



On the Fundamentals and the Use of Tripodal Tris(silanolate) Ligands: Air-Stable Alkyne Metathesis Catalysts & Lewis Acids for Menthol Synthesis

Dissertation

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Johannes Nepomuk Korber

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1. Berichterstatter: Prof. Dr. Alois Fürstner
2. Berichterstatter: Prof. Dr. Norbert Krause

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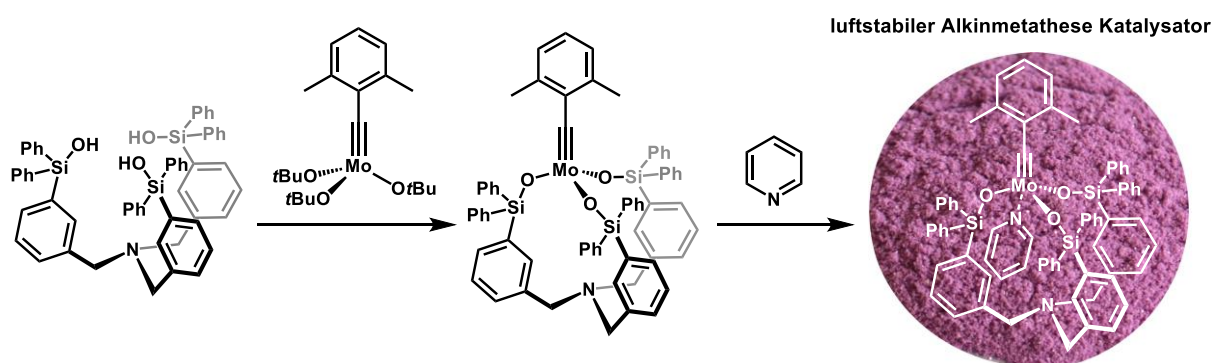
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Zusammenfassung

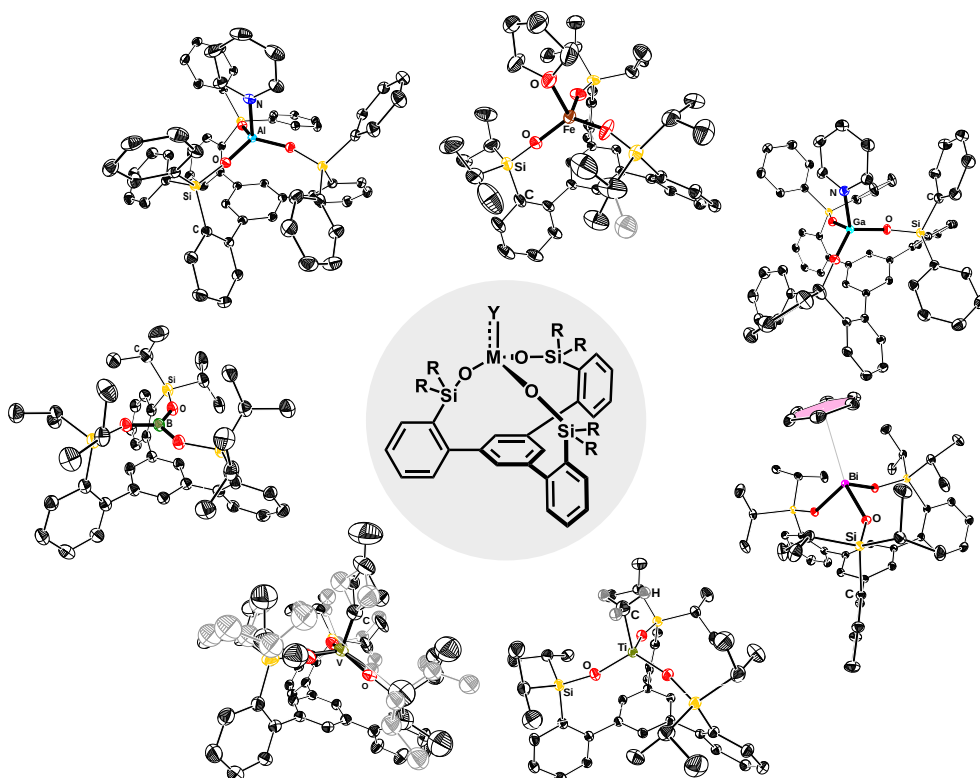
Die Alkinmetathese ist eine Reaktion von strategischem Wert in der organischen Chemie im Allgemeinen und im Besonderen für die Naturstoffsynthese. Die Verbreitung ihrer Anwendung wird jedoch durch den Mangel an leicht verfügbaren und stabilen Katalysatoren behindert. Im ersten Teil der vorliegenden Arbeit wird eine neue Generation an Alkinmetathese Katalysatoren vorgestellt, die zum Ziel hat diese Beeinträchtigung zu überwinden. Die Molybdän-Alkyldin-Komplexe des unten abgebildeten Typs mit einem neuartigen tripodalen Tris(silanolat)-Liganden zeichnen sich durch eine beispiellose Stabilität und Nutzerfreundlichkeit aus, ohne dabei die Vorzüge früherer Katalysatorgenerationen einzubüßen.



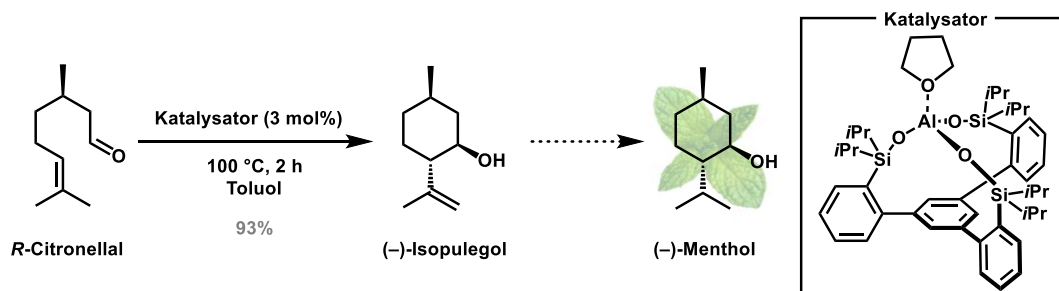
Der Schlüssel zum Erfolg lag in der Kombination mehrere Designelemente, darunter das neue flexiblere tripodale Ligandengerüst sowie ein externer stabilisierender Ligand. Das abgebildete Addukt konnte im Gramm-Maßstab hergestellt werden und lässt sich routinemäßig an der Luft handhaben. In Lösung ist das Pyridin jedoch labil und gibt bei Raumtemperatur durch spontane Dissoziation den aktiven Katalysator frei. Über eine standardisierte Testreaktion wurde die katalytische Aktivität der neuen Komplexe mit einer Reihe von Katalysatoren aus vorhergehenden Generationen verglichen. Zudem wurde erstmals auch die Luftstabilität der Komplexe untersucht. Das gezeigte Addukt bleibt über viele Monate hinweg an Luft intakt und übertrifft damit alle bisherigen Hochleistungskatalysatoren.

Die Komplexe sind äußerst leistungsfähige Katalysatoren, die eine bemerkenswerten Kompatibilität mit diversen funktionellen Gruppen aufweisen. Ihre Nützlichkeit konnte anhand einer Reihe anspruchsvoller Ring-Schluss-Metathesen mit Zwischenstufen aus vorangegangenen Naturstoffsynthesen bewiesen werden. Der entscheidende Fortschritt besteht darin, dass die neuen Katalysatoren weder in irgendeiner Weise aktiviert werden müssen noch eine Schutzgasatmosphäre für deren Lagerung und Handhabung notwendig ist. Es wird erwartet, dass die verbesserte Stabilität der Katalysatoren die Methodik einem größeren Anwenderkreis zugänglich macht und damit zu einer häufigeren Anwendung dieser überaus nützlichen Reaktion führt.

Im zweiten Teil dieser Arbeit werden explorative Untersuchungen zur Koordinationschemie einer besonderen Klasse tridentater Silanolat-Liganden vorgestellt. Die ‚Canopy-Liganden‘ wurden ursprünglich für die Alkinmetathese entwickelt und zeichnen sich durch ihre starke Präferenz für eine C_3 -symmetrische Konformation aus. Aus diesem Grund sind sie für die Herstellung von Komplexen von Interesse, die an Metallzentren auf Kieselgeloberflächen in der heterogenen Katalyse erinnern. Die Synthese einer Reihe von Komplexen unterschiedlichster Metalle in vielfältigen Oxidationsstufen konnte die Anpassungsfähigkeit dieser Liganden demonstrieren.

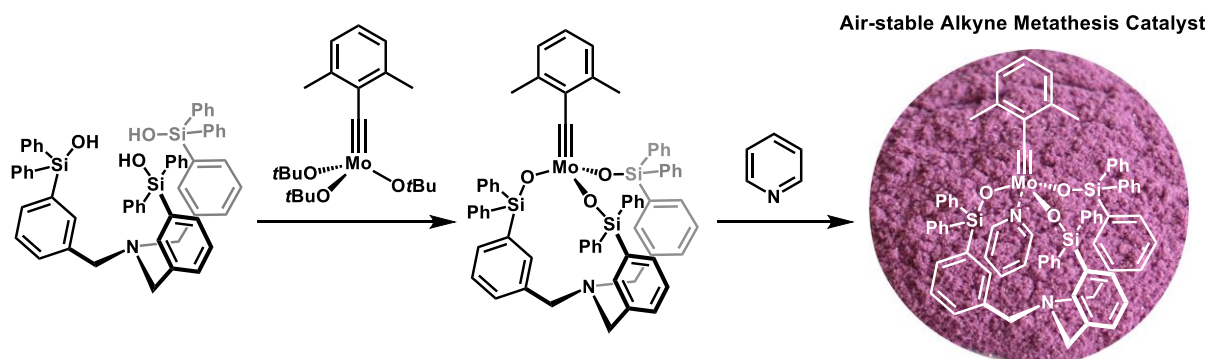


Abschließend wird das Potential der neuartigen Komplexe für Anwendungen in der Katalyse anhand eines Beispiels veranschaulicht. Ein einschlägiger Aluminium Komplex katalysiert die Zyklisierung von Citronellal zu Isopulegol mit guter Diastereoselektivität und ausgezeichneter Chemoselektivität. Die Temperaturstabilität des Komplexes übertrifft das bisherige Standard-Katalysatorsystem der Industrie und ermöglicht es, das Produkt und den Katalysator durch Destillation voneinander zu trennen. Die Wiederverwendbarkeit des Katalysators eröffnet Möglichkeiten für eine potenziell effizientere (industrielle) Synthese von (-)-Menthol.



Abstract

Alkyne metathesis is a reaction of high strategic value in the synthesis of natural products and in general organic chemistry. Widespread use of the transformation has been hampered by the lack of easily accessible and stable catalysts. In the first part of this work, a new generation of alkyne metathesis catalysts is presented that addresses the issue. Molybdenum alkylidyne complexes of the type shown below, comprising a novel tripodal tris(silanolate) ligand, are distinguished by an unprecedented level of stability and practicality without sacrificing the chemical virtues of their predecessors.

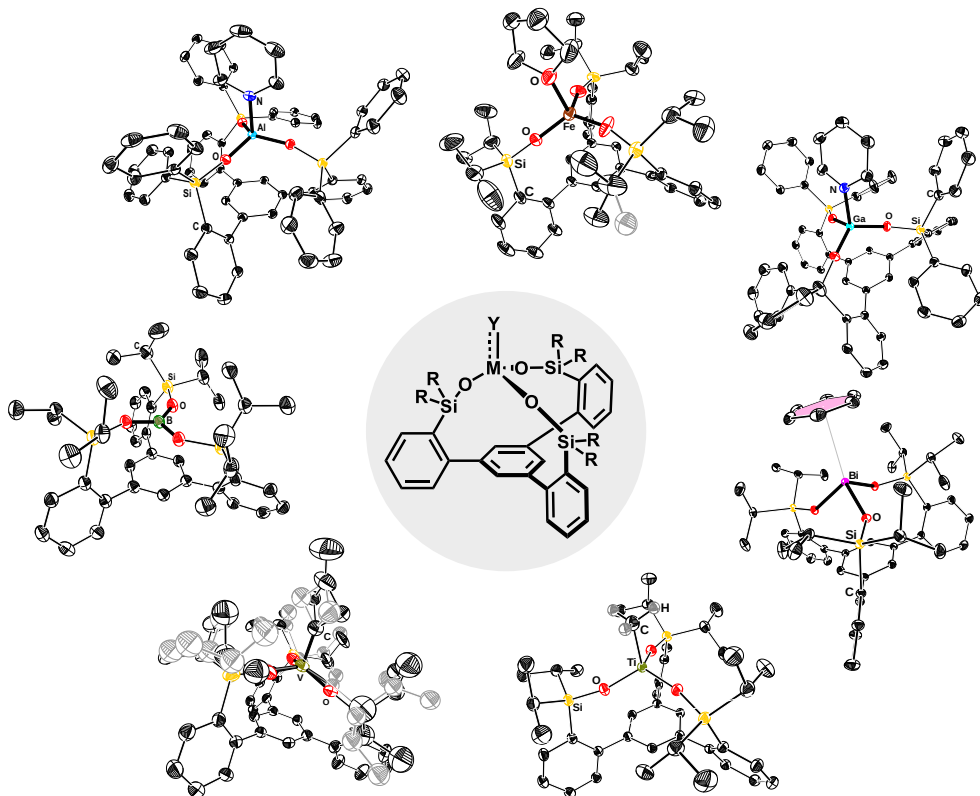


Key to the success was a combination of features, including the design of a more flexible tripodal ligand scaffold and the addition of an external stabilizing ligand. The depicted adduct could be prepared on gram scale and can be routinely handled in air. In solution at ambient temperature the pyridine is labile and reveals the active catalyst by spontaneous dissociation. The catalyst's activity was benchmarked in a standardized reaction against a library of catalysts from previous generations. For the first time, these complexes were also compared with respect to their stability in air. The novel complex remained intact on the bench for many months, outperforming all previous highly-active catalysts. In addition, the critical parameters for the activity and stability could be elucidated by varying different features in the overall design.

The adduct is an exceedingly enabling catalysts with an outstanding functional group tolerance. Its excellent performance is highlighted in a row of challenging ring-closing alkyne metathesis reactions on highly functionalized intermediates from previous natural product synthesis campaigns, with the key advancement being that the novel catalyst neither needs preactivation nor a glovebox for handling and storage. It is expected that the catalyst's enhanced stability will also enable non-expert users to apply alkyne metathesis and promote a more widespread adoption of this strategic transformation.

The second part of this thesis contains an exploratory study of the coordination chemistry of a special class of tripodal tris(silanolate) ligands. The 'canopy ligands' were originally developed for application in alkyne metathesis catalysis and are characterized by their preorganization into a C_3 -symmetrical conformation. For this reason, they are considered to be of interest for forming complexes reminiscent of metal sites supported on silica in heterogeneous catalysis.

This work ventures beyond molybdenum and tungsten alkylidynes and was aimed at expanding the range of complexes attainable with ‘canopy ligands’. The synthesis of a library of complexes containing seven different metals and metalloids in varying oxidation states is reported, vividly illustrating the adaptability of the ‘canopy ligands’.



The obtained complexes were characterized by crystallographic and spectroscopic means, including solid-state NMR and cyclic voltammetry. Special attention is paid to the changes in the coordination geometry of the complexes when compared to their congeners with untethered silanolate ligands. Seminal differences in the electronic influence on the metal center as well as the steric bulk surrounding it are described.

Lastly, the potential of the novel complexes for catalysis is demonstrated. An aluminum complexes catalyzes the cyclization of citronellal to isopulegol with good diastereoselectivity and excellent chemoselectivity. The stability of the complex at elevated temperatures allows for a separation of product and catalyst *via* distillation, opening the prospect of a potentially more efficient industrial synthesis of (–)-menthol.

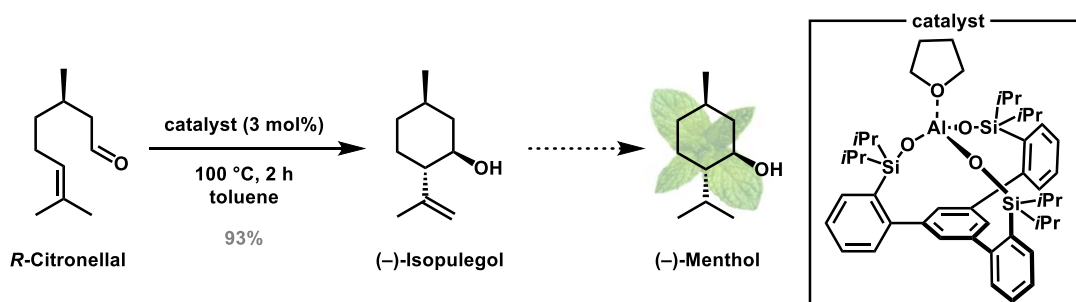


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I An Air-Stable Catalyst for Alkyne Metathesis

I.1 Introduction

I.1.1 Metal Alkylidyne Complexes

Carbon-metal multiple bonds have been a source of fascination for chemists since the first complex with such a motif was isolated by *Ernst Otto Fischer* 60 years ago.^[1] The discovery sparked a flurry of research.^[2] Some of the most renowned chemists of the 20th century devoted their careers to the synthesis, characterization, and use of complexes containing carbon-metal multiple bonds.^[3] This effort led to countless scientific achievements, including Grubbs catalysts, complexes bearing *N*-heterocyclic carbenes, and Tebbe's reagent – compounds which have become canonical and indispensable tools for organic synthesis.^[4]

Most of these accomplishments relate to carbon-metal double bonds, which are conventionally referred to as carbenes (or alkylidenes).^[5] The sibling class of carbon-metal triple bonds has arguably received less attention.^[6] Still, a large number of complexes containing such a motif have been reported since the first carbon-metal triple bond was described by *E. O. Fischer* in 1973 (*table 1*).^[7]

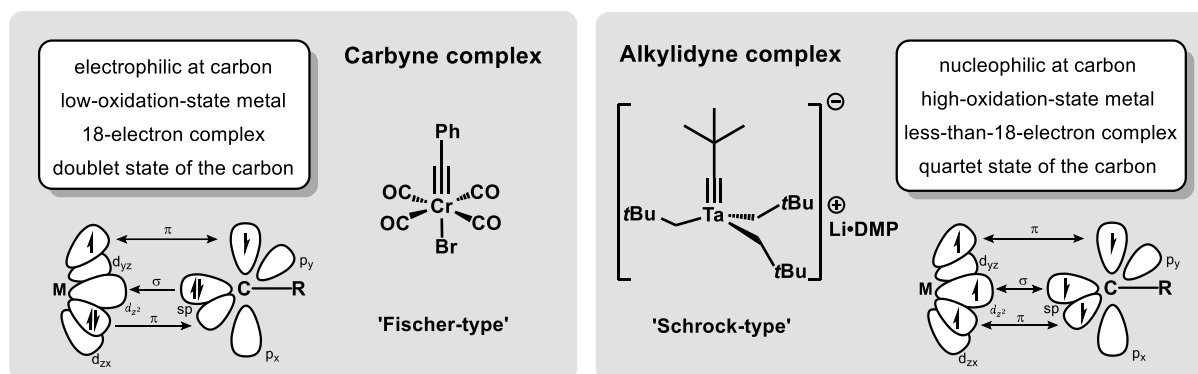
Table 1: Occurrence of isolated complexes with carbon-metal triple bonds (reported; not reported).^[8]

Group of transition metals									
3	4	5	6	7	8	9	10	11	12
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

An important distinction has been made by classifying the complexes as carbynes or alkylidyne, analogous to the terminology used for metal-carbon double bonds (carbenes and alkylidenes).^[9] These designations help to understand the reactivities of carbon-metal triple bonds resulting from disparate bonding situations. The terms are used interchangeably with 'Fischer-type' (carbyne) and 'Schrock-type' (alkylidyne) complexes in deference to the discoverers of these compound classes.^[7, 10] In the following, a brief introduction is given on how to distinguish the two categories and the main properties of the respective complexes. It is, however, necessary to remember that the examples demonstrate the two extreme ends of a range with a large ambiguous space in between.

Considering the first complexes reported for each class, the carbyne $[\text{Br}(\text{CO})_4\text{Cr}\equiv\text{C}-\text{Ph}]$ ^[7] and the alkylidyne $[\text{((}t\text{BuCH}_2)_3\text{Ta}\equiv\text{C}-t\text{Bu})\text{Li}\cdot\text{DMP}]$ ^[10], a distinction can be made immediately based on the geometry and the number of valence electrons (*scheme 1*). The 'Fischer-type' complex is octahedral with an 18-electron count, whereas the 'Schrock-type' complex is

pseudo-tetrahedral with a sub-18-electron count.^[6a] Generally carbyne complexes include metals in low oxidation states and are regarded as ‘low-valent’, whereas alkylidyne complexes encompass metals in higher oxidation states and are designated ‘high-valent’.^[11] Following convention, the carbyne ligand in ‘Fischer-type’ complexes is counted as monoanionic (*ergo* Cr^{+II}) and the alkylidyne ligand in ‘Schrock-type’ complexes as trianionic (*ergo* Ta^{+V}). Assigning oxidation states in this manner is, however, only a formalism and, although useful, should not be seen as a representation of the absolute electron distribution.^[9, 12]



Scheme 1: Characteristics of carbyne and alkylidyne complexes demonstrated on the bases of classical examples.

This description reflects the bonding model that considers the carbyne ligand to be in a doublet state. In contrast, an alkylidyne ligand is assumed to be in a quartet state.^[9, 13] In the case of the ‘Fischer-type’ carbon-metal triple bond this results in a σ -bond *via* donation of 2 e^- from the sp -orbital of the carbyne and a π -bond with 1 e^- each from a p -orbital of the carbyne and a d -orbital of the metal. Additionally, a π -bond is formed through back donation of 2 e^- from a d -orbital into an empty p -orbital on the carbyne fragment. Overall, the triple bond comprises a mixture of dative bonding (σ -donation, π -back-donation) and one electron-sharing π -bond.^[14]

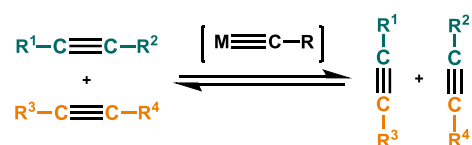
In a ‘Schrock-type’ case all the orbitals (sp , p_z , p_y) at carbon are singly occupied due to the quartet state. Therefore, three covalent bonds are formed, with the metal and carbon fragment each contributing 1 e^- to all bonds.^[6b] In this description of alkylidyne complexes, the carbon atom becomes a pure donor ligand, which is reflected in its reactivity. ‘Schrock-type’ complexes are usually nucleophilic at the carbon; ‘Fischer-type’ complexes are electrophilic. This observable property is perhaps the most reliable and meaningful measure for classifying carbon-metal triple bonds into the two categories.

Carbyne and alkylidyne complexes display rich chemistry and possess intriguing photophysical properties.^[15] Alkyne metathesis is by far the most prominent reactivity and is almost exclusively limited to alkylidyne complexes, a fact that underlines the relevance of the distinction between ‘Fischer-type’ and ‘Schrock-type’ complexes summarized above.^[8, 16] Alkyne metathesis is the focus of this work and will be discussed in detail in the following chapters (*vide infra*).

Other reactions of carbyne and alkylidyne complexes include the metathesis of heteroatom-containing triple bonds (e.g., $\text{N}\equiv\text{CR}$, $\text{N}\equiv\text{NR}^+$, $\text{P}\equiv\text{CR}$, or $\text{M}\equiv\text{CR}$)^[17], the formation of various metallacycles, some of which are relevant to the synthesis of cyclic polymers,^[18] oxidations or reductions transforming ‘Fischer-type’ into ‘Schrock-type’ complexes or *vice versa*,^[19] nucleophilic or electrophilic reactions at the carbon atom,^[20] and the formation of polynuclear complexes with bridging carbyne or alkylidyne ligands.^[21]

1.1.2 Alkyne Metathesis

Alkyne metathesis, the redistribution of the alkylidyne fragments in a pair of alkynes (Greek: μετατίθημι, ‘*metatithemi*’ = to reposition)^[22] is a compelling synthetic method for the formation of carbon-carbon bonds (*scheme 2*). These chemical entities are ubiquitous throughout biological active molecules, polymers, and functional materials alike. Accordingly, alkyne metathesis has emerged as highly enabling tool for organic chemists, along with being a fundamentally intriguing reactivity.^[16a, b, 23]



Scheme 2: General reaction scheme of alkyne metathesis.

Long overshadowed by alkene metathesis, alkyne metathesis has been recognized as having its own value for the synthetic chemist by displaying some seminal differences from its extraordinarily successful cousin.^[16a, 24] The formation of carbon-carbon triple bonds offers ample opportunities for postmetathesis transformations providing access to rich chemical space.^[25] One of the simplest among them is the stereoselective semireduction of the alkyne unit to *E*- or *Z*-alkenes.^[26] The stereoselectivity issue has plagued alkene metathesis since its discovery and has, despite great advances, never been resolved to complete satisfaction.^[27] Another notable difference is the reluctance of metal alkylidynes to react with alkenes making the method orthogonal and suitable for polyunsaturated substrates. The merits of alkyne metathesis as a method for synthetic chemistry will be further elaborated with some examples in *chapter 1.1.6*.

The history of alkyne metathesis is inextricably linked to the development of catalysts. Only the advent of easier attainable catalysts with improved functional group tolerance at the turn of the millennium made the surge in applications over the last 25 years possible.^[16b] Some important milestones in the history of alkyne metathesis research are shown in *figure 1*.

The first report of alkyne metathesis stems from *Pennella, Banks, and Bailey* working at the Phillips Petroleum Company in 1968. They described the “disproportionation” of pent-2-yne

into but-2-yne and hex-3-yne over tungsten trioxide on silica at high temperatures.^[28] Beyond that, the communication also linked the phenomenon to a related reaction known for alkenes (alkene metathesis) and proposed a four-membered transition state. In 1972, the French scientists *Mortreux* and *Blanchard* reported on alkyne metathesis over a similar system containing molybdenum; thereby introducing the second of two transition metals that dominate the field.^[29] The same group was the first to transfer the reaction from a heterogeneous system to the liquid phase using molybdenum hexacarbonyl with pre-treated silica as a catalyst.^[30] Already in these early embodiments the role of silica was suspected to go beyond simple dispersion of the metal complex – an observation which had great impact on later catalyst development.^[31] The first fully homogeneous catalyst system consisted of molybdenum hexacarbonyl and resorcinol and allowed for reduced reaction temperatures (160 °C).^[32] Although elegantly simple, the lack of clarity concerning the active species together with competing polymerization made the early systems unattractive for the application to more complex molecules.^[33]

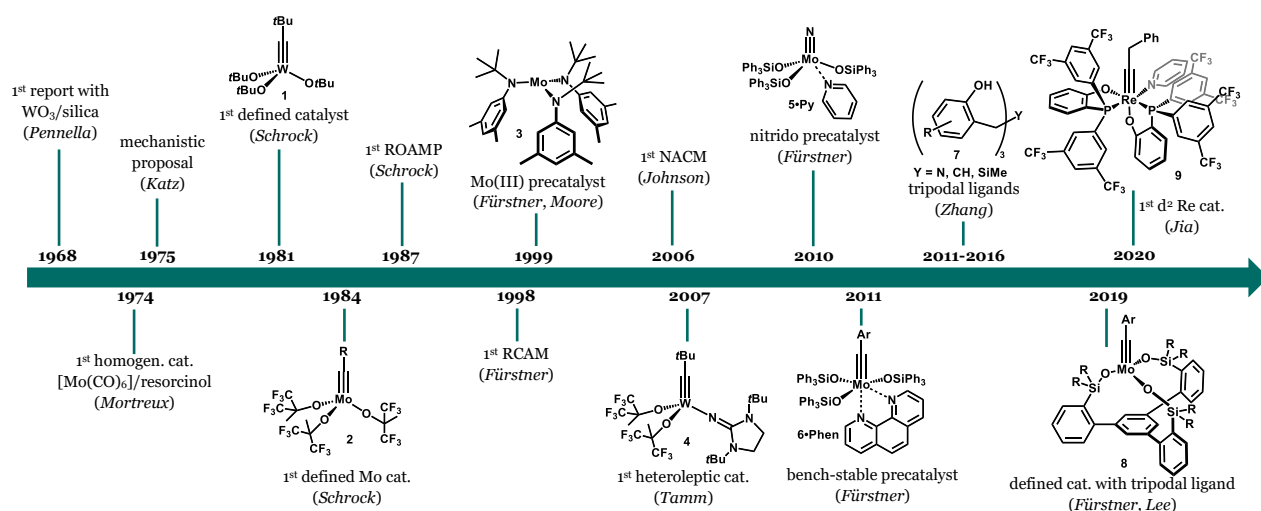
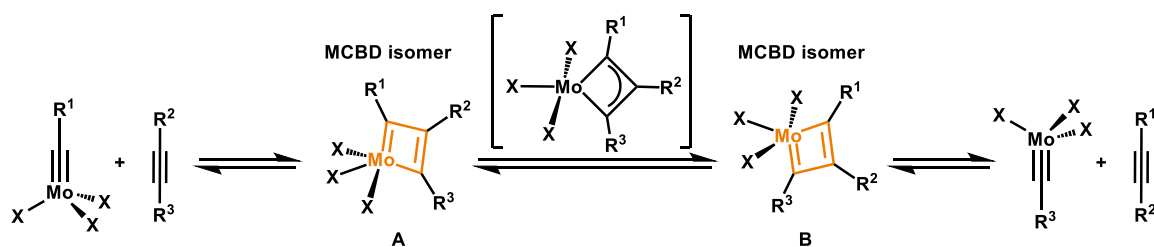


Figure 1: Milestones in alkyne metathesis research.

Concurrent with the development of these initial catalytic systems, *E. O. Fischer* reported the first metal carbyne complexes in 1973.^[7] Prompted by this discovery and the mechanism discussed for alkene metathesis *Katz* and coworkers put forward a mechanistic proposal for alkyne metathesis (*scheme 3*).^[34]



Scheme 3: Canonical mechanism of alkyne metathesis.

Metallacyclobutadienes (MCBD) were invoked as the intermediates resulting from a [2+2]-cycloaddition of the alkyne to the alkylidyne complex. The distorted square-pyramidal intermediate **A** then undergoes a tautomerization to its isomer **B** through a trigonal bipyramidal transition state. Cycloreversion releases the product and a new catalytically active propagating species.^[35] The mechanism is widely accepted today, but recent studies by *Fürstner* and coworkers revealed an additional Berry pseudorotation of the MCBD to be necessary for catalysts with tripodal ligands.^[36]

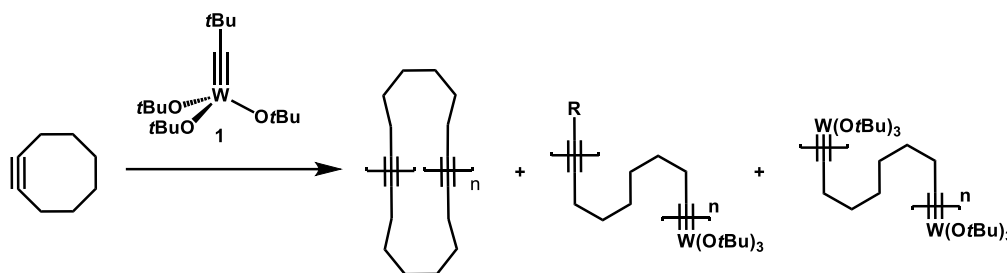
In contrast to the suggested catalytic species, the ‘Fischer-type’ carbynes known at that time were all inactive in alkyne metathesis. It took until 1981 and the arrival of the first well-defined tungsten alkylidyne complexes to gain experimental proof for the proposed mechanism.^[37] In this landmark paper *Schrock* and coworkers reported on the alkyne metathesis activity of several tungsten (VI) alkylidyne complexes with the most notable being $[(OtBu)_3W\equiv C-tBu]$ (**1**): the only alkyne metathesis catalyst commercially available to this day. The mechanism was confirmed in the following years through the isolation of tungsten metallacyclobutadienes which were catalytically competent.^[38]

The first discovery was followed by detailed studies from *Schrock* and coworkers covering structures, catalytic performance, an array of different ligands, substrate scope, and decomposition pathways (*chapter 1.1.4*).^[5] In due course the first molybdenum alkylidyne complex capable of catalyzing alkyne metathesis reactions was reported.^[39] Fluorinated alkoxide ligands were necessary to promote the reaction due to the inherently lower electrophilicity of molybdenum (VI) when compared to tungsten (VI). However, the synthesis of molybdenum alkylidynes *via* α -hydrogen abstraction, a route which served well for tungsten alkylidynes, was troublesome and not scalable.^[40] In 1988, the rhenium complex $[(NAr)(OCMe(CF_3)_2)_2Re\equiv C-tBu]$ was reported to convert hep-3-yne into hex-3-yne and oct-4-yne, revealing an additional metal to be able to productively catalyze alkyne metathesis.^[41] However, until recently, rhenium alkylidynes have only played a minor role in alkyne metathesis catalysis.^[42]

The initial catalytic alkyne metathesis reactions were of purely academic nature and not intended to deliver synthetically valuable products. It is noteworthy that in the proposed mechanistic scheme (*vide supra*) the reaction is in equilibrium and gives a mixture of products. To be synthetically meaningful, the equilibrium must be perturbed by the continuous removal of one of the products. In modern alkyne metathesis catalysis, internal alkyne substrates with methyl end-caps are commonly employed, yielding but-2-yne as a by-product. The low-boiling alkyne can be removed at elevated temperatures, under gentle vacuum or by adsorption into molecular sieves (5 Å).^[31b, 43] Precipitation-driven reactions have been reported, but they do not find widespread use due to the need for specifically tailored end-groups.^[44]

The first real hint at a practical application came from *Schrock* and coworkers in the form of ring-opening-alkyne-metathesis polymerization (ROAMP) in 1987 (*scheme 4*).^[45] In this

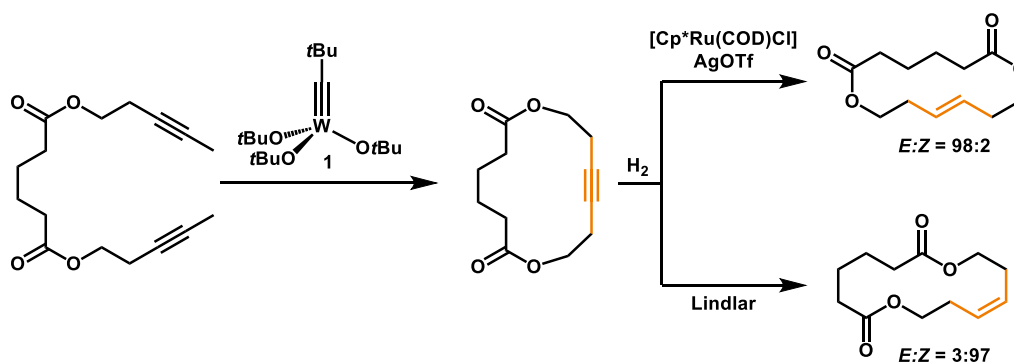
embodiment, the equilibrium was influenced by employing a highly strained cyclic alkyne as substrate. However, contrary to the initial classification of the reaction as a living ROAMP, subsequent investigations revealed the major product to be cyclic oligomers.^[46]



Scheme 4: First example of ROAMP by Schrock and coworkers.

The high activity of the tungsten alkylidyne catalyst prevented kinetic control of the reaction towards product distributions with a lower polydispersity index. Subsequent efforts by several research groups have overcome this issue with ingenious catalyst design.^[47] More details on the applications of alkyne metathesis in the synthesis of polymers are presented in chapter 1.1.6.3.

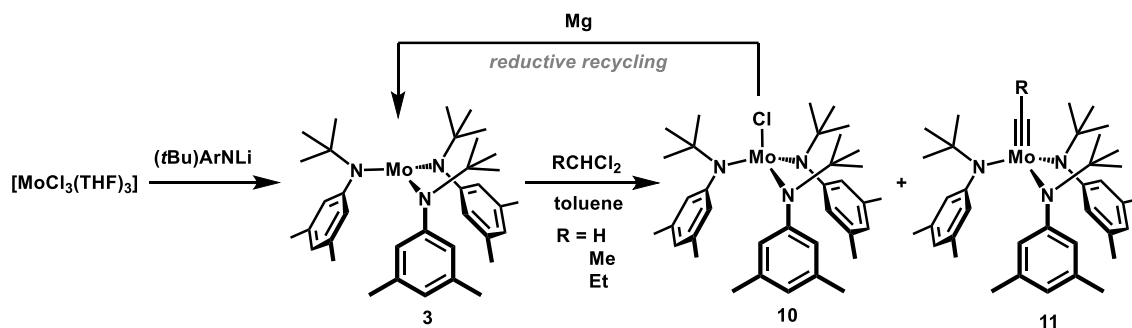
The true potential of alkyne metathesis for organic synthesis was revealed by *Fürstner* and coworkers in 1998 with the first ring-closing-alkyne-metathesis (RCAM).^[48] Cyclizing diynes to give macrocyclic products has become the dominant application of alkyne metathesis over the last 25 years.^[16a] Initially proposed as an alternative strategy to alkene metathesis for accessing unsaturated macrocycles with control over the alkene geometry, RCAM evolved into a strategic transformation in its own right (scheme 5).^[49] *Fürstner* and coworkers have proven its value and versatility by conquering numerous increasingly challenging macrocyclic natural products (chapter 1.1.6.1).^[24]



Scheme 5: Stereoselective synthesis of *E*- and *Z*- alkenes via RCAM and semi-reduction.

The surge in applications starting around the turn of the century was accompanied by continuous catalyst development. *Schrock's* tungsten alkylidyne complex proved to have a rather narrow functional group tolerance, thereby constraining its applicability concerning more complex substrates. In 1999, *Fürstner* and coworkers discovered an *in situ* generated catalyst system based on a molybdenum (III) complex (**3**) introduced by *Cummins* a few years earlier.^[50] The complex had originally risen to fame for its ability to cleave dinitrogen under

homogeneous conditions.^[51] The high-spin state of the molybdenum (III) with three unpaired electrons was a tantalizing partner for a ‘Schrock-type’ alkylidyne fragment.^[52] *Fürstner* and coworkers were able to activate the complex with dichloromethane to give a mixture of molybdenum (IV) chloride **10** and a molybdenum (VI) methylidyne complex **11** which proved to be active in alkyne metathesis. The switch from tungsten to the inherently less Lewis acidic molybdenum significantly improved the functional group tolerance, permitting substrates containing donor groups.^[53] *Moore* and coworkers were able to amend the activation strategy by employing higher *gem*-dihalides to provide the corresponding molybdenum alkylidyne complexes. Together with the reductive recycling of the molybdenum (IV) chloride complex **10** through the addition of magnesium, higher yields of the ‘activated’ complex could be obtained (scheme 6).^[54] The isolated molybdenum alkylidyne enabled researchers to modify the ancillary ligand sphere by *in situ* protonolysis of the basic amine ligands with phenols.^[44a]

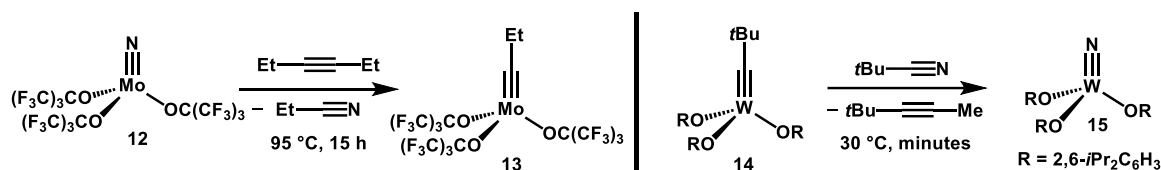


Scheme 6: Activation of Mo(III) complex **3** with organo-*gem*-dihalides and reductive recycling strategy.

Although highly enabling, the system also had some considerable drawbacks mainly concerning the handling of the extremely sensitive molybdenum (III) precursor **3**. Trace oxygen and water have to be strictly excluded and manipulations under argon atmosphere are mandatory due to its ability to cleave nitrogen.^[16a] Further, the isolation of derivatives obtained from the molybdenum alkylidyne complex proved to be difficult due to persistent contamination with the free aniline ligand as well as decomposition products.^[44a] Additionally, the polymerization of but-2-yne, the by-product generated from substrates with methyl endcaps, posed an undesirable side reaction.^[55] Given these challenges, the search for more robust alkyne metathesis catalysts continued.

An alternative approach was investigated by the group of *M. Johnson*, who reported the first nitrile-alkyne-cross-metathesis (NACM) in 2006.^[56] The reaction of an electrophilic molybdenum nitrido complex **12** with an excess of hex-3-yne gave the corresponding molybdenum alkylidyne species **13** and a nitrile (scheme 7). Accordingly, molybdenum nitrido complexes with a variety of ligands could be used to catalyze alkyne metathesis reactions with the actual active species being formed *in situ*.^[57] Notably, the reverse reaction from an alkylidyne to a nitrido complex turned out to be thermodynamically unfavorable for molybdenum, although well known for tungsten.^[58] The enticing prospect of a catalytic

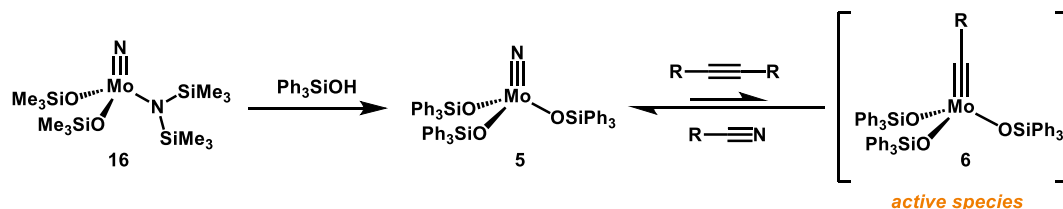
metathesis of nitriles to give dinitrogen and alkyne products could therefore never be realized.^[17a]



Scheme 7: First NCAM with a molybdenum catalyst and the reverse reaction with a tungsten catalyst.

In parallel, the group of *M. Tamm* continued to pursue an approach based on tungsten. Their design sought to temper the pronounced Lewis acidity with a heteroleptic ligand sphere. In their 2007 publication, one of the alkoxide ligands in the original *Schrock* design was exchanged with an imidazolin-2-iminato ligand (*figure 1, 4*).^[59] The resulting complexes were superior to their homoleptic predecessors with respect to activity. The outcome was ascribed to a ‘push-pull-effect’ from the electron-withdrawing fluorinated alkoxide ligands and the electron-releasing nitrogen based ligand.^[60] This observation aligns with the varying electronic exigencies throughout the catalytic cycle of alkyne metathesis: the cycloaddition demands a highly Lewis acidic metal center, whereas the cycloreversion is favored with a less Lewis acidic metal.^[61]

Nonetheless, research groups with a focus on applying the methodology to natural product synthesis continued to concentrate on molybdenum-based catalysts. Building on *Johnson’s* results, *Fürstner* and coworkers employed the readily accessible molybdenum nitrido complex **16** to screen for optimal ligands. Thus far the field had been dominated by the fluorinated alkoxide ligands originally proposed by *Schrock* and phenolates pioneered by *Mortreux*. In 2009, the search revealed silanolate ligands to synergize exceedingly well with molybdenum nitrido/alkylidyne complexes in catalyzing alkyne metathesis.^[57b] In retrospect, the discovery is not entirely surprising, since heterogeneous systems with molybdenum (or tungsten) grafted on silica had played a key role in the discovery of alkyne metathesis.^[55, 62] In any case, the transfer into the sphere of homogeneous catalysis opened the doors to the golden era of alkyne metathesis. Due to their unique electronically adaptive properties silanolate ligands continue to dominate high-performance alkyne metathesis today (*chapter 1.1.3*).^[16a, 61, 63]



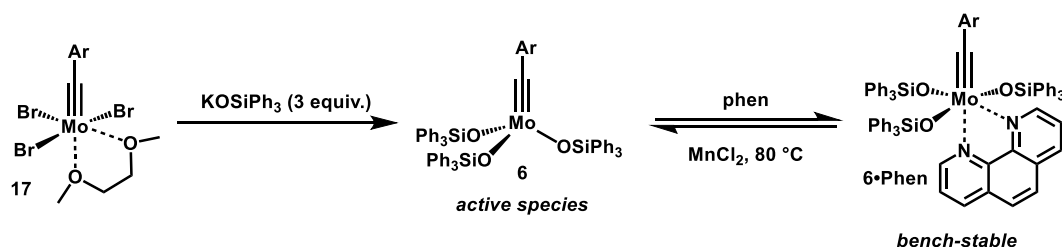
Scheme 8: A molybdenum nitrido complex with silanolate ligands as precatalyst for alkyne metathesis.

The stabilization of the molybdenum nitrido complex **5** with labile nitrogen donor ligands (initially pyridine and subsequently phenanthroline) allowed for its isolation and even storage on the bench (*figure 1*).

Surprisingly, closer inspection revealed the equilibrium between the nitrido and alkylidyne complexes to be largely on the side of the precatalyst (*scheme 8*); an observation which stands in contrast to the case described by *Johnson*.^[31b] The discrepancy likely stems from the different ligand spheres and resulting electrophilicities of the molybdenum center. In any case, the catalytically active mixture contained only small amounts of complex **6** highlighting its exceptional activity. However, in order to prepare meaningful amounts of the molybdenum alkylidyne another synthetic route was required.

The adaptation of a procedure by *Mayr* and coworkers that relies on the oxidation of a low-valent ‘Fischer-type’ carbyne to a ‘Schrock-type’ alkylidyne with bromine, enabled the synthesis of molybdenum alkylidynes on gram scale.^[64] The approach was independently pursued and published by the groups of *Tamm* and *Fürstner*.^[31b, 65] In combination with triphenylsilanolate ligands, a highly active catalyst was obtained allowing for a significant reduction in catalyst loadings (*scheme 9*). Its extensive application to natural product syntheses is a testimony to its excellent performance and user-friendliness.^[66]

Moreover, the stabilization strategy for the molybdenum nitrido complexes could be extended to the molybdenum alkylidyne complexes. Phenanthroline adducts of type **6•Phen** remain intact for years when exposed to air and moisture, a fact which is utterly inconceivable for earlier catalyst generations based on the *Schrock* design or the highly sensitive molybdenum (III) complex **3**. However, somewhat harsh conditions are necessary to liberate the active species from the bench-stable precatalyst.^[43a]



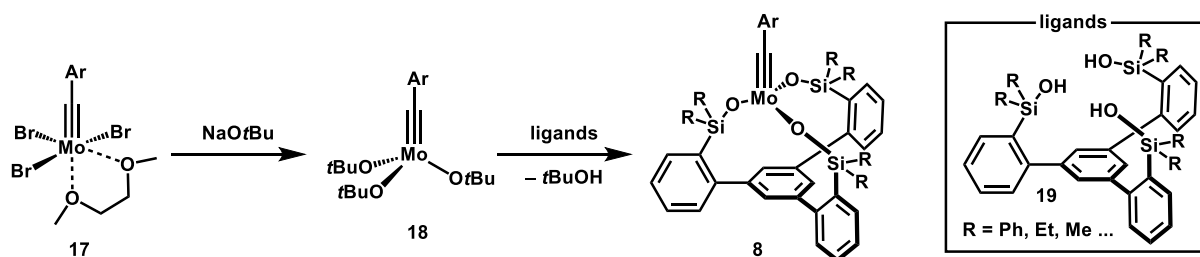
Scheme 9: Highly active molybdenum alkylidyne complex **6** with silanolate ligands: synthesis & stabilization.

In parallel to the ascent of alkyne metathesis to strategy level status in natural product synthesis, the group of *Zhang* developed a row of tripodal ligands for alkyne metathesis applications in material science (*figure 1, 7*). Their focus lies on the field of ‘molecular architecture’ which aims to create shape-persistent compounds with peculiar structures and unique properties (*chapter 1.1.6.2*).^[67] Alkynes, with their rigid and linear geometry, are therefore appealing building blocks. In addition, the reversibility of alkyne metathesis makes it highly suitable for dynamic covalent chemistry (DCC) – a common strategy to obtain structures out of reach for traditional methods.^[68] However, catalyst stability throughout the reaction is a key element to ensure the thermodynamic product is obtained. Early experiments using the activated molybdenum (III) complex **11** struggled with the polymerization of the by-product but-2-yne and catalyst decomposition.^[44a, 69]

For this reason, *Zhang* and coworkers put forth a row of multidentate ligands aimed at increasing stability. In these ligands three phenols are connected through a nitrogen, silicon or carbon-based tether.^[69b, 70] The proposed mechanism for but-2-yne polymerization proceeds through a ring-expansion mechanism of the metallacyclobutadiene intermediate and therefore requires two substrate-binding sites on the catalyst.^[71] The tripodal ligands effectively block the position *trans* to the alkylidyne moiety, largely suppressing polymerization. Yet, definitive proof of the actual composition and configuration of the active species in these systems is still missing. All of them are created *in situ* from precursor **3** requiring (at least part of) the handling to take place under inert atmosphere. Nevertheless, the systems have found widespread application in the synthesis of molecular cages and rigid macrocycles.^[72]

The *Fürstner* group adopted the concept and devised their own tripodal ligands, based on trisilanols.^[73] In their case the primary objective was to utilize the chelate effect to keep the ancillary ligands bound to the metal center in the presence of protic functional groups. Protonation of the weakly basic silanolates in the presence of substrates comprising, e.g., alcohols had turned out to be a fundamental deficiency in the functional group tolerance of catalyst **6**.^[74] Similar to the systems developed by *Zhang* the first generation of tripodal ligands failed to give well-defined molybdenum alkylidyne complexes; likely due to excessively flexible alkyl chains used for connecting the ligands to the tether. Still, in combination with precursor **3**, catalytically active mixtures were obtained. While their exact constitution remains unclear, their performance regarding protic functional groups vindicated the design concept. The catalyst systems tolerate phenols, primary and secondary alcohols and are able to form highly challenging products with two propargylic alcohols. Beyond that, the presumed oligomeric structure of the catalyst enabled the metathesis of densely decorated substrates previously inaccessible with structurally defined catalysts.^[75] However, the systems still relied on the same difficult-to-handle precursor complex **3**, which constituted a step backwards in terms of user-friendliness compared to stabilized complexes such as **6•Phen**.

In 2019, *Fürstner* and coworkers were able to overcome the oligomerization issue with a new set of rigid tridentate ligands **19**.^[76] In combination with a mild complexation method the preorganized ligands gave the first well-defined alkyne metathesis catalysts **8** with a tripodal ligand framework (*scheme 10*).



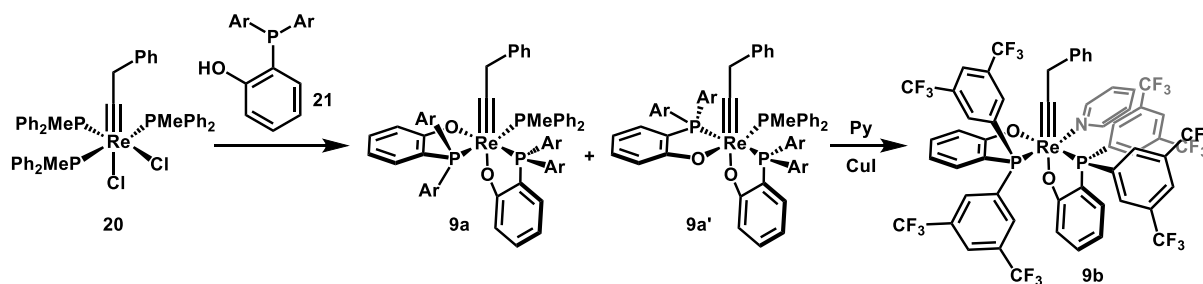
Scheme 10: Synthesis of the first well-defined alkyne metathesis catalysts with a tripodal ligand framework.

With a nod to the shielding of the complexes by the ligand backbone, the term ‘canopy catalysts’ was coined to describe this latest generation of catalysts.^[74] The group of *S. Lee* also published on the same ligand design.^[77] The structurally defined nature of the ‘canopy catalysts’ allowed for detailed studies into the structure-activity relationship of the ligand sphere.^[61, 78] While the derivative closest to the parent complex **6** carrying phenyl substituents on the silanolate ligands showed considerably reduced activity, changing the groups to methyl substituents restored the excellent reactivity.^[74]

These results, in conjunction with computational evidence, suggest higher energy barriers in catalysts with ridged frameworks for passing through the different geometries required during the catalytic cycle. Additionally, to complete the isomerization of the MCBs a pseudorotation over one of the ligand arms is necessary. The finding was corroborated through the isolation of an off-cycle metallatetrahedran (MTH) which is mechanistically connected to the pseudorotation.^[36]

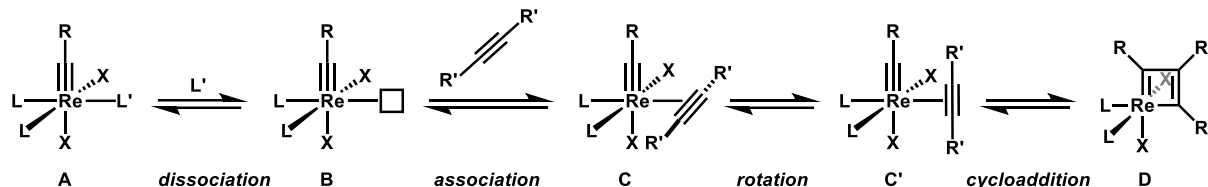
With well-defined catalysts in hand, a more detailed investigation of the substrate scope was undertaken: a host of protic groups, C-H acidic sites, potentially coordinating Lewis-basic moieties and other functional groups that are oftentimes detrimental to transition metal catalysts, such as azides, alkyl halides, and thio-esters, were well tolerated. The most advanced iteration of the ‘canopy catalysts’ has found application in several natural product syntheses.^[79] The close scrutiny allowed for by the possibility to isolate the defined complexes also revealed potential deactivation pathways. The rigidity of the ligands, as previously discussed, was instrumental for the successful complexation, but resulted in ring strain in the formed complexes which could be released under certain conditions to give cyclo-oligomeric structures.^[17d] Even more concerningly, the most active catalyst with slender methyl groups succumbed to a bimolecular decomposition pathway under conditions relevant to catalysis. The resulting binuclear Mo≡Mo species is a thermodynamic dead end and does not engage in alkyne metathesis.^[80]

While a high level of sophistication has been reached in catalyst design using molybdenum alkylidyne, rhenium alkylidyne had been neglected for most of alkyne metathesis history. All the more surprising was the presentation of the first non-d⁰ rhenium alkylidyne complex **9** capable of catalyzing alkyne metathesis by the group of *Jia* in 2020 (*scheme 11*).^[42]



Scheme 11: Preparation of the first catalytically active Re(V) alkylidyne complex.

Stoichiometric alkyne metathesis had previously been achieved with rhenium (V) complex **20** and insightful reasoning had led to the design of bidentate phosphino-phenolates (**21**) as suitable ligands for rendering the process catalytic.^[81] For alkyne metathesis with a six-coordinate rhenium (V) complex, a slightly different mechanistic sequence has to be considered (*scheme 12* and *chapter 1.1.5*).^[82]



Scheme 12: Mechanism for alkyne metathesis reactions of six-coordinate Re(V) alkylidyne complexes.

The first and presumably rate determining step is the dissociation of a labile ligand to free a coordination site for the incoming alkyne (**B**).^[83] Upon association there are two possible coordination modes for the substrate. In rhenium (V) complexes the electronically preferred isomer is **C** with the alkyne perpendicular to the alkylidyne unit.^[81a] To promote the rotation into the conformation **C'** necessary for productive cycloaddition ligands have to be chosen which destabilize **C**. This can be accomplished by placing steric bulk in the *cis* position of the alkyne forcing it into a conformation parallel to the alkylidyne ligand so that the MCB **D** can be formed. Another design feature of the ligands is their bidentate nature, which ensures further ligand dissociation towards an unproductive five-coordinated species to be suppressed. The resulting complexes exhibit good reactivity even though frequently high temperatures are needed. The true strength of these complexes lies in their superb functional group tolerance: protic groups pose no problem and even substrates containing carboxylic acids are compatible, which instantly deactivate molybdenum (VI) or tungsten (VI) alkylidyne catalysts.^[84] Furthermore, several of the complexes were shown to be air-stable. To date, these recent catalysts have not been tested in the synthesis of truly complex molecules (e.g., natural products), but the generally better stability of middle/late transition metals towards oxygen and water holds great promise for the future.^[3c]

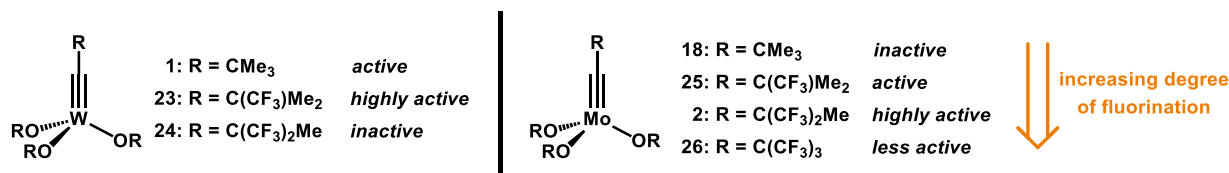
The synopsis of the most important milestones in alkyne metathesis history highlights how far this fundamental reactivity has come in half a century. The reaction mechanism is fairly well understood, active catalysts with three different transition metals have been identified and several reaction types useful for organic synthesis have been put forward. So far the interest in alkyne metathesis has largely been of academic nature and practical aspects remain underexplored. Accordingly, the use of the knowledge gained for designing catalysts and reactions with an orientation towards a more general applicability is a major concern of current alkyne metathesis research.

Subsequent chapters offer a more thorough examination of selected aspects deemed pertinent to the research that follows.

1.1.3 Molybdenum Alkylidyne Catalysts

While the first well-defined catalysts for alkyne metathesis were tungsten alkylidynes, a majority of the modern systems are based on molybdenum. This may appear counterintuitive, given that initial research indicated molybdenum alkylidynes to be comparatively less reactive.^[39-40] The molybdenum complex **18** analogous to *Schrock's* original tungsten catalyst **1** is virtually inactive and more electron-deficient donor ligands were required to obtain a good catalyst (*scheme 13*). Ironically however, exactly the inherently higher Lewis acidity of tungsten (VI) complexes limits their potential for applications. Even the fairly tame complex **1** was deactivated by substrates containing a thioether, a pyridine or an electron deficient alkyne.^[49] In contrast, molybdenum alkylidynes tolerate all these potentially coordinating functional groups.

A reinvestigation of the early catalyst systems by the group of *Tamm* outlines the fundamental differences in reactivity and highlights the importance of the ancillary ligands.^[85]

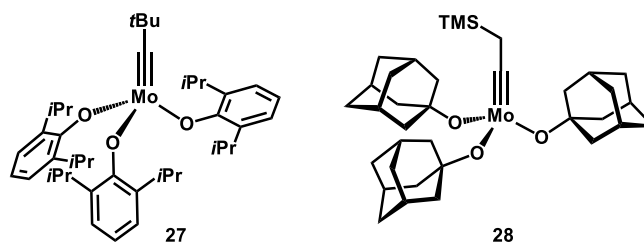


Scheme 13: Differences in the reactivity of (fluoro)-alkoxide supported tungsten and molybdenum alkylidynes.

As the degree of fluorination on the supporting alkoxide ligands increases, the reactivity is first enhanced and then diminishes again (**24** is already completely inactive). However, the peak in terms of activity is reached for different degrees of fluorination in tungsten (**23**) and molybdenum (**2**). The data indicates the necessity for striking a fine balance in order to avoid over stabilizing any state on the catalytic cycle. For the relatively electron-rich **18** the barrier for the cycloaddition is too high and for the extremely electron-poor **26** the cycloreversion from the MCBP is disfavored. For the latter, this fact has allowed the relevant MCBPs to be isolated.^[35b, 85]

Accordingly, the ancillary ligands have to be carefully chosen in order to make the metal center sufficiently electrophilic but not overly electrophilic. With a formally d⁰-metal, reactivity depends largely on the donor capabilities of the ligands. Early on, electron-rich alkyl as well as thiolate ligands were shown to have a detrimental effect on catalytic performance.^[39-40, 84, 86] Phenolates, fluorinated alkoxides, and silanolates on the other hand were found to yield active catalysts.^[39-40, 57b] A deviation from this rule are aniline ligands, which support the catalysts obtained *in situ* from **3**.^[50] A thorough investigation of the electronic effects exerted by the ligands in these species has not been undertaken. However, for related systems the aniline ligands were described to be exchanged by protonolysis for phenolate or silanolate ligands in order to obtain better catalytic performance.^[54, 87]

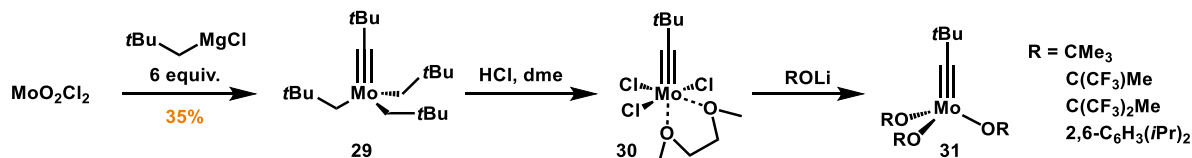
The ligand size also seems to play a role (*scheme 14*).^[39, 52b] The ligands must exhibit sufficient bulk to prevent decomposition through bimolecular processes and to avoid polymerization of substrates through an associative pathway.^[17d, 38c]



Scheme 14: Examples of molybdenum based alkyne metathesis catalysts with sterically demanding ligands.

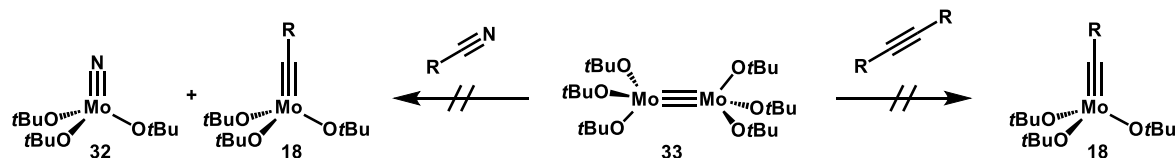
Ligands with large steric bulk destabilize the MCB intermediate with its more crowded trigonal bipyramidal geometry. As a consequence, the energetic barrier for substrate association is raised. Conversely, cycloreversion and product expulsion are in turn more favored.^[38b] Akin to the electronic influences, a fine balance has to be found.

To access the plethora of molybdenum alkylidyne catalysts known today, an efficient route for their synthesis had to be found. The first examples were obtained through exhaustive alkylation and subsequent α -hydrogen abstraction on a molybdenum (VI) complex.^[88] A parallel route had been successfully employed to access the first tungsten neopentylidyne complexes. Unfortunately, in the case of molybdenum the synthesis was low yielding and not scalable (*scheme 15*).^[39]



Scheme 15: Synthesis of early molybdenum alkylidynes via alkylation and α -hydrogen abstraction.

The second route developed to synthesize tungsten alkylidynes also failed in the case of molybdenum.^[89] The cleavage of metal-metal triple bonds in binuclear molybdenum complexes (**33**) with alkynes or nitriles is generally disfavored (*scheme 16*).^[71a, 80]



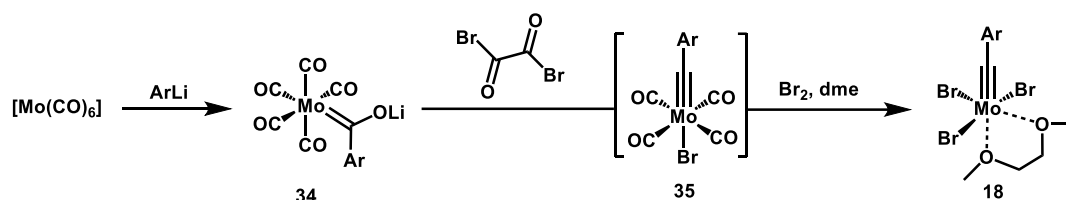
Scheme 16: Examples for the unsuccessful cleavage of binuclear molybdenum complexes.

For this reason, most initial insights concerning alkyne metathesis were obtained from tungsten alkylidynes. It was not until the turn of the century and the discovery of *in situ* activated systems by *Fürstner* and coworkers for molybdenum to move into the focus.^[50] The incomplete understanding of this activation process will be discussed in *chapter 1.1.3.1*. For now, it suffices to say, that the system did not lend itself to the straightforward synthesis of a large library of molybdenum alkylidyne catalysts. Although a few well-defined and structurally

characterized complexes are known, in the majority of cases the actual catalytic species is formed by *in situ* complexation with a range of ligands.^[43b, 44a, 73, 90]

The strategy explored by *Johnson*, which involved the transformation of molybdenum nitrido complexes into molybdenum alkylidyne complexes, also lacked the necessary degree of generality.^[56] The equilibrium appears to be highly contingent on the ligand sphere which complicates the targeted synthesis of alkyne metathesis catalysts with specific ligands.

Faced with this problem the groups of *Fürstner* and *Tamm* revived carbyne/alkylidyne chemistry which had been known since the 1980s.^[31b, 65] The pertinent route starts with molybdenum hexacarbonyl and relies on the oxidation of a low-valent ‘Fisher-type’ carbyne into a ‘Schrock-type’ alkylidyne (*scheme 17*). Consequently, the term ‘low-oxidation-state’ route was coined to differentiate it from the traditional ‘high-oxidation-state’ route starting with molybdenum (VI) complexes.



Scheme 17: ‘Low-oxidation-state’ route to access molybdenum alkylidyne complexes.

The synthesis is based on several publications by *Mayr* and coworkers and starts with the nucleophilic addition of an aryl lithium species to molybdenum hexacarbonyl.^[19] The resulting ‘Fisher-type’ carbene **34** is treated with oxalyl bromide to formally abstract an oxide from the acyl ligand.^[64b, c] The obtained carbyne **35** is highly instable. It is directly oxidized at $-78\text{ }^{\circ}\text{C}$ with bromine into a molybdenum (VI) ‘Schrock-type’ alkylidyne **18** and supported with a bidentate ligand such as dimethoxyethane (DME).^[64a] The halide ligands in precursor **18** can be replaced *via* salt metathesis with the desired anionic ligands of choice. In the initial publications the counterion of carbene **34** was exchanged to give an air-stable intermediate, but a subsequent reoptimization showed the step can be skipped as long as all procedures are carried out under inert-atmosphere.^[91] Overall, the ‘low-oxidation-state’ route has been demonstrated to be reasonably scalable and has allowed a variety of molybdenum catalysts to be synthesized.^[16a, 31b] It currently serves as the standard in the field.

Building on this groundwork, the group of *Buchmeiser* was able to obtain a series of cationic molybdenum alkylidyne complexes.^[92] The underlying idea stems from the field of alkene metathesis, where cationic complexes have been very successful. Adding strongly σ -donating NHCs to complexes such as **26** or **2** leads to the (partial) dissociation of an alkoxide ligand, revealing highly active catalysts.^[93] Although reports on their use in synthesis are scarce so far, this conceptually different approach might hold merit in the future.

1.1.3.1 *In situ* activated Systems

This chapter will discuss catalyst systems in which the catalytically active species is either unknown or has to be generated *in situ*.

The ‘*Mortreux* system’ is the oldest among the catalysts for homogeneous alkyne metathesis.^[32] Originally referring to a mixture of molybdenum hexacarbonyl and resorcinol, the concept extends to an assortment of molybdenum sources and additives (*figure 2*).^[30]

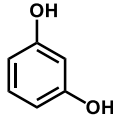
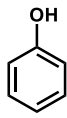
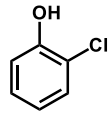
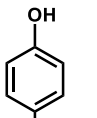
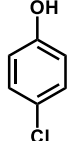
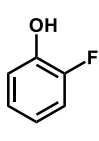
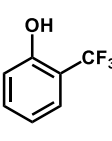
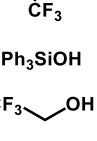
Molybdenum sources		Additives/Ligands			
[Mo(CO) ₆]	[Mo(CO) ₃ (COD)]				
[Mo(CO) ₃ (MeCN) ₃]	[Mo(CO) ₄ (ndb)]				
[Mo(CO) ₃ (PhCN) ₃]	[Mo(CO) ₃ (mes)]				
[Mo(CO) ₃ (Py) ₃]	[MoO ₂ (acac) ₂] / AlEt ₃				
[Mo(dppe) ₂ (N ₂) ₂]	[MoCl ₂ (NO) ₂ (Py) ₂] / AlEt ₃				

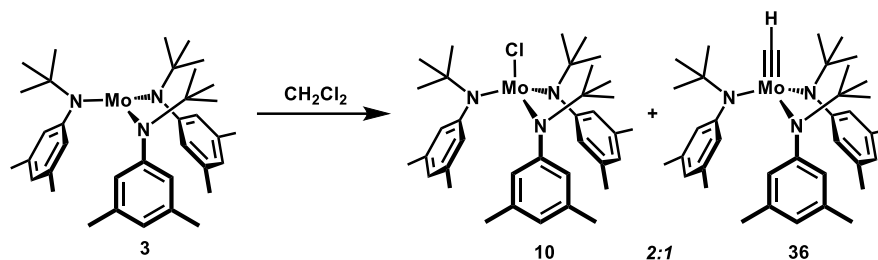
Figure 2: Examples of molybdenum sources and additives used in ‘*Mortreux*-type’ catalytic systems.

Most reported metal precatalyst are low valent. The two exceptions, namely [MoO₂(acac)₂] and [MoCl₂(NO)₂(Py)₂] were reported by *Mortreux* to require alkyl aluminum reagents as co-reactants.^[94] In these cases, an activation pathway through alkylation and α -hydrogen abstraction similar to *Schrock*’s route to high-valent alkylidynes, is conceivable. However, for the molybdenum (o) precursors the mechanism by which the active species is generated remains unclear. Empirical studies have shown that replacing some carbonyl ligands in the molybdenum source with more labile ligands (e.g., COD) is beneficial to the overall catalytic activity. The result suggests at least partial dissociation of the carbonyl ligands is necessary.^[95] Further, the addition of phenols, silanols or alcohols is essential to obtain reactivity.^[63, 96] The assortment of suitable additives has a suspicious overlap with the ligands for well-defined molybdenum alkylidyne catalysts, suggesting the (at least transient) formation of such species in the reaction mixture. In line, more electron deficient phenols and silanols were found to be rate accelerating.^[63] Different forms of activation were shown to be effective: the traditional approach of heating the system in the presence of an alkyne demonstrated turnovers starting at 110 °C; microwave irradiation has been employed to the same effect.^[96a, 97] Interestingly, UV light was recently reported to activate the system at ambient temperatures.^[63] However, issues with conversion and catalyst deactivation ensued.

In summary, the ‘*Mortreux*-system’ remains poorly understood despite considerable research efforts.^[30, 98] Together with the harsh conditions required (temperatures above 110 °C), typically high concentrations of the additives (0.5 to 1.5 equiv.), and limited functional group tolerance, the catalyst system does not invite application to the synthesis of complex molecules.^[49] On the other hand, the *off-the-shelf* nature (availability and low price of the components) makes the system attractive to the wider chemical community which is not

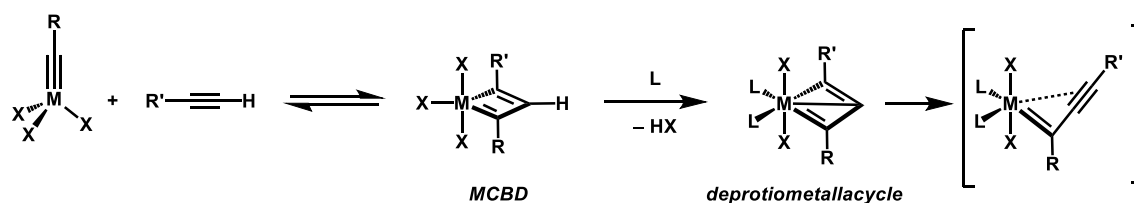
specialized on alkyne metathesis catalysis. Accordingly, some applications from the field of dynamic covalent chemistry and in the total syntheses of (–)-nakadomarin A and the turrianes have been reported.^[33, 97, 99]

At the turn of the century, *Fürstner* and coworkers were on the search for an improved molybdenum-based catalyst due to the discussed issues with the ‘*Mortreux*-system’ and the limited functional group tolerance of well-defined tungsten catalysts. Activation of the highly reactive molybdenum (III) trisamide complex **3** with methylene chloride gave a mixture with excellent catalytic reactivity (*scheme 18*).^[50]



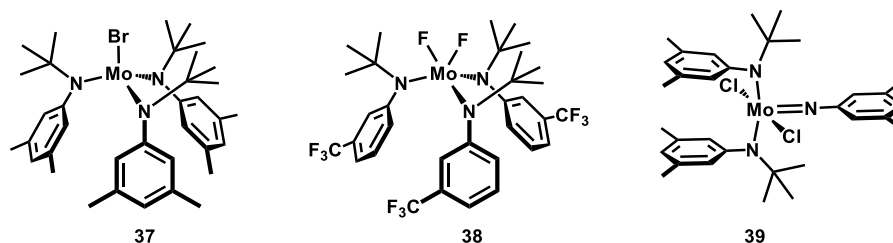
Scheme 18: Activation of the Mo(III) complex with methylene chloride gives a catalytically active mixture.

Careful analysis of the activation reaction revealed chloride complex **10** and methylidyne complex **36** as the major products. Counterintuitively, the later was shown to be catalytically inactive after one turn-over.^[53] A probable decomposition pathway is the deprotonation of the formed MCBd under concomitant ligand-loss: a phenomenon that has been observed in alkyne metathesis reactions of terminal alkynes with tungsten alkylidynes (*scheme 19*).^[40, 100]



Scheme 19: Catalyst deactivation pathway proposed by Schrock in the metathesis of terminal alkynes.

In contrast, the molybdenum (IV) chloride complex **10** was able to sustain alkyne metathesis reactivity. The exact mechanism of how the molybdenum chloride reacts with an alkyne to form the propagating species has never been elucidated.



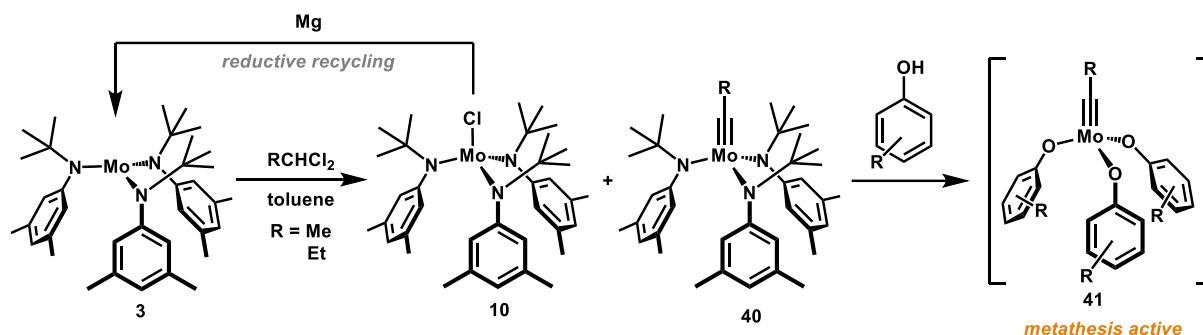
Scheme 20: Catalytically active molybdenum species with mixed halide/amine ligand spheres.

However, several related species containing halogenated molybdenum centers were also shown to be catalytically active for alkyne metathesis (*scheme 20*).^[53] It could be speculated that molybdenum alkylidynes with mixed halide/amide ligand spheres are competent alkyne

metathesis catalysts. In one instance *Schrock* referred to an undefined impurity likely containing a tungsten chloride/amide complex as the catalytically active species, but no clear results were ever reported.^[101] Further circumstantial evidence comes from related systems generated from molybdenum alkylidyne trisamide complex **40** and tridentate phenol ligands **7** which demand chlorinated solvents in order to sustain catalytic activity. Other commonly used solvents (e.g., toluene) led to a significant reduction in turnovers, suggesting an active involvement of the solvents (carbon tetrachloride, chloroform, or chlorobenzene).^[43b]

Be that as it may, the combination of the molybdenum (III) complex **3** and dichloromethane was applied for RCAM reactions in the synthesis of numerous macrocyclic natural products.^[102] The mixture exhibits a robust functional group tolerance, transforming substrates containing thioethers, pyridines, sulfones, aldehydes, nitro groups, nitriles, and primary alkyl chlorides.^[53] The new protocol was proven superior in direct comparison with the ‘*Mortreux* system’ and *Schrock*’s catalyst in several instances.^[102f, g, 103] The enhanced activity also allowed for generally lower reaction temperatures (approx. 80 °C). Still, working with the molybdenum (III) complex **3** requires rigorously dried solvents and strict exclusion of air and moisture throughout the reaction. Arguably a drawback in practical terms when compared to the more forgiving ‘*Mortreux* system’.

Based on the *in situ* activation strategy, a more elaborate approach was developed by *Zhang* and *Moore* for synthesizing molybdenum alkylidynes from complex **3**. Using higher *gem*-chlorides instead of dichloromethane the ethylidyne and propylidyne variants could be prepared (*scheme 21*).^[44a, 54]



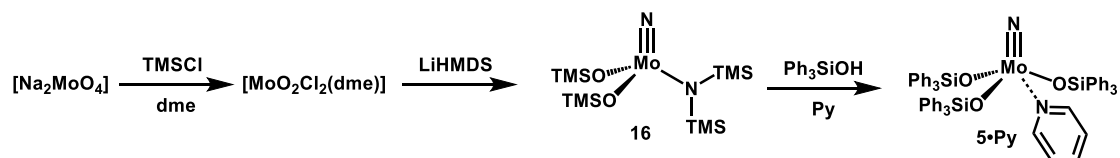
Scheme 21: ‘Second-generation’ activation strategy and reductive recycling of the chloride complex.

The loss of two-thirds of the submitted molybdenum into the chloride complex **10** was prevented by the recycling of the halide complex into the starting material with a suitable reductant. Overall, nearly quantitative yields of the molybdenum alkylidynes **40** could be isolated. Although direct reports on the alkyne metathesis activity of these complexes are scarce, protonolysis with a variety of (preferably electron deficient) phenols (or fluorinated alcohols and later also silanols)^[87] are presumed to give complexes of type **41**, which show good reactivity even at ambient temperature.^[44a] However, the isolation of the formed alkoxide and phenoxide complexes proved to be troublesome and characterization by X-ray crystallography has only been reported for one example.^[52b] For this reason, these types of complexes are

grouped into the section for catalysts with unknown active species. Nevertheless, the first method for synthesizing preparative meaningful amounts of molybdenum alkylidyne in a straightforward manner has had a large impact on the field.^[23b, 69, 73] The *in situ* combination with phenol or silanol ligands has been regularly applied in material sciences and immobilized variants have been reported.^[44b, 55, 67, 87, 104]

1.1.3.2 Molybdenum Alkylidyne Complexes with Silanolate Ligands

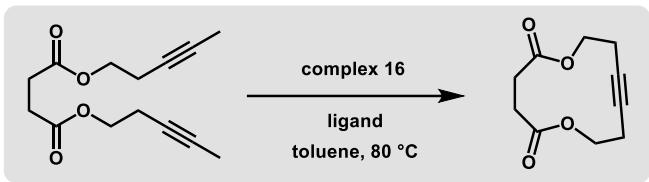
The continued search for a route providing facile access to molybdenum alkylidyne without a detour through the highly sensitive and difficult to manipulate molybdenum (III) complex **3**, led to the synthesis of the molybdenum nitrido precursor **16** (*scheme 22*).^[57b] Fürstner and coworkers devised a novel route that avoids the large scale use of sodium azide employed by Johnson in his related synthesis of molybdenum nitrido complexes.^[17a, 56]

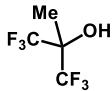
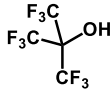
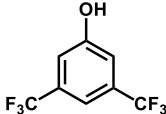
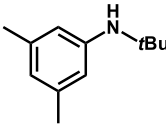
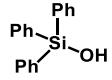


Scheme 22: Preparation of the precatalyst molybdenum nitrido complex with silanolate ligands.

To effect this, sodium molybdate, a readily available salt, was treated with trimethylsilyl chloride, resulting in the formation of the dimethoxyethane stabilized bis-chloride complex. Reaction with lithium hexamethyldisilazide provided nitrido complex **16** in good overall yield (*scheme 22*). The complex was used to screen for alkyne metathesis activity with a row of ligands (*table 2*). The best results were obtained in combination with triphenylsilanol. In an attempt to move away from systems relying on *in situ* complexation, considerable efforts were undertaken to characterize the actual complex. Ultimately, addition of pyridine enabled the isolation of precatalyst **5**. Moreover, the labile ligand turned out to have a positive impact on the overall stability making it possible to weigh complex **5•Py** in air, which marks a substantial improvement considering the sensitivity of previous precatalysts such as molybdenum (III) complex **3**.

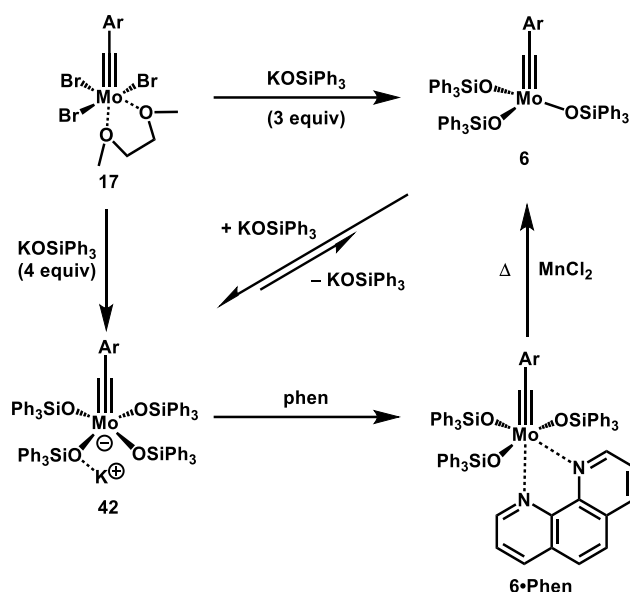
The more important point, however, was the first report of silanolate ligands enabling higher activity in direct comparison with fluorinated alcohols, phenols, and amides (*table 2*). While there had been several reports of silanols in the context of alkyne metathesis, these reports failed to notice the large potential of such ligands for homogeneous alkyne metathesis catalysis.^[105] The robust activity exhibited by nitrido complex **5•Py** is truly impressive considering its nature as a precursor for the actual catalytic species, even more so since NMR studies showed only small amounts of the complex are being transformed into the active molybdenum alkylidyne.^[31b]

Table 2: Screening of selected ligands for alkyne metathesis with precatalyst **16**.^[57b]


Ligand	t [h]	NMR yield
	18	<5%
	18	19%
	18	<5%
	18	<5%
	1.5	83%

Shortly after the initial publication, *Moore* and coworkers showed that the catalytic activity of nitrido complexes can be enhanced by Lewis-acid activation of the nitride.^[57a] Despite the solid performance of nitrido precatalysts, they were only briefly in use before further catalyst development made them irrelevant.^[106]

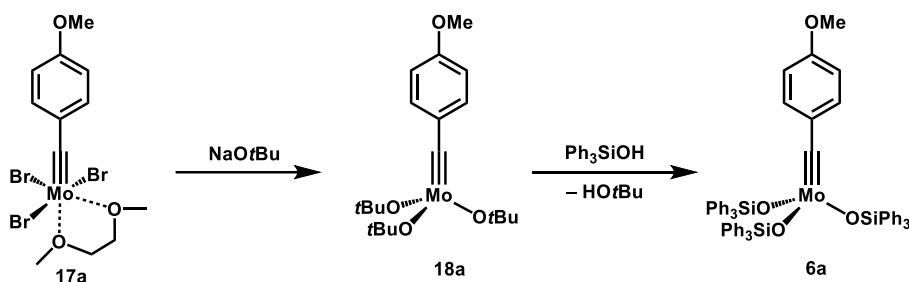
Fürstner and coworkers, convinced of the favorable properties of the newly discovered ligands, targeted the synthesis of the elusive silanolate supported molybdenum alkylidyne, hypothesizing that this was the actual active species during the reaction. With the aid of the 'low-oxidation' state route delineated in *scheme 17*, they were able to obtain trisbromide complex **17**.^[31b, 43a] Salt metathesis with potassium triphenylsilanolate gave the desired complex **6**. Inaccuracies in the equivalents of the ligand salt, or too hasty addition, resulted in the formation of the related ate-complex **42** (*scheme 23*). Steric influences from differently substituted benzylidyne units also had an effect on which complex was obtained. In solution partial dissociation of the fourth silanolate releases the neutral complex. Owing to these hurdles in preparing the pure neutral complex **6**, references to the use of the ate-complex **42** or the diethyl ether adduct of complex **42** or **6** as catalysts can be found in the older literature. An alternative route to the neutral complex leads through the stabilization with 1,10-phenanthroline.



Scheme 23: Synthesis and stabilization of a triphenylsilanolate molybdenum benzylidyne complex.

Originally investigated as an alternative to the pyridine in the nitrido complex **5•Py**, adducts of the type **6•Phen** were shown to be entirely bench-stable for >1 year. In solution removal of the bidentate ligand with the aid of a Lewis acid and raised temperatures releases the neutral species **6**.^[31b]

In 2021, *Fürstner* and coworkers published an updated and improved direct synthesis of the neutral complex **6**.^[16a, 91] *Scheme 24* shows the synthesis of the most active variant (**6a**) of complex **6** with an anisol benzylidyne unit. Herein, first a salt metathesis with highly sterically demanding sodium *tert*-butoxide gives the neutral metathesis-inactive alkoxide complex **18a**. Due to the higher acidity of silanols in lieu of alcohols, mild protonolysis with triphenylsilanol afforded complex **6a** on gram scale.



Scheme 24: Improved synthesis of the most commonly used variant of complex **6**.

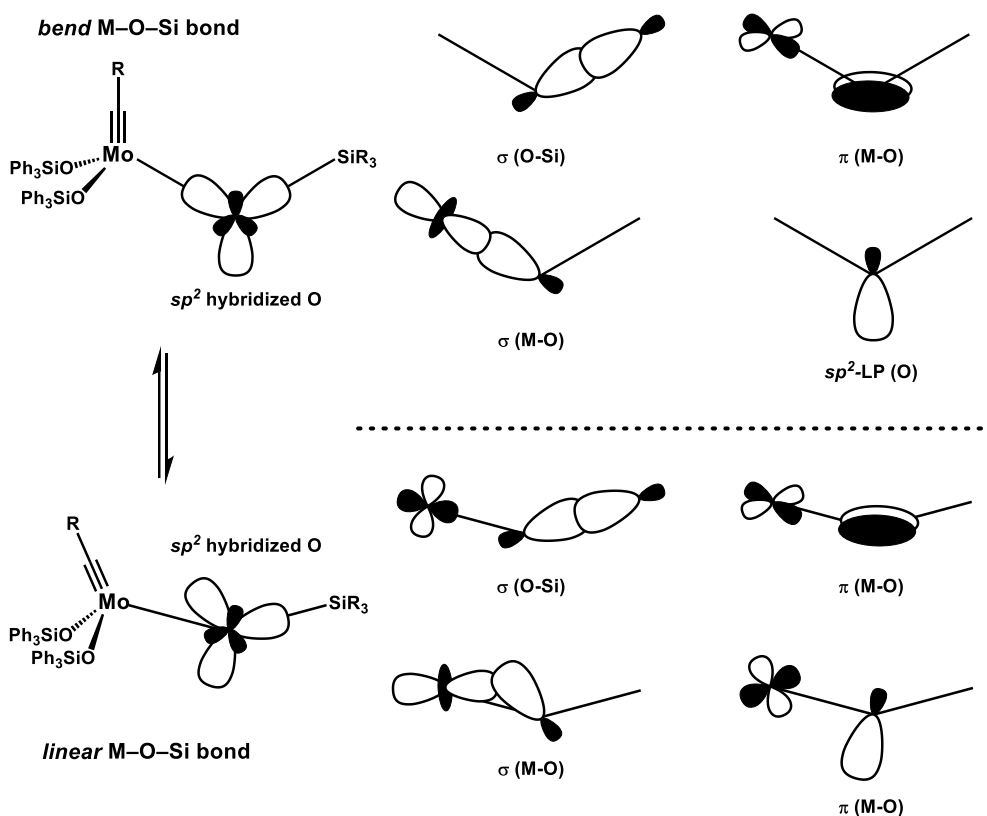
Complex **6** constituted the first highly active well-defined molybdenum alkylidyne catalyst which could be readily synthesized on gram scale after a decade of using *in situ* activated systems and precatalysts. This facilitated comprehensive investigations into alternations within the ligand sphere, as well as the mechanism and decomposition pathways.^[43a, 107] The excellent synergy between silanolate ligands and molybdenum alkylidynes manifests itself in an outstanding activity. In direct comparison to *Schrock's* complex **1**, the only other available well-defined catalyst, full conversion was reached in the homodimerization of 1-phenyl-prop-

1-yne within three minutes, whereas the tungsten alkylidyne converted only 20% of the substrate in 60 min at ambient temperature.

The exceptional performance was reasoned to be a consequence of the adaptive ligand properties of silanolates. As previously mentioned, a delicate electronic balance has to be maintained in order to be able to proceed through the whole catalytic cycle.

Considering the bonding situation of silanolate ligands with the metal, it is evident that both a σ -bond as well as π -bonds are formed. Since the molybdenum (VI) has a formal configuration of d^0 , the electron density at the metal strongly depends on the bond strength or rather the dominating factor herein: the electron donation from the ligands. However, π -donation is reduced in silanolates due to back-bonding of the filled sp^2 -orbitals (O) into the empty low lying σ^* -antibonding orbitals of the Si–C bond. Thus silanolates are considered weaker net donors in comparison with alkoxides, upregulating the Lewis acidity of the molybdenum center.^[108]

Beyond that, the true advantage of silanolates is their changing donor properties, which are dependent on the O–Si–Mo bond angle. The linkage is highly flexible and can freely change between a bend (120°) or approximately linear (180°) geometry at ambient temperature (scheme 25).



Scheme 25: Illustrative molecular orbitals explaining the angle-dependent bonding of silanolates.

Initially, the bend conformation was postulated to render the molybdenum more Lewis acidic. This was based on the unfavorable overlap of the lone-pairs at the oxygen with the d -orbital at the metal.^[16b] However, more recent computational studies by Füstner and Neese revealed

the σ -bond to be the deciding factor.^[61] Although the π -bonds formed between the sp^2 -orbitals (O) and the d -orbitals (Mo) are stronger in the linear geometry, the decreased orbital overlap for the σ -bond overcompensates the effect (*scheme 25*). Accordingly, the linear conformation renders the molybdenum center more Lewis acidic. The hypothesis could be substantiated by means of the ^{95}Mo ssNMR shifts, which can be correlated with the electron density at the metal.^[78]

Independent of which geometry corresponds to a more Lewis acidic metal, the fundamental concept of adaptive silanolate ligands remains the same. For this reason, it is believed that molybdenum catalysts supported by silanolate ligands are capable of efficiently addressing the disparate electronic demands of the alkyne metathesis cycle. In 2021, supplementary experiments led to the isolation of the intermediate MCBD formed from parent complex **6** with hex-3-yne, showcasing the effortless accessibility of the necessary intermediates (*figure 3*).^[36a]

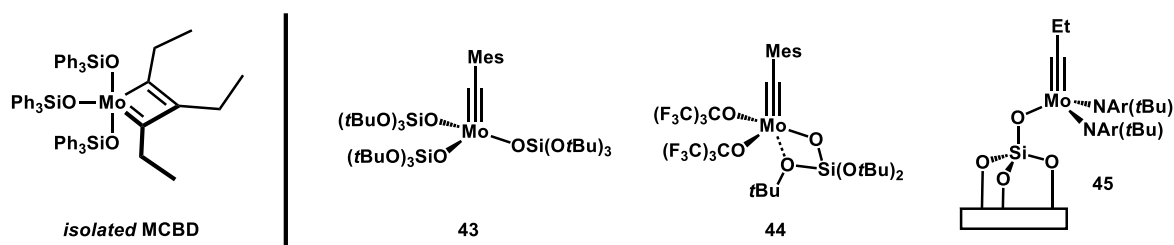


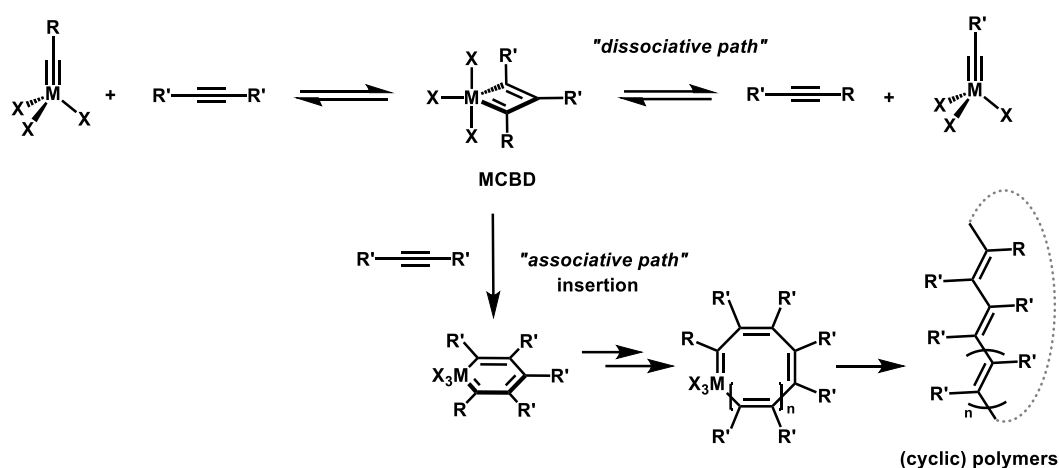
Figure 3: Isolated MCBD with Ph_3SiO -ligands and representatives of other silanolate-supported catalysts.

Besides the complex carrying triphenylsilanolate ligands, a row of other silanolate supported molybdenum alkylidynes are known. Three representatives are shown in *figure 3*. The use of *tert*-butoxysilanols as ligands led to reduced catalytic activity (**43**), presumably due to the changed electronic properties of the silanolates, as well as the excessive steric bulk.^[109] Heteroleptic complex **44** with a ligand sphere containing silanolates and fluorinated alkoxides showed good activity in alkyne metathesis.^[110] The *tert*-butoxysilanolate somewhat counterbalances the perfluorinated alkoxide ligands, which had previously been shown to decrease the catalytic activity through rendering the metal overly Lewis acidic. The secondary molybdenum oxygen interaction present in the molecular structure obtained from X-ray diffraction analysis is dynamic in solution and presumably of little relevance to catalysis.^[111] Complex **45** represents one of the first attempts at immobilizing well-defined molybdenum alkylidynes on silica surfaces.^[55, 105c] Several other catalysts have been grafted onto silica showing good activity, but only few applications have been reported.^[85, 110, 112]

In contrast, complex **6** is arguably the most commonly applied alkyne metathesis catalyst in natural product synthesis. Its discovery was followed by a burst of reports from the *Fürstner* laboratory and other groups on the syntheses of natural products obtained *via* RCAM.^[25, 66a, c, d, f, j, 113] The introduction of silanolates as privileged ligands for alkyne metathesis also led to their application in the before-hand described *in situ* systems.^[87]

1.1.3.3 Molybdenum Alkylidyne Complexes with Tripodal Ligands

In parallel to the developments around silanolate based molybdenum alkylidynes, another important innovation for alkyne metathesis catalysis was made by the group of *Zhang*. They introduced a tridentate ligand design with the intent of preventing undesirable polymerization of alkyne substrates.^[69b] This side reaction had plagued alkyne metathesis catalysis since its beginning and was proposed by *Schrock* to arise through the reaction of the MCBF with an additional substrate *via* an ‘associative path’ (*scheme 26*).^[71b]

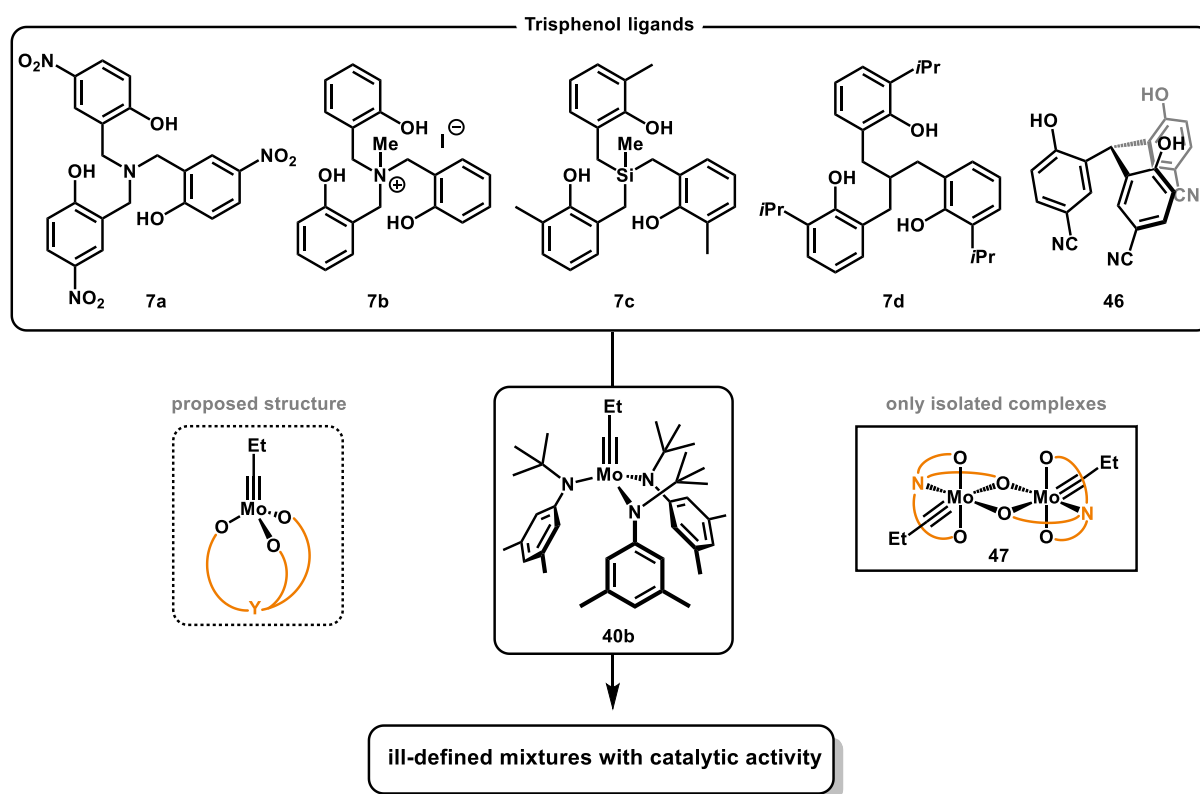


Scheme 26: Productive ‘dissociative path’ or ‘associative path’ leading to polymerization.

A recent review on generating cyclic polymers from alkynes indicates the picture to be somewhat more complicated, with several possible mechanisms and linear as well as cyclic polymers being formed.^[18] In any case, the loss of material towards polymeric products is a frequent problem when working with catalyst adorned with ‘slimmer’ ligands or ill-defined systems.^[44a, 114] For this reason, sterically demanding ligands, such as triphenylsilanolates, are frequently preferred in catalyst design, as they impede the binding of an additional substrate. On the other hand, excessive steric hindrance can prevent the RCAM of densely decorated diynes.^[66h, i, 115] The expedient removal of the small, polymerization-prone by-product (e.g., but-2-yne) also plays a decisive role. However, for applications in dynamic covalent chemistry where reaching the thermodynamic equilibrium is the goal, this approach is not applicable. With this in mind, *Zhang* and coworkers combined the ligand **7a**, comprising three phenols tethered together by an amine linker, with the molybdenum alkylidyne **4ob**. The resulting mixture showed good activity in alkyne metathesis and did not give rise to any signs of polymerization, even when subjected to a substantial excess of but-2-yne.^[69b]

In the following years, the group of *Zhang* was able to extend the strategy to several generations of the conceptually same design (*scheme 27*). In the first iteration, the amine tether was alkylated to prevent the nitrogen from binding to the highly Lewis acidic molybdenum (VI) metal.^[90a] Indeed an increase in activity was observed, but the poor solubility of the ammonium

salt **7b** constituted a major disadvantage.^[70a] Switching to a neutral silicon atom as the linchpin remedied the issue (**7c**). To increase the overall stability the next generation **7d** used a central carbon atom instead of the silicon tether due to concerns about the carbon-silicon bond strength.^[70b] The latest iteration **46** changed the overall blueprint by removing the methylene spacer from the design in order to create an even tighter 'binding pocket'. This system was reported to enable alkyne metathesis reactions under open-to-air conditions.^[43b] However, attempts to do so by another laboratory have been met with failure.^[116]



Scheme 27: Catalyst systems with various generations of trisphenol ligands pioneered by Zhang and coworkers.

Overall, the systems show high alkyne metathesis reactivity and were able to transform substrates comprising challenging functionalities such as aldehydes, nitro groups, and electron deficient alkynes. Aldehydes are especially difficult since molybdenum alkylidyne complexes equipped with silanolates as well as tungsten catalysts decompose in their presence (presumably *via* a 'Wittig-type' reaction of the alkylidyne with the carbonyl).^[31b, 58, 96c]

Notwithstanding their performance, considerable doubts about the actual constitution of the catalytically active species persist. No structural data from single crystal X-ray diffraction has ever been reported that shows the ligands binding in a tripodal manner to a monomeric complex. The only data available for the solid-state stems from phenolate bridged dimers carrying nitrogen tethered ligands of the type **47** which were isolated from the catalyst mixtures.^[69b] In these, the nitrogen was shown to bind *cis* rather than *trans* to the molybdenum alkylidyne. What is more, the dimers were described as essentially inactive in alkyne metathesis, and some are stable in air and could even be purified by chromatography on silica.

The *Nuckolls* group managed to activate such a bridged compound by adding excess of a protic solvent (presumably breaking up the dimer).^[90b] The resulting mixture showed some alkyne metathesis activity, but again the exact nature of the species could not be determined. Extensive efforts to elucidate the structures of the created complexes in solution through NMR studies gave an ambiguous picture. On the one hand, free aniline ligand from the precursor could be detected, indicating the successful protonolysis with the phenol ligands. On the other hand, several signals for alkylidyne units were observed, indicating the formation of multiple species.^[43b, 70b] Thus, more information on these complexes is required to warrant the depiction of the ligands as binding in a tripodal manner.

Another prominent handicap of *Zhang's* catalyst systems is their need for chlorinated solvents (as discussed above). Hepatotoxic, ozone-depleting, and potentially carcinogenic carbon tetrachloride was repeatedly shown to give the best results.^[43b]

Motivated by the systems' favorable resistance against polymerization, the group of *Fürstner* presented their own set of tridentate ligands **48/49** with the important distinction of carrying three silanol ligands instead of the phenols propagated by *Zhang* and coworkers (*figure 4*).^[73] These systems met the same fate as described above: together with complex **40b** catalytically active mixtures were obtained, but the constitution of the active species as well as the exact binding mode of the ligands could never be elucidated. Even attempts at preorganizing the ligands in a tripodal fashion by selecting a 1,3,5-trisubstituted-2,4,6-triethylbenzene platform as the connecting unit did not change the outcome. These kind of benzene derivatives are known to adopt an alternating orientation and are widely used in the synthesis of cage compounds.^[117]

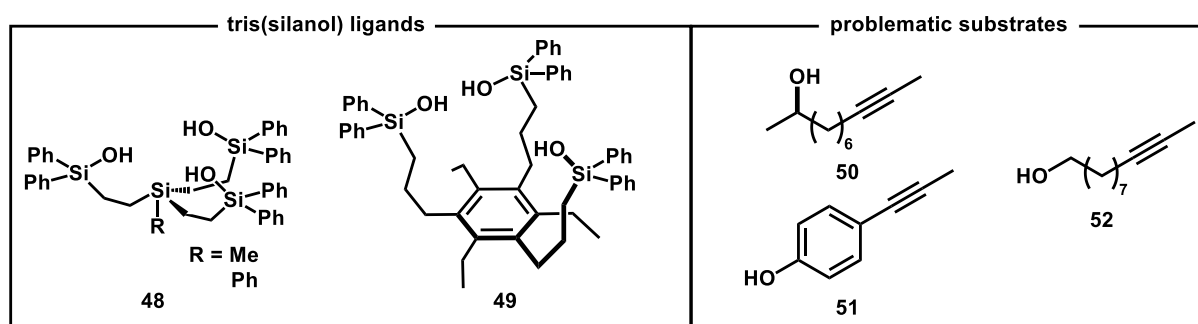


Figure 4: First generation tridentate tris-silanol ligands and substrates with problematic protic moieties.

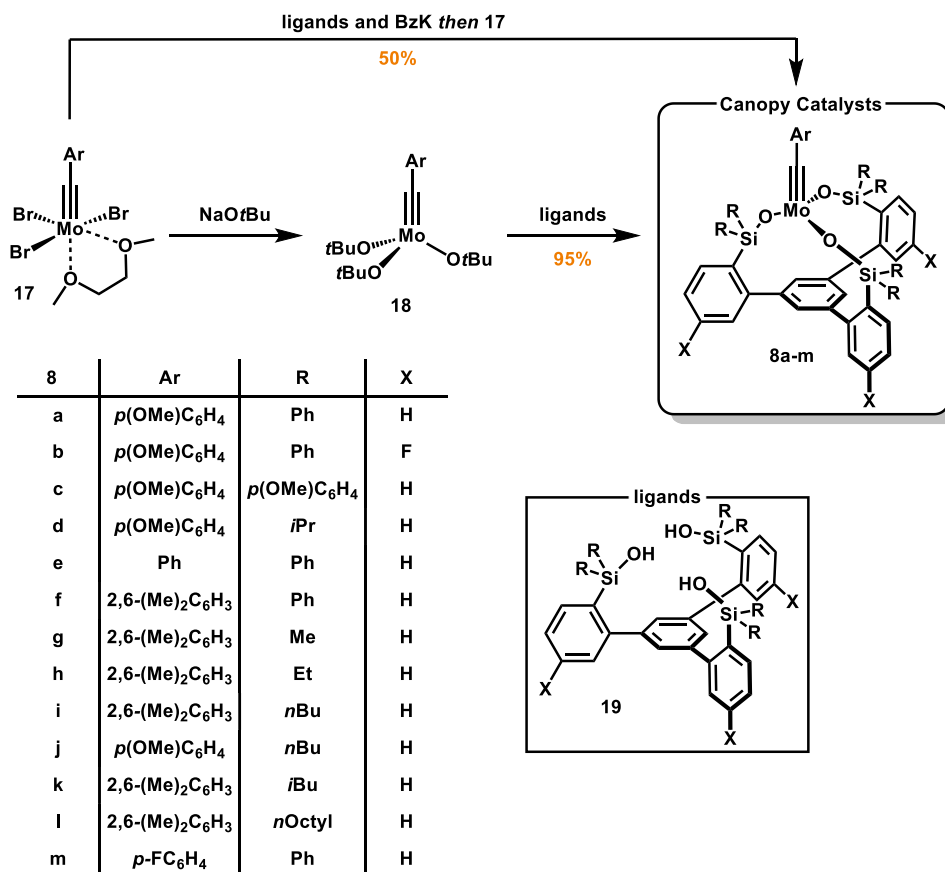
Over the years protic functional groups had emerged to be a challenge for complex **6** endowed with monodentate silanolate ligands. Although substrates carrying secondary alcohols (**50**) and phenols (**51**) could be transformed under somewhat forcing conditions, primary alcohols marked an important limit of its functional group compatibility. With respect to this, a key advantage of catalyst systems with tridentate tris-silanol ligands became apparent: these catalysts were able to transform substrates such as **52** in acceptable yields.^[73] The difference in performance was explained with the chelate effect; in the version with monodentate ligands,

the alcohol will eventually replace the silanolates in the presence of excess substrate, rendering the complex inactive for alkyne metathesis. In the case of the tridentate ligand, the loss of all silanolates is statistically less likely and the partial protonolysis presumably reversible.

An additional benefit of the ill-defined systems is their ability to catalyze the RCAM of densely functionalized diynes into highly strained rings as exemplified in the synthesis of (–)-Sinulariadiolide or Guangnamycin A alcohol.^[75b, c] Presumably this capability stems from the oligomeric nature of the catalyst systems. NMR-investigations indicated the presence of a multitude of species with generally broad signals. The ligands **48** and **49** are assumed to take the role of “cross-linkers” connecting several metal centers.^[73] A key factor seems to be the conformational flexibility caused by the alkyl chains connecting the ligands to the tether. The same reason is responsible for the reluctance of the system to form a well-defined complex with the ligand binding in a tripodal manner, which prevented the use of the more readily accessible tribromide precursor complex **17**. Despite considerable experimentation, all attempts at salt metathesis reactions towards a structurally defined complex or even catalytic reactivity failed.^[118]

The second generation of catalysts with tridentate silanolate ligands **8**, published by *Fürstner* and coworkers in 2019, made two pivotal changes to the design: a more rigid ligand **19** with only *sp*²-hybridized carbons in the scaffold, and a milder complexation method *via* protonolysis (*scheme 28*).^[76]

Molecular structures of the ligands obtained by X-ray diffraction showed them to be preorganized into the tripodal shape with the silanols orientated into an ‘all-inward’ and ‘all-upward’ conformation. Through this conformation, oligomerization could be avoided and the first well-defined molybdenum alkylidyne complexes with a tripodal ligand framework were obtained. The clean complexation was aided by the use of alkoxide precatalyst **18** prepared *via* salt metathesis with sodium *tert*-butoxide from trisbromide **17**. Although not strictly necessary, as shown by a publication from the *Lee* group on the same catalyst design without the use of precatalyst **18**, protonolysis has the advantage of being reversible.^[77] Undesirable crosslinking can thus be corrected in favor of the targeted tripodal conformation. This is reflected in higher yields obtained *via* the protonolysis route.^[36b]



Scheme 28: Synthesis of the ‘Canopy-catalysts’ and evaluated variations in the ligand sphere.

A large library of complexes with the same general blueprint was prepared (the table in *scheme 28* shows the iterations from the *Fürstner* group).^[74] Modifications at specific sites in the ligand sphere allowed for insights into their effects on the alkyne metathesis reaction. The prototype catalyst **8a** with phenyl substituted silanolate ligands and a *para*-methoxy benzylidyne unit closely resembles the parent complex **6a**. Comparison in a standardized benchmark reaction revealed it to be considerably less active for alkyne metathesis. Presumably, the rigidified podand form impedes the distortions necessary to reach the different geometries along the catalytic cycle.

Furthermore, complexes bearing the *para*-methoxy benzylidyne motive in combination with phenyl groups on the silanolates were plagued by an aggregation issue (**8a-c**, **e**, **m**). C-H/ π -interactions of the *ortho* protons on the benzylidyne unit with the phenyl rings on the ligands likely enabled the formation of dimers.^[91] Disruption of the interaction by changing to *iso*-propyl substituents on the silicon resulted in a monomeric complex (**8d**), but no activity was observed in the benchmark reaction at ambient temperature. Tackling the issue from the other side by changing the benzylidyne unit to 2,6-di(methyl) phenyl also gave a monomeric complex (**8f**). This motive was already reported to be instrumental in obtaining the neutral complexes instead of the ate versions in renditions with monodentate silanolate ligands.^[43a]

However, a price in the form of slower catalyst initiation must be paid for the steric bulk imposed by the two methyl substituents (**8a** vs. **f** and **i** vs. **j**).

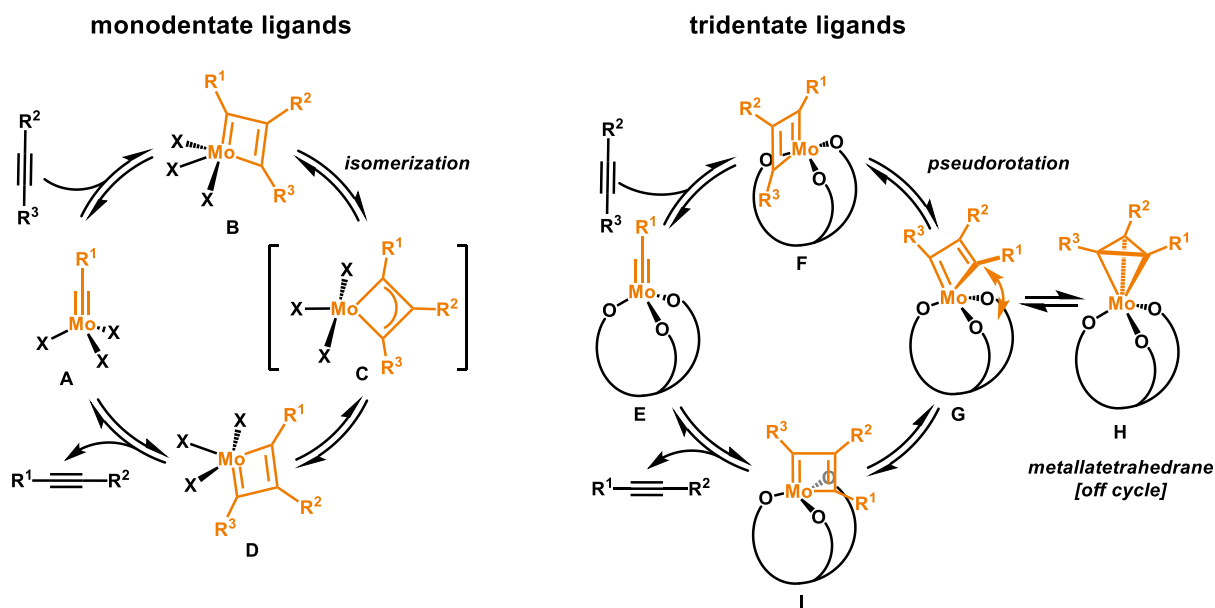
In turn, reducing the peripheral bulk of the tripodal ligand by exchanging the phenyl groups on the silanolates for smaller alkyl substituents had a drastic effect. The activity of catalyst **8g** equipped with methyl groups rivaled the monodentate parent complex.^[74] It was therefore named ‘turbo canopy catalyst’ as the most active variant of the whole family. Presumably, substrate binding is more facile with a smaller ‘fence’ around the metal center. Stepwise elongation of the alkyl substituents on the silicon led to an incremental reduction in reactivity (**8h-i**, **l**), although good overall activity is maintained as long as no branching is introduced (**8d**, **k**).

Adjusting the electronic influence of the ligands by substitution (**8b** and **c**) had little impact on the catalytic activity. The same applies to the electronic influence of the benzyldiene cap (**8a**, **e**, **f** and **m**), which is not surprising since it is lost during the first turnover of the catalyst.^[119]

The original study used solution state ⁹⁵Mo NMR to decode the electronic effects of different ligand classes on the catalytic activity.^[74] The obtained data was later corroborated with ssNMR data and indicated good catalytic activity for complexes with ⁹⁵Mo $\delta_{iso} > 350$ ppm.^[78] Through this, the explanation for the long known inactivity of molybdenum alkylidyne complexes with *tert*-butoxide ligands (excessive electron donation) was finally substantiated by directly probing the electronic character of the metal center (**18a**: ⁹⁵Mo $\delta_{iso} = 80$ ppm, Ar = *p*-MeOC₆H₄).

From the host of catalysts available, mainly **8a** and **8g** were investigated with regard to their functional group tolerance. Once more, the tridentate ligands paid valuable dividends, enabling the transformation of substrates containing primary alcohols with yields that parallel those achieved with catalysts comprising the first-generation tridentate ligands. A notable difference is that the ‘canopy catalyst’ are available as well-defined complexes in contrast to the ill-defined catalytic mixtures of the first-generation, which have to be prepared *in situ*. Overall, both catalysts were shown to have a similar scope, with **8g** transforming the substrates more quickly and in some cases reducing the amount of dimeric side products formed. For this reason, the ‘turbo canopy catalyst’ has become the catalyst of choice for natural product chemists in recent years.^[79, 120]

Having access to well-defined alkyne metathesis catalysts with tripodal ligands also allowed the groups of *Fürstner*, *Neese*, and *Lee* to investigate the mechanism by which these catalysts function. Addition of hex-3-yne to complex **8a** gave rise to a metallatetrahedran **H** (MTH) instead of the expected MCBD intermediate.^[36, 77] As already mentioned, only the MCBD was observed and isolated in the case of monodentate silanolate ligands. The discrepancy in behavior hinted at subtle changes in the mechanism (*scheme 29*).



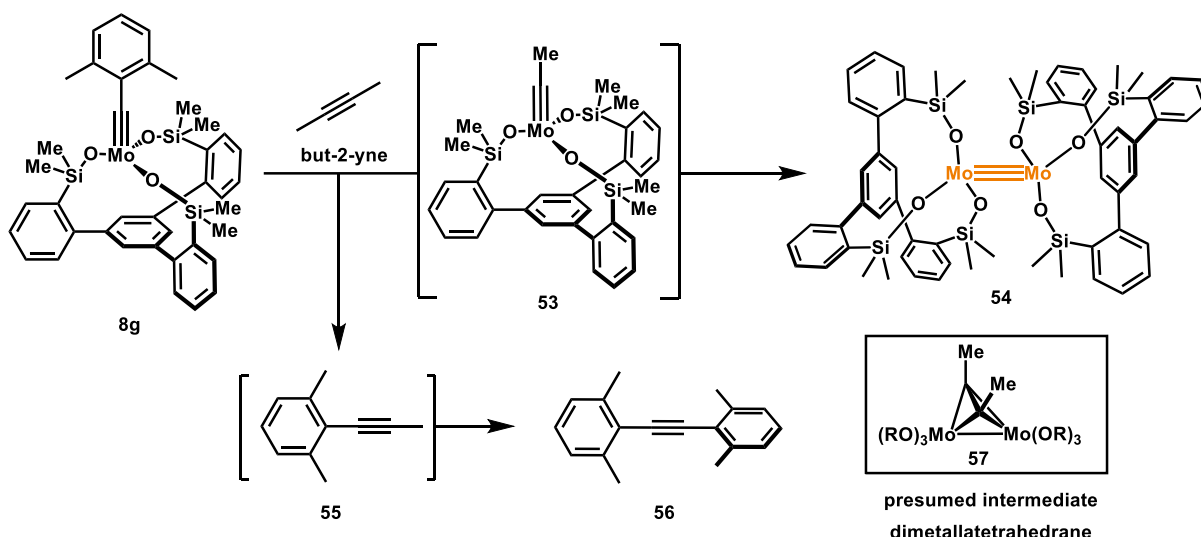
Scheme 29: Catalytic cycle for alkyne metathesis catalysts with tripodal ligands including a pseudorotation.

Considering the fundamental difference between the two types of ligands, it becomes obvious that the tether connecting the ligands in the tripodal version prevents the canonical isomerization of **B** into **D** through a trigonal bipyramidal transition state **C**. Being connected through the backbone hinders the ligands from passing through the mirror plan and reaching the productive isomer **D**.

Nevertheless, alkyne metathesis reactivity is observed for complexes with tripodal ligands. A combination of calculations, NMR-experiments, and crystallographic data strongly indicates a pseudorotation of **F** into **I** to be operative.^[36a] For this, the MCBF has to pass through a distorted conformation **G** rotating over one of the tethered ligand arms. This mechanism can also explain the observed MTH **H**, which arises from **G** and seems to be an off-cycle reservoir. Although itself not a productive intermediate for alkyne metathesis, its formation is reversible. The mechanistic ‘twist’ further clarifies why the steric bulk exhibited by substituents on the silanolates plays such a central role for the catalytic activity of the ‘canopy catalysts’.

Although the performance of the slimmest variant **8g** is truly impressive, in some applications high catalyst loadings were necessary.^[74, 79b] A closer inspection of possible decomposition pathways was therefore warranted.

Complications that arose during the synthesis of **8g** (e.g., an inseparable oligomeric impurity or the necessity of high dilution) had already foreshadowed this specific ligand to be the lower limit regarding steric bulk.^[74] Indeed, upon addition of but-2-yne to a catalyst solution the large ‘protective’ benzyldiyne unit is removed and after a short time the binuclear molybdenum (III) dimer **54** was observed (scheme 30).^[17d]

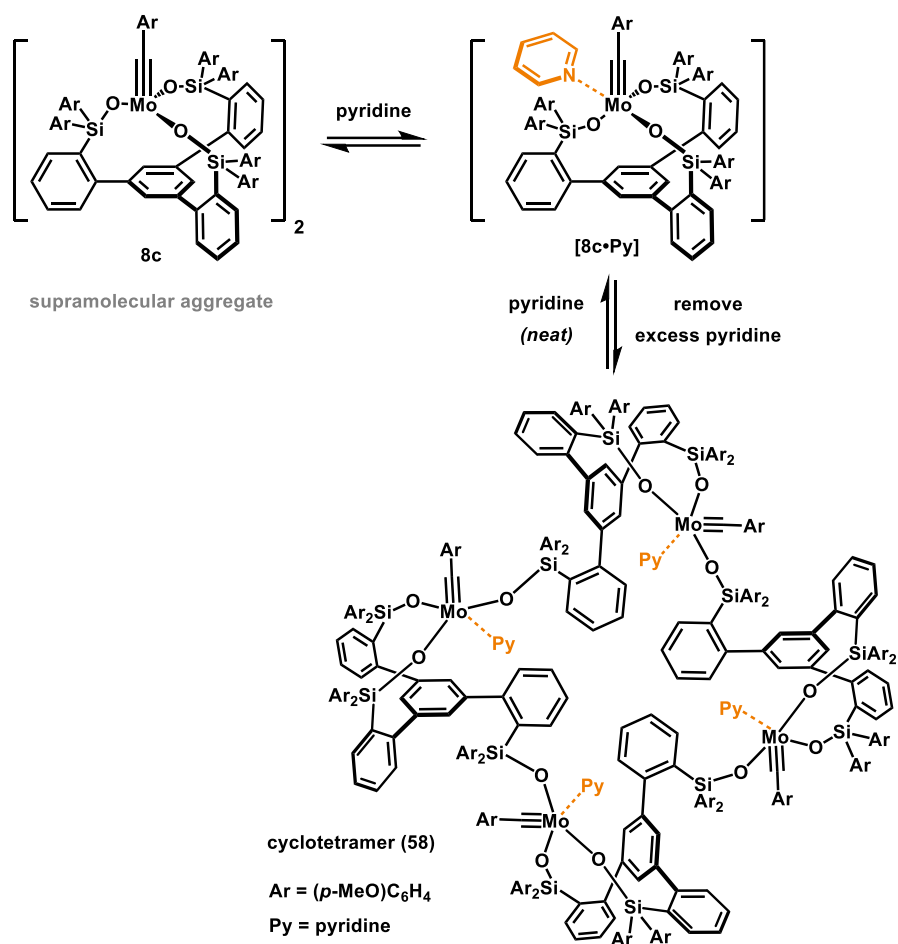


Scheme 30: Deactivation of the methyl variant **8g** through dimerization resulting in a binuclear complex.

Its formation is proposed to proceed *via* the tenuous ethylidyne complex **53** and the dimetallatetrahedran **57**. The latter arises upon collision with a second fragment and such a species had been previously observed as a decomposition product of the parent complex **6**.^[43a] The organic by-product **56** of the transformation was also detected, providing further evidence for the pathway. Binuclear Mo≡Mo complexes have been thoroughly investigate by the group of *Chisholm*, but generally do not display any activity in alkyne metathesis due to the thermodynamically stable metal-metal triple bond.^[80, 121] A single report exists on the cleavage of a Mo≡Mo dimer with a terminal alkyne, however, the present binuclear complex **54** did not react with either terminal or internal alkynes.^[71a] Therefore, it represents a fatal impasse for complex **8g** under catalysis-relevant conditions.

A second weakness of the ‘canopy catalysts’ emerged during an attempt to break the previously mentioned supramolecular aggregates. In specific cases, the addition of pyridine led to the opening of the tripodal ligand framework and ‘cross-linking’ to form large cyclo-tetramers (**58**) (*scheme 31*). *Fürstner* and coworkers reasoned this to be the result of strain release. Notably, different Si–O–Mo angles in the complexes with tripodal ligands when compared to the monodentate parent complex indicated the buildup of ring strain by the overly rigid ‘canopy ligands’.^[17d, 74]

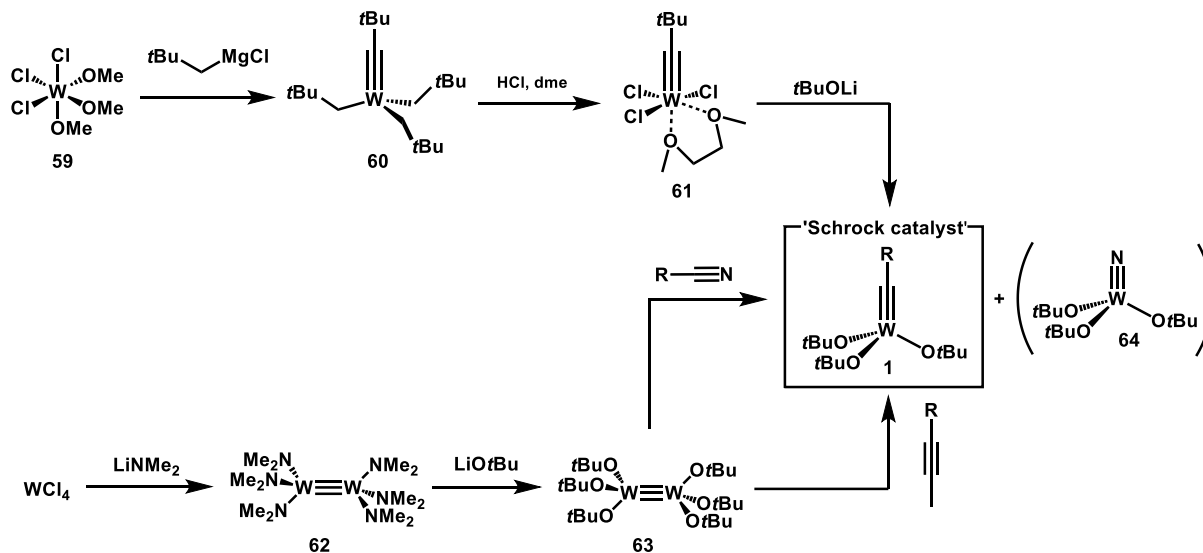
While no direct correlations can be established between the two described decomposition pathways and the high catalyst loadings necessary in some advanced applications, it seems plausible that they are (at least partially) operative under harsh conditions (i.e. refluxing toluene). These observations also serve as convenient starting points for further catalyst development for alkyne metathesis.



Scheme 31: Formation of a cyclo-tetrameric array driven by strain release.

1.1.4 Tungsten Alkylidyne Catalysts

Despite being the historic lead compounds for alkyne metathesis catalysis, tungsten alkylidynes have been largely superseded by molybdenum alkylidynes due to aforementioned reasons (limited functional group tolerance and propensity for polymerization).^[16a, c] Nevertheless, the present chapter is dedicated to providing a brief summary of the historic tungsten alkyne metathesis catalysts and some more recent attempts at their revival.



Scheme 32: Classical routes to tungsten alkylidyne alkyne metathesis catalysts.

The classical 'Schrock catalyst' **1** can be prepared *via* three routes (*scheme 32*). The original route proceeds *via* alkylation of tungsten (VI) precursor complex **59** and double intramolecular α -hydrogen abstraction to give tris(neopentyl)neopentylidyne complex **60**. Chlorination with hydrochloric acid and stabilization with 1,2-dimethoxyethane afforded the trichloride complex **61**. Ligand exchange *via* salt metathesis gave access to a row of alkoxide and phenolate complexes with the most pertinent shown in *scheme 32*.^[88, 122]

The remaining two routes are connected and rely on the metathetic cleavage of tungsten-tungsten triple bonds.^[89, 123] The more prominent of the two involves the reaction of binuclear **63** with an internal alkyne to give the corresponding tungsten alkylidyne complex **1**. The reaction was shown to be highly dependent on the ancillary ligands.^[124] For instance, complex **62** with amide ligands did not react in the same manner. The size of the ligands and the resulting weakening of the triple bond through steric repulsion were speculated to play a role. In the final route, the binuclear complex **63** was cleaved by a metathesis reaction with nitriles.^[89] Since half the submitted material is lost into the nitrido complex **64**, the route is not suited for preparative purposes. However, the observation has some relevance for efforts to develop efficient catalysts for NACM.^[17a]

A modern fourth synthesis has been established in tandem with the 'low-oxidation-state' route described for molybdenum alkylidynes in *chapter 1.1.3*.^[31b, 65] However, since the classical routes already offer convenient access to tungsten alkylidynes on good scale and with

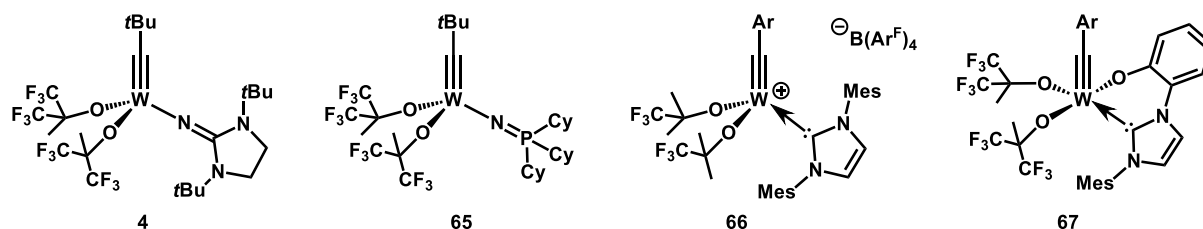
satisfactory yields, the ‘low-oxidation-state’ route has not gained as much traction as it has for molybdenum alkylidynes.^[47b]

The ancillary ligands of tungsten alkylidynes are of the uttermost importance for their competence as alkyne metathesis catalysts. Overly electron-donating ligands such as alkyl, amide, or thiolate ligands render the cycloaddition of alkynes to the tungsten alkylidyne unfavorable, whereas unduly electron-withdrawing ligands such as halides, and carboxylates over-stabilize the formed intermediates.^[37, 71b, 84, 86, 88, 125] *Schrock* and coworkers showed bulky alkoxide and phenolate ligands to deliver tungsten alkylidyne complexes, which are active in alkyne metathesis.^[37, 38c] Sterically demanding ligands are necessary to prevent the polymerization of substrates *via* the ‘associative pathway’. Simply changing ligands from a larger tertiary fluorinated alkoxide to a marginally slimmer secondary fluorinated alkoxide resulted in the exclusive formation of polymeric products.^[38c]

During early applications of alkyne metathesis, tungsten alkylidynes of the general type **1** were demonstrated to tolerate a number of functional groups, but reached their limits when confronted with aldehydes, donor moieties such as pyridines, thiophenes or thiazoles, acid-sensitive functionalities like epoxides or acetals, and traces of moisture.^[49, 84] Another general limitation of alkyne metathesis was discovered with these types of complexes: internal alkynes can often be transformed in good yields, but terminal alkynes have the tendency to initiate polymerization and to deactivate the catalysts.^[100, 126] While this is true for both tungsten- and molybdenum-based alkyne metathesis catalysts, the higher Lewis acidity of tungsten makes the derived catalysts especially susceptible to the polymerization pathway. Notwithstanding the limited number of reports of successful alkyne metathesis reactions with terminal alkynes, the vast majority of applications concern internal alkynes (e.g., with a methyl cap).^[105b, 127]

Modern iterations of alkyne metathesis catalysts based on tungsten sought to mitigate the high Lewis acidity of the metal center with a heteroleptic ligand sphere. Inspired by the use of arylimido ligands in alkene metathesis catalysts, *Tamm* and coworkers replaced one of the fluorinated alkoxide ligands in a classical ‘*Schrock* complex’ with a monoanionic imidazolin-2-imide (*scheme 33*).^[59-60, 128] The resulting complex **4** demonstrated increased activity compared to the parent complex **1** and certain challenging functional groups, including nitro groups, were tolerated. The concept was extended to several tungsten alkylidynes with heteroleptic ligand spheres including ligands such as phosphoraneiminato (**65**), alkyl, and amides.^[60b, 129] However, their serviceability for organic synthesis remains difficult to assess since only limited information about their scope and functional group tolerance is available. Another approach was pursued by the group of *Buchmeiser*. They had previously investigated cationic alkene metathesis catalysts which showed exceptionally high activity and sought to transfer the concept to alkyne metathesis (*scheme 33*).^[92] The synthesis of cationic complexes such as **66** carrying a neutral NHC ligand was accomplished, but the resulting compounds

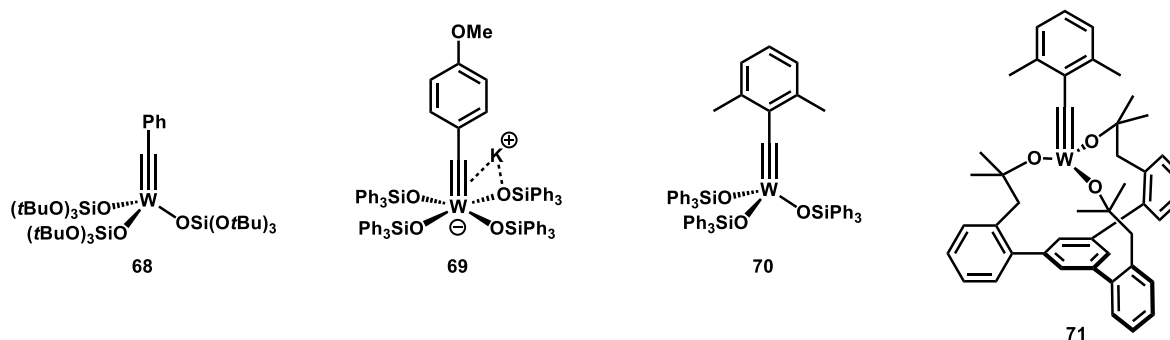
exhibited only marginal reactivity in alkyne metathesis. Given the propensity of low-coordinated cationic complexes of this general design scheme to undergo bimolecular decomposition, bidentate or even tridentate NHC containing ligands were employed in an attempt to stabilize the species. However, the syntheses failed to deliver the targeted cationic species and the corresponding neutral complexes naturally showed low reactivity due to the substrate binding site being blocked by the neutral NHC ligand (e.g., **67**).^[93b, 130]



Scheme 33: Heteroleptic ligand spheres on tungsten alkylidynes and NHC adducts.

The excellent synergy of silanolate ligands with molybdenum alkylidynes does not translate to the tungsten congeners. In 2011, the group of Tamm reported a closely related tri-siloxy complex **68**, which showed activity in alkyne metathesis. However, the preparation of neutral complexes with less encumbered silanolate ligands proved to be challenging, preventing extensive studies (*scheme 34*).^[131] The higher Lewis acidity of tungsten leads to a strong preference for the formation of ate-complexes (**69**) and to decomposition *via* C–H activation processes in the absence of an appropriate additional ligand.^[31b] It was only through the implementation of *Fürstner's* modification of the complexation method in 2020 that the targeted synthesis of neutral tungsten alkylidynes (such as **70**) was successfully achieved.^[132] Alkoxide tungsten benzyldiyne complexes were used as precursors and the ligands were replaced *via* protonolysis with silanolates. The resulting complexes turned out to be inactive in alkyne metathesis.

An investigation into the electronic situation at the metal center *via* ^{183}W NMR revealed tungsten alkylidynes carrying silanolate ligands to be highly electron-deficient. As a consequence, the MCB intermediate is over-stabilized and could be isolated in certain cases.



Scheme 34: Tungsten alkylidynes with silanolates ligands and a tripodal alkoxide ligand.

Following the success of tripodal ligands in broadening the functional group tolerance for molybdenum alkylidynes, tridentate alkoxide ligands for tungsten alkylidynes were

devised.^[132] Indeed, the obtained complex **71** was able to transform substrates containing an acid labile epoxide, a thiazole, and an elimination-prone aldol subunit, which had been a fatal match for the parent ‘*Schrock* catalyst’. In addition, the complex with a tripodal ligand outcompeted **1** in a benchmarking experiment. The enhanced reactivity is likely attributable to a moderating effect by the ligand on the Lewis acidity of the metal. The tether restricts the conformation of the ligand and thereby alters its donating capability.

Notwithstanding the recent advances in the field, catalysts based on tungsten alkylidynes are no match in terms of activity and especially functional group tolerance for state-of-the-art molybdenum alkylidyne systems, such as the ‘canopy catalysts’. Therefore, they have seen little use in natural product synthesis, but recent developments indicate them to be highly relevant for the synthesis of polymers (*chapter 1.1.6.3*).^[18, 133]

1.1.5 Rhenium Alkylidyne Catalysts

A number of the challenges faced in catalyst development with molybdenum and tungsten alkylidynes (e.g., stability in the presence of protic functional groups and air/moisture) could potentially be addressed by a shift to noble transition metals.^[134] Such a change is widely regarded to have aided the development of alkene metathesis. The departure from sensitive molybdenum alkylidenes in favor of the more stable ruthenium-based Grubbs catalysts was the prelude for the extraordinary surge in applications within academia and the chemical industry.^[3c, 135]

However, early reports from *Schrock* and coworkers on the synthesis and activity of rhenium (VII) alkylidyne complexes had been discouraging. Although complexes, such as **72** and **73**, could be synthesized *via* a similar alkylation and double α -hydrogen abstraction strategy previous employed for the tungsten congeners, they did not show activity in alkyne metathesis (figure 5).^[136]

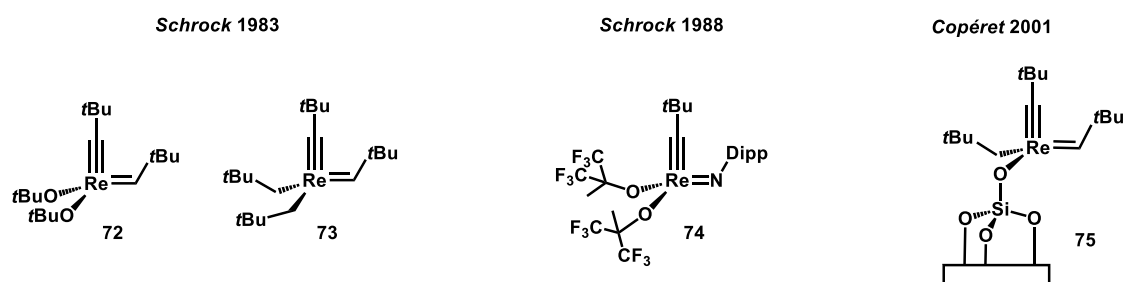
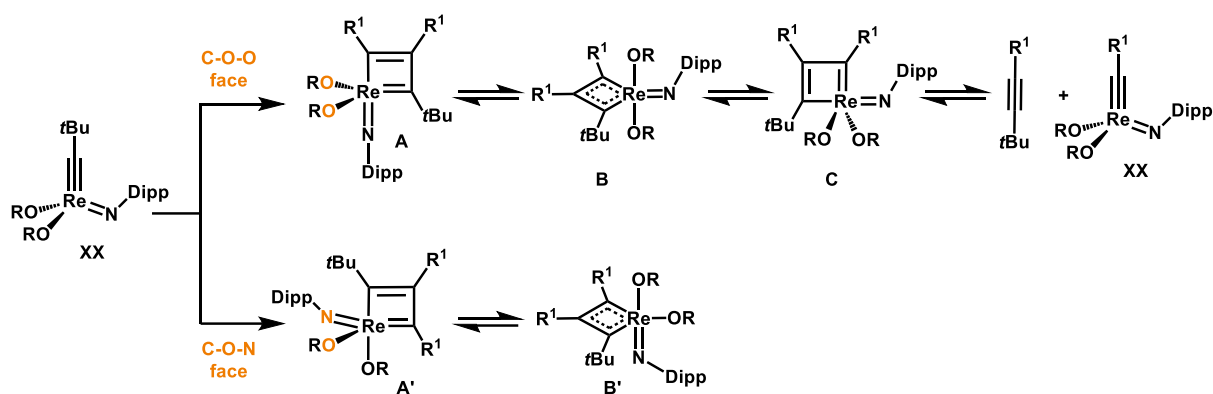


Figure 5: Rhenium (VII) alkylidyne complexes with and without activity in alkyne metathesis.

On the contrary, the addition of a Lewis acid resulted in the ability of the mixed alkylidyne-alkylidene complexes to scramble simple alkenes.^[137] Hence, including alkylidene ligands in the design of alkyne metathesis catalysts risks losing one of the fundamental advantages of the methodology: its orthogonality to alkenes.

In 1988, *Schrock* and coworkers presented an updated version in which the alkylidene had been replaced by an imido ligand and fluorinated alkoxy ligands had been added in order to enhance the electrophilicity of the rhenium center.^[41, 138] Complex **74** was shown to catalyze the metathesis of internal alkynes, but only acetylene derivatives with bulky substituents gave satisfactory turnovers.

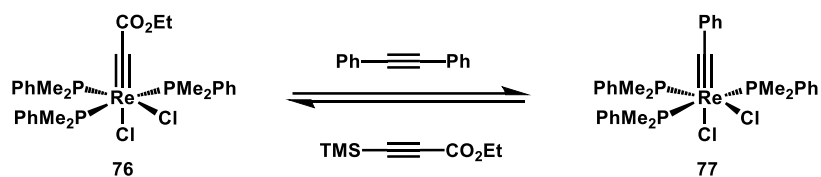
The unsymmetrical nature of complex **74** results in two possibilities for the formation of a MCB, depending on the face from which the alkyne approaches the catalyst. *Schrock* proposed only one of the intermediates to contribute to the catalytic turnover (scheme 35). Association from the C-O-O face gives MCB **A** which can isomerize into MCB **C**. The strong *trans*-effect exerted by the imido ligand, which is located in the same plane as the MCB, aids the [2+2]-cycloelimination to expel the product. The other pathway (C-O-N face) leads to the imido ligand being positioned perpendicular to the MCB (**A'**). The intermediate is overstabilized and an unproductive thermodynamic dead-end.^[138]



Scheme 35: Electronically distinct metallacyclobutadienes formed upon cycloaddition from different faces.

Due to these complications, as well as the difficult syntheses and the high prize of rhenium metal, preference was given to tungsten and molybdenum alkylidyne catalysts. The field was largely dormant for nearly 20 years with a single interlude from the group of *Copéret*, which published on a version of **75** immobilized on silica.^[139] Metathesis activity was observed; however, the complex reacted with alkenes as well as alkynes.

In 2016, *Jia* and coworkers revitalized the research area by discovering reversible stoichiometric alkyne metathesis activity for the d²-rhenium (V) complex **76** (scheme 36).^[81a]



Scheme 36: Reversible, stoichiometric alkyne metathesis with d²-rhenium (V) alkylidyne complex **76**.

The report was startling because, thus far, alkyne metathesis had been almost exclusively confined to high valent d⁰-complexes. The only exception had been an account describing the stoichiometric reaction of an alkyne with a tungsten (IV) carbyne complex, which took two weeks to complete the exchange of the carbyne substituent.^[140] The following reasons had been cited to explain the virtual inactivity of non-d⁰ tungsten, molybdenum, and (so far) rhenium carbon triple bonds for alkyne metathesis: the insufficient Lewis acidity of the metal centers and their preference for coordinating alkynes in a perpendicular mode to the alkylidyne/carbyne ligand.^[81a]

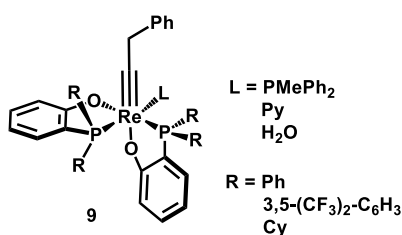


Figure 6: Alkyne metathesis catalysts based on d²-Re(VI).

By carefully assessing which properties allowed complex **76** to overcome these hurdles and by elaborating on them with ingenious ligand design, the group of *Jia* managed to turn the

stoichiometric reaction into a catalytic process (*figure 6*).^[42, 81b, c, 141] Replacing the phosphines in complex **76** with sterically less encumbered trimethyl phosphine caused a marked decrease in the rate of the reaction in comparison to that observed with bulkier ligands. From this, they deduced steric bulk to be a prerequisite for the productive binding of the alkyne in a parallel manner to the alkylidyne.^[82] In addition, bidentate ligands were chosen in order to impede the rearrangement into unproductive five-coordinated square pyramidal intermediates upon dissociation of the labile ligand. Phosphino-phenolates were selected due to the π -donating properties of the phenolate, which could aid the first step of the catalytic cycle (dissociation of the labile ligand; see *scheme 12*).^[142] First iterations carrying methyldiphenylphosphine as the labile ligand showed marginal catalytic activity under harsh conditions (neat, 150 °C). The addition of copper iodide as a phosphine scavenger increased the turnover, suggesting the dissociation to be the rate limiting step. Replacing the phosphine with a more labile pyridine resulted in a substantial increase in reactivity, enabling reactions to occur at 100 °C within reasonable timeframes.

More electron-withdrawing trifluoromethyl substituted ligands decreased the reaction rate, which is consistent with the loss of the pyridine as the rate limiting step. The best results were obtained with electron-donating cyclohexyl substituted phosphines.

Recently, an update version of the catalyst was reported by the *Jia* group with water as the labile ligand instead of pyridine.^[83] The respective complex was found to catalyze alkyne metathesis reactions at ambient temperature – a first for rhenium (V) based systems that typically require elevated temperatures (>100 °C). The fact that water can be used as a component in rhenium (V) alkylidyne complexes, emphasizes their amenity when compared to the highly moisture-sensitive molybdenum (VI) and tungsten (VI) catalysts. As in alkene metathesis, the shift to a more noble transition metal paid valuable dividends in terms of general stability. Most of the catalysts are reported to be bench stable as solids. Only complexes containing alkyl-substituted phosphine ligands degraded in contact with air and moisture. The rhenium-based catalysts excellent performance in the presence of protic functional groups is also remarkable; primary alcohols, phenols, anilines, benzylic alcohols, and even carboxylic acids were tolerated. Additionally, challenging moieties such as aldehydes and nitro groups posed no problem. Their only established limitation are substrates containing donor ligands such as pyridine. In summary, although the reactivity of these catalysts currently still lags behind its molybdenum-based cousins, their functional group tolerance is complementary.

The development of rhenium (V) based alkyne metathesis catalysts has prompted a re-evaluation of long-standing principles within the field, opening up new prospects to explore. A re-examination of non-d⁰ alkylidyne complexes of molybdenum and tungsten, as well as other transition metal alkylidynes (e.g., Ru, V) with respect to their activity in alkyne metathesis may be warranted.

1.1.6 Applications of Alkyne Metathesis

1.1.6.1 Natural Product Synthesis

The total synthesis of natural products has emerged as the most prominent field of application for alkyne metathesis. Starting with first forays around the turn of the millennium, the group of *Fürstner* has since synthesized numerous, mostly macrocyclic, target molecules.^[24a, 143] Their ambition to tackle increasingly challenging substrates contributed decisively to the development of ever more advanced catalysts (*vide supra*).^[16a]

A selection of targets, conquered with the aid of alkyne metathesis, is shown in *figure 37* demonstrating the diversity of structural motives which can be generated from the acetylene derivatives obtained in the reaction.^[16a, b, 79a, 120a, 144]

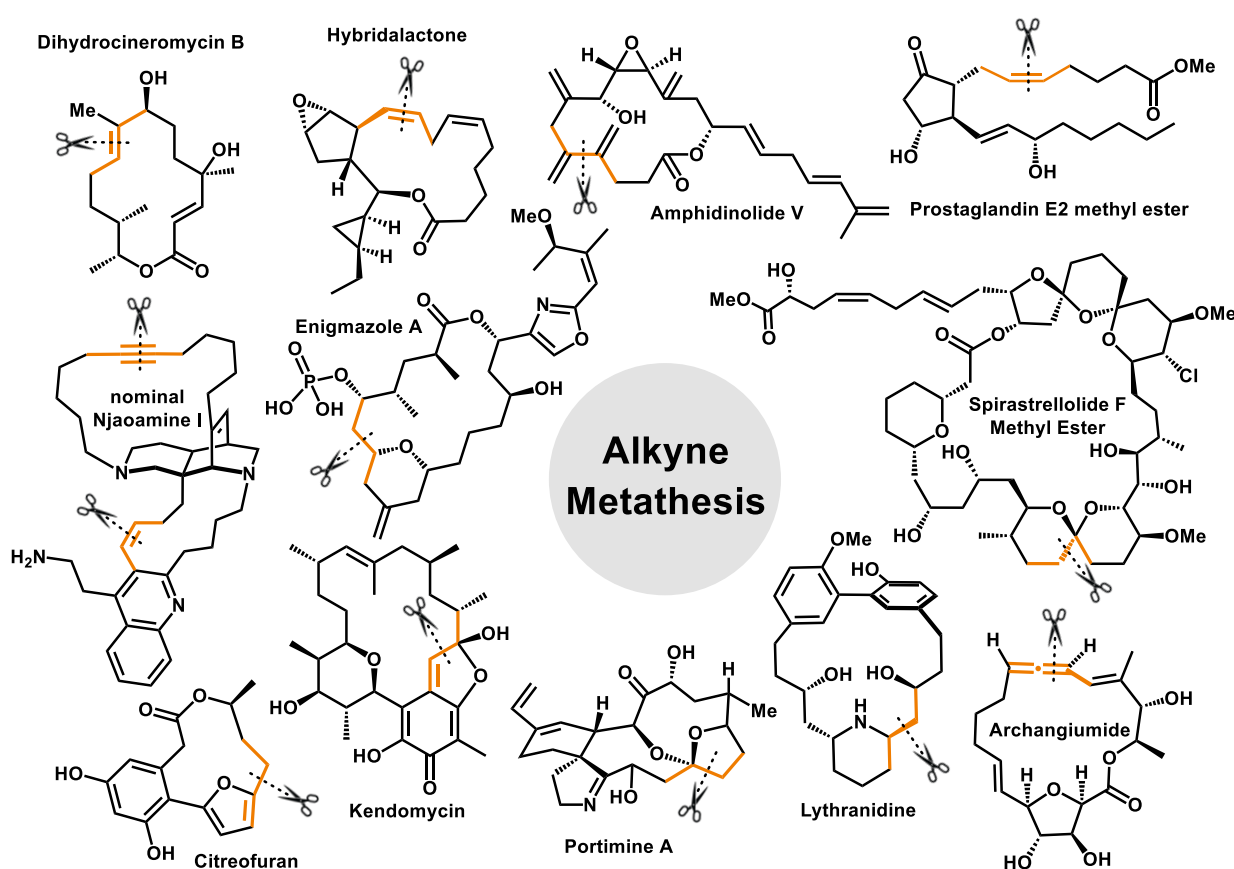
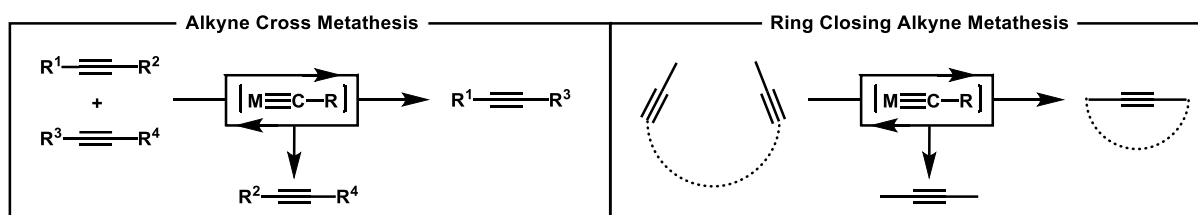


Figure 7: Selected natural products synthesized with the aid of alkyne metathesis.

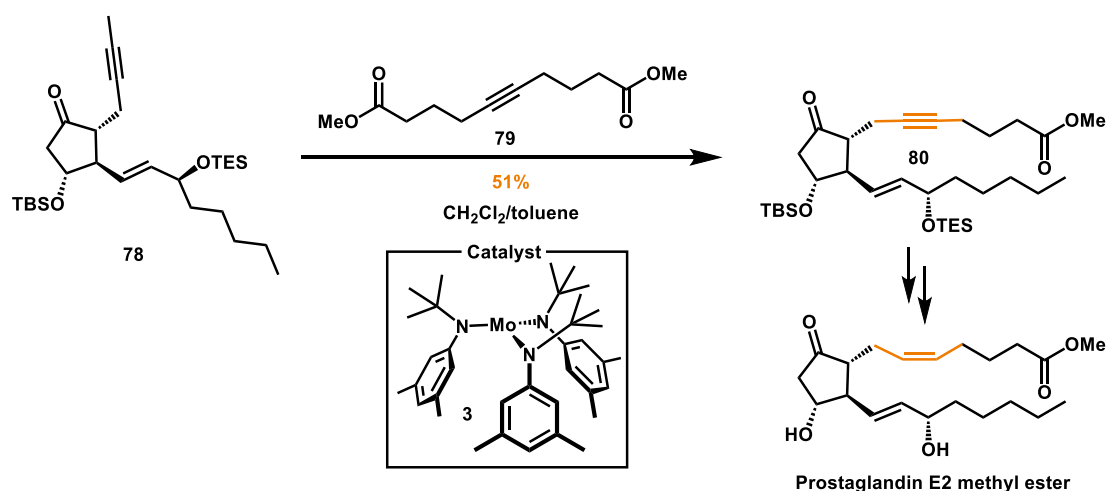
Alkyne metathesis can be applied to the synthesis of natural products in two fundamental reaction modes: intermolecularly as alkyne cross metathesis (ACM) and intramolecularly as ring closing alkyne metathesis (RCAM) (*scheme 37*). In ACM two internal alkynes are combined into the desired acetylene derivative concomitant to the formation of equimolar amounts of a by-product. In the case of methyl capped alkynes ($R^2 = R^3 = \text{Me}$), the equilibrium can be shifted to the side of the desired product by selectively adsorbing the formed but-2-yne into molecular sieves. The fundamental challenge in metathesis reactions lies in preventing an indiscriminate mixture of cross- and homo-metathesis products. Introducing a bias towards

the targeted product based on electronic or steric factors is possible.^[103] For instance, substrates with bulky quaternary centers next to the alkyne or alcohols in the propargylic position generally do not undergo homo-metathesis reactions.^[31b, 57b, 127b]



Scheme 37: The two fundamental reaction modes of alkyne metathesis in natural product synthesis.

However, due to the linear nature of alkynes and them only carrying two substituents, there are fewer opportunities than in alkene metathesis for steering the outcome of the reaction. As a consequence, ACM has found only limited application in natural product synthesis. The synthesis of Prostaglandin E₂ methyl ester by *Fürstner* and coworkers might serve as an example (scheme 38). Through the addition of an excess of the inexpensive symmetrical alkyne **79** the desired product **80** could be formed in moderate yield. Deprotection and selective reduction to the *Z*-alkene gave the targeted molecule.^[145]

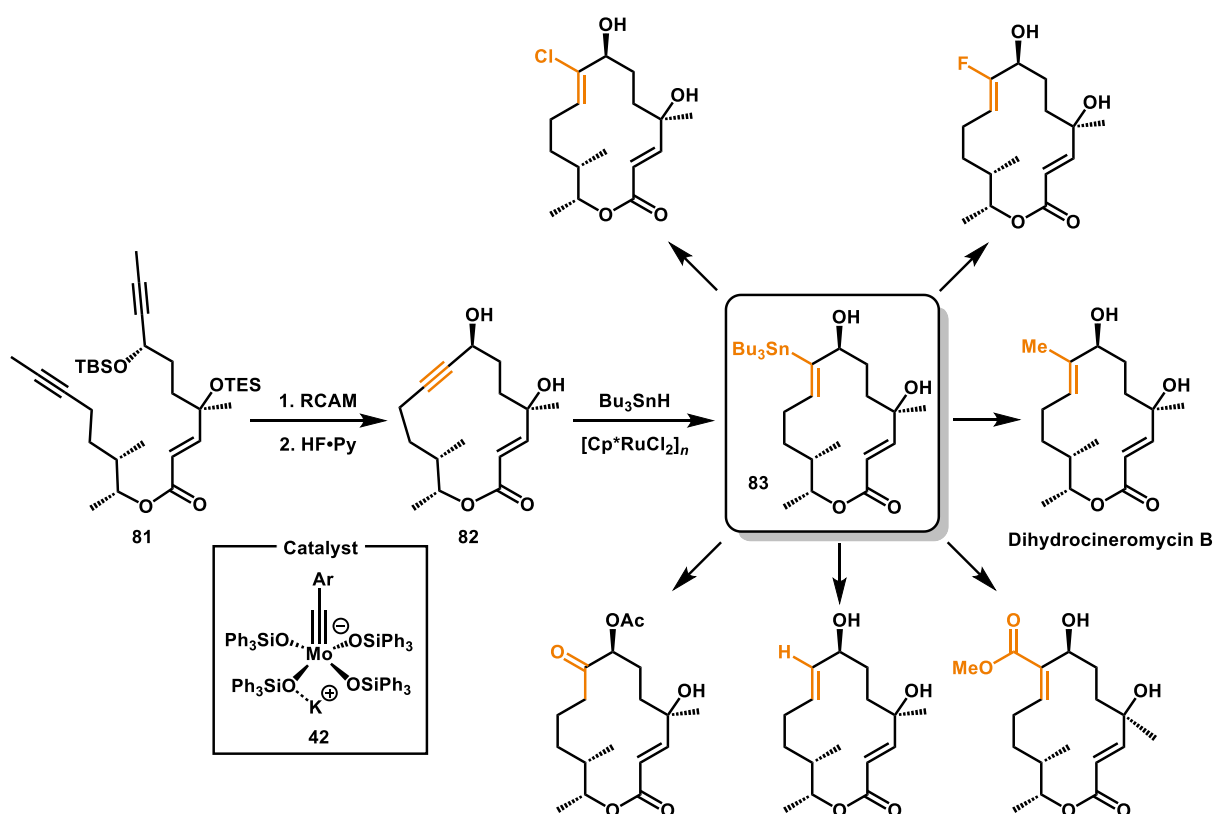


Scheme 38: Alkyne cross metathesis in the synthesis of Prostaglandin E₂ methyl ester.

RCAM, in contrast, has established itself as a powerful method for forging macrocyclic rings. RCAM is only suitable for rings containing more than eleven atoms due to the rod-like shape of alkynes. When targeting smaller cycles, the ring strain becomes excessive, resulting in the predominance of dimerization and subsequent formation of larger rings.^[81c] Although the RCAM of terminal alkynes has been reported and mixed reactions with one internal and one terminal alkyne have even been executed in total synthesis (Mandelalide A)^[66j, 113b], methyl capped internal alkynes are by far the most common precursors.^[66b] At its outset, RCAM was predominantly applied to unbiased alkynes in large ring systems (e.g., Epilachnene or Sophorolipid lactone)^[49, 102b], but over time it was shown that also densely functionalized

smaller rings and electronically biased alkynes are amenable (e.g., Guanganmycin A alcohol)^[75c].

In the context of strategic disconnections, RCAM's most significant strength lies in the diversity of structural motives that can be traced back to alkyne moieties. In *figure 7* the sites, at which RCAM took place during the synthesis, are highlighted. Not only the obvious alkynes and *E*- and *Z*-alkenes can be obtained, but also allenes, furans, spiroketals, 1,3-aminoalcohols, lactols, trisubstituted alkenes, tetrahydropyrans and a 1,2-bis-methylene unit (and more) have been shown to be viable sites for retrosynthetic disconnections based on RCAM. In addition, its exquisite selectivity allows RCAM to be performed on highly functionalized precursors at an advanced stage of the synthesis. Especially noteworthy in this context is the π -bond selectivity of alkyne metathesis which leaves alkenes untouched and enables the synthesis of unsaturated target molecules (e.g., Hybridalactone, Amphidinolide V or Neurymenolide A).^[146] Even the simultaneous construction of the two rings in a bicyclic oligopeptide through an orthogonal one-pot alkene and alkyne metathesis reaction was possible.^[147]



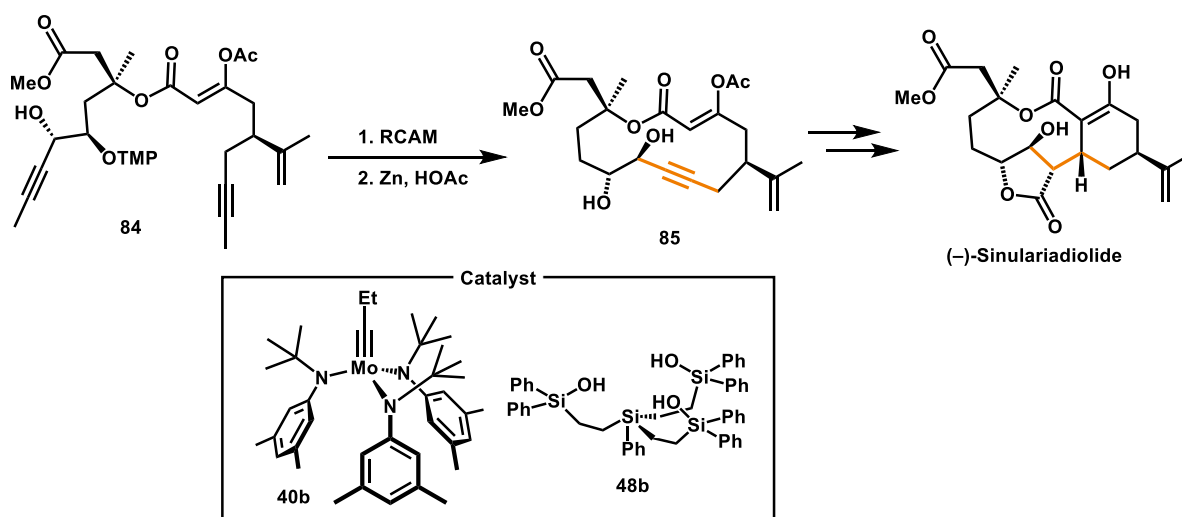
Scheme 39: Trans-hydrometalation of the RCAM product as a path to various analogs of Dihydrocineromycin B.

Trans-hydrometalation is highlighted in *scheme 39* as one of the most powerful postmetathesis functionalizations.^[79d, 148]

In these ruthenium catalyzed reactions, the propargylic alcohol has a directing effect, affording trisubstituted alkenes in a regioselective manner. Subsequent cross coupling with methyl iodide gives access to the 2-methyl-but-2-en-1-ol motive, a prevalent structural element in

polyketide and diterpene natural products. In the shown case, alkenylstannane **83** could be further diversified to give a host of natural product analogs.^[25, 149]

The application of RCAM as strategic disconnection is not confined to macrocyclic natural products – congested medium sized rings are also amenable, provided that they can be traced back to a larger ring. A recent example from the *Fürstner* group is the total synthesis of Sinulariadiolide, which contains a six- and a nine-membered ring, in addition to a butanolide.^[75b]

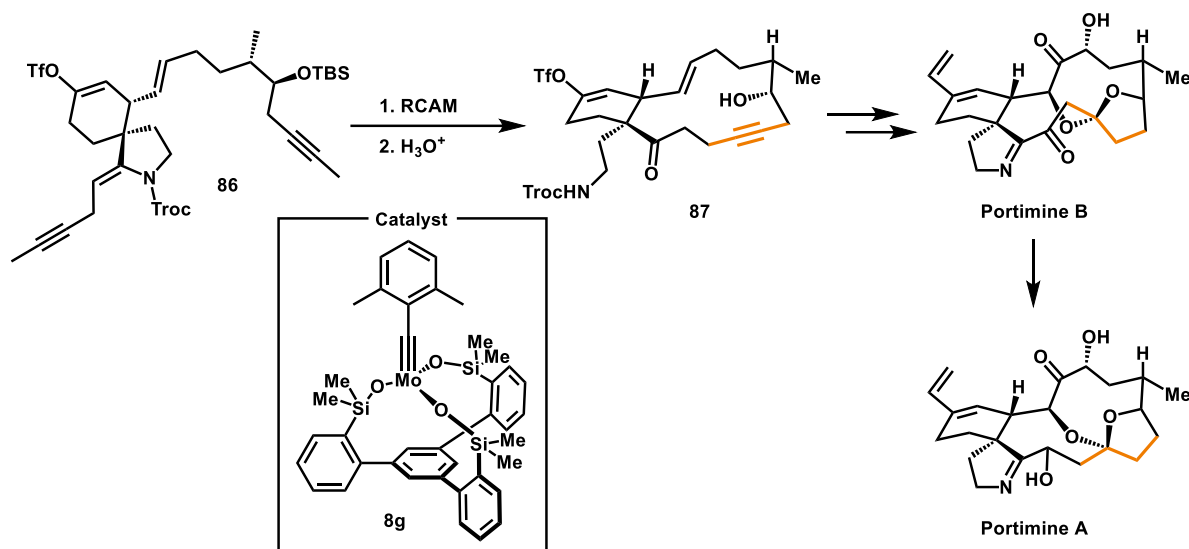


Scheme 40: An example for the formation of a macrocycle via RCAM followed by a transannular reaction.

The three rings can be derived from the macrocyclic precursor **85** with their connectivity being build up from the alkyne moiety using a transannular Michael addition cascade. The necessary 14-membered ring could be formed *via* RCAM; the *in situ* generated system with the tridentate silanolate ligand **48b** was able to transform the diyne **84** comprising an unprotected propargylic alcohol in good yield.

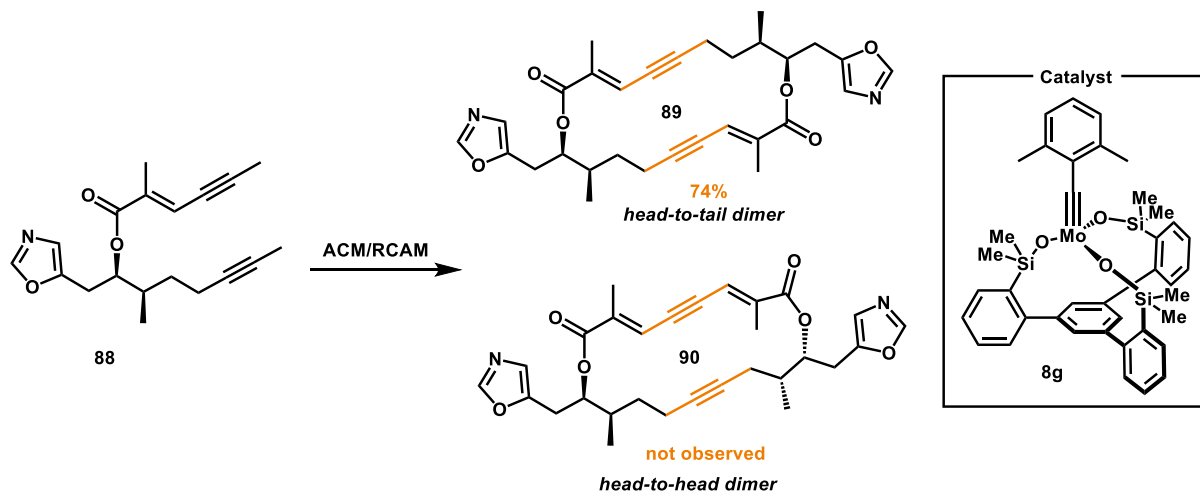
Another prominent total synthesis using transannular reactivity was disclosed by the group of *Baran*.^[79a] The structures of Portimine A and B contain five rings including a spiro-fused five-membered cyclic imine. This daunting, highly oxygenated scaffold could be traced back to 14-membered macrocycle **87** containing all the necessary C-C connections, which was synthesized *via* RCAM.

While a substrate containing the free cyclic imine could be transformed with the ‘turbo canopy catalyst’ **8g**, protecting it with a 2,2,2-trichloroethanoxycarbonyl (Troc) group (**86**) made catalyst loadings as low as 2 mol% possible. Extensive oxidations and the transannular nucleophilic addition of a hydroxyl group to a cyclic oxonium species afforded Portimine A and B (scheme 41).



Scheme 41: Total synthesis of Portimine A and B through the construction of the carbon-scaffold by RCAM.

As a final illustration of the diverse application modes of alkyne metathesis, the cyclodimerization approach pioneered by the group of *Hulme* will be discussed.^[113a] Essentially a combination of ACM and RCAM, the method allows C_2 -symmetric dimers to be synthesized. The posed challenge was to exclusively obtain the desired head-to-tail product **89** instead of the head-to-head dimer **90** of the unsymmetrical diyne precursor **88** (scheme 42). Employing an electron-deficient enyne and an electronically unbiased alkyne in the substrate led to the formation of the desired isomer in good yields.^[120b]



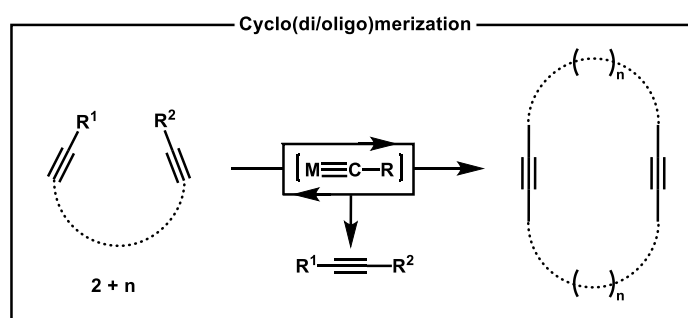
Scheme 42: Cyclodimerization via alkyne metathesis in the total synthesis of Samroiymycin A.

Ruthenium catalyzed *trans*-hydrometalation followed by protodemetalation gave the *E*-configured alkenes of the target molecule Samroiymycin A.

It exceeds the scope of this work to provide a comprehensive overview of all the strategic considerations and different formats in which alkyne metathesis can be applied to the synthesis of natural products. Authoritative reviews have been published on the matter.^[16a, 24a, 150] The provided examples are merely intended to highlight the diversity of the target molecules to which alkyne metathesis has been successfully applied.

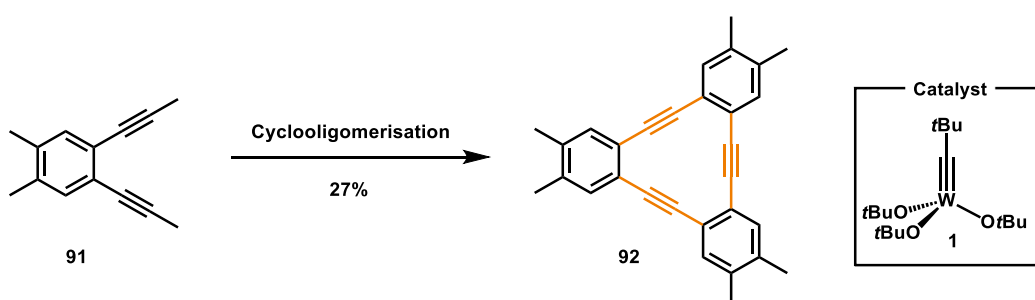
1.1.6.2 Molecular Architecture

The synthesis of shape-persistent organic structures is another domain in which alkyne metathesis has found application. When targeting rigid molecular architectures, alkynes with their linear geometry are attractive building blocks.^[67, 69a] Specifically, macrocycles that are composed of arylene-ethynylene units have garnered significant interest in the fields of supramolecular and materials chemistry and alkyne metathesis is uniquely positioned to provide them. The abundance of π -electrons in these highly conjugated systems opens up possibilities for host-guest binding as well as photophysical and electronic applications.^[72a, 151]



Scheme 43: General reaction scheme for cyclo(dimerization or cyclooligomerization).

The synthesis of shape-persistent structures involves a reaction mode of alkyne metathesis, which is referred to as cyclo(dimerization or cyclooligomerization) (scheme 43). Two or more diynes are combined into a macrocyclic product under the extrusion of an acetylenic by-product. In the case of but-2-yne, it is routinely removed through the application of gentle vacuum or molecular sieves, but in the field of molecular architectures precipitation driven approaches have also played a larger role.^[44b, 104b] Generally, symmetrical precursors are employed to avoid head-to-tail versus head-to-head selectivity issues (*vide supra*).



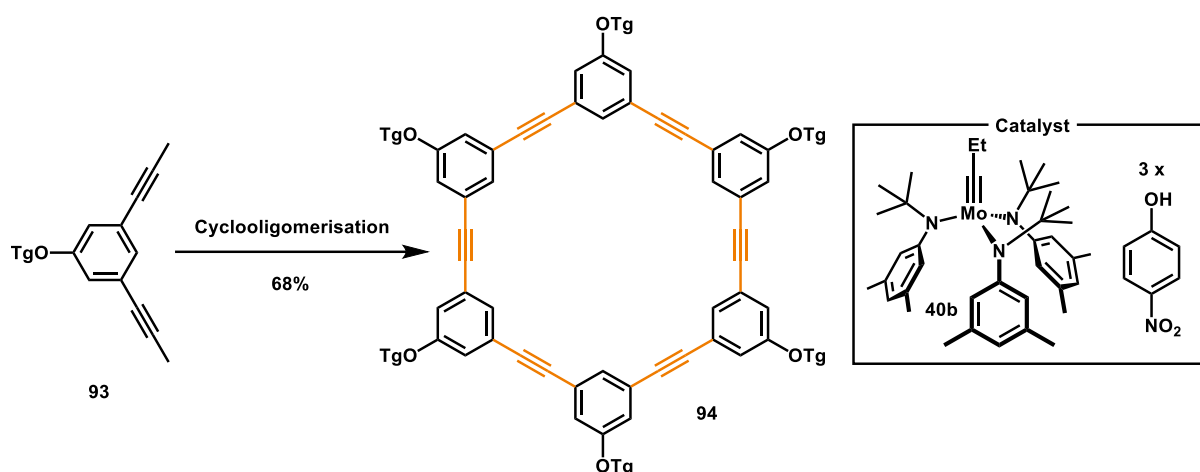
Scheme 44: Cyclotrimerization of ortho-dipropynylated arenes with the aid of 'Schrock's catalyst'.

Early pioneers in the field were *Bunz* and *Vollhardt* with their synthesis of arylene-ethynylene macrocycles.^[99a, 152] Scheme 44 shows a trimeric example **92** realized with the aid of 'Schrock's catalyst' **1**. However, only low to moderate yields could be obtained, and high catalyst loadings were necessary.

For the efficient synthesis of thermodynamically stable, highly ordered structures reversible covalent bond formation is beneficial. Dynamic Covalent Chemistry (DCC) allows for

connectivity ‘mistakes’ to be corrected and the thermodynamic equilibrium to be reached.^[68] In principle, alkyne metathesis fulfills the reversibility criteria for DCC, given its indiscriminate scrambling of carbon-carbon triple bonds. However, in the present case, decomposition of the catalyst and polymerization likely prevented the system from reaching the full equilibrium. Consequently, more reliable catalyst systems were in demand.

Indeed, the molybdenum-based *in situ* generated catalytic mixture introduced by *Moore* provided the related hexamer **94** in good yield.^[44b]

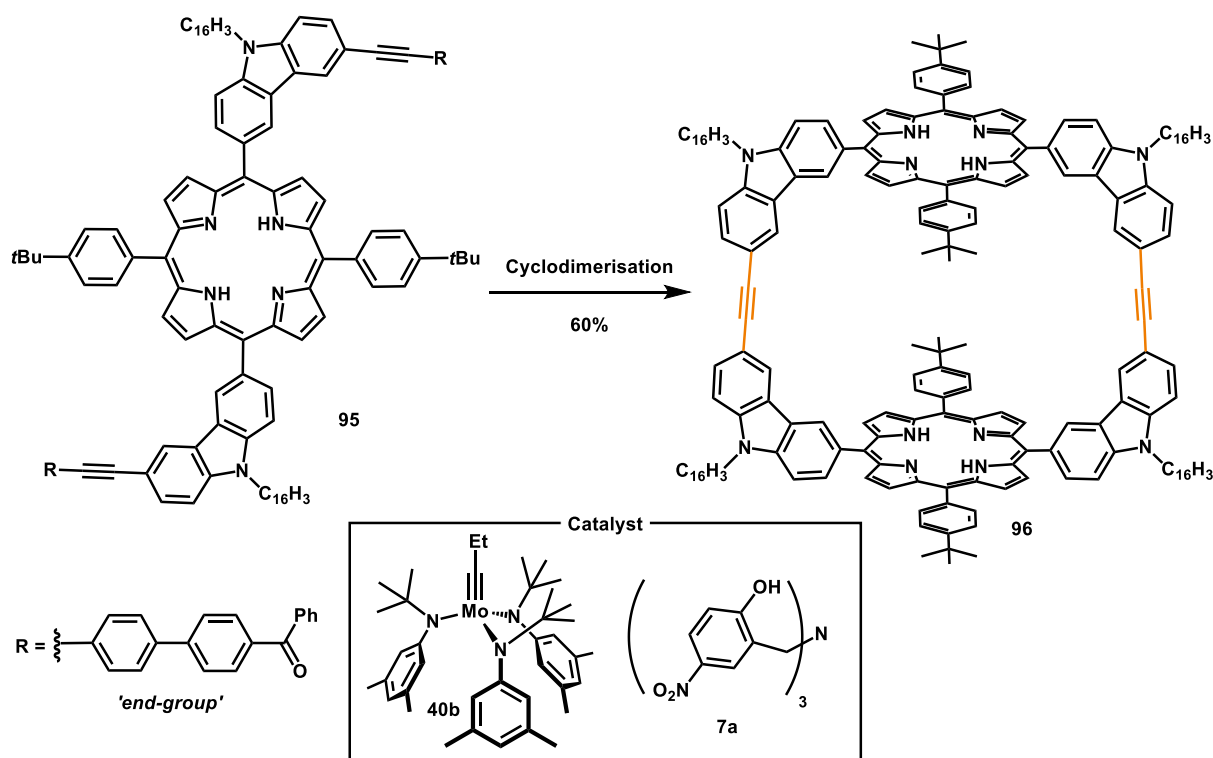


Scheme 45: Synthesis of an ethynylene-linked hexamer **94** with a highly active *in situ* generated catalyst.

The positioning of the two propargyl units at the arene monomer **103** dictates which product is thermodynamically preferred and ultimately formed – an advantage over previously used kinetically driven cross-coupling reactions. A multitude of 2D and 3D ethynylene-linked structures have been synthesized through varying the angles and geometries in the monomer.^[69a, 72a, 153] The formation of the compounds generally occurs *via* a two stage process. First, the monomer is rapidly converted into oligomers, which then reorganize more slowly into the preferred macrocycle.^[44b] Yet, not all alkyne metathesis cyclooligomerisation reactions are under perfect thermodynamic control. Unexpectedly, also kinetically trapped products have been reported.^[72b, 104a] Possible reasons for the phenomenon are: difficult to activate intermediates, which are formed through fast intramolecular ring-closing reactions, or the precipitation of insoluble larger oligomers.

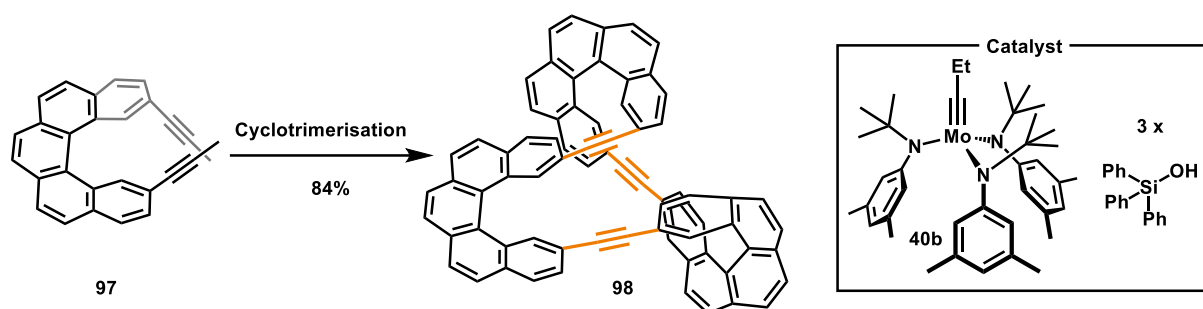
During efforts to scale up reactions of the type shown above (*scheme 44 and 45*), it was observed that the polymerization of the by-product (but-2-yne) had a detrimental effect on the catalyst lifetime. The group of *Zhang* resolved the issue with their tridentate ligands **7**, which prevent polymerization by blocking the ‘associative pathway’.^[69b, 70b, 90a] An alternative solution evaluated for solving the problem involved circumventing the presence of the small alkyne by-products altogether. Specifically designed end-groups at the alkyne termini of the monomers **95** gave insoluble by-products upon engagement in alkyne metathesis, thereby shifting the equilibrium of the reaction by precipitating from solution (*scheme 46*). However,

this strategy entails a large loss of mass and does not meet modern standards of atom-economy.^[154]



Scheme 46: Precipitation driven synthesis of the dimeric porphyrin based macrocycle **96**.

To conclude, a last example is given in order to underline the power of alkyne metathesis for the synthesis of unusual molecular architectures. *Moore* and coworkers were able to obtain the conjugated molecule **98** with a shape reminiscent of a Möbius strip (*scheme 47*).^[87]



Scheme 47: Synthesis of a shape-persistent molecule with Möbius topology.

Previous campaigns towards compounds with this topology struggled with low overall yields and multiple step procedures.^[155] In contrast, the cyclotrimerization of monomer **97** using a molybdenum-based catalyst with silanolate ligands gave the desired product in a single step and with a high yield.

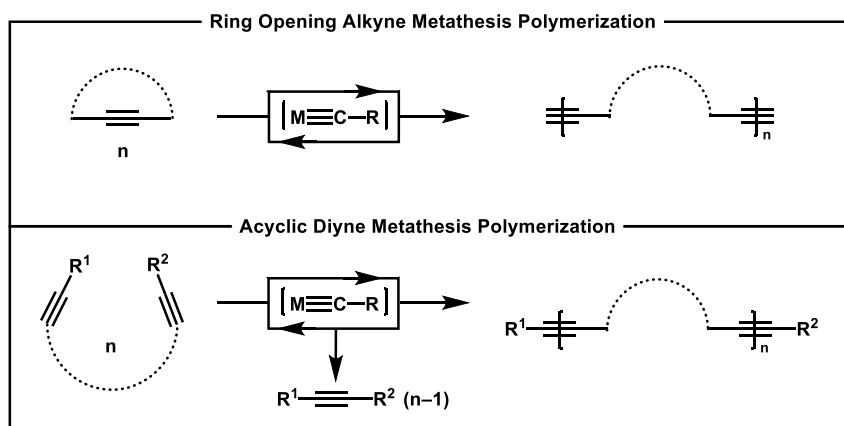
Surprisingly, structure **98** does not embody the thermodynamically favored product, but results from kinetic trapping. Considerably different barriers for the formation of the two initial, highly distorted MCBs and a facile cycloreversion led to its formation. This fact emphasizes the intricacy encountered when designing the synthesis of shape-persistent molecules with alkyne metathesis.

I.1.6.3 Polymers

The synthesis of polymers is the third and final field in which alkyne metathesis finds application. Up to this point, polymerization has only been mentioned as detrimental side reaction.

The generally accepted mechanism for the polymerization of small alkynes in the presence of alkylidyne catalysts proceeds through the association of an additional alkyne substrate to the intermediate MCBD, followed by insertion to give a ring expanded metallacycle (*scheme 26*).^[16b] Of late, an increased interest in the resulting polymers has led to the development of special catalysts, which selectively promote the ring expansion pathway (e.g., vanadium alkylidynes).^[18, 133a, 156] In spite of that, this mechanistic sequence is not regarded as a ‘true’ alkyne metathesis reactivity since the obtained products do not contain carbon-carbon triple bonds. Consequently, it will not be discussed in detail.

There are two polymerization reaction modes for alkyne metathesis, in which alkyne moieties are retained in the products (*scheme 48*).

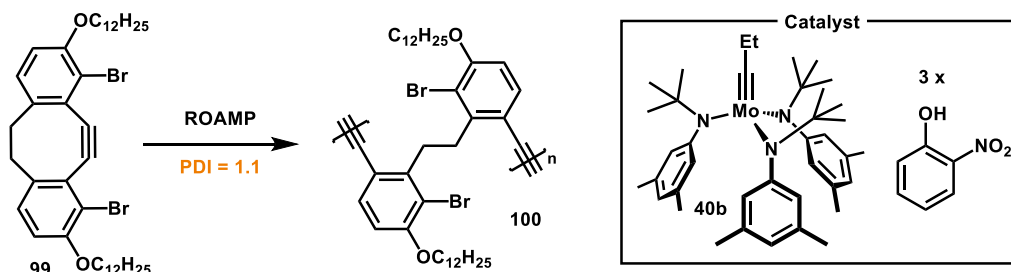


Scheme 48: Reaction modes of alkyne metathesis for polymer synthesis.

Ring opening alkyne metathesis polymerization (ROAMP) has already been alluded to and relies on the ring strain of cyclic alkynes as the substrates. The second reaction mode is acyclic diyne metathesis polymerization (ADIMET). Herein, the positioning of the propylidyne units in the inflexible monomers prevents the formation of entropically favored cycles and yields linear polymers. The resulting poly(arylene-ethynylenes) (PAEs) are of interest for the manufacturing of electronic components and luminescence materials.^[157]

The group of *Schrock* reported the first ROAMP with cyclooctyne as a monomer.^[45-46] However, the highly active ‘*Schrock catalyst*’ indiscriminately engaged the monomer (productive) or the polymer chain (unproductive). Ultimately, products with large polydispersity indexes (PDI) were obtained. While backbiting and chain transfer processes could be reduced with less reactive catalysts (such as molybdenum alkylidyne and heteroleptic tungsten alkylidyne complexes), no truly satisfactory dispersity could be attained.^[46, 158]

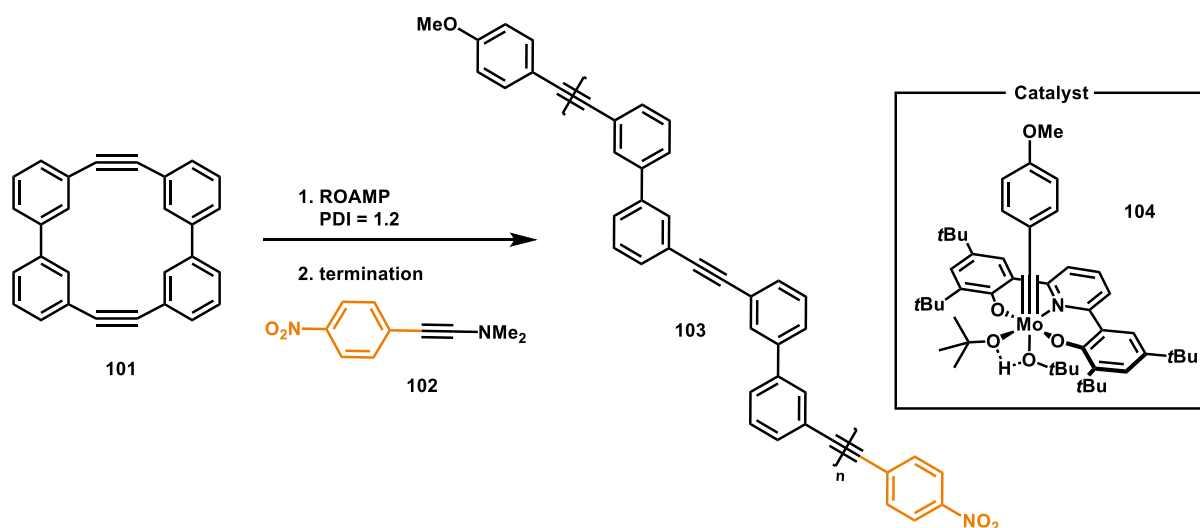
For living ROAMP reactions fast initiation as well as the ability of a catalyst to differentiate between the triple bonds of the substrate and the growing polymer chain is crucial. To this end, *Fischer* and *Nuckolls* took advantage of the kinetic selectivity of a molybdenum-based catalyst for engaging benzo[*a,e*]-[8]-annulene **99**, which exhibits an even higher angle strain than cyclooctyne.^[47a]



Scheme 49: First living ROAMP with an engineered, highly strained substrate.

The strategy also leveraged the slower reaction rate of aryl-alkynes in comparison to alkyl-alkynes such as those present in the backbone of poly(octyne). The reaction represents the first true living ROAMP yielding linear polymers **100** with PDIs as low as 1.1.

The group of *Fischer* extended the concept by purposefully designing less reactive catalysts (**104**), which only engage with strained alkynes.^[47c] By introducing a planar tridentate ligand they restricted the geometries allowed for the catalysts coordination sphere (*scheme 50*). The barrier for the initial [2+2] cycloaddition of unstrained alkynes was raised causing a kinetic selectivity for favorably preorganized strained alkynes (**101**) with bond angles similar to the sp^2 -hybridization in the formed MCB. At the same time, the sterically encumbered ligand prevented chain-transfers through bimolecular catalyst decomposition.



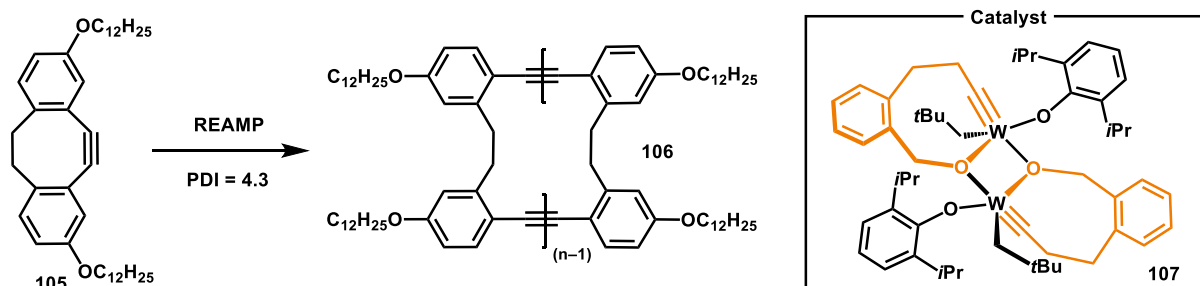
Scheme 50: ROAMP and termination to give an end-functionalized arylene-ethynylene polymer.

The group also developed termination reagents (**102**) for cleaving off the propagating catalyst species from the polymer chain, deactivating it and at the same time installing a defined end-group to give telechelic polymers (**103**).^[159] These reagents capitalize on the polarization in the

triple bonds of ynamines, which preferentially transfer the electron-rich part of the alkyne to the catalyst.

Changing to cyclo(phenylene-ethynylene) monomers (**101**) allowed *Fischer* and coworkers to access PAEs, which had been difficult to make *via* ROAMP before.^[160] The use of appropriate termination reagents also prevented the formation of cyclic polymers with low molecular weight and attached handles for copolymerization.

Moving into the opposite direction, the group of *Veige* deliberately targeted the synthesis of cyclic polymers due to their distinct properties.^[18] They have lower intrinsic viscosities, are less prone to nanoparticle aggregation, and exhibit higher glass transition temperatures.^[161] The approach was named ring expansion alkyne metathesis (REAMP, *scheme 51*).



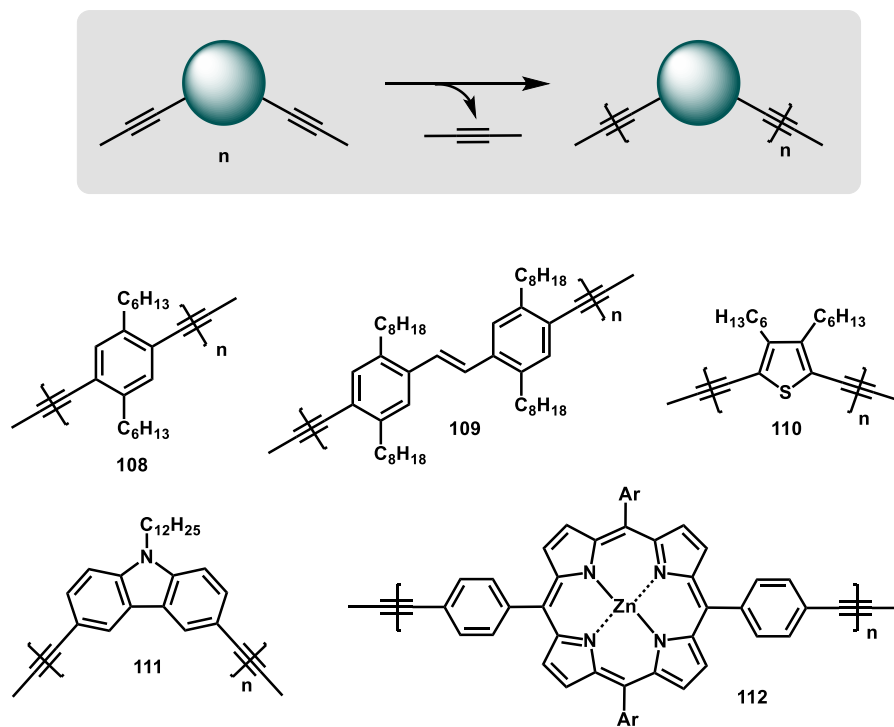
Scheme 51: Ring expansion alkyne metathesis polymerization with a tethered tungsten catalyst.

To facilitate the formation of polymeric rings, catalysts with tethered alkylidyne units were introduced.^[133b] The dimeric tungsten complex **107** functions as a cyclic initiator, inherently leading to cyclic polymers through ring expansion. The product **106** is released through an intramolecular reaction with any of the internal alkynes in the polymeric ring.

ADIMET was developed by the group of *Bunz* and others around the turn of the millennium as an alternative synthetic entry for PAEs.^[157a, c] Traditional approaches for their synthesis relied on cross-coupling methodologies, but were plagued by low molecular weight and defect structures.^[162] In contrast, alkyne metathesis provided high degrees of polymerization. Initial experiments using the ‘*Mortreux* system’ as the catalyst demonstrated simple hydrocarbon monomers to be adequate, with the polymer chain length being predominantly influenced by solubility.^[99b, 163] This property could be tuned through the length of appropriate alkyl residues in the monomers.

However, the rudimentary catalyst system failed when applied to monomers containing heteroatoms in the vicinity of the alkyne units. Also the ‘*Schrock* catalyst’ failed to polymerize thiophene-based monomers (**110**).^[157a] Only milder and more functional group tolerant molybdenum-based catalyst systems with phenol ligands were successful.^[164]

The synthesis of porphyrin-based arylene-ethynylene polymer **112**, obtained in high molecular weight and with low polydispersity employing catalysts with tridentate ligands, provides further testimony to the power of alkyne metathesis in polymer synthesis.^[90a]



Scheme 52: Selected examples of polymers prepared by ADIMET.

1.2 Motivation and Aim

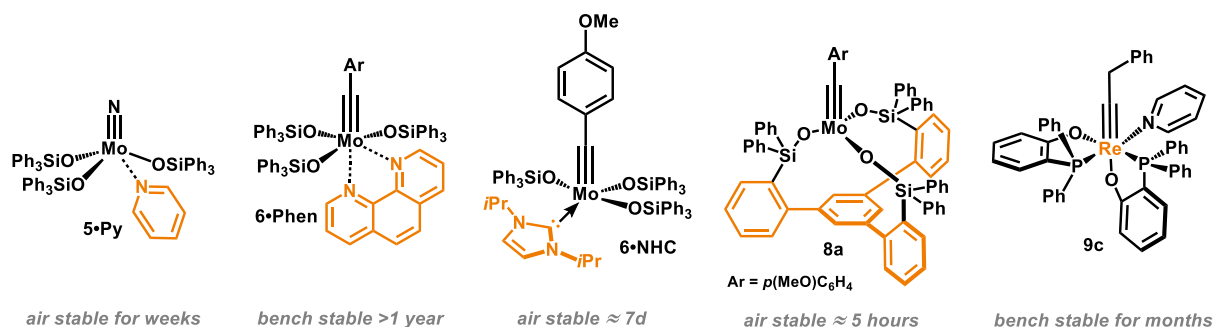
At the inception of the presented work, alkyne metathesis had left its role as an academic curiosity behind and had moved into the focus of synthetic organic chemists. Its value had been demonstrated through applications in the fields of natural product total synthesis, material, and polymer sciences. The fundamental understanding of catalysts, including the mechanisms of their working, was well advanced.^[16a]

Despite these developments, the methodology had so far not been incorporated into the community's exclusive repertoire of routinely applied reactions. To rise to such a status, a method must not only provide a unique reactivity, but must also be robust, accessible, and user-friendly. Early commercialization and the resulting widespread availability of the Grubbs catalysts in combination with their excellent stability, played a crucial part in the swift inclusion of alkene metathesis into the standard toolbox of organic chemists.^[135]

To date, the only commercially available catalyst for alkyne metathesis is *Schrock's* original tungsten alkylidyne complex (**1**). Together with *off-the-shelf* systems, such as the one from *Mortreux*, they have long been shown to be inadequate for advanced applications. In contrast, all the state-of-the-art catalysts require lengthy, difficult synthesis and cannot be bought. Notwithstanding recent advances, the catalysts stability remains their Achilles' heel and has so far prevented commercialization. Accordingly, alkyne metathesis, as a synthetic methodology, has been restricted to expert laboratories, given the required organometallic expertise for producing the catalysts.

The central aim of the presented thesis was to liberate alkyne metathesis from this limitation by designing and synthesizing an air-stable catalyst. Such a catalyst would allow also non-expert users to harness the power of alkyne metathesis and was anticipated to foster more regular use of this enabling transformation in general. The current popularity of macrocyclization strategies in medicinal chemistry would, for example, present a plethora of potential applications.^[165] Additionally, the presented work set out to remedy the decomposition issues of the 'canopy catalysts' delineated in *chapter 1.1.3.3*.

Molybdenum alkylidyne complexes are generally vulnerable to air and moisture, decomposing rapidly when exposed to the ambient atmosphere.^[109a, 166]



Scheme 53: Efforts towards stabilizing alkyne metathesis (pre)catalysts.

Some progress towards more stable catalysts has been made and will be discussed in the following.

Bindl et. al. reported the addition of pyridine to have been instrumental in isolating the molybdenum nitrido complex **5** (*scheme 53*).^[57b] The catalyst precursor was mentioned to be “sufficiently robust to be weighed in air” indicating the overall stability to benefit from forming an adduct with a donor ligand. *Heppekaussen et. al.* extended the concept by stabilizing their molybdenum alkylidyne complex with phenanthroline (**6•Phen**).^[31b] The adduct is bench stable for years but itself catalytically inactive. The stabilizing chelate ligand has to be removed through the addition of a Lewis acid and prolonged heating to liberate the active species. While the presented work was in progress, a similar approach was disclosed by the group of *Buchmeiser*. They stabilized the same complex **6** using neutral NHC ligands.^[167] Solid samples had limited lifetimes in air, contingent on the steric bulk of the ligand, with the most durable (**6•NHC**) lasting approx. seven days. The inferior stability was compensated for with less drastic activation conditions: simply heating to 80 °C provided decent metathesis reactivity. Stabilization efforts by *Hillenbrand et al.* are conceptually distinct, employing a tripodal chelating ligand.^[74] The higher resilience in regard to protic functional groups has already been discussed, but the tridentate ligands led only to minor improvements in the stability towards air and moisture. Yet another approach stems from the group of *Zhang*, who formulated a catalytically active mixture in paraffin wax for benchtop storage.^[43b] However, the catalyst’s activity decreased significantly over the course of one month.

Lastly, rhenium alkylidyne catalysts **9** were revealed to be largely air-stable as discussed in *chapter 1.1.5*.^[42] In any case, their activity thus far lags behind that of most molybdenum alkylidyne catalysts, and they have yet to demonstrate their effectiveness with advanced substrates.

Accordingly, there is a demand for a novel catalyst which (1) should be air-stable for extended periods of time, (2) exhibit reactivity without the need for preactivation ideally at ambient temperature, (3) have a functional group tolerance on par with state-of-the-art catalysts and (4) be accessible on scale with limited cost.

1.3 Results

1.3.1 Design Features of an Air-Stable Alkyne Metathesis Catalyst

As a first step, a general blueprint **113** for an air-stable alkyne metathesis catalyst was proposed (figure 8). Maximal stability was sought, while aiming to maintain the chemical virtues of its predecessors. The design was based on the insights gained from 25 years of catalyst development in the *Fürstner* group. Molybdenum alkylidynes were selected, since they are the most promising catalyst class (see chapter 1.1.3) and detailed studies on ligand effects had already been undertaken.^[17d, 43a, 73-74]

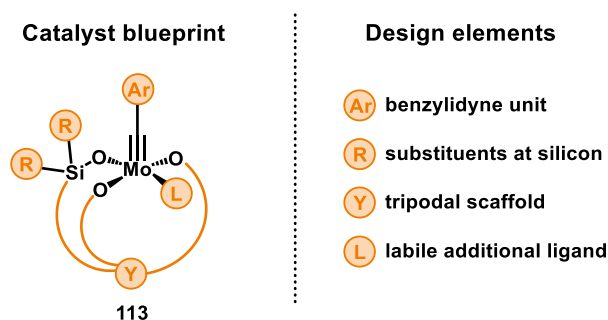


Figure 8: Design elements in a general blueprint for an air-stable alkyne metathesis catalyst of type **113**.

Four design features were identified as the primary elements influencing catalyst stability: (1) the benzylidyne unit, (2) the substituents at the silanolate ligands, (3) the tripodal ligand scaffold, and (4) an additional neutral, labile donor ligand.

Firstly, the alkylidyne unit must exhibit sufficient steric bulk to protect the metal center in the bulk material. Since it is ablated upon the first turn-over of the catalytic cycle, only a minor impact on the activity is expected. Additionally, bulky benzylidyne units were shown to be of importance for obtaining structurally defined catalysts.^[31b] For instance, the complexation failed to give the desired tripodal cage structure when a molybdenum alkylidyne precursor carrying a less encumbered *para*-methoxy substituted benzylidyne unit and the ‘slimmest’ of the canopy ligands (**19**, R = Me) were employed.^[17d]

Secondly, the substituents at silicon have to be considered. In general, silanolates were selected as ancillary ligands due to them synergizing exceedingly well with molybdenum alkylidynes. The residues generating a ‘fence’ around the catalytically active molybdenum alkylidyne unit have a crucial impact on the reactivity and are suspected to also impact the catalyst’s stability.^[119] In order to gather additional information on this second tentatively claimed correlation a sample of the most active catalyst from the ‘canopy series’ was exposed to ambient atmosphere and its decomposition followed by NMR spectroscopy (figure 9).

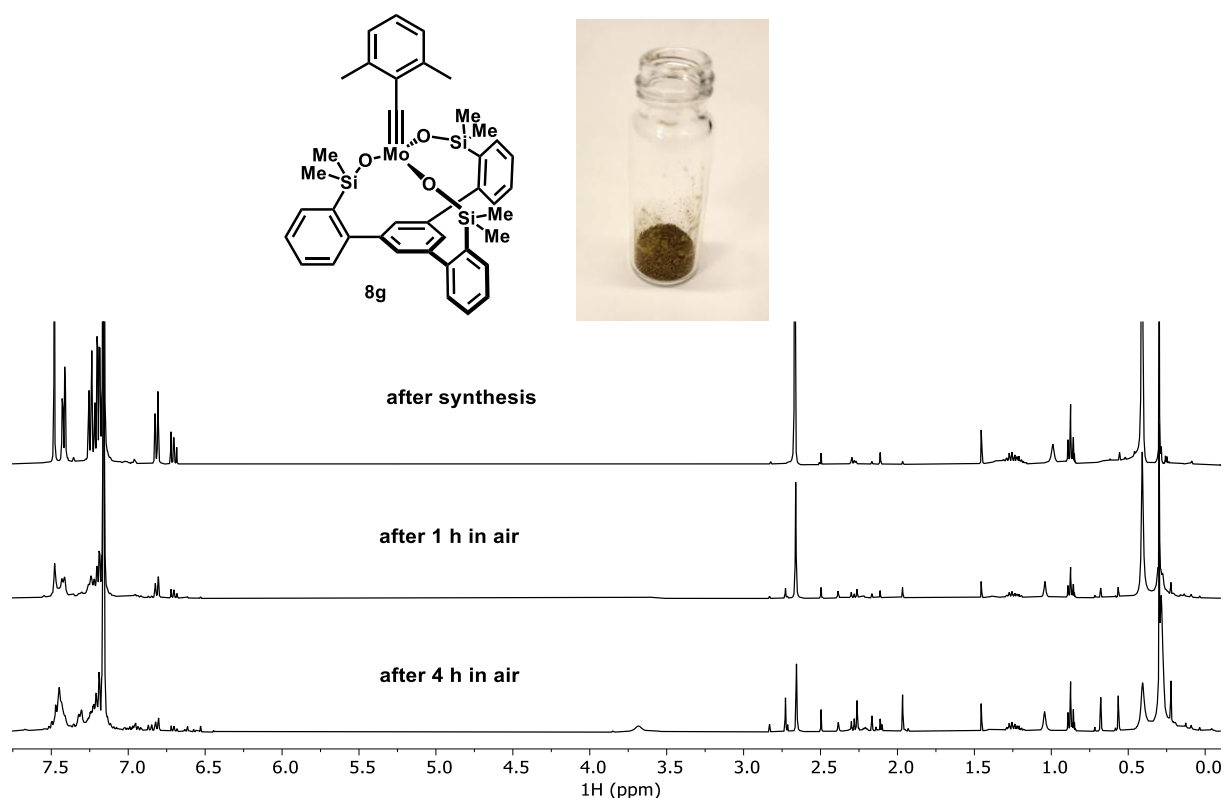
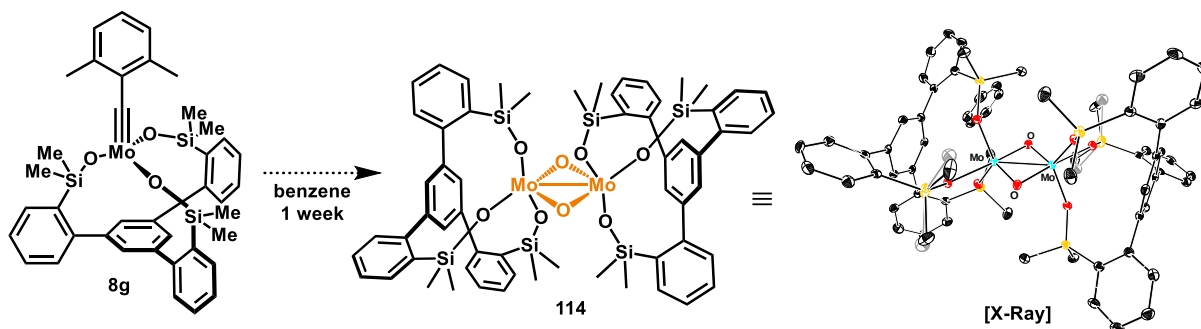


Figure 9: ^1H NMR spectra of aliquots taken from the sample exposed to air at the indicated time intervals.

The result was clear; the batch of complex **8g** underwent an immediate color change from yellow to brown/black upon exposure to air, with the majority of the catalyst decomposing within one hour. After approx. four hours, the alkylidyne unit had completely vanished and free silanol ligand was detected. The observed disintegration is considerably faster than that reported by *Hillenbrand et al.* for another member of the ‘canopy series’ carrying phenyl substituents on silicon (**8f**: half lifetime of approx. 5 h).^[91] Thus, it is reasonable to predict a new stable catalyst would require sterically demanding residues on the silanolate ligands. This is particularly true since larger substituents also safeguard against the bimolecular decomposition of the catalyst during the reaction.^[17d]



Scheme 54: Formation and structure of an oxygen bridged dimer **114** from a solution of complex **8g**.

In addition to the known $\text{Mo}\equiv\text{Mo}$ dimer that forms from **8g**, a new oxygen bridged dimer (**114**) was observed during crystallization attempts of the ‘turbo canopy’ (scheme 54). This underscores the potential risk of bimolecular decomposition. A similar unsymmetrical Mo_2O_2 core structure had been previously disclosed by *Heppekausen et al.*^[43a]

Thirdly, a tripodal ligand scaffold was favored since the chelate effect prevents the ligands from falling off the metal center in the presence of protic substrates. It further shields the coordination site *trans* to the alkylidyne, thus obstructing polymerization *via* the ‘associative pathway’. A general beneficial effect on the overall stability was also anticipated.

From previous catalyst generations it became apparent that a fine balance had to be struck between flexibility and rigidity in regard to the framework. Excessive flexibility leads to the formation of oligomers comprising several metal centers during the synthesis, whereas overly rigid ligands give monomeric complexes with reduced catalytic activity.^[73-74] The most recent design (‘canopy series’) overshoot the target with a framework exclusively consisting of sp^2 -hybridized carbon atoms. As a consequence, a slightly less rigid scaffold was targeted. This would allow for the use of aryl substituents at the silanolates in order to shield the metal center without unduly impacting the catalytic activity. In a more flexible scaffold the larger lateral substituents are expected to be able to bend out of the way of incoming substrates and readily accommodate the different geometries mandated by the catalytic cycle.^[36a]

Lastly, adduct formation with a stabilizing yet labile external ligand was anticipated to render the formally 12-electron complex air-stable. On the one hand, the ligand must bind tightly enough to the molybdenum to withstand spontaneous dissociation in the solid-state, on the other hand the ligation must be reversible in solution to release the active species. Bidentate iterations, such as the formerly successfully employed phenanthroline, are precluded by the tripodal ligand.

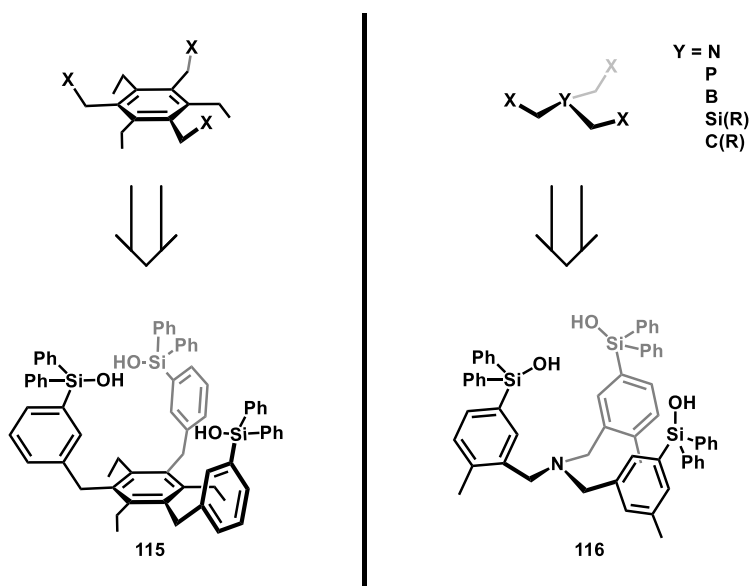


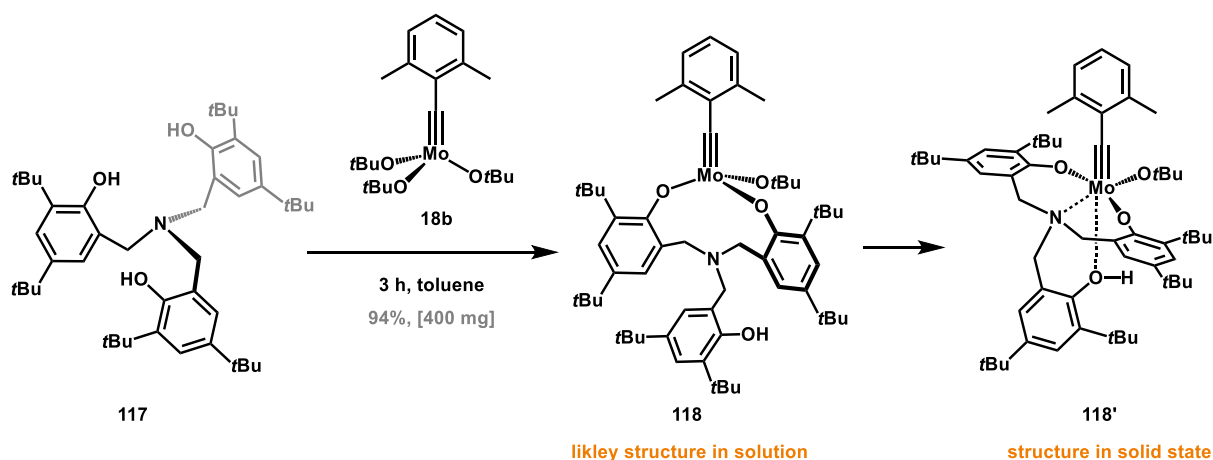
Figure 10: General designs considered for the ligand scaffold.

Overall, the design must walk to a fine line between the often opposing parameters of stability and catalytic activity. The ligand scaffold was regarded as the design feature with the most significant potential for influencing both factors. Two different designs were considered for the tether (*figure 10*).

For both scaffolds preliminary work from within the laboratory existed. A hexasubstituted benzene ring would potentially be able to arrange the three ligands into a tripodal conformation. The sp^3 -hybridized methylene linkers to the basal benzene would increase the flexibility in comparison with the ‘canopy catalysts’. However, previous efforts by *Schaubach et al.* had failed to deliver structurally defined complexes (*chapter 1.1.3.3*).^[73] Preliminary studies conducted during the author’s master’s thesis had shown that by replacing the extended alkyl chain linkers in the first ligand generation (**49**) with more rigid arenes (**115**) allowed for the formation of defined complexes.^[119] However, the synthesis of a slimmer version of this ligand with methyl residues at the silanols had failed due to the formation of siloxanes.

The second design is heavily inspired by the ligands develop by the *Zhang* group.^[69b, 70b] A central atom is used to tether three ligand arms together and methylene linkers provide the desired flexibility. In 2017, Dr. *T. Fukino* had explored the design in the *Fürstner* laboratory employing a central nitrogen as the linchpin (**116**). He pursued a ligand equipped with silanols instead of the phenols favored by the *Zhang* group and aryl substituents at the silicon in order to attain the necessary rigidity. However, the same fate befell this endeavor as *Schaubach*’s previous one: no structurally defined catalyst was obtained in combination with the molybdenum alkylidyne precursor complexes **40b** or **17**. On this basis heteroatoms had been excluded from consecutive ligand designs.^[76]

Due to the inconclusive data in the literature concerning the tripodal nature of the ligands in complexes with this scaffold design and the discouraging results obtained by *Fukino*, additional information was sought. For this purpose amine tethered trisphenol **117** with essentially the same structure as the ligands pioneered by *Zhang* and coworkers was employed to investigate their coordination behavior. The substitution with *tert*-butyl groups was intended to preclude dimerization.^[69b, 90b]



Scheme 55: Sterically demanding *N*-tethered ligand **117** fails to bind in a tripodal manner in complex **118**.

The reaction of **117** with the precatalyst **18b** resulted in the clean formation of a monomeric species. NMR spectroscopy revealed the tridentate ligand to have bound, but one *tert*-butoxide from the starting material was retained. Consequently, a tripodal conformation could not have formed. X-ray diffraction of single crystals showed the molybdenum center to have an

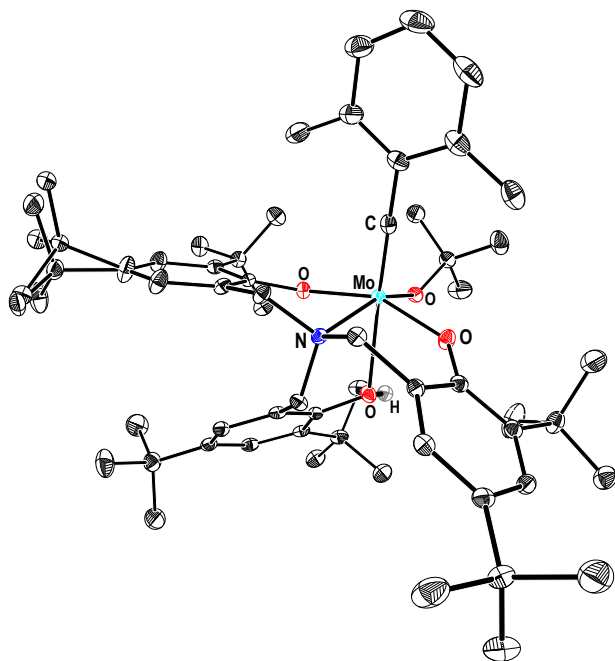


Figure 11: Structure of complex **118** in the solid-state; H-atoms were omitted for clarity with the exception of the phenolic –OH.

octahedral coordination geometry in the solid-state (figure 11).

In addition to two phenolate ligands, the nitrogen tether and the remaining alkoxide are bound to the metal in the equatorial plane. The axial positions are occupied by the alkylidyne unit and the third phenol from the tridentate ligand, which remains protonated.

The bond to the third phenolic O appears to be weak (2.474 Å) likely due to the strong *trans* effect of the alkylidyne. In combination with the ^{15}N shift of the nitrogen tether, which does not change significantly from the ligand to the complex, a tetrahedral coordination

geometry of the complex in solution is assumed ([2D ^1H - ^{15}N HMBC]: ligand $\delta = -329$ ppm; complex $\delta = -324$ ppm).

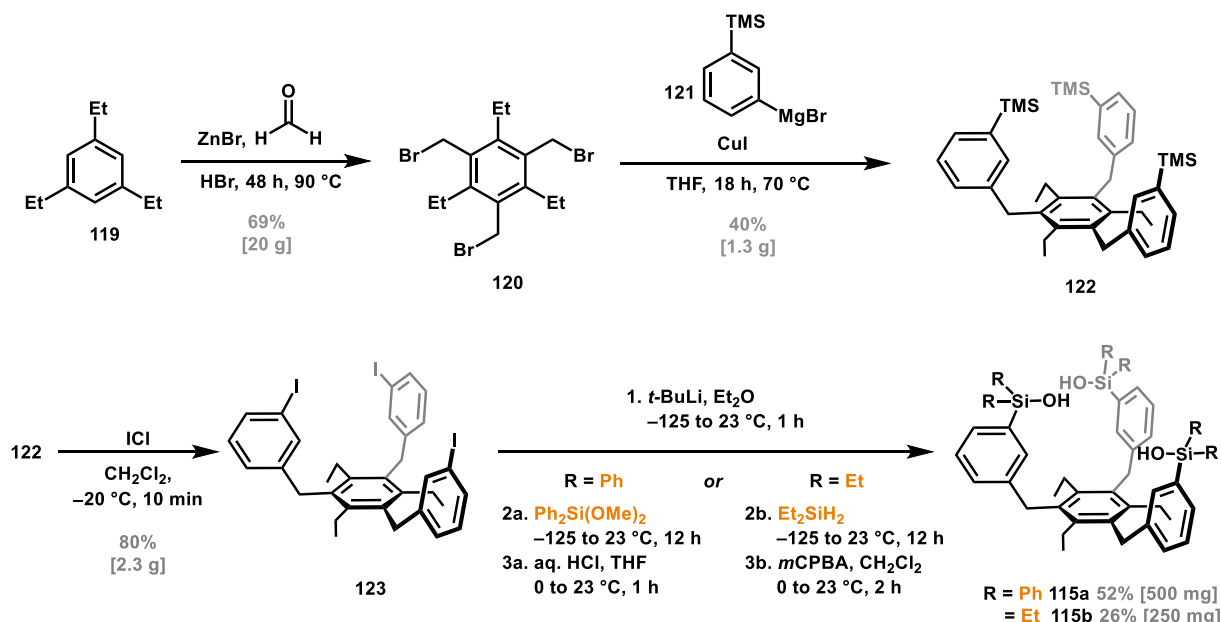
Overall, ligand **117** failed to bind in a tripodal manner. The data stands in stark contrast to the way complexes with analogous ligands are commonly drawn in the literature. Aside from that, the coordination of the metal center by the nitrogen tether does not appear to be as strong as feared and reversible in solution – an observation which reflects well on the chances of success with ligands of design **116**.^[90a]

Strategically moving the positioning of the ligand from *ortho* to *meta* in reference to the placement of the linker, as shown in the design, should further obviate detrimental binding of the tether. In addition, the change was anticipated to result in the relaxation of the ligand geometry, thereby promoting the formation of a complex in which the ligand is bound in a tripodal configuration.

With a comprehensive blueprint for an air-stable alkyne metathesis catalyst in hand and two design ideas for the critical, tripodal ligand framework, it was time to transfer the plan from the drawing board into the laboratory.

I.3.2 Ligand Synthesis

For both designs preliminary work from within the group existed. In the case of the scaffold based on a hexasubstituted benzene ring, the author had already shown during his master's thesis that ligand **115a** carrying phenyl substituents was attainable through the route outlined in *scheme 56*.^[119]

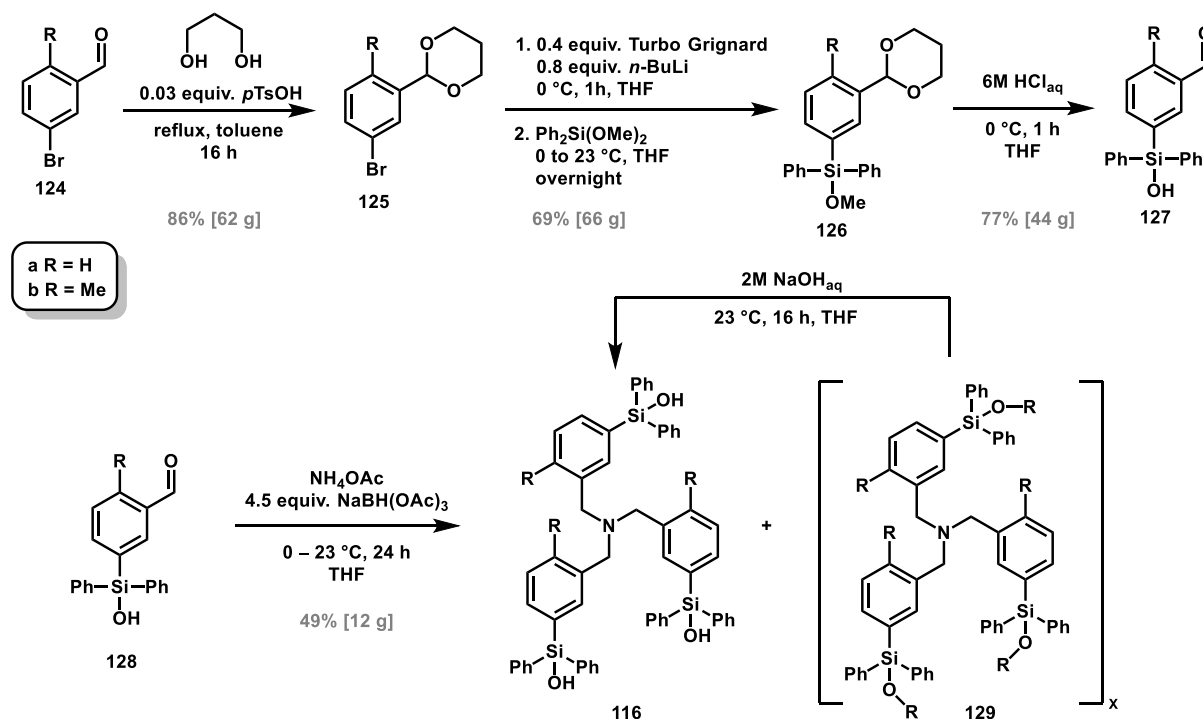


Scheme 56: Divergent synthesis for ligands based on a hexasubstituted benzene with Ph or Et on the silanols.

However, the catalyst formed with the help of **115a** proved to be no match for the ‘turbo canopy’ catalyst in terms of activity. As a consequence, a slimmer array of substituents at the silanols was targeted in this work to increase reactivity. Iododesilylation of compound **122**, which could be reached *via* literature known procedures, gave the tri-iodide **123**. Exhaustive lithium-halogen exchange was followed by quenching with an appropriate silane. In contrast to di(aryl)di(alkoxy) silanes, di(alkyl)di(alkoxy) silanes are not suitable in the reaction, making a small change in the procedure necessary. Employing diethylsilane gave the hydrosilane in acceptable yield. However, the subsequent oxidation proved to be troublesome, even under buffered conditions. Presumably, the flexible ligand arms permit intra- and intermolecular siloxane formation reactions – a common problem when working with sterically less encumbered silanols.^[168] Most likely, the issue had simply not arisen during the synthesis of the slimmer versions in the ‘canopy series’ because the exceedingly rigid ligand scaffold precluded intramolecular reactions and the hydrogen bonding kept the silanols oriented inward. Regardless, a small quantity of the desired ligand **115b** could be obtained.

The synthesis of ligands with a single atom linchpin could rely on a route previously developed by *T. Fukino*. A tertiary amine was chosen as the tether because the preparation was expected to be facile and scalable. Execution of the synthesis proved straightforward with only minor

adjustments in the conditions necessary (*scheme 57*). The synthetic work was conducted together with *Christian Wille*.



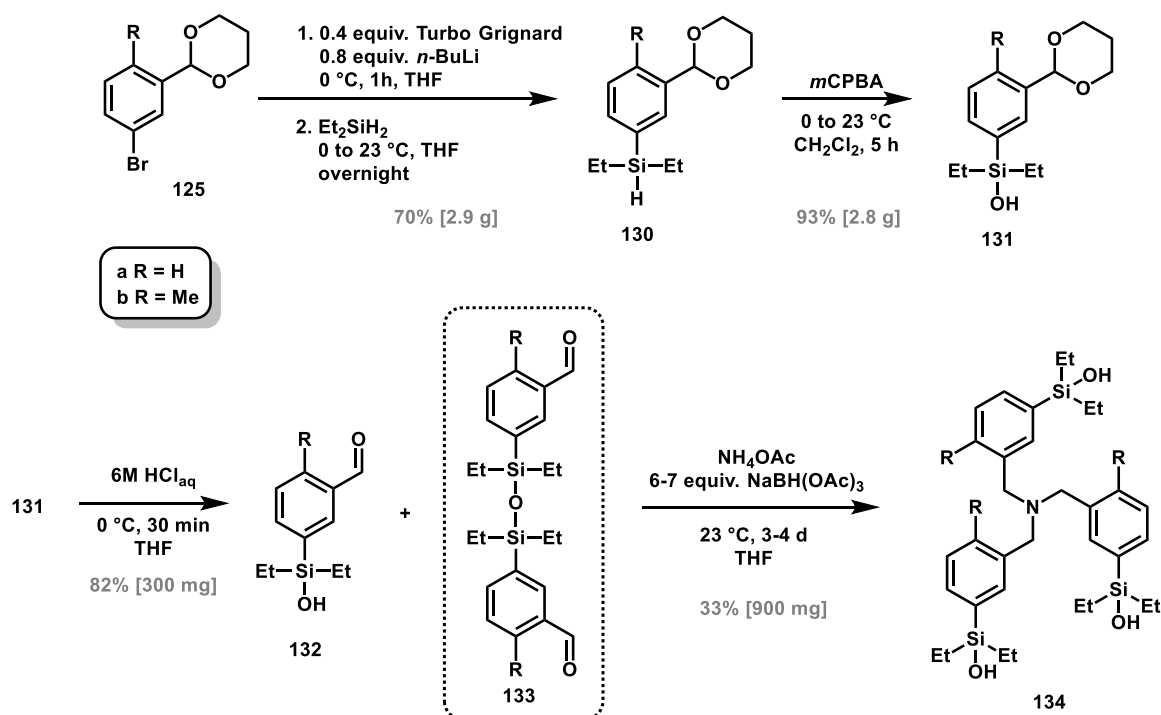
Scheme 57: Preparation of amine tethered tris(silanol) ligand **116** on multigram scale (yields given for $R = \text{H}$).

Initially, the ligand **116** was prepared with methyl substituents in the position *para* to the silanols. Further into the project, the moiety turned out to have no influence on the conformation of the ligand. Hence, when scaling the route to ligand **116**, the methyl substituent was omitted solely due to the reduced cost of the starting material **124a**.

The aldehyde **124** was protected as an acetal prior to a mild metal-halogen exchange at non-cryogenic temperatures.^[169] The resulting organometallic species was quenched with di(phenyl)di(methoxy) silane to afford **126**. Simultaneous hydrolysis of the alkoxy silane and cleavage of the acetal with aqueous hydrochloric acid set the stage for the reductive amination. However, as soon as the silanol moiety is revealed, there is the danger of siloxane formation. The reactions have to be performed at high dilutions and it is essential to diligently neutralize the reaction mixtures before concentrating in order to evade this side reaction. Still, during the reductive amination the formation of varying amounts of inter- and/or intramolecular siloxanes (**129**) could not be fully prevented. The issue could be remedied by stirring the oligomeric fraction with aqueous base overnight, cleaving the siloxanes to afford the desired ligand **116**. On smaller scale (4 g) yields of ca. 60% could be obtained. When increasing the scale, the degree of dilution was limited by the size of the glassware, resulting in a reduced yield (49% for 12 g; single largest batch).

Overall, the synthesis of ligand **116** was accomplished in 22% yield over five steps from cheap commercial starting materials without resorting to expensive transition metal catalysts or harsh conditions.

Next, a slimmer version of the ligand was envisioned. To obtain the ethyl variant of the ligand, minor changes had to be made in the route (*scheme 58*). The reasoning for targeting an embodiment with ethyl rather than even slimmer methyl groups at the silanol ligands was twofold: on the one hand ethyl residues had been shown to effectively prevent the bimolecular decomposition in the ‘canopy series’ and on the other hand the likelihood of troublesome siloxane formation during the ligand synthesis increases for less shielded silanols.



Scheme 58: Synthesis of the ethyl variant **134** (yields given for R = H).

Utilizing acetal **125** from the previous synthesis and the same mild metalation conditions, the reaction with diethyl silane afforded compound **130**. In contrast to the experience with the other ligand scaffold, in this case, the oxidation with *meta*-chloridoperoxybenzoic acid furnished the silanol **131** in good yield. However, unveiling the aldehyde under acidic conditions was precarious. High dilution and a strict reaction control was necessary to minimize the formation of dimer **133**. Even the neat product **132** is prone to spontaneous siloxane formation. Hence, it was immediately used in the next step. Unsurprisingly, the following reductive amination proved to be less effective for the synthesis of the ethyl variant. Only low yields of ligand **134** could be obtained with the analysis of the crude reaction mixture showing a host of different cross-linked species. Efforts to rectify the issue with base were not effective in this instance. Further, attempts at purifying the product through flash chromatography revealed silica to catalyze the condensation to siloxanes.

Although sufficient material could be obtained to continue the investigation, an alternative route had to be found. Producing the troublesome silanols during the last step in a clean reaction, without the need for purification, would reduce the risk of siloxane formation. An

exploratory study showed the required trisilane **136** to be obtainable in moderate (unoptimized) yield. A brief screening for appropriate oxidation conditions towards the tris(silanol) was undertaken (*table 3*).

Table 3: Conditions screened for a revised synthesis of the ethyl ligand.

entry	conditions	comments	results
1	3.3 equiv. <i>m</i> CPBA, CH ₂ Cl ₂ , 1 h		aldehyde 135 and dec.
2	a) CSA, CH ₂ Cl ₂ , 1 h b) 3.3 equiv. <i>m</i> CPBA, CH ₂ Cl ₂ , 30 min	salt formation successful	reaction incomplete
3	a) TFA, CH ₂ Cl ₂ , 1 h b) 3.3 equiv. <i>m</i> CPBA, CH ₂ Cl ₂ , 6 h		decomposition
4	a) BF ₃ ·Et ₂ O, Et ₂ O, −78 °C, 1 h b) 3.3 equiv. <i>m</i> CPBA, CH ₂ Cl ₂ , 1.5 h	adduct formation successful	decomposition
5	a) BH ₃ ·Me ₂ S, THF, −78 °C, 1 h b) Oxone, methanol/water, 12 h		decomposition
6	KMnO ₄ , THF, sonication, 18 h		reaction incomplete
7	Pd/C, dioxane/buffered H ₂ O, 3 h	purification with Florisil®	30% of 134a

Formerly effective conditions with *meta*-chloroperoxybenzoic acid did not yield the desired ligand (*entry 1*). The oxidation of the tertiary amine to the *N*-oxide was speculated to be a detrimental side reaction. Efforts to evade this by quaternizing the amine through protonation or adduct formation did not lead to a clean reaction (*entry 2-4*). Different oxidations were tested but resulted in decomposition or very slow turnover (*entry 5+6*).^[168a] The best result was obtained in a heterogeneous catalytic oxidation with water.^[170] However, the crude mixture still required purification and even using neutral Florisil® siloxane formation ensued. Based on these results, *B. Breustedt* went on to find a method for the clean and quantitative oxidation of the trisilane **136** into the desired ligand utilizing a manganese (I) catalyst and water as the terminal oxidant.^[168b, 171]

The NMR spectra of all the synthesized ligands are in accordance with perfect *C*₃-symmetry in solution – a fact which foreboded well for binding in a tripodal manner during the

complexation. The preorganization is also present in the solid-state structure of ligand **116b**, exhibiting intramolecular hydrogen bonding between the silanols (*figure 12*).

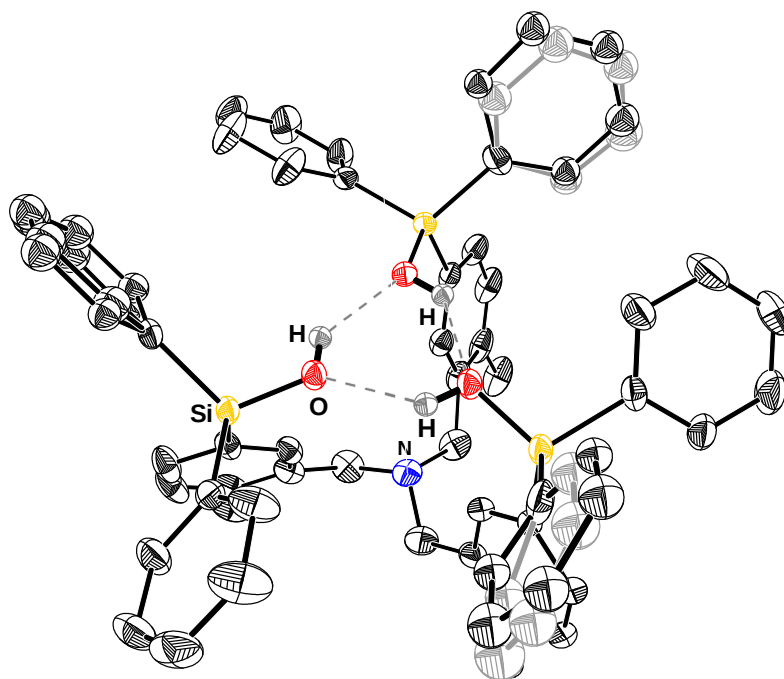
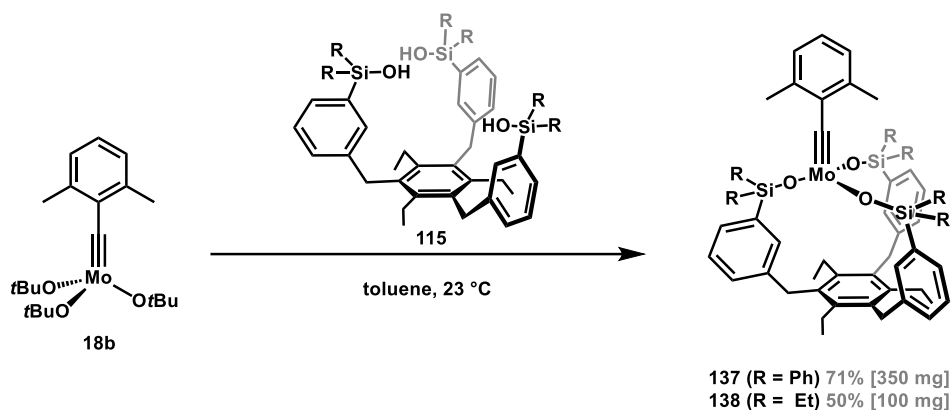


Figure 12: Structure of ligand **116b** in the solid-state; all H-atoms were omitted for clarity, except those involved in the mutual hydrogen bonding of the silanol groups and disordered parts are shown in grey.

1.3.3 Complexation and Adduct Formation

With the ligands in hand, the complexation with a suitable precursor complex was the next step in the synthesis of an air-stable alkyne metathesis catalyst. Precatalyst **18b** was selected due to its bulky benzyldiyne unit and the anticipated facile ligand exchange *via* protonolysis with release of *tert*-butanol, which can be removed under high vacuum.^[76]

In the first ligand class, the phenyl variant **115a** (R = Ph) had already been shown to afford the desired complex **137** in good yield.^[119] Disappointingly, stirring a solution of precatalyst **18b** with ligand **115b** (R = Et) resulted only in moderate yields of complex **138**. NMR analysis of the crude reaction mixture showed broad signals in the background, indicating the formation of oligomers. Extraction with dichloromethane and precipitation through the addition of an excess of pentane, afforded the complex **138** in reasonable purity (*scheme 59*).

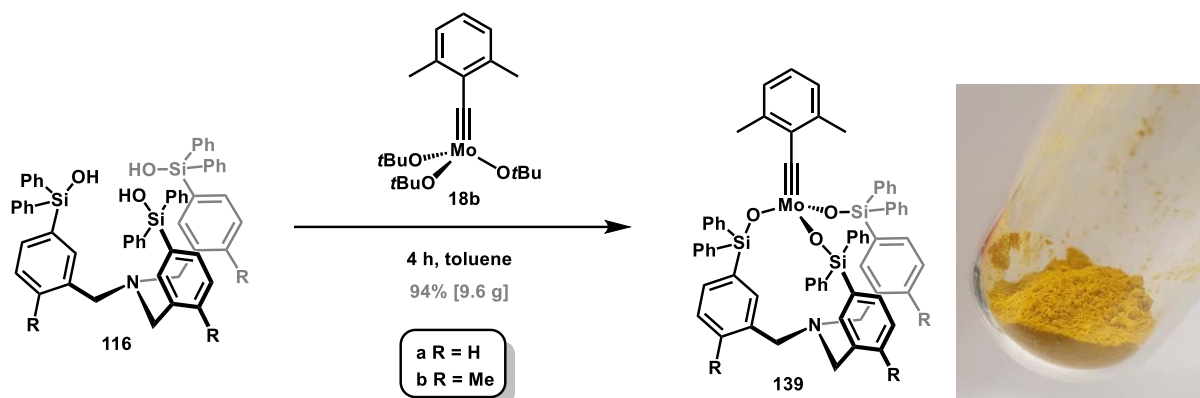


Scheme 59: Complexation of precatalyst **18b** with ligands **115** to give catalysts **137** and **138**.

In accordance with the proposed structure, the recorded spectral data of **138** in [D₈]-toluene showed the C₃-symmetry of the ligand to be retained. The formation of a monomeric species could further be confirmed by high resolution mass spectrometry. The complex carrying ethyl substituents on the silanolate ligands turned out to be less stable than its congener **137**. During NMR analysis, heating a solution of **138** to 60 °C entailed decomposition and appearance of broad background signals. The combination of a more flexible ligand scaffold with slimmer residues at silicon appears to favor the detrimental oligomerization side reaction, impacting the yield of the complexation. Despite these discouraging results, a small amount of the desired complex could be secured for testing in catalysis.

The second ligand class, on the other hand, afforded the desired complexes **139a** and **b** in excellent yields (*schemes 60*). No interference from competing oligomerization was observed. Simple removal of the solvent gave complex **139** in analytically pure form as a bright yellow powder. The reaction proved scalable with 9.6 g being the largest batch of the catalyst isolated so far. When preparing the complex on a multigram scale, stripping the crude material several times with pentane is recommended to remove residual toluene. Alternatively, the material can

be dissolved in a small amount of dichloromethane and the complex precipitated by addition of the solution to a large excess of pentane.



Scheme 60: Synthesis of alkyne metathesis catalyst **139** and a photograph of the solid material (yield for **139a**).

The recorded NMR spectra of **139** supported the proposed conformation with the ligand binding in a tripodal manner. The ^{15}N NMR shifts of the free ligand and the complex are very similar, indicating that the nitrogen is not bound to the metal center ([2D ^1H - ^{15}N HMBC]: ligand $\delta = -335$ ppm; complex $\delta = -333$ ppm).

Orange single crystals suitable for X-ray diffraction could be grown from a saturated benzene solution of complex **139b** (figure 13). Indeed, a distance of 5.30 Å between the nitrogen tether

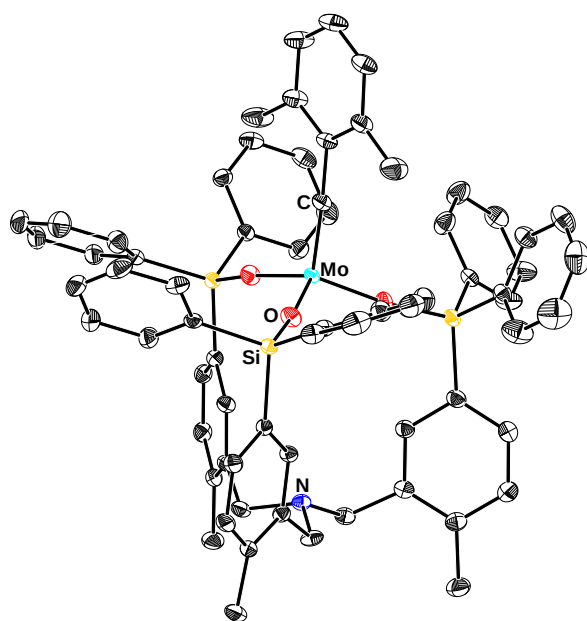


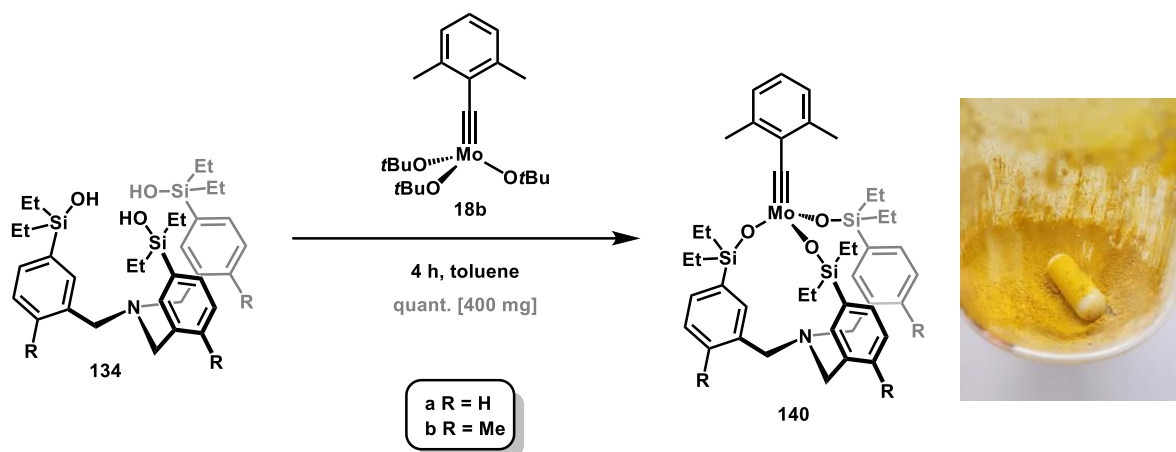
Figure 13: Structure of complex **139b** in the solid-state.

and the molybdenum atom makes any interaction highly unlikely, even though the nitrogen lone-pair is directed into the tripod formed by the ligand. Overall, the design considerations discussed above are largely vindicated. By moving the attachment point of the ligands *meta* to the linkers the nitrogen linchpin is too distant from the metal center to bind. Also, the relaxed ligand architecture manifests itself in changed torsion angles for the Si–O–Mo–C units: 112.3°, 32.4° and 36.5°. These are considerably smaller when compared to an example from the canopy series (**8f**: –105.0°, –124.0°, –147.2°)^[74] and more similar to the angles of the parent complex **6** with monodentate ligands (–98.3°, –4.4°, –1.2°)^[43a]. The ‘concave’ binding mode of the new ligand is considered evidence for the absence of ring strain in the complex – a property which might allow a fourth stabilizing ligand to bind without the danger of ring-opening as observed for the ‘canopy series’.^[17d] The Mo≡C bond length (1.747 Å) and the angle of the alkylidyne unit (176.9°) fall into the expected range.^[74] The C–Mo–O angles (107.0°,

and the molybdenum atom makes any interaction highly unlikely, even though the nitrogen lone-pair is directed into the tripod formed by the ligand. Overall, the design considerations discussed above are largely vindicated. By moving the attachment point of the ligands *meta* to the linkers the nitrogen linchpin is too distant from the metal center to bind. Also, the relaxed ligand architecture manifests itself in changed torsion angles for the Si–O–Mo–C units: 112.3°, 32.4° and 36.5°. These are considerably smaller when compared to an example

107.4°, 105.6°) show a close-to-ideal tetrahedral coordination geometry around the molybdenum.

Combining precatalyst **18b** with the ethyl variant of the ligand in toluene afforded complex **140** in excellent yield (*scheme 61*). With this scaffold design even the slimmer substituents do not entail oligomer formation, indicating its preorganization to be superior in comparison to the other tested framework.



Scheme 61: Synthesis of the alkyne metathesis catalyst **140** with ethyl substituents at silicon.

The resulting complex was obtained as a bright yellow solid and was highly soluble in most organic solvents (except for pentane) rendering crystallization challenging. Its constitution was therefore confirmed by NMR spectroscopy and elemental analysis.

In addition to surveying the standard NMR nuclei, ^{95}Mo shifts of the molybdenum alkylidyne complexes were recorded (*figure 14*).

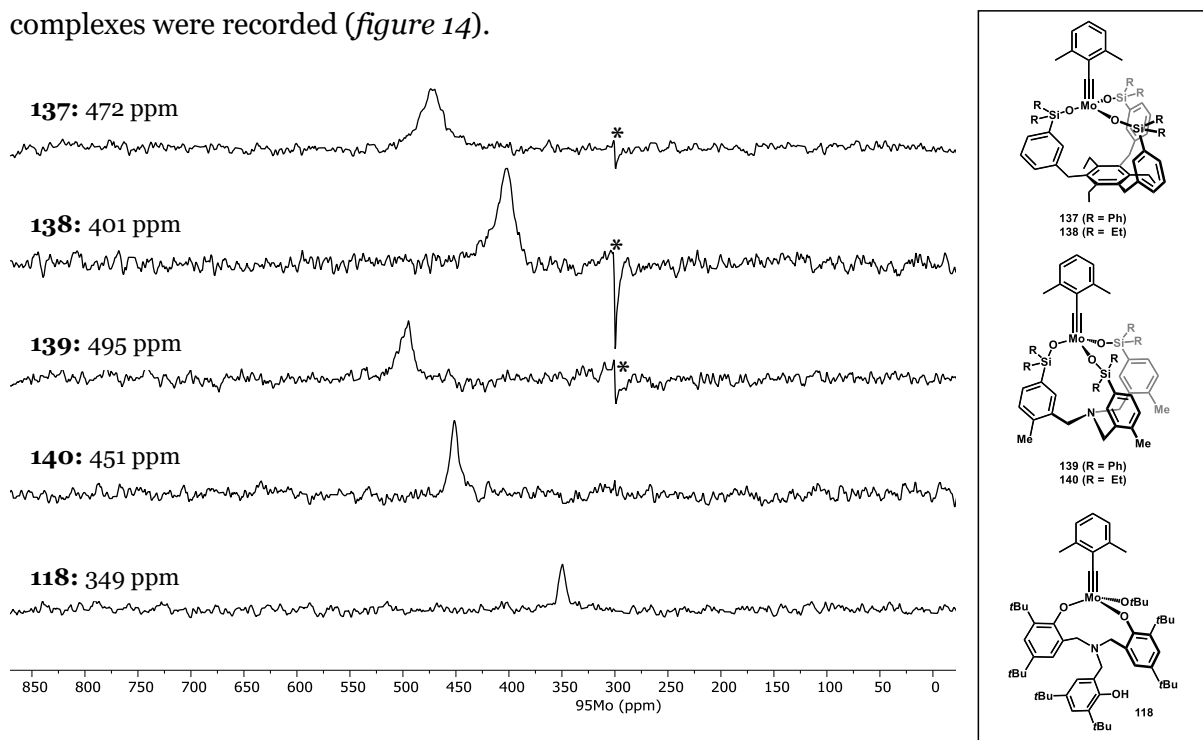


Figure 14: ^{95}Mo NMR spectra of different molybdenum alkylidyne complexes; recorded at 60 °C with the exception of **138** (25 °C); *offset artefacts.

For the most part, the spectra were measured at 60 °C in order to slow the quadrupolar relaxation and obtain sharper signals. Only **138** had to be investigated at ambient temperature due to it decomposing at 60 °C. The complexes showed signals in the expected range (δ = 472 ppm (**137**); 401 ppm (**138**; at 25 °C); 495 ppm (**139**); 451 ppm (**140**)) with the aryl substituted ligands resulting in more deshielded nuclei.

Fürstner and *Copéret* recently demonstrated the most active, molybdenum-based alkyne metathesis catalysts to exhibit shifts in the region above 350 ppm.^[78] Following this parameter, good activity was expected for all the newly synthesized complexes equipped with silanolate ligands.

A comparison to the complex **118** carrying two phenolate and an alkoxide ligand is instructive; in this case, the detected molybdenum shift (δ = 349 ppm (**118**)) is exactly at the border defined for good catalytic activity. Hence, the complex was expected to demonstrate some reactivity in alkyne metathesis, yet to be less effective than silanolate-based catalysts. Indeed, it only showed activity at elevated temperatures (for more details see *chapter 1.3.5*).

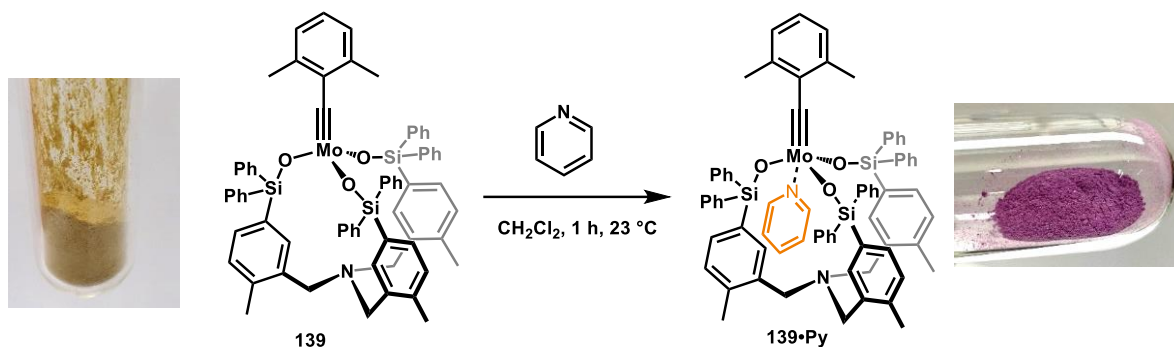
In any case, it is imperative to exercise caution when using ⁹⁵Mo NMR spectroscopy as a predictive tool for the reactivity of catalysts. The NMR shifts are influenced by a multitude of factors including solution state dynamics and the geometry of the ligand sphere. The same is valid for the catalytic activity, which does not only depend on the electronic situation at the metal center, but also on factors such as steric hindrance and catalyst stability. Therefore, ⁹⁵Mo NMR shifts can merely be taken as an indicator of reactivity among closely related complexes.

The final piece required for synthesizing an air-stable catalyst for alkyne metathesis was the incorporation of an additional stabilizing ligand that is also labile. Complex **139** was selected as a test case for the screening for an appropriate candidate. The scaffold design of **137** and **138** had proven challenging in the synthesis and had been prone to oligomer formation during complexation. It was therefore excluded from further synthetic efforts towards an air-stable catalyst. While **140** was also accessible on a reasonable scale, the better shielding of the molybdenum alkylidyne unit through the phenyl residues in **139** was expected to pay dividends in terms of stability.

An ideal neutral ligand would bind tightly to the molybdenum in the solid-state and be labile in solution. The group of *Buchmeiser* had already shown NHCs to coordinate with excessive strength to similar complexes and they were excluded from consideration.^[167] Simple pyridine was selected as a starting point.

Addition of 1.5 equivalents of pyridine to a yellow solution of complex **139** resulted in a prompt color change to deep lilac (*scheme 62*). Ensuing experiments demonstrated this to be an excellent indicator for judging if an adduct had formed. Removal of the solvent under high vacuum afforded **139•Py** as a purple powder in quantitative yield. Investigating the adduct by NMR at ambient temperature produced broad peaks in the spectrum (*figure 15*). Upon cooling

the sample to 253 K, sharp signals were detected, corresponding to a species in which the C_3 -symmetry of the starting complex was broken. The coordination of the pyridine leads to a C_S -symmetry in the ligand backbone resulting in signals for the ligands arms in a ratio of 2:1.



Scheme 62: Synthesis of the pyridine adduct **139•Py**.

Variable temperature (VT) NMR studies suggested the binding of pyridine to be reversible (*figure 15*). The signal broadening at ambient temperature is caused by an equilibrium on the NMR time scale between the adduct and the free complex alongside with dissociated pyridine. Warming the sample to 323 K showed the peaks to coalesce into sharper signals corresponding to the free complex **139**. The process is accompanied by the characteristic color change from the deep lilac of the adduct to the yellow/orange of the catalyst. The reversible complexation/decomplexation of pyridine is therefore facile, nondestructive, and temperature dependent.

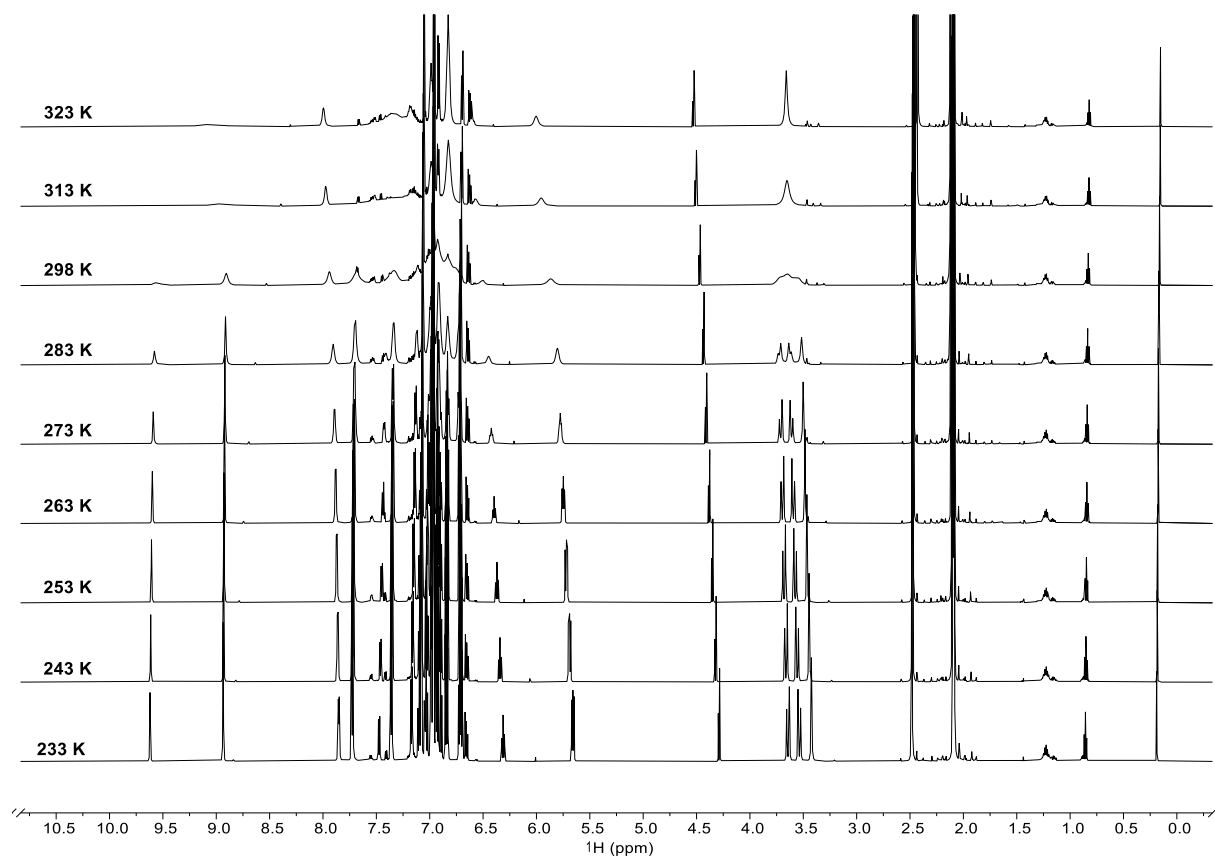
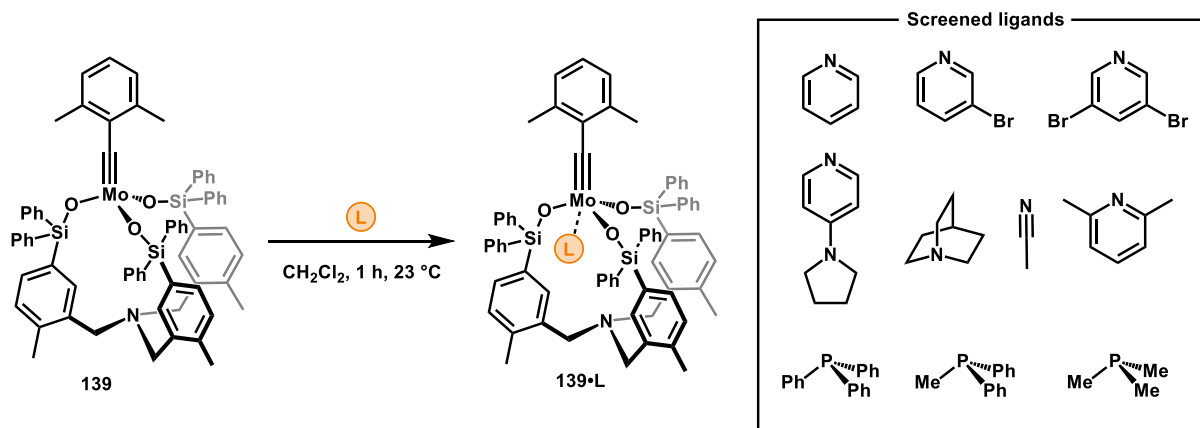


Figure 15: ^1H NMR of **139•Py** in $[\text{D}_8]\text{-toluene}/\text{CD}_2\text{Cl}_2$; 323 – 233 K.

Following this example, a row of other ligands were screened (*scheme 63*). Generally, the presence of the adduct could be easily deduced from the color of the reaction solution.



Scheme 63: Ligands screened for forming stable adducts with complex **139**.

To start, commercially available pyridines with different σ -donating strength were surveyed. 3-Bromopyridine behaved similar to pyridine, whereas 3,5-dibromopyridine proved far more labile: the additional ligand was partly removed when washing the solid with pentane at ambient temperature and even at 228 K the ^1H signals of the adduct did not fully sharpen. ^[172] On the opposite site, the more electron rich 4-pyrrolidino-pyridine binds tightly to the molybdenum, showing no equilibrium with the free complex at ambient temperature. The bicyclic amine quinuclidine and acetonitrile also form adducts, but are largely removed again when washing the obtained material with pentane and drying it under high vacuum. They were not further investigated. The more sterically demanding 2,6-lutidine did not bind at all and the solution of the complex remained yellow. The same is true for triphenylphosphine. While methyldiphenylphosphine binds to the complex, it turned out to be too labile, likely on steric grounds. Finally, trimethylphosphine afforded a satisfactory adduct, exhibiting an equilibrium with the free complex at ambient temperature. However, the low boiling point and the propensity of alkyl phosphines for oxidation made it a less attractive choice than the benign pyridine. ^[81c]

The survey of additional stabilizing ligands suggested the initial pyridine to be a good compromise. It forms stable adducts with complex **139**, but is sufficiently labile to readily reveal the free catalyst, even at ambient temperature. Crystals of two embodiments of **139·Py** (**a** and **b**) could be grown from dichloromethane/pentane solutions through slow evaporation of the solvents (*figure 16*).

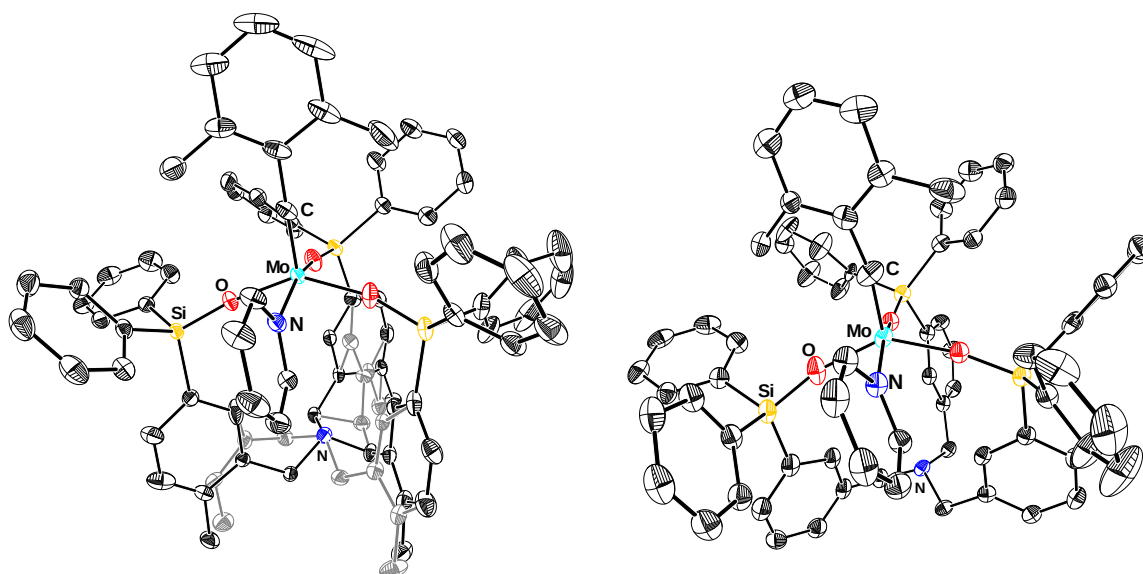
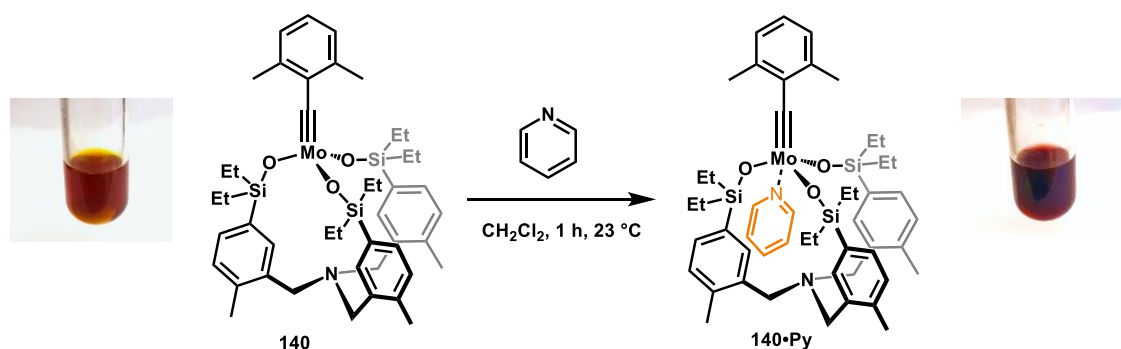


Figure 16: Solid-state structures of the pyridine adducts of complexes **139a** and **139b**; disordered parts in grey.

As expected, the pyridine is tightly bound in the solid-state (**139b**•Py: Mo–N 2.255 Å). The coordination geometry around the molybdenum changes in the adduct to square-pyramidal with the angles between the oxygen atoms (O–Mo–O: 95.8° and 94.0°) being slightly larger than between oxygen and nitrogen (O–Mo–N: 80.9°). Also, the alkyldiene unit is somewhat more bend than in the free complex (171.9°) angling away from the additional ligand. The phenyl residues on the silanolates are arranged in a ‘protective’ fence around the metal center, thereby effectively shielding it in the solid-state.

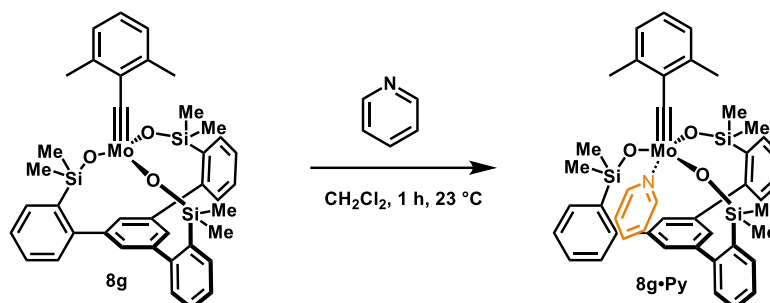
Displaying both structures side-by-side demonstrates that there is barely any difference between the two and the methyl groups *para* to the silanolate ligands do not impact the overall conformation. Hence, the properties of **139a** and **139b** (and their respective adducts) are virtually the same.

With pyridine determined as the optimal additional ligand, adducts of **140** and the most active complex from the ‘canopy series’ **8g** were prepared. This enables a comparison between catalysts with different ligand designs with respect to their stability.



Scheme 64: Adduct formation of complex **140** with pyridine.

Complex **140** readily formed an adduct with pyridine as indicated by the characteristic color change (*scheme 64*). However, the additional ligand appears to bind somewhat less tightly to **140**, since sharp ^1H NMR signals could only be detected at 233 K. The finding is in line with the more electron-releasing alkyl substituents on the silanolate ligands and the therefore presumably reduced Lewis acidity of the molybdenum center.



*Scheme 65: Adduct formation of ‘turbo canopy’ **8g** with pyridine.*

The adduct of catalyst **8g** with pyridine could be prepared in the same manner as described above (*scheme 65*). Also in this case, the NMR signals only combined into sharp peaks at very low temperatures (233 K) – for comparison **139•Py** could be characterized at a temperature 20 Kelvin higher (253 K).

In summary, the synthesis of a new structurally well-defined complex was accomplished following the blueprint for an air-stable alkyne metathesis catalyst laid out in *chapter 1.3.1*. The more promising ligand scaffold of two initial designs was singled out and an appropriate neutral ligand for the adduct formation was selected. Several versions of the complexes, following the same general design, had been synthesized and were available for assessing their stability. A ‘stabilized’ version of the latest catalyst generation could also be prepared for comparison.

1.3.4 Stability Studies

The central hypothesis of the project rests on the assumption that ligation of the catalyst with an additional, neutral ligand enhances the stability. To validate this premise, it was first necessary to determine the baseline stability of the unligated complex. To this end, a sample of **139** was removed from the protective argon atmosphere in the Schlenk flask and exposed to the ambient atmosphere. The batch was stored in an open vial on the bench and the degree of decomposition was assessed by NMR analysis of aliquots taken from the batch at the indicated time intervals (*figure 17*).

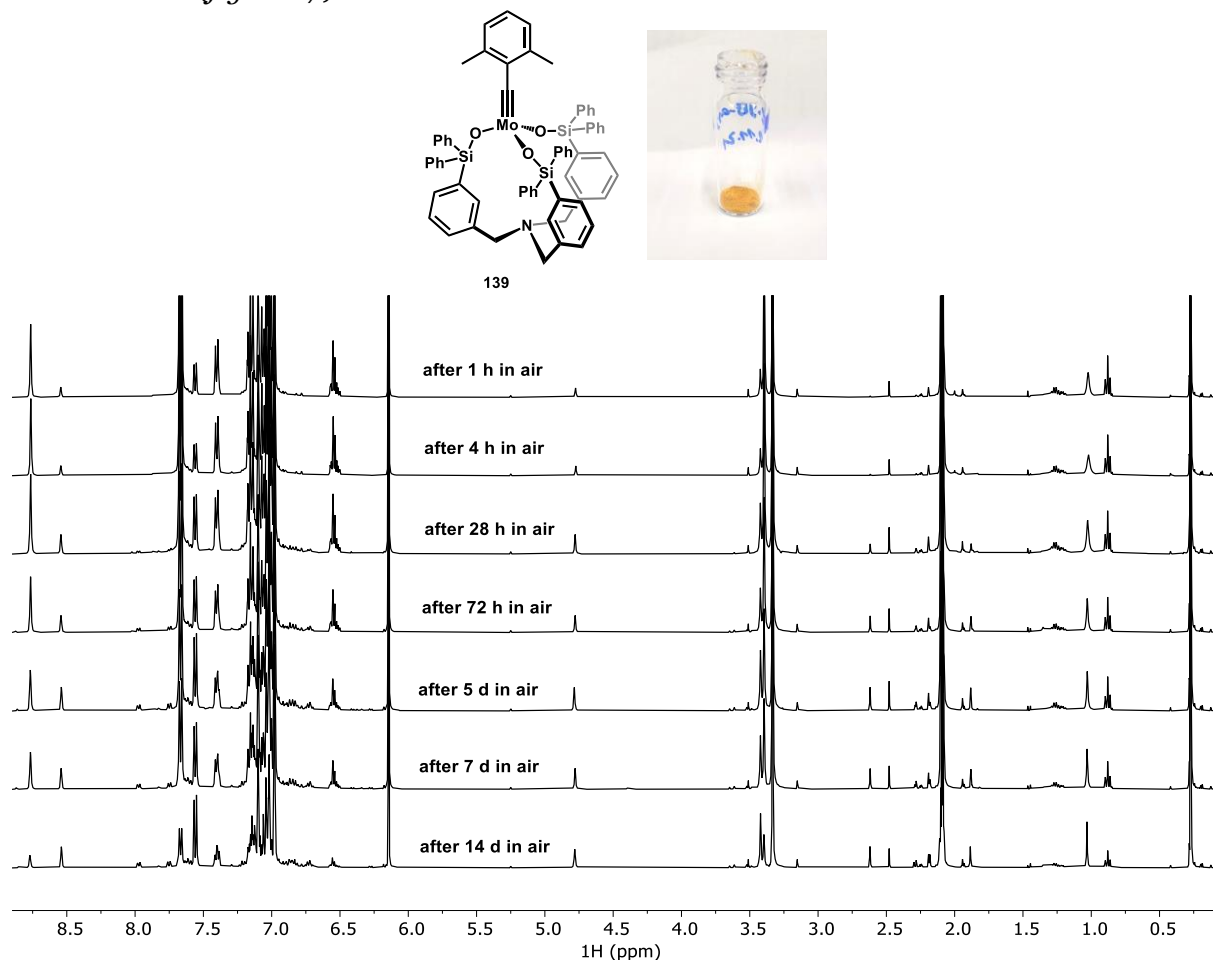


Figure 17: ¹H NMRs tracing the decomposition of **139** when exposed to the ambient atmosphere.

The ¹H-signal of the aromatic protons, located between the silanolate ligands and the linkers, was found to be the most diagnostic signal ($\delta = 8.76$ ppm). It can be clearly distinguished and the signal emerging in close proximity is attributed to the hydrolyzed ligand.

Already the unligated complex has a half-life on the order of days. Its enhanced stability is a marked improvement when compared to the ‘canopy catalysts’, which decomposed within hours when kept in air (see *figure 9*).^[74] The result can be seen as an affirmation of the protective properties of the different features of the general design: namely the bulky alkylidyne unit, the protective ‘fence’ of phenyl residues around the metal center and the

tripodal scaffold. Catalyst **139** can be weighed and handled in air for short periods of time without any particular precautions.

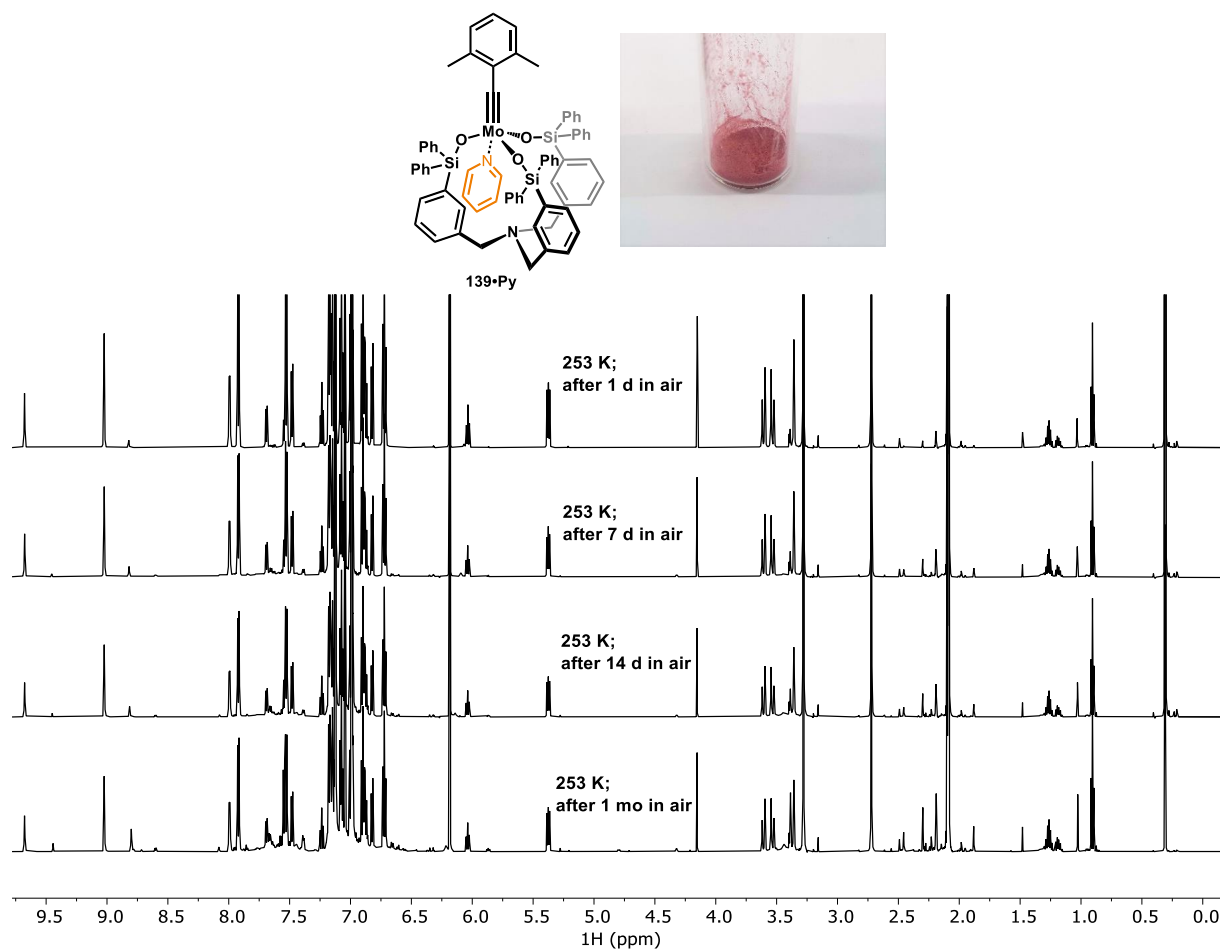


Figure 18: Stability of a powder sample of **139•Py** exposed to the ambient atmosphere assessed by ^1H NMR at 253 K.

Next, a powdered sample of the pyridine adduct **139•Py** was exposed to the ambient atmosphere (*figure 18*). Since the NMR spectra of **139•Py** is broad and featureless at ambient temperature, the stability had to be assessed at 253 K. The data clearly showed ligation with pyridine to be beneficial for the stability. Whereas the free complex had completely disintegrated after 14 days, the adduct exhibited only minimal signs of degradation at that time. Even after 1 month, the majority of the sample was still intact.

The favorable outcome represents a major step forward for alkyne metathesis considering the sensitivity of most catalysts to air and moisture. The longest timespans outside of the glovebox achieved for molybdenum-based alkyne metathesis catalysts were on the scale of hours. Still, over extended periods hydrolysis became more prominent even for **139•Py**. Efforts to render the sample fully air-stable will be discussed later on.

With the benefit of an additional ligand established, some of the other adducts of **139** were submitted to the same conditions and their stability appraised *via* ^1H NMR after approximately one month.

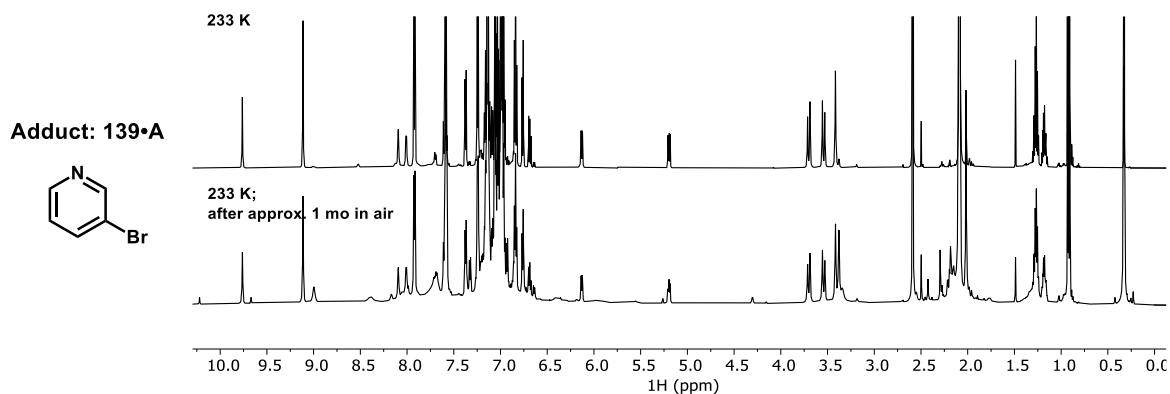


Figure 19: ^1H NMRs assessing the stability of adduct **139•A** when exposed to the ambient atmosphere.

The adduct with 3-bromopyridine behaved similarly to **139•Py**, as expected from the complexation experiments (figure 19). However, a rather broad background was detected in the NMR spectrum, indicating the presence of unidentified decomposition products.

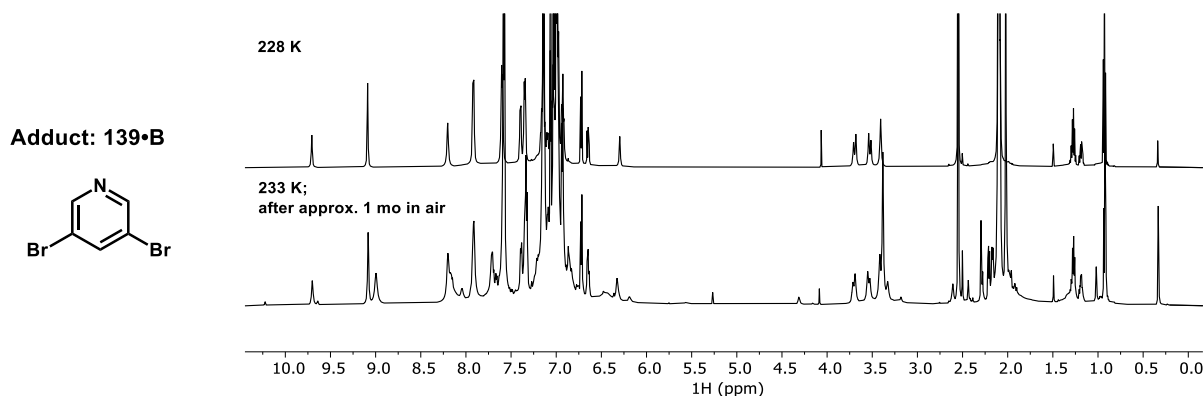


Figure 20: ^1H NMRs assessing the stability of adduct **139•B** when exposed to the ambient atmosphere.

Next the 3,5-dibromopyridine adduct was investigated (figure 20). Here, the decay was clearly more pronounced and the sample turned brown after ca. 14 days in air. As already indicated by the VT-NMR study, the reduced electron density at nitrogen leads to the pyridine being only weakly bound to the molybdenum. Apparently, decoordination in the solid-state is possible, leaving the complex vulnerable to decomposition.

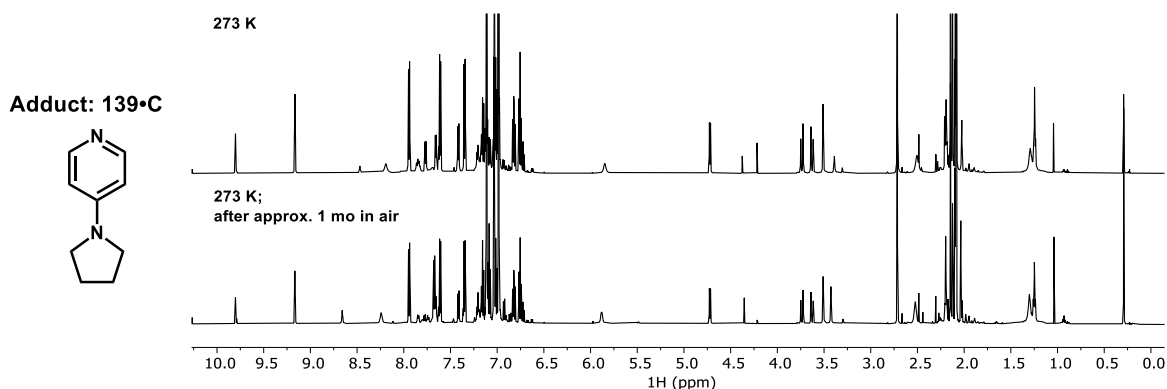


Figure 21: ^1H NMRs assessing the stability of adduct **139•C** when exposed to the ambient atmosphere.

4-Pyrrolidino-pyridine, on the other hand, is a far better Lewis base and coordinates strongly to the formally d^0 -metal.^[173] As a consequence, the sample was in good shape after one month in air (*figure 21*). The few additional signals belong to a small amount of unligated 4-pyrrolidino-pyridine, which was already present in the original sample and could not be removed. The result demonstrates that the stability can be further increased with strongly binding ligands. However, the VT-NMR data for the adduct showed almost no equilibrium with the free complex at ambient temperature, forecasting low reactivity. Hence, a difficult compromise between stability and catalytic activity has to be found.

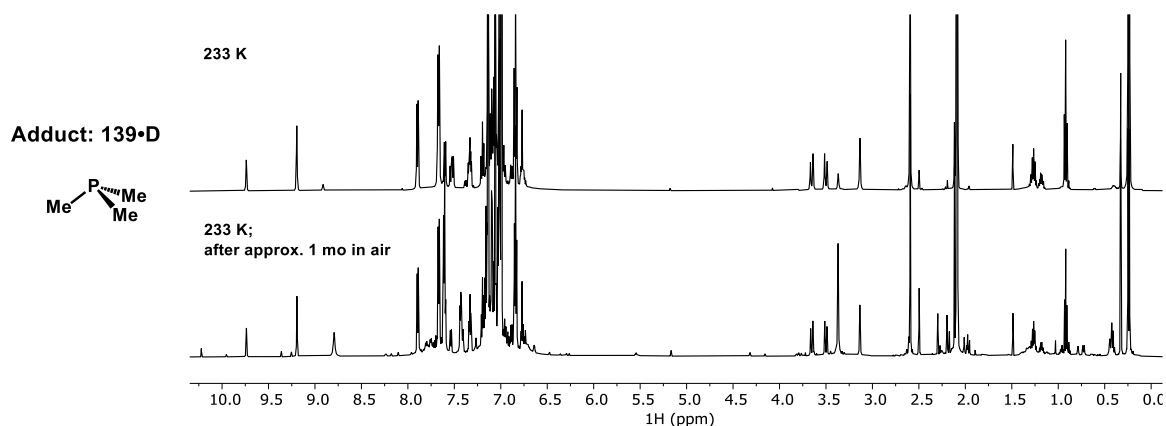


Figure 22: ^1H NMRs assessing the stability of adduct **139•D** when exposed to the ambient atmosphere.

Lastly, the adduct with trimethylphosphine was examined. Some intact complex remained after one month, but decay had clearly set in (*figure 22*). As anticipated, the presence of phosphine oxides could be detected in the ^{31}P NMR spectrum, suggesting oxidation of the stabilizing ligand to be an additional issue.

The stabilization studies consolidated the status of unsubstituted pyridine as the most suitable stabilizing ligand. Utilizing more weakly coordination ligands compromised the desired air-stability, whereas employing more tightly binding derivatives did not bring a large enough benefit to justify the likely lower reactivity.

To even further increase the resistance of **139•Py** towards decomposition in air, a crystalline sample was prepared from a mixture of dichloromethane and pentane. The underlying hypothesis was that a reduction in the surface area of the sample would substantially decelerate the hydrolysis and render the adduct even more stable. The obtained batch of small crystals was stored in air over the spring and summer, during which the atmospheric humidity reached 80% on certain days.

Gratifyingly, the sample showed hardly any signs of degradation, even after eight months (*figure 23*). Accordingly, **139•Py** can be confidently referred to as air-stable in the crystalline state. This quality allows for the handling, potential shipping, and longer term storage of samples of the complex without resorting to inert gas techniques.

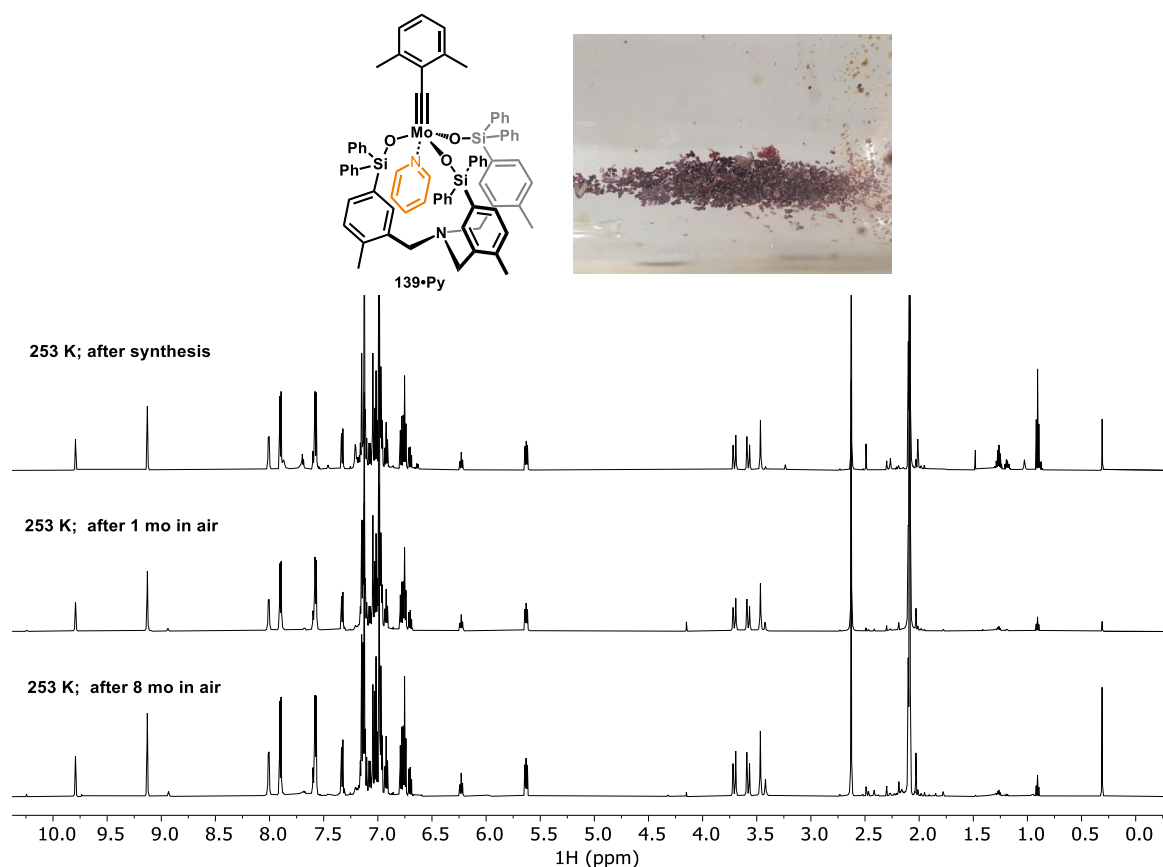


Figure 23: Stability of a crystalline sample of **139•Py** exposed to the ambient atmosphere; assessed by ^1H NMR.

Because controlling the exact morphology and size of crystals is challenging, two alternative storage conditions for the bulk material were examined. A powder sample was kept in an air-filled desiccator over a drying agent and a second sample was stored in an argon flushed standard screw-cap vial in the freezer. Both conditions are easy to realize in every chemical laboratory and routinely applied for storing more sensitive chemicals (e.g., second generation Grubbs catalyst or $\text{Ni}(\text{stb})_3$).^[174]

The desiccator was opened at regular intervals, aliquots were taken from the batch, and analyzed *via* ^1H NMR spectroscopy (figure 24). Under these storage conditions, **139•Py** exhibited good stability with the amount of free ligand resulting from hydrolysis visibly reduced when compared to the powder sample stored on the benchtop (figure 18).

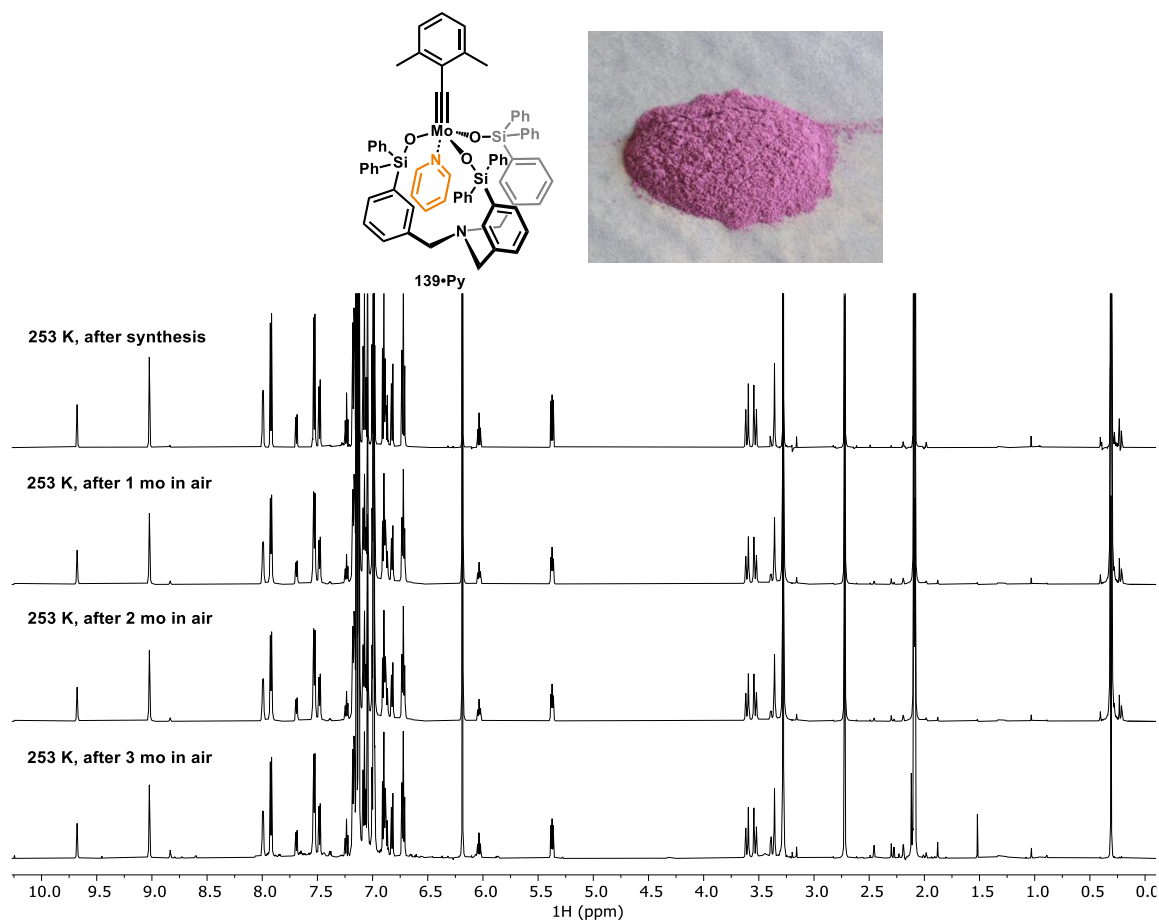


Figure 24: Stability of a powder sample of **139•Py** stored in an air-filled desiccator assessed by ^1H NMR.

Also, after keeping **139•Py** in a screw-top vial in the freezer ($-20\text{ }^\circ\text{C}$) for up to five months, barely any signs of decomposition were detectable (*figure 25*). The batch was brought to ambient temperature at regular intervals for the removal of aliquots. Afterwards, the vial was flushed with argon (as is common practice for sensitive chemicals), closed again with a screw-cap, and stored at $-20\text{ }^\circ\text{C}$. After four months, a sample was submitted to combustion analysis resulting in the same outcome as obtained with a fresh batch of **139•Py**.

Following these experiments, **139•Py** is deemed air-stable in its crystalline form and storage-stable for extended periods under easily produced conditions, even in non-expert laboratories. Still, the complex remains a sensitive chemical and should be treated as such. Hydrolysis of the silanolates continues to be the greatest danger and contact with water must be avoided. When a batch of the adduct loses its characteristic dark to light lilac color, decomposition has likely set in and the purity should be reassessed through NMR spectroscopy.

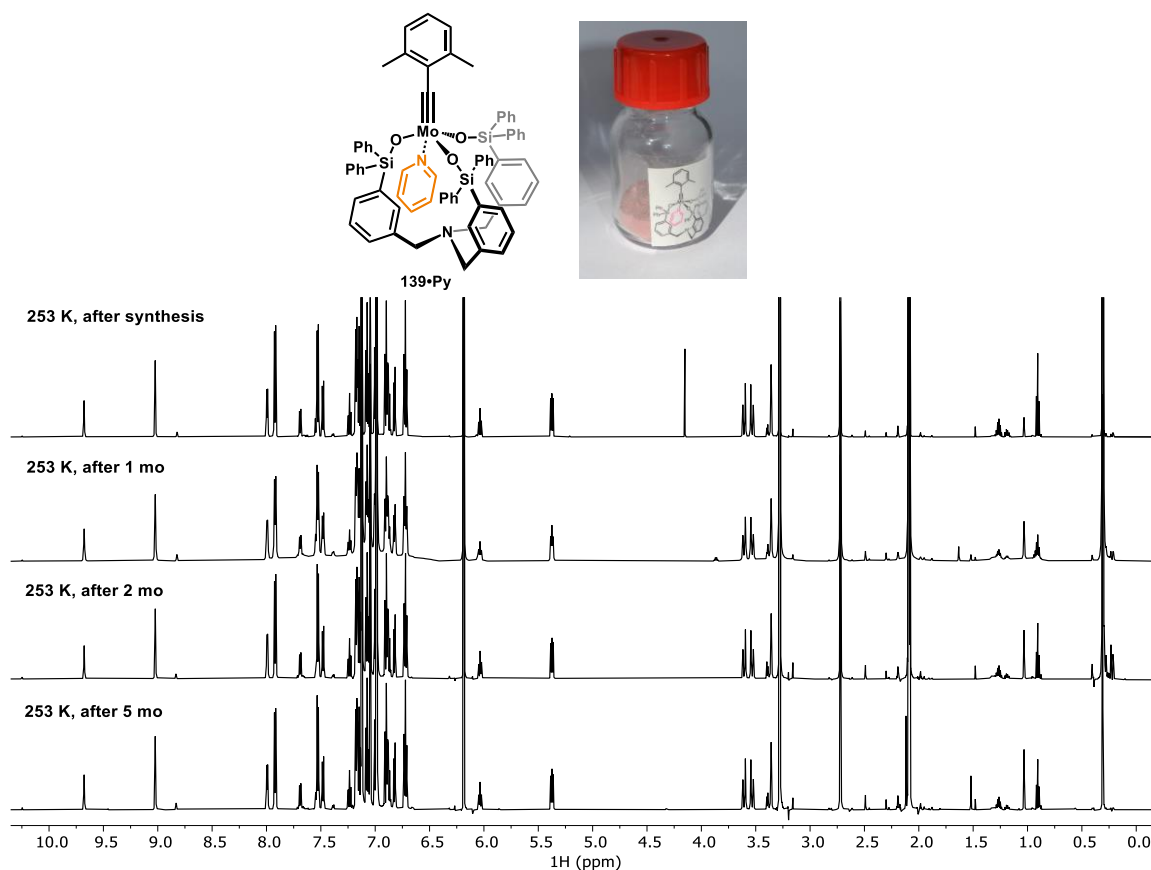


Figure 25: ¹H NMRs assessing the stability of **139•Py** as a powder stored in an argon flashed vial at -20°C .

To illustrate the progress made in terms of air-stability, **139•Py** is compared to some catalyst systems from the literature. The ‘turbo canopy catalyst’ (**8g**) has already been discussed in *chapter 1.3.1*. It was shown to rapidly decompose within minutes/hours in air (*figure 9*). Additionally, a catalyst system based on the molybdenum alkylidyne complex **4ob** and a tridentate trisphenol ligand was investigated.^[70b] Ligand **7d** was chosen because it had been shown to result in a robust catalyst system in solution. However, the solid obtained from the mixture of complex **4ob** and the ligand was not stable upon exposure to the ambient atmosphere. None of the signals belonging to the original catalytically active mixture could be detected *via* NMR spectroscopy after 12 h in air (*figure 26*). Instead, signals attributed to the free ligand **7d** and the aniline derived from **4ob** could be identified. More importantly, the ‘aged’ sample was incapable of catalyzing a simple alkyne metathesis reaction. Furthermore, the commonly used precursor complex **4ob** itself, as well as molybdenum alkylidyne **18b** used to synthesize well-defined catalysts, were both shown to decompose rapidly in air.

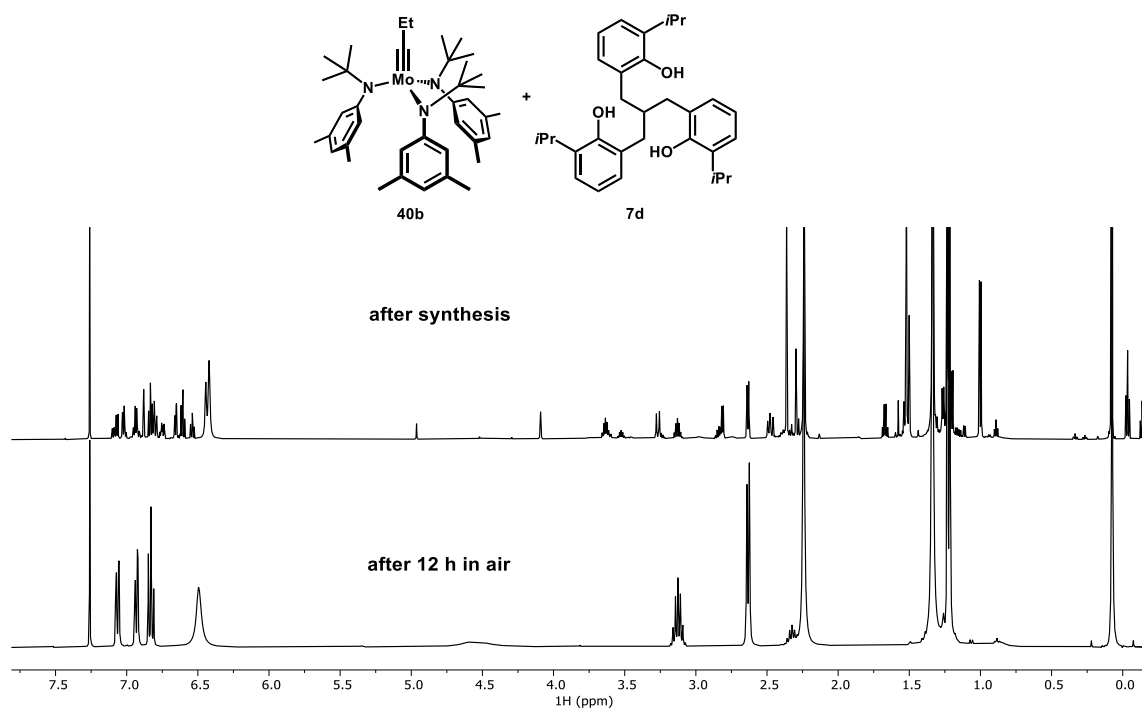


Figure 26: ^1H NMRs showing the catalytically active mixture obtained upon mixing **40b** and **7d** and the free ligand together with $\text{HN}[(\text{Ar})(\text{tBu})]$ derived from complex **40b** obtained after storing the mixture in air for 12 h.

Efforts at extending the pyridine ligation tactic to stabilize other complexes did not bear fruit. While **8g•Py** could be synthesized, the material turned dark brown within days when exposed to the ambient atmosphere. A control NMR spectrum after one month revealed the adduct to have fully decomposed (*figure 27*).

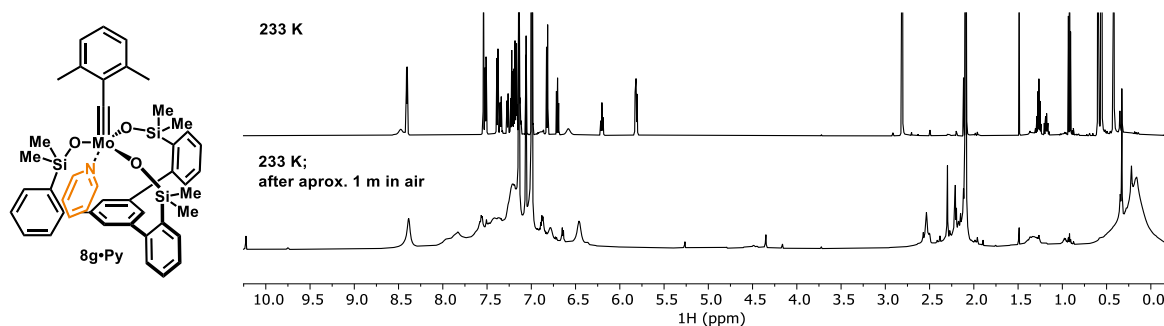


Figure 27: ^1H NMRs assessing the stability of adduct **8g•Py** when exposed to the ambient atmosphere.

Also, the ethyl variant **140** proved less amenable to stabilization with pyridine (*figure 28*).

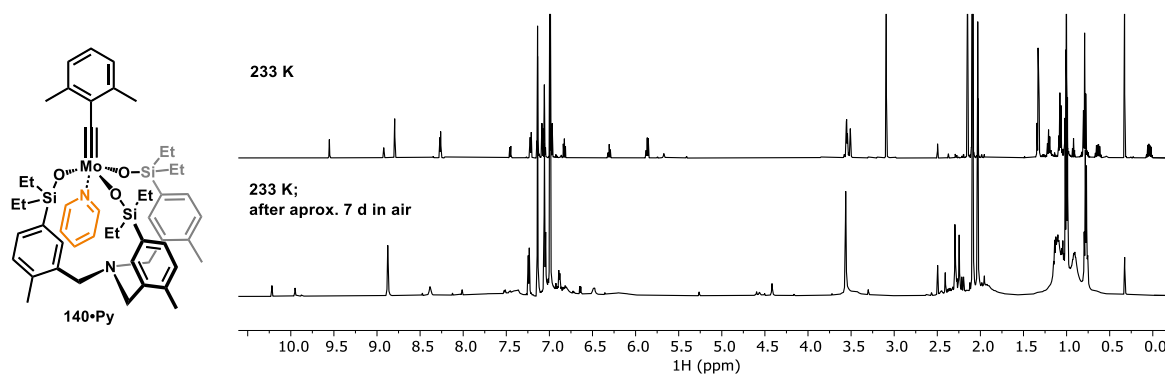


Figure 28: ^1H NMRs assessing the stability of adduct **140•Py** when exposed to the ambient atmosphere.

The result indicates that all elements of the original blueprint for an air-stable alkyne metathesis catalyst must be present to ensure durability. Merely replacing the phenyl substituent in **139** with sterically less demanding alkyl substituents (**140**) had a drastic impact on the stability in air. Additionally, the electron-releasing alkyl residues in **8g•Py** and **140•Py** might result in a weaker coordination of the external pyridine.

So far, the discussion has been confined to the stability of **139•Py** in the solid-state. In solution, the adduct is more vulnerable to hydrolysis and should be kept under inert atmosphere. However, in the absence of water and oxygen a solution of **139•Py** in deuterated toluene showed no signs of degradation after a week. The adduct also exhibits good thermal stability. Heating a toluene solution of **139•Py** to 120 °C for 24 h caused no change.

As a final matter, the question of chemical stability was addressed. The member **8g** from the ‘canopy series’ with the slimmest ligand is vulnerable to bimolecular decomposition (*scheme 30*). In the presence of but-2-yne the complex rapidly converted into a binuclear molybdenum (III) dimer **54**, which proved to be catalytically inactive.

To test if the newest generation of catalysts is also susceptible to this particular deactivation pathway, complex **139** was subjected to the same conditions. The unligated complex was used due to the dynamic equilibrium of **139•Py** in solution at ambient temperature, rendering NMR-analysis challenging.

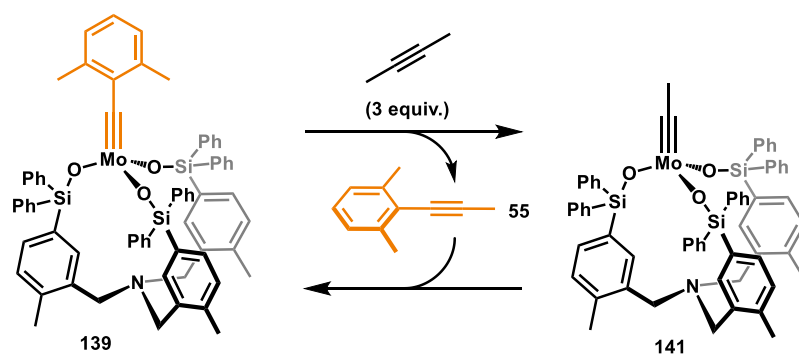


Figure 29: **139** is resilient against bimolecular decomposition in the presence of but-2-yne.

Complex **139** behaved distinctly different when exposed to but-2-yne. Tracing the reaction *via* ^1H NMR, a rapid reaction with the small alkyne was observed and the known by-product **55** derived from the benzylidyne cap of the catalyst was formed. Over 1.5 h, the signal corresponding to the excess of but-2-yne became broad, indicative of a polymerization process, and finally vanished completely. With no further substrate available the catalyst reacted with alkyne **55** to generate the original complex with its characteristic 2,6-dimethylbenzylidyne unit. At no point during the experiment was a dinuclear complex observed. Hence, **139** (and by extension supposedly **139•Py**) is far less prone to perilous binuclear decomposition than the ‘turbo canopy catalyst’ **8g**.

Yet, the investigation had resummoned the old specter of polymerization as a detrimental side reaction. Indeed, exposing **139** to a solution of oct-2-yne confirmed also other aliphatic alkynes

to eventually polymerize. However, the side reaction occurs at a much slower rate than productive alkyne metathesis. In any case, practitioners should be aware of this danger, when conducting alkyne metathesis reactions with sluggish conversions or odd mass-balance. It also shows that tripodal ligands in the catalyst design do not guarantee the prevention of polymerization, thereby raising questions about the exact mechanism by which the reaction occurs.

In conclusion, the findings demonstrate that ligation to pyridine significantly enhances the stability of **139**. The resulting adduct, **139•Py**, is air-stable for months and can be stored outside of a glovebox under appropriate conditions for extended periods of time. Notably, the shelf life of this catalyst exceeds everything so far reported for molybdenum alkylidyne catalysts.

1.3.5 Benchmarking of the Catalytic Activity

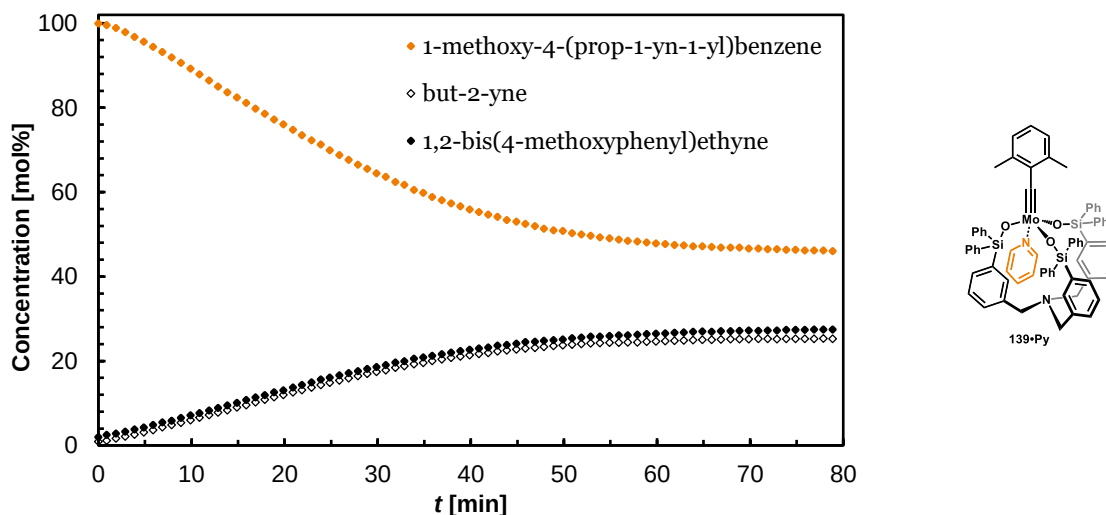
With the stability of the complexes established, their activity as alkyne metathesis catalysts was evaluated. To this end, a standardized benchmark reaction was used to facilitate comparison between the different catalysts. Additionally, data was collected for select systems reported in the literature to create a comprehensive overview.



Scheme 66: Reaction for benchmarking the reactivity of different catalysts in alkyne metathesis.

The homometathesis of alkyne **142** to the tolane derivative **143** and but-2-yne was selected (scheme 66). More electron-rich alkynes, tested for the benchmark reaction, equilibrated overly fast, making the reaction challenging to trace. Substrates with more electron-deficient alkynes were partly reluctant to undergo homometathesis at 25 °C or crystallized from the solution, eliminating them from consideration.

The reactions were performed in deuterated toluene in the absence of molecular sieves. ¹H-NMR spectroscopy was employed to determine when the equilibrium was reached (approx. 50 mol% **142** and each 25 mol% of **143** and of but-2-yne; see graph 1).

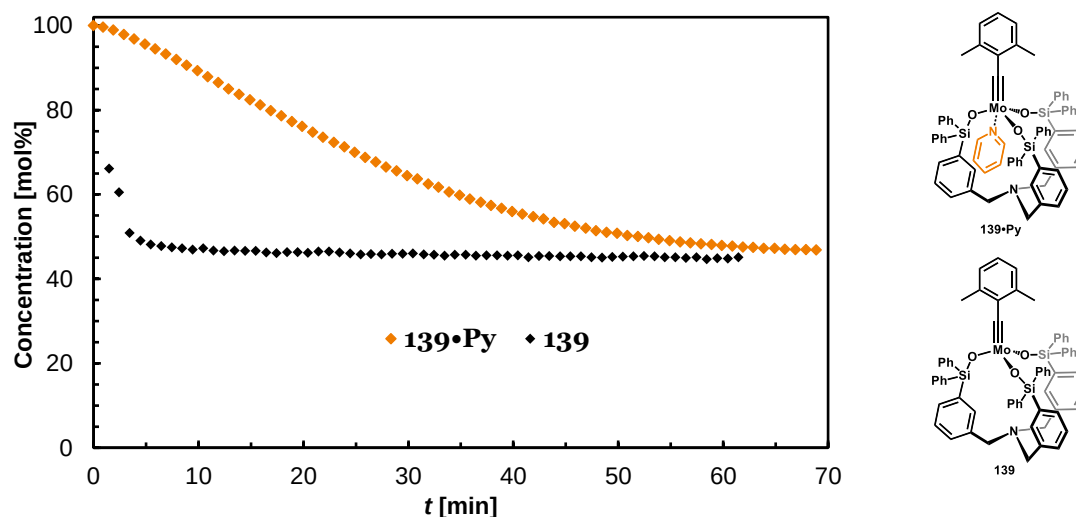


Graph 1: Consumption of alkyne **142** and generation of product **143** and but-2-yne in [D₈]-toluene in the benchmark experiment using adduct **139•Py** as catalyst (5 mol%), as monitored by ¹H NMR spectroscopy at 25 °C.

Adduct **139•Py** exhibited good reactivity at ambient temperature reaching the equilibrium in approx. 60 minutes. The result is consistent with the presence of both the pyridine adduct and the free complex **139** in solution at 25 °C, as suggested by the VT-NMR data. Spontaneous dissociation of the pyridine reveals the catalytically active species **139** by unblocking a site for substrate association. However, only small amounts of the free complex are present in solution

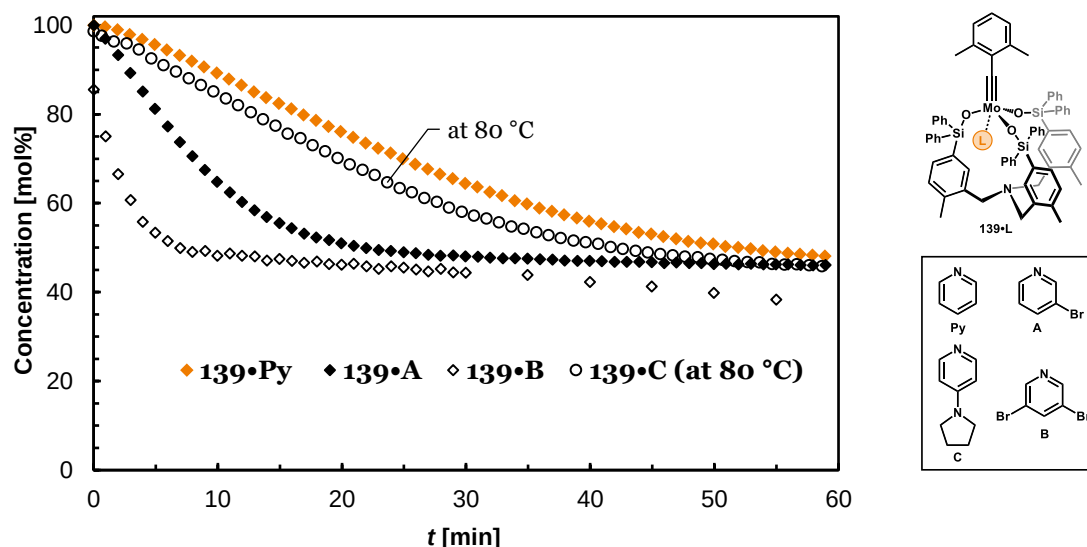
at ambient temperature. Heating favors the dissociation of the pyridine and results in a massive rate acceleration.

The intrinsic reactivity of the free complex **139** is much higher than that of the adduct **139•Py** (*graph 2*). When comparing the reactivities of different complexes, for the sake of clarity, only the data points for the consumption of the starting material **142** are shown.



Graph 2: Consumption of alkyne **142** in benchmark experiments using either the pyridine adduct **139•Py** or the free complex **139** (5 mol%) as catalyst in $[D_8]$ -toluene, as monitored by 1H NMR spectroscopy at 25 °C.

The excellent performance of the free complex **139** (≤ 5 min to equilibrium) rivaled the speed reported for the ‘turbo canopy’ catalyst.^[74] It further indicated the dissociation of the labile pyridine from **139•Py** to be the overall rate-limiting step (at least at 25 °C).



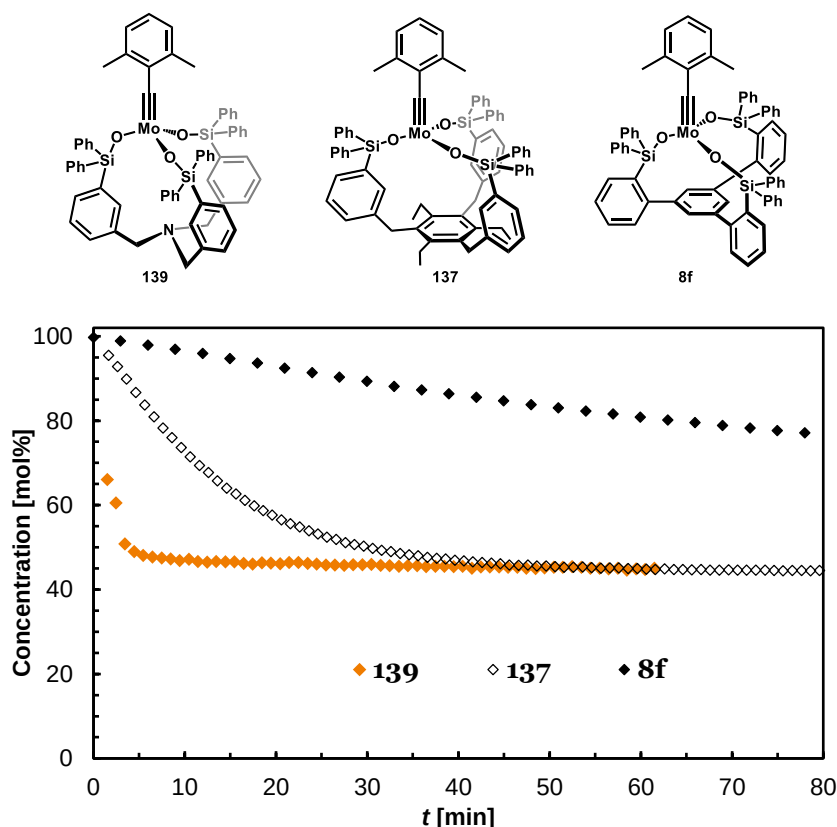
Graph 3: Consumption of alkyne **142** in benchmark experiments using the adducts of **139** (5 mol%) as catalyst in $[D_8]$ -toluene, as monitored by 1H NMR spectroscopy at 25 °C; except for the reaction with **139•C**, which was carried out at 80 °C.

To further probe this aspect, a row of adducts comprising pyridine derivatives with varying σ -donating capabilities were tested (*graph 3*). The trend discernible from the VT-NMR data also manifested itself in the benchmark reaction. Adducts with weaker Lewis bases (**A** and **B**)

exhibited increased reactivities at ambient temperature, implying a higher concentration of the free complex to be present. In accordance with the equilibrium of **139**•**B** at 25 °C being predominantly on the side of the dissociated pyridine and complex **139**, adduct **139**•**B** virtually reaches the performance of the free complex.

The adduct with a stronger Lewis base (**C**) did not react with the substrate at 25 °C. The VT-NMR predicted higher temperatures to be necessary for releasing meaningful amounts of the free complex. Indeed, at 80 °C adduct **139**•**C** showed reasonable activity. The data highlights the precarious balance that must be achieved in order to form a stable adduct, while concurrently maintaining sufficient reactivity. At the outset of the project, one of the objectives was to identify a catalyst that functions at ambient temperature without the need for (thermal) preactivation. Pyridine is therefore deemed to be the best compromise.

In order to probe the effect of the newly designed ligand scaffold, a comparison was made to the second proposed design and to a member of the previous catalyst generation ('canopy series').¹ Note, that the catalysts only differ in the ligand framework and otherwise carry the same benzyldiyne unit and the same residues on the silanolates (*graph 4*).^[74, 119]



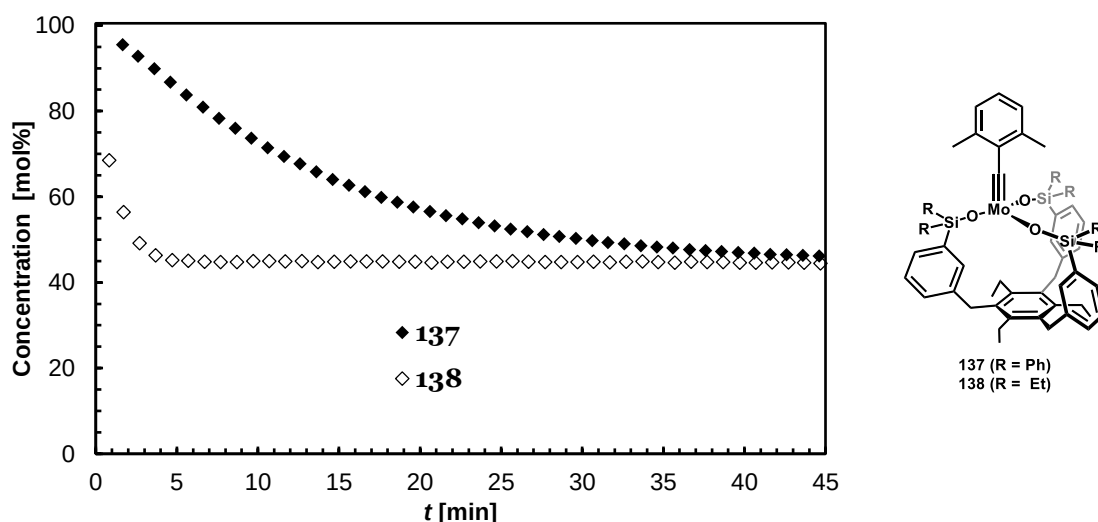
Graph 4: Consumption of alkyne **142** in benchmark experiments using either the **139**, **137** or **8f** (5 mol%) as catalyst in [D₈]-toluene, as monitored by ¹H NMR spectroscopy at 25 °C.

The clear trend in performance is presumably attributable to the increase in flexibility when moving from the rigid, all *sp*²-hybridized ligand framework of the 'canopy series' over the

¹ The data for **8f** was provided by Dr. Hillenbrand and the data for **137** was already presented in the author's master's thesis.

hexasubstituted benzene based design to the amine tethered scaffold with the sp^3 -hybridized linkers. The latter is sufficiently pliable to readily accommodate the different coordination geometries that the reactive intermediates pass through during the catalytic cycle. In a stiffer ligand framework the sterically demanding aryl substituents at the silanolate ligands have a larger impact on reactivity, because they cannot swerve out of the way with the same ease. For complexes with tripodal ligands the flexibility assumes particular importance due to the Berry pseudorotation over one ligand arm, which is a prerequisite for productive alkyne metathesis in their case.^[36a]

Next, the effect of tuning the size of the residues on the silanolate ligands was investigated. Complex **137** was compared to the new variant **138** equipped with slimmer ethyl groups on the silanolate ligands (*graph 5*).²



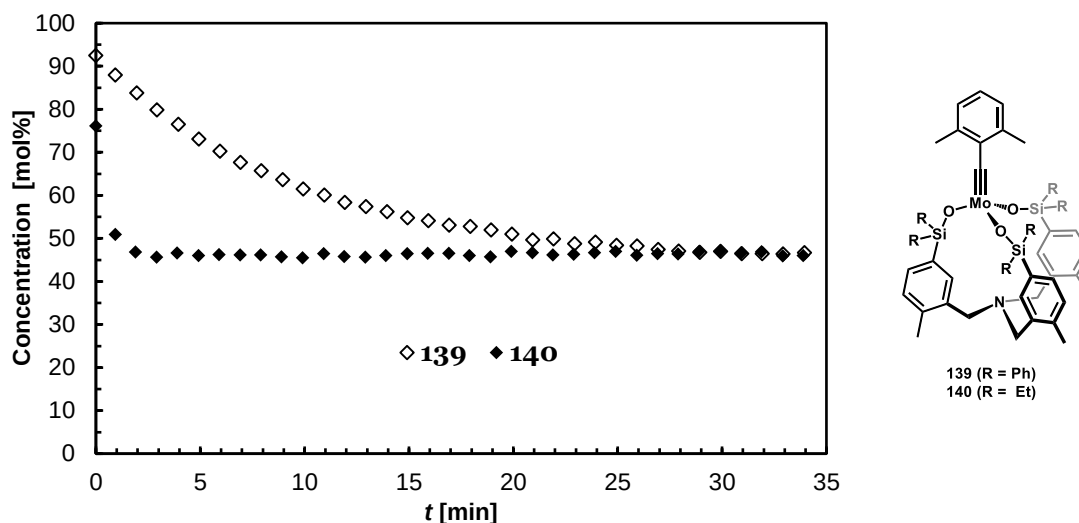
Graph 5: Consumption of alkyne **142** in benchmarking experiments using either complex **137** or complex **138** (5 mol%) as catalyst in $[D_8]$ -toluene, as monitored by 1H NMR spectroscopy at 25 °C.

In the ‘canopy series’ this parameter had played an outsized role (**8g** (R = Me) $\gg$ **8f** (R = Ph)) due to the reasons alluded to above (*chapter 1.1.3.3*). The trend observed for the new complexes was essentially the same, with complex **138** (R = Et) performing better than complex **137** (R = Ph). However, the influence on the reactivity was less pronounced in the present case. Apparently, with an increase in flexibility the significance of the lateral ‘fence’ around the active center declines.

When an attempt was made to benchmark the reactivity of **139** and **140** at ambient temperature, no difference was discernable, because in both cases the equilibrium was reached within the first two/three measurements. As a consequence, the benchmark reactions were performed at 0 °C. There is little precedent for carrying out alkyne metathesis reactions below 25 °C, since RCAM reactions are (at least in theory) favored by higher temperatures.^[43a] Nevertheless, **139** and **140** both exhibited excellent reactivity at 0 °C. The former so much so,

² The data for **137** was already presented in the author’s master’s thesis.

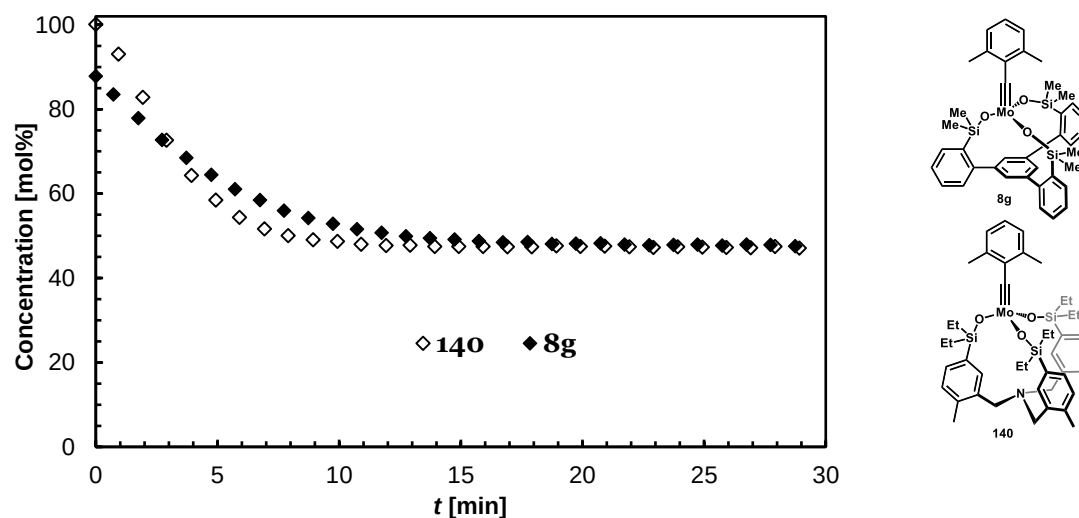
that it again reached the equilibrium within 1-2 min, while the latter took ca. 30 min to equilibrate the reaction mixture (*graph 6*).



Graph 6: Consumption of alkyne **142** in benchmark experiments using either complex **139** or complex **140** (5 mol%) as catalyst in $[D_8]$ -toluene, as monitored by 1H NMR spectroscopy at 0 °C.

Again, the influence of the substituents at the silanolate ligands was less pronounced, when compared to the ‘canopy series’. The effect is believed to be of high importance for the balance between stability and activity of the catalysts. The increased flexibility in solution allows complex **139** to carry bulky phenyl substituents while maintaining a high degree of reactivity. In the solid-state, the same phenyl groups form a protective, rigid ring around the alkylidyne unit. In contrast, the sterically less encumbered complexes **140** and **8g** excel in terms of activity, but are not stable in air.

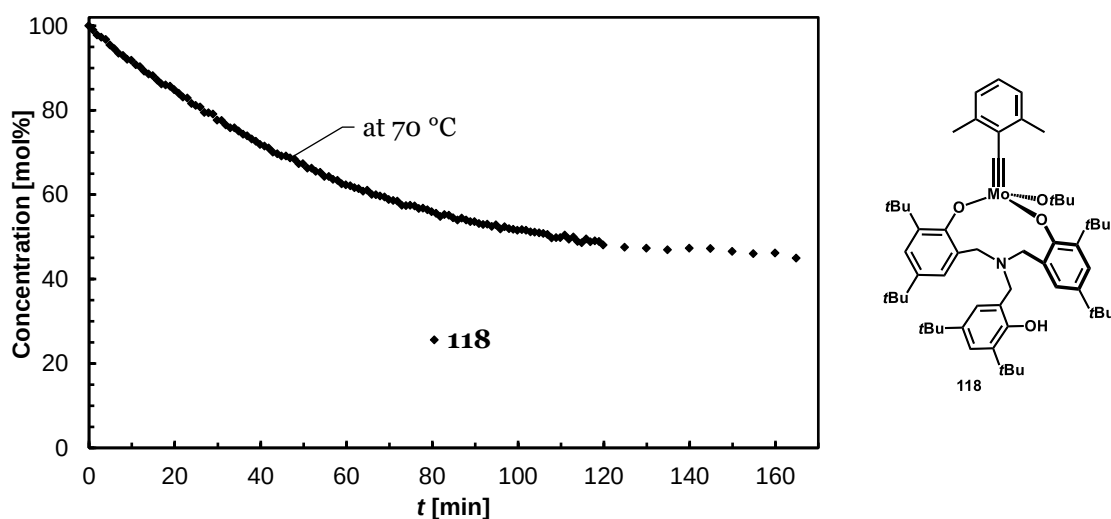
To reliably benchmark the actual reactivity of ‘turbo canopy catalyst’ **8g** and **140** remained challenging, but an attempt was made at -20 °C (*graph 7*).



Graph 7: Consumption of alkyne **142** in benchmark experiments using either complex **8g** or complex **140** (5 mol%) as catalyst in $[D_8]$ -toluene, as monitored by 1H NMR spectroscopy at -20 °C.

At this temperature, the equilibrium was reached in 15 min with both catalysts. The ‘turbo canopy catalyst’ is even more active than previous data at ambient temperature suggested. It easily outcompetes **139** in terms of performance. Complex **140**, on the other hand, seems to be on par with the most reactive variant from the last catalyst generation. There appears to be a slight difference in the rate of initiation, but the effect lies within the error margin of the experiment. In general, toluene becomes increasingly viscous at these low temperatures and it is unclear how much impact the rate of diffusion in the unstirred reaction mixture has on the overall rate at this point. Still, it is in itself remarkable that alkyne metathesis can be carried out at such a low temperature and the reaction bears testimony to the excellent reactivity of molybdenum alkylidyne complexes with silanolate ligands.

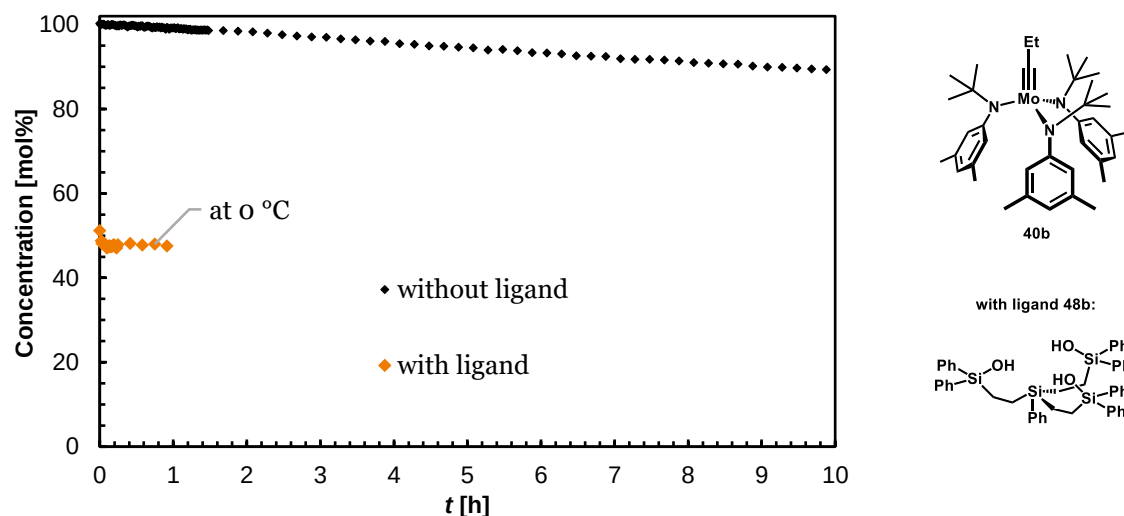
For comparison, complex **118** endowed with two phenolate and one alkoxide ligand was submitted to the benchmark reaction (*graph 8*). The catalyst did not react with the substrate at 25 °C and the temperature had to be raised to 70 °C to be able to detect turn-over. Even at this temperature, the conversion was sluggish and the equilibrium was only reached after approx. 120 min. The data confirms the prediction made for the complex from its ^{95}Mo NMR shift (*see chapter 1.3.3*). However, the mediocre reactivity of complex **118** cannot solely be blamed on the insufficient Lewis acidity of the molybdenum center. Steric factors from the bulky ligands certainly also play a role.



Graph 8: Consumption of alkyne **142** in a benchmark experiment using complex **118** (5 mol%) as catalyst in $[\text{D}_8]\text{-toluene}$; as monitored by ^1H NMR spectroscopy at 70 °C.

To give a more comprehensive picture, three additional catalyst systems from the literature were investigated *via* the benchmark reaction. First, complex **40b**, originally reported by the group of Moore, was examined.^[54] There was no data available on the activity of the trisamido complex itself. Therefore, it was deemed imperative to establish a baseline for the reactivity of **40b** in order to assess the effect of the different ligands added. The corresponding ^{95}Mo NMR shift was detected at 304 ppm, forecasting low activity.

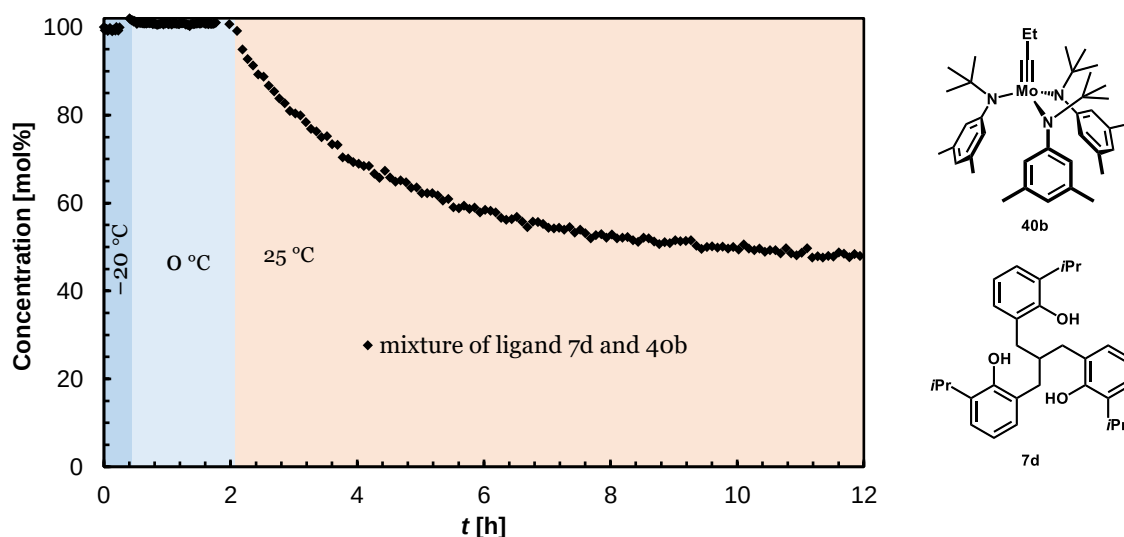
While complex **40b** did catalyze the benchmark reaction at ambient temperature, the conversion was extremely slow. It took over 80 h until an equilibrium was reached (*graph 9*).



Graph 9: Consumption of alkyne **142** in benchmark experiments using complex **40b** (5 mol%) as catalyst with or without ligand **48** in $[D_8]$ -toluene; as monitored by 1H NMR spectroscopy at 25 °C (without ligand) and at 0 °C with the ligand.

All the more impressive is the effect of ligand **48b**. When mixing complex **40b** and the ligand **48b** before the substrate is added, the formed species catalyzes the reaction with the highest efficiency. Even at 0 °C, the equilibrium had been reached upon the first NMR measurement (≤ 2 min). The experiment highlights the extraordinary impact silanolate ligands have on the activity of molybdenum alkylidyne catalysts for alkyne metathesis.

The last catalyst system investigated was originally published by the group of Zhang.^[70b]

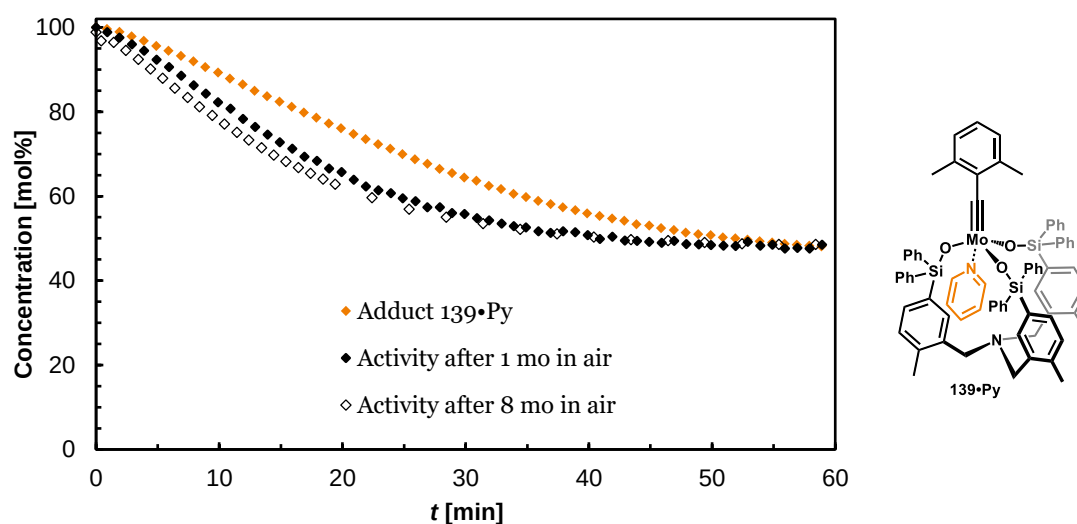


Graph 10: Consumption of alkyne **142** in a benchmark experiment using a catalyst generated in situ from the molybdenum alkylidyne **40b** and ligand **7d** (5 mol% each) in a mixture of $CDCl_3$ and $[D_8]$ -toluene, as monitored by 1H NMR spectroscopy at 253 K (-20 °C), 273 K (0 °C) and 298 K (+25 °C).

Good activity had been reported at ambient temperature, but no reactions at lower temperatures had been attempted. As previously mentioned, chlorinated solvents had to be added to the reaction to obtain a catalytically active mixture.

Interestingly, the system did not give any conversion of the test substrate at $-20\text{ }^{\circ}\text{C}$ or $0\text{ }^{\circ}\text{C}$. When warming the sample to $25\text{ }^{\circ}\text{C}$, homometathesis was observed and the equilibrium was reached after approx. nine hours. The performance of the system based on a trisphenolate ligand stands in stark contrast to the excellent reactivities observed with tridentate silanolate ligands.

Returning to the main concern of the described project, the synthesis of an air-stable alkyne metathesis catalyst, the activity of samples stored in air over extended periods was examined. More specifically, aliquots from the crystalline batch of **139•Py** were taken after one month and eight months respectively and used as catalysts in the benchmark reaction (*graph 11*).



Graph 11: Consumption of alkyne **142** in benchmark experiments using samples of crystalline adduct **139•Py** (5 mol%) in $[D_8]$ -toluene as catalyst as monitored by ^1H NMR spectroscopy at $25\text{ }^{\circ}\text{C}$. The samples were either freshly prepared, or had been stored in air for 1 month or 8 months.

The homometathesis occurred with largely unchanged rate and efficiency. The slight deviation of the curves is within the margin of error and presumably caused by differences in mixing before inserting the sample into the NMR spectrometer.

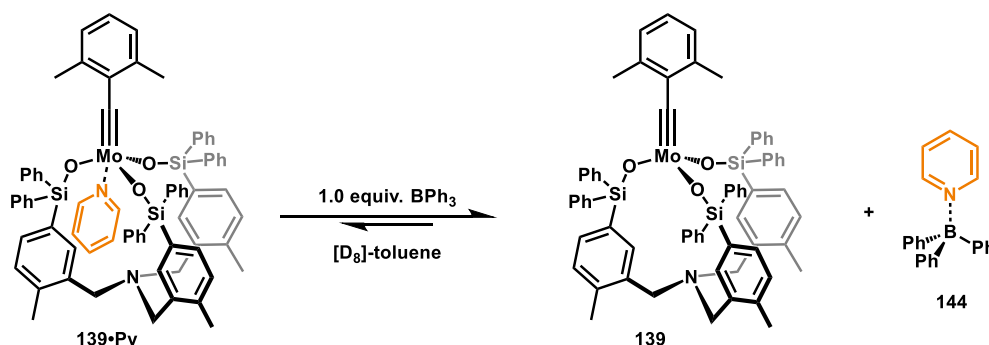
In summary, the air-stable adduct **139•Py** was shown to exhibit good reactivity in a benchmark reaction at ambient temperature without the need for preactivation. It was compared to a library of complexes and select systems from the literature. The effects of tuning different parts of the general catalyst design could be elucidated and the stability of **139•Py** was proven by demonstrating the activity of samples ‘aged’ in air.

I.3.6 Pyridine Scavenger Strategy and Reactive Intermediates

The previous chapter established air-stable **139•Py** to be a fully competent catalyst for alkyne metathesis at ambient temperature without requiring any preactivation. However, the stabilization with pyridine entails a significant reduction of the reaction rate compared to the unligated complex **139**. Raising the temperature is one way to accelerate the reaction by shifting the equilibrium towards the dissociation of the pyridine. For cases where this method is not applicable (e.g., temperature sensitive substrates or competing side reactions), a strategy was developed to promote the reaction at ambient temperature or below.

In previous iterations of stabilized alkyne metathesis catalysts hard Lewis acids such as zinc chloride in combination with high temperatures were required to remove the additional ligand.^[43a] Since these harsh conditions are less than ideal when working with highly functionalized substrates, a milder alternative was sought. The ability of boron Lewis acids to form stable adducts with pyridine derivatives is well established.^[175]

Indeed, when one equivalent of triphenylborane was added to a solution of **139•Py**, the characteristic color change from lilac to orange was observed (*scheme 67*).



Scheme 67: Abstraction of the stabilizing pyridine with triphenylborane.

Inspection of the obtained mixture *via* NMR spectroscopy confirmed the equilibrium to have largely shifted into the direction of the free complex **139** and the Lewis acid/base adduct **144**.

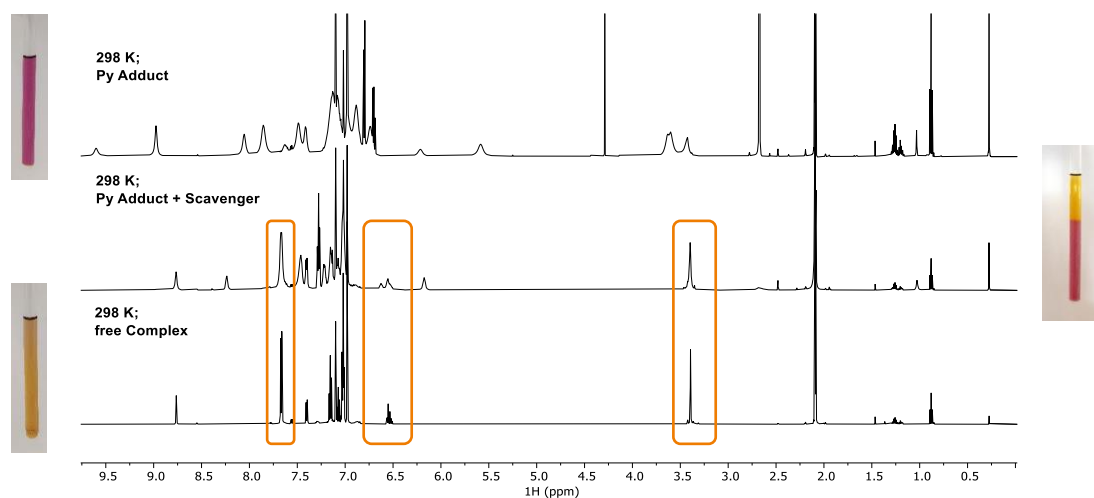
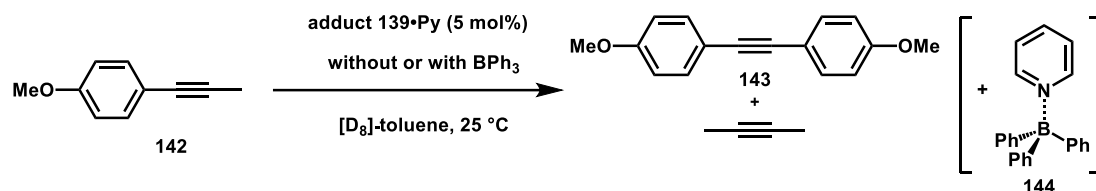


Figure 30: ^1H NMR spectra of solutions of **139•Py**, **139•Py** after the addition of BPh_3 and the unligated complex **139** in $[\text{D}_8]\text{-toluene}$ and photographs of the pertinent samples.

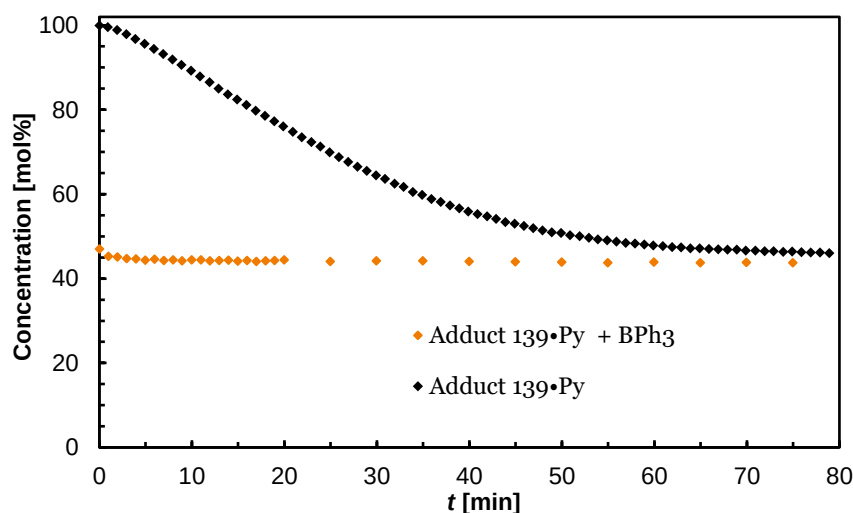
The presence of the latter was confirmed with ^{11}B NMR. No detrimental interaction of the Lewis acid with the tertiary amine in the ligand backbone was detected.

In order to assess the effect of the pyridine scavenger on the reaction rate, the mixture of triphenylborane with the adduct **139•Py** was submitted to the benchmark reaction (*scheme 68*).



Scheme 68: Benchmarking experiment with and without the addition of BPh_3 as pyridine scavenger.

Tracing the reaction with ^1H NMR spectroscopy revealed triphenylborane to be an excellent promoter. Approximately the same reactivity as with the unligated complex **139** was observed (*graph 12*).



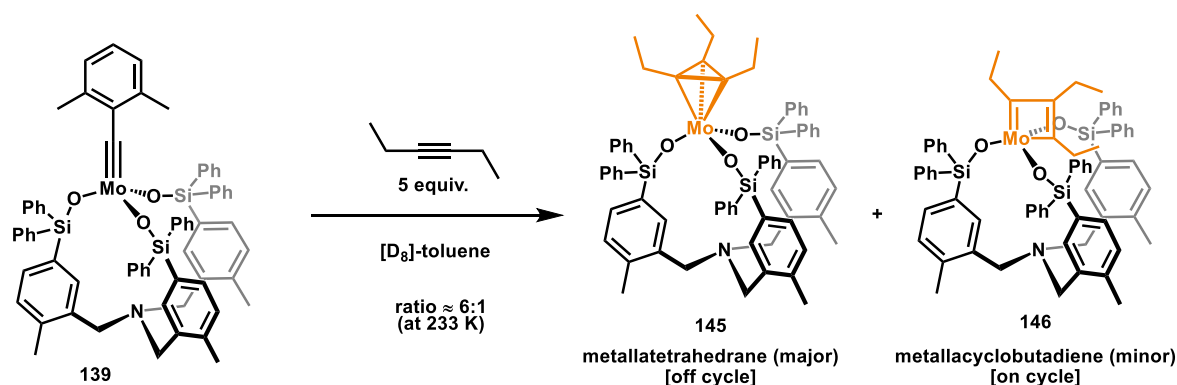
Graph 12: Consumption of alkyne **142** in benchmark experiments using adduct **139•Py** (5 mol%) as catalyst in $[\text{D}_8]\text{-toluene}$ with or without the addition of BPh_3 (5 mol%); as monitored by ^1H NMR spectroscopy at 25°C .

While other scavengers for pyridine can be imagined, commercially available, crystalline triphenylborane is well suited due to the ease of operation and its relatively mild Lewis acidity, which likely poses little risk to highly functionalized substrates.^[176] Also, a higher Lewis acidity of the scavenger did not invariably translate into a greater rate acceleration in the benchmark reaction. Tris(pentafluorophenyl)borane promoted the reaction, but at a slower rate than triphenylborane and boron trifluoride etherate quenched all reactivity, likely due to non-innocent interactions with the tertiary amine in the ligand scaffold of the catalyst.

The pyridine scavenger strategy also enabled the air-stable adduct **139•Py** to catalyze reactions below ambient temperature and with challenging terminal alkynes (see *chapter 1.3.7*).

A brief study of the intermediates formed in alkyne metathesis with the novel catalysts was undertaken. A recent investigation had revealed the ‘canopy series’ to operate *via* a mechanism distinct from the canonical catalytic cycle of alkyne metathesis (see *chapter 1.1.3.3*).^[36a] The constrictions imposed by the tripodal ligand make a pseudorotation over one of the ligand arms necessary. From the distorted intermediary metallacyclobutadiene (MCBD) an off-cycle metallatetrahedran (MTH) arose, which could be identified in the NMR spectra of catalytic mixtures. The objective was therefore to ascertain whether the new complexes operate through the same distinct mechanism.

Complex **139** was selected as the test case, because omitting the labile pyridine facilitated NMR spectroscopy. Addition of five equivalents of hex-3-yne to a solution of complex **139** in deuterated toluene gave rise to a dynamic mixture with two main organometallic components.



Scheme 69: Reaction of **139** with hex-3-yne and the intermediates observed in the reaction mixture at 233 K.

The sample was cooled to 233 K to facilitate the characterization of the two metallacycle intermediates.³ The major product could be identified as metallatetrahedran **145**. Its presence indicates a similar pseudorotation to be operational as for the ‘canopy series’.

In the ‘canopy series’ the off-cycle species had been speculated to be stabilized through CH $\cdots\pi$ -interactions between the ethyl substituents in the MTH unit and the lateral phenyl residues of the ligand.^[36b] Evidence had been found in the ^1H NMR spectrum: the peak of the relevant methylene protons split into signals corresponding to diastereotopic protons at lower temperatures. With the novel complex, however, this phenomenon was not observed. The change in behavior may be attributed to the higher flexibility of new ligand scaffold, which allows the phenyl rings to tilt out of the way – an indication for the required pseudorotation to be more facile in the new catalyst series, which is also reflected in the higher reactivity of **139** when compared to the relevant complex from the ‘canopy series’ (see *graph 4*).

A second indication is the presence of the metallacyclobutadiene **146** in the reaction mixture. Due to the lower symmetry and low concentration of the minor species not all signals could be unambiguously assigned, but all characteristic signals supported the proposed structure. It is undoubtedly the intermediate through which the catalytic cycle for productive alkyne

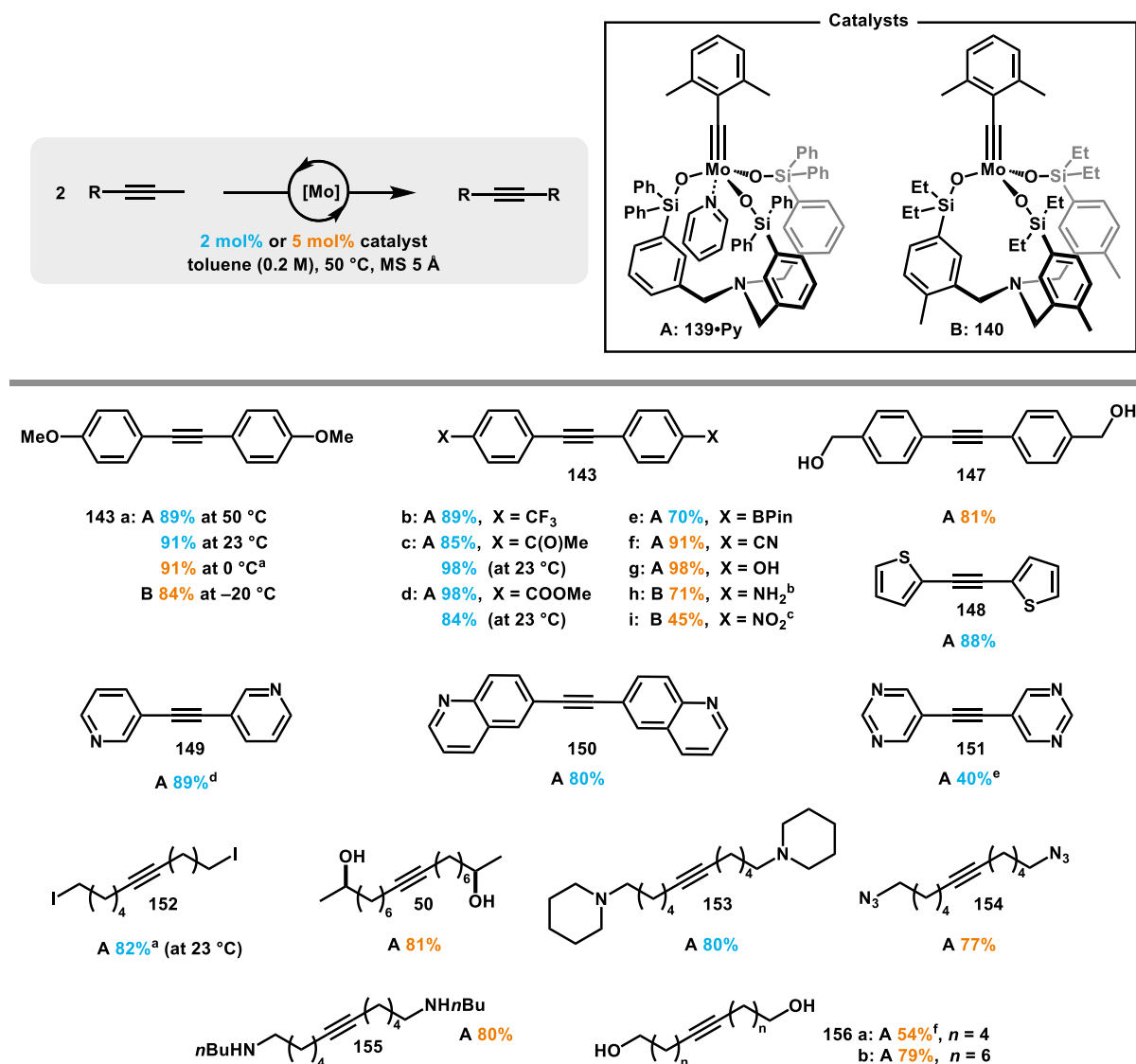
³ The NMR experiments were carried out in close cooperation with Dr. Markus Leutzsch.

metathesis has to proceed. In accordance with this, the MCB_D in the current experiment underwent dynamic exchange with free hex-3-yne even at 233 K, whereas exchange with the MTH was only observed at ambient temperature. The presence of both species in the reaction mixture might indicate that the off-cycle MTH is not as energetically favored in relation to the on-cycle MCB_D as in the case of the ‘canopy series’. There, in the analogous experiment, the MCB_D had not been encountered in significant amounts.^[36a]

1.3.7 Scope and Application

The initial evaluation through the benchmark reaction had predicted good reactivity for the novel catalysts. Their performance in alkyne metathesis reactions on a preparative scale was assessed with a large number of substrates comprising varied functional groups.

In a first foray, the homometathesis of a series of methyl capped alkyne derivatives was investigated. While the obtained products are not particularly valuable, the reactions serve as a good indicator for the functional group compatibility of **139•Py** (scheme 70).



^awith added BPh₃; ^bat 110 °C; ^cwith 7 mol% catalyst at 110 °C; ^dat 90 °C; ^eat 100 °C; ^fwith MS 4 Å.

Scheme 70: Homometathesis reactions of functionalized substrates with the air-stable adduct **139•Py** or **140**.

Most reactions were performed with 2 mol% of air-stable **139•Py** as the catalyst in toluene at 50 °C in the presence of molecular sieves (5 Å) as scavengers for the released but-2-yne. While reactions at ambient temperature are certainly possible, as proven by the examples of **143a**, **c** and **d**, slightly elevated reaction temperatures were chosen as the standard conditions to also allow electron-deficient alkynes to reach full conversion within a reasonable time span.

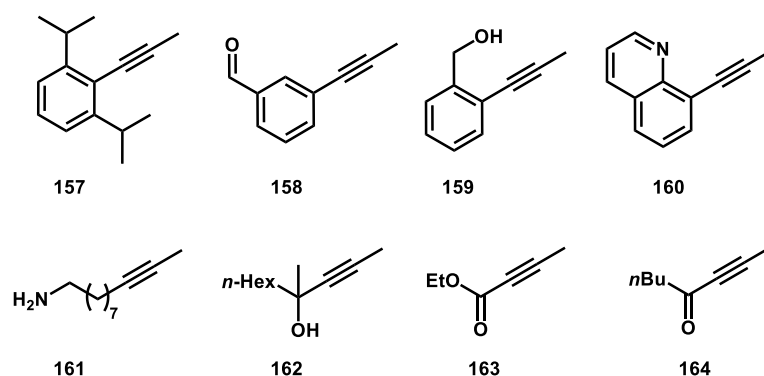
Reaction temperatures below ambient temperature are also possible. At 0 °C, product **143a** could be obtained with **139•Py** by employing the pyridine scavenger strategy. For a reaction at –20 °C, the unligated and slimmer variant **140** had to be used.

Substrates comprising protic groups are challenging for molybdenum alkylidyne complexes with silanolate ligands, and 5 mol% of the catalysts were deployed to drive the reactions towards full conversion. Satisfyingly, the complex **139•Py** with its tridentate ligand was operative in the presence of a primary and secondary aliphatic, as well as a benzylic alcohol, a phenolic –OH, and a secondary amine. Molecular sieves with a smaller pore size were used for substrate **156a**, as short linear-chain alcohols can be absorbed in larger cavities.^[177]

The presence of donor sites had marked an important limitation for some catalysts in the past.^[102a] As forecasted by the reversible stabilization with pyridine, **139•Py** was able to convert substrates containing a nitrile, pyridine, pyrimidine, quinoline, thiophene, and a tertiary aliphatic amine. Alkyl iodides and azides can be troublesome functional groups for the classical Grubbs catalysts as they react with the phosphine ligands contained therein.^[135] **139•Py**, on the other hand, formed the products **152** and **154** in high yields. The synthesis of alkyl iodide **152** was the only reaction with internal alkynes during which polymerization was observed as a competing side reaction. Lowering the reaction temperature to 23 °C in conjunction with the promoter triphenylborane ensured a high yield (*cf.* at 50 °C: 60%).

Overall, the new catalysts have a similarly favorable functional group tolerance as the previous generation, with the notable distinction that **139•Py** could be weighed out and handled in air. The new ease of operation, avoiding the preparation of catalyst stock solutions under inert atmosphere, is deemed a marked improvement for the practitioner.

Perhaps even more interesting than the functional groups, which are tolerated, are motifs which should be avoided when attempting an alkyne metathesis. Some limitations of the current catalysts are summarized and discussed in the following (*scheme 71*).



Scheme 71: Unreactive substrates in homometathesis reactions demonstrating limitations.

The highly sterically encumbered substrate **157** did not undergo homometathesis. It is likely that very bulky substrates denote a general limitation for catalysts with a tripodal ligand framework. A substrate comprising aldehyde **158** also failed to react. The incompatibility of the moiety with catalysts equipped with silanolate ligands is well documented, whereas

Next, the catalysts performance in the RCAM of diynes into macrocycles of different sizes was investigated (*scheme 72*). In order to favor ring closure, the reactions are carried out at high dilution (2 mM in toluene) and in the presence of molecular sieves.

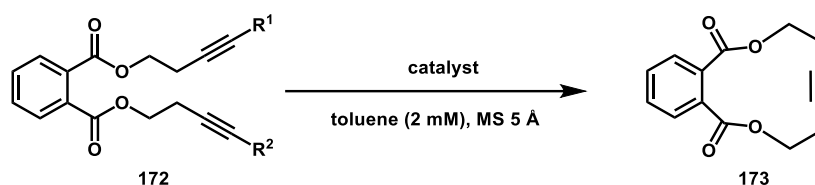
Twelve-membered cycles are the smallest attainable with alkyne metathesis and two simple examples **165** and **166** were prepared in excellent yields. The reactions can be performed at ambient temperature or above, and a short survey demonstrated that the catalyst loading can be reduced to 1 mol% for such uncomplicated cases. Also larger macrocycles (e.g., 18-membered **167**) can be formed at variable temperatures.

As alluded to above, ynoates can be challenging substrates in alkyne metathesis and were shown to be beyond the scope of *Schrock's* catalyst.^[49, 179] Only a molybdenum alkylidyne equipped with monodentate silanolate ligands was previously able to form macrocyclic ynoate **168** *via* RCAM. The new, air-stable catalyst **139•Py** also belongs to this elite class.

Even more formidable substrates are diynes comprising two propargylic alcohols. Such alkynes react slowly, giving the detrimental side reaction of the flanking –OH groups with the complex time to proceed. As a consequence, only molybdenum alkylidynes with tripodal silanolate ligands and less oxophilic rhenium-based catalysts had engendered such ring closures.^[73-74, 81c] Satisfyingly, both **139•Py** and **140** were able to catalyze the transformations, albeit also with moderate yields. These types of substrates are currently the most stringent benchmark for alkyne metathesis catalysts and all complexes developed in the future should be submitted to this litmus test.

Interestingly, the slimmer, unligated version **140** did not perform significantly better with these challenging substrates. In the ‘canopy series’, all but the most active ‘turbo catalyst’ had failed to afford product **170**. This is seen as further proof that the differences in terms of activity between the air-stable **139•Py** and **140** are small and only of relevance in very specific cases.

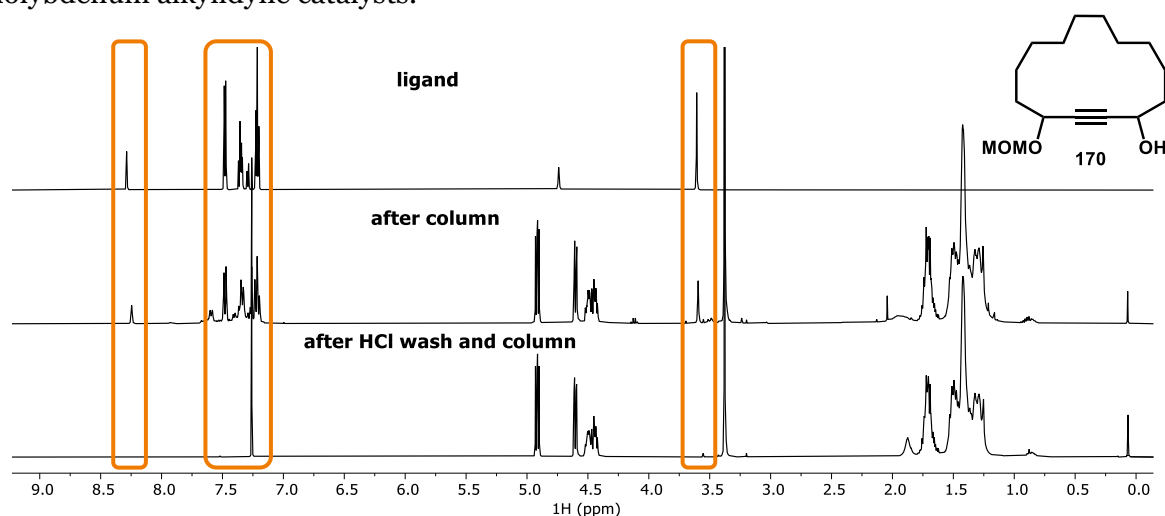
At this point, a short survey was conducted to elucidate how different end-caps on the starting material alkynes impact the outcome of the RCAM reaction (*table 4*). As mentioned before, cyclization of substrates bearing methyl end-caps are preferred, but the reaction with **172b** carrying propyl groups was equally effective.^[153b] Introducing methyl capped alkynes into a molecule frequently involves the use of gaseous prop-1-yne, which is more difficult to handle than the liquid hex-1-yne employed for generating acetylene derivatives with propyl end-caps. The result offers an uncomplicated alternative to chemists planning the synthesis of their RCAM substrate. The same is true for substrate **172c** comprising a silyl terminus and a methyl end-cap, although more forcing conditions and longer reaction times were necessary. Diynes with two silyl termini do not undergo RCAM as can be deduced from the accumulation of diyne **172f** ($R^1 = R^2 = \text{TMS}$) as a side product in the reaction under *entry 3*.

Table 4: Survey of the effect exerted by different alkyne caps on the RCAM.

Entry	Substrate	R ¹	R ²	Catalyst	Additive	T (°C)	Yield
1	172a	Me	Me	139•Py (5 mol%)	—	23	90%
2	172b	C ₃ H ₇	C ₃ H ₇	139•Py (5 mol%)	—	50	90%
3	172c	Me	SiMe ₃	139•Py (5 mol%)	—	100	86% ^a
4	172d	Me	H	139•Py (5 mol%)	—	23/50	— ^b
5				139 (5 mol%)	—	23	66%
6				139•Py (10 mol%)	BPh ₃ (10 mol%)	23	92% ^c
7	172e	H	H	139•Py (10 mol%)	BPh ₃ (10 mol%)	23	16% ^c

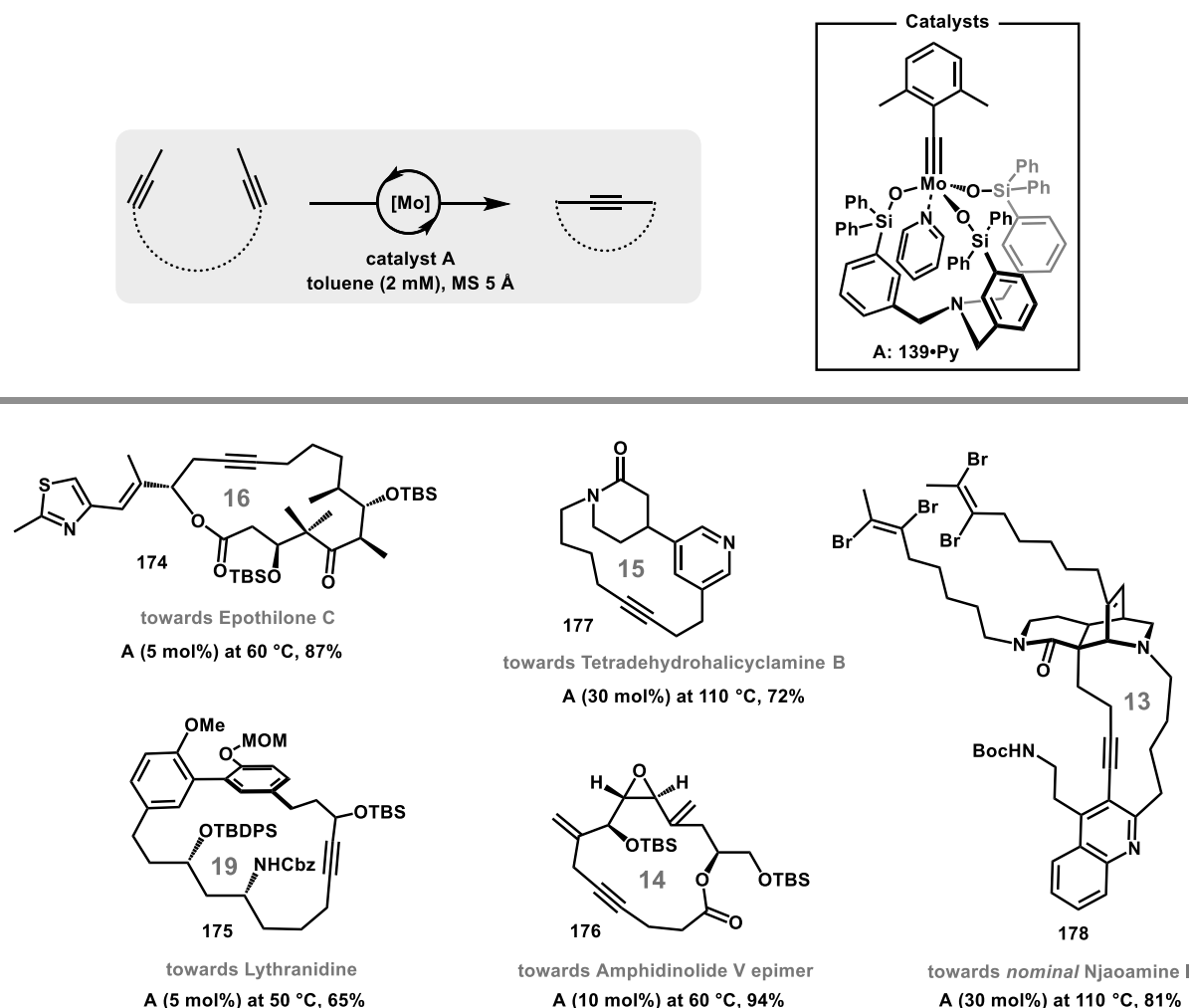
^aThe reaction was performed in the absence of MS; Diyne **172f** with R¹ = R² = SiMe₃ was formed as a side product (ca. 7%). ^bNo reaction at 23 °C and polymerization at 50 °C. ^cin the presence of MS 4 Å and MS 5 Å.

Terminal alkynes are known to be difficult substrates for alkyne metathesis, although some success with cross-metathesis reactions of methyl capped alkynes and terminal alkynes has been reported.^[127b] However, with **139•Py** polymerization prevailed. Presumably, the pyridine acts as a base in aiding the detrimental deprotonation of the MCBP. In line with this notion, the reaction with the unligated complex **139** gave the desired product in good yield. Likewise, when triphenylborane was introduced as a pyridine scavenger, **139•Py** was also capable of affording the product in excellent yield. In the reaction with substrate **172e**, comprising two terminal alkynes, polymerization was dominant and the product was only obtained in poor yield. Therefore, terminal alkynes remain beyond the scope of the current silanolate-based molybdenum alkylidyne catalysts.

**Figure 31:** ¹H NMRs of the ligand, the sample after flash chromatography and after an acid wash and flash chromatography.

Another practical feature of the new catalysts is the nitrogen acting as the tether of the ligand. It can be used for the removal of the hydrolyzed silanol ligand from the product after work-up. *Figure 31* shows an example in which the ligand coeluted with the product (**170**). Difficulties in separating tris(silanol) ligands or fragments thereof from the targeted compounds through flash chromatography have been noted in the past, in particular, as silanols have the tendency to interact with the silica used for purification.^[79b, d] Simply washing the crude reaction mixture with diluted aqueous hydrochloric acid before submitting it to flash chromatography was sufficient to remove traces of the new ligand.

The overall encouraging outcome of the model reactions provided the motivation for attempting a final round of evaluation using advanced intermediates from previous natural product syntheses (*scheme 73*). Testing the air-stable catalyst **139•Py** on these highly functionalized ‘real life’ substrates is arguably the most rigorous trial possible.



Scheme 73: Application of the air-stable catalyst **139•Py** to advanced intermediates of previous natural product syntheses.

No attempts were undertaken at optimizing the presented reactions towards, e.g., lower catalyst loadings, because the available amounts of the substrates were limited. The first macrocycle **174**, an intermediate en route to Epothilone C, was obtained in good yield with low

catalyst loading (5 mol%) at 60 °C within two hours. The substrate has become a classical application for alkyne metathesis providing control over the geometry of the alkene in the final structure *via* Lindlar reduction of the alkyne.^[53] The successful formation of intermediate **175** under equally mild conditions further illustrates the prowess of air-stable **139•Py**. A propargylic silyl ether, an acetal and a carbamate were tolerated in the formation of this precursor for the alkaloid Lynthranidine.^[66a] An even greater challenge was posed with a substrate from the synthesis of an epimer of Amphidinolide V: the vinyl epoxide and the allylic ether are sensitive to both acid/base and the resulting cycle is fairly strained.^[146b] Yet, air-stable **139•Py** afforded the product **176** in excellent yield under the previously reported conditions. Note, that the alkenes in the compound remain untouched. Similarly, the 15-membered **177** could be formed, which had served the total synthesis of *epi*-Tetradehydro-halicyclamine B. Pyridines, although a challenge for the venerable Grubbs catalysts, pose no problem for advanced molybdenum alkylidyne catalysts, as is evident from the stabilized catalyst **139•Py**. The *meta/para* substitution pattern in **177** brings additional strain to the formed cycle, explaining the high temperature necessary for its formation. The RCAM reaction affording the polyfunctionalized intermediate **178** was chosen as an ultimate test. The structure comprises a secondary amine, a quinoline, a tertiary amine, *vic*-bromoalkenes, and an amide. Regardless, **139•Py** affected the macrocyclization of the strained lower ring without difficulties. The obtained product had been a key intermediate in the total synthesis of the polycyclic *nominal* Njaoamine I.^[79b] Its formation is a powerful testimony to the functional group compatibility of the new catalyst.

The encouraging performance of **139•Py** in numerous examples positions it among the best alkyne metathesis catalysts known to date. On top, the adduct's reactivity is paired with an unrivaled ease of operation. Air-stable **139•Py** can be stored, weighed, and handled without the need for a glovebox. Its overall favorable application profile is expected to make it an expedient tool for organic chemists.

1.3.8 Miscellaneous Catalyst Designs

This chapter is dedicated to miscellaneous catalyst designs pursued in parallel to the main project of the thesis.

In reviewing the literature on molybdenum-based alkyne metathesis catalysts, it is conspicuous that two ‘schools’ have emerged (*figure 32*).

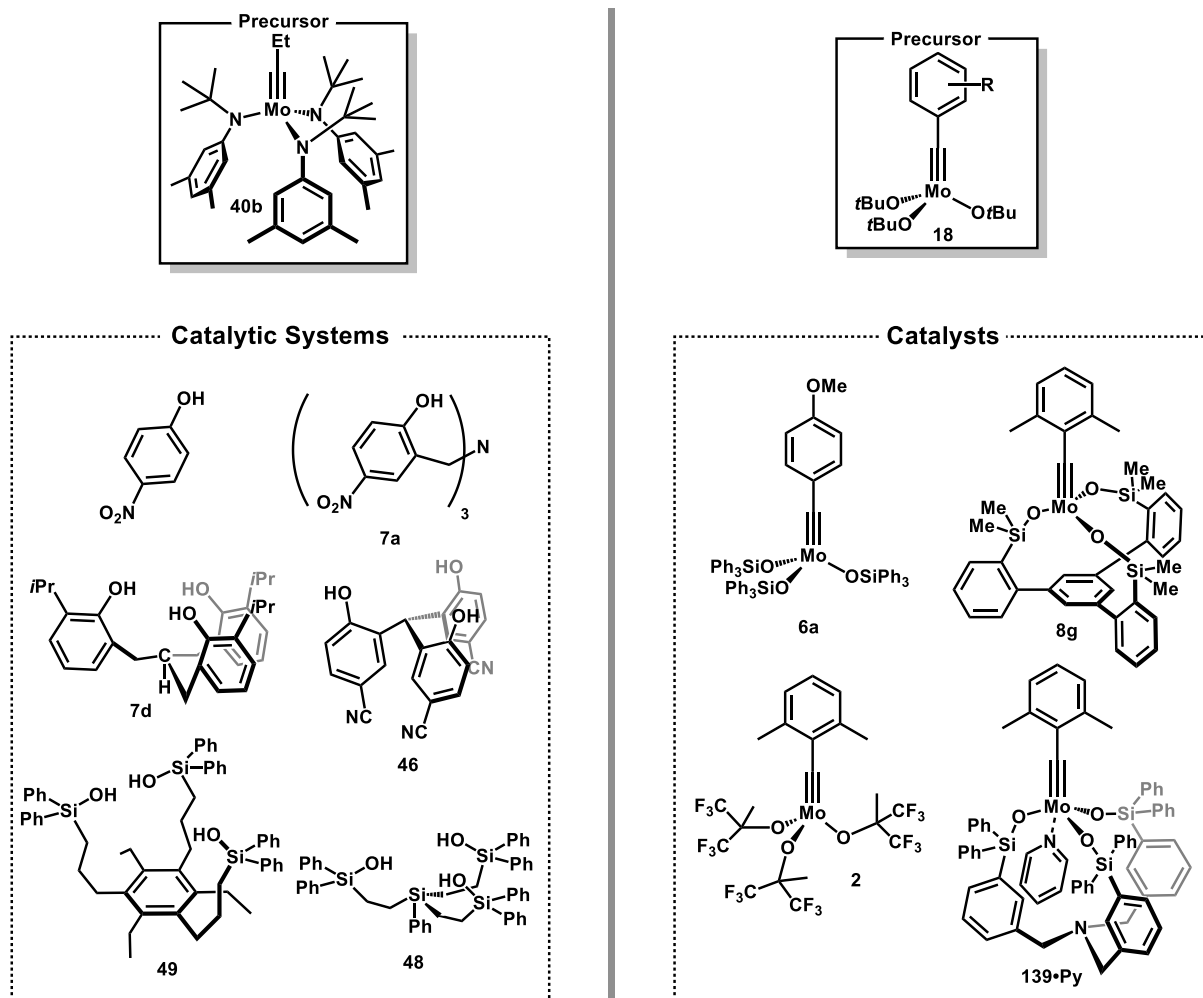


Figure 32: The two dominant molybdenum alkylidyne precursors for alkyne metathesis systems.

One of them relies on precursor **40b** derived from molybdenum (III) complex **3** and *in situ* complexations with a variety of ligands.^[43b, 44a, 69b, 73] The other one prefers the molybdenum alkoxide precursor **18**, which is obtained *via* the ‘low oxidation route’, for the formation of structurally defined complexes.^[74, 78] While both methods have their merits, precursor **40b** is unsuitable when user-friendliness is the primary goal. Its synthesis requires strict exclusion of moisture, oxygen, and nitrogen and is always accompanied by varying amounts of the free aniline ligand. Its storage stability is unreliable, even under argon at low temperatures, and complexations often require chlorinated solvents. Therefore, it was investigated if precursor **40b** can be replaced by the precursor complex **18**.

To that end, it had to be investigated if molybdenum alkylidyne catalysts stay operational in the presence of *tert*-butanol, which is formed *in situ* when replacing the alkoxides in **18** with

the desired ligand. Surprisingly, it was even possible to perform the standard test reaction using *tert*-butanol as a solvent. Modest to good yields were obtained with catalysts **139** and **6a** (table 5); **8g** also gave good conversion, but the product was not isolated.

Table 5: Testing the compatibility of molybdenum alkylidyne complexes with *tert*-butanol and water.



Entry	Catalyst	Conditions	solvent	Yield
1	139 (18 mol%)	4 h, 40 °C, 4 Å MS	<i>t</i> BuOH (0.2 M)	50%
2	8g (18 mol%)	4 h, 40 °C, 4 Å MS	<i>t</i> BuOH (0.2 M)	53% conv. ^a
3	6a (18 mol%)	4 h, 40 °C, 4 Å MS	<i>t</i> BuOH (0.2 M)	67% ^a
4	139 (5 mol%)	4 h, 40 °C	water/TPGS750M/toluene	no conv.

^adetermined via GC/MS as a ratio of the starting material and the product.

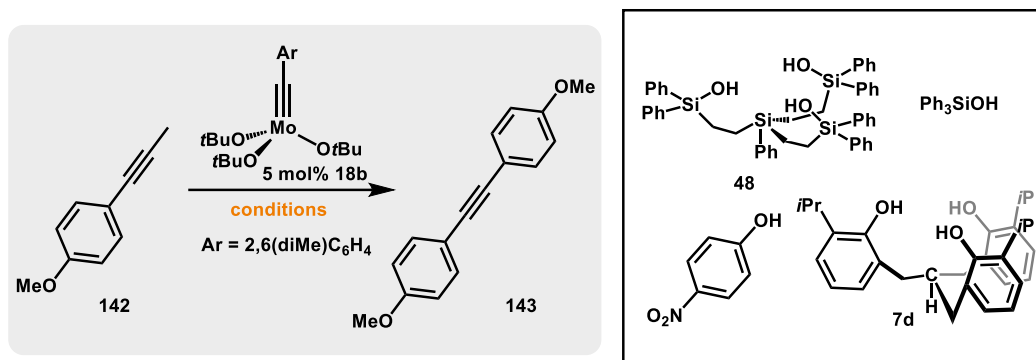
The catalysts stability in the protic solvent did not depend on whether they contained a tripodal ligand or not. It is likely that the steric bulk of *tert*-butanol slows down the detrimental protonolysis reaction, irrespective of the catalyst used.

Encouraged by these result, an alkyne metathesis reaction in water was attempted employing a surfactant developed by the group of Lipshutz (entry 4).^[180] No conversion was observed. Water remains highly detrimental to molybdenum alkylidyne catalysts in solution.

The performance of complex **18** as a precursor for *in situ* generated catalyst systems was evaluated using the standard test reaction (table 6). Addition of a mixture of **18** and the tridentate tris(silanol) ligand **48b** to a substrate solution of **142** entailed a rapid homometathesis reaction. Full conversion was reached within approx. one hour and product **143** was isolated in excellent yield.

Combining 4-nitrophenol with precursor **18b** in toluene caused precipitation. Addition of dichloromethane partially redissolved the precipitate, but overall low conversion was observed. In combination with triphenylsilanol, precursor **18** lead to a high conversion within a short timeframe, whereas the triphenol ligand **7d** was unsuitable for catalyzing the reaction in pure toluene. Only when premixing the ligand with the precursor complex in chloroform and then adding the catalyst solution to the substrate in toluene, the desired product was obtained.

In summary, the molybdenum alkoxide complex **18** can serve as a precursor for catalytically active mixtures with different ligands. However, it did not obviate the need for chlorinated solvents in combination with phenol ligands.

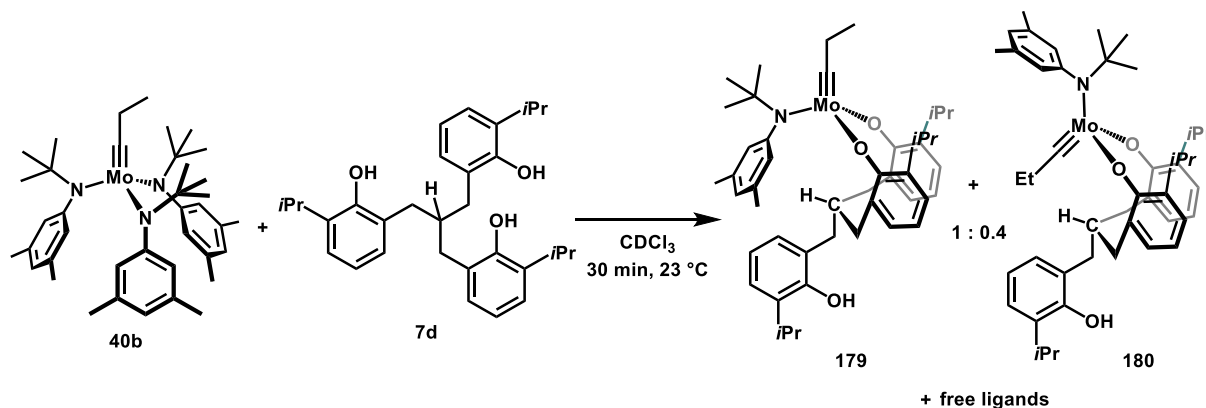
Table 6: Test reactions evaluating the performance of precursor **18b** with different ligands.

Entry	ligand	Conditions	Solvents	Conversion ^a
1	48d	1 h, 23°C, 5 Å MS	toluene (0.2 M)	98% (91%)
2	4-nitrophenol (15 mol%)	16 h, 23°C, 5 Å MS	toluene + CH ₂ Cl ₂ (0.2 M)	10%
3	Ph ₃ SiOH (15 mol%)	3 h, 23°C, 5 Å MS	toluene (0.2 M)	99%
4	7d	3 h, 23°C, 5 Å MS	toluene (0.2 M)	15%
5	7d	16 h, 40°C, 5 Å MS	18 and 7d premixed in CHCl ₃ reaction in toluene (0.2 M)	93%

^adetermined *via* GC/MS as a ratio of the starting material and the product; isolated yield in parenthesis.

A related investigation focused on the composition of the species formed during *in situ* complexations of precursor **40b** and triphenol ligands. The synthesis and characterization of complex **118** discussed in *chapter 1.3.1* showed the coordination chemistry to be more complex than suggested in the literature. However, ligand **117** containing a nitrogen atom in the tether, which coordinates to the metal in the solid-state, can be regarded as a special case and the question remained open for the other ligands.

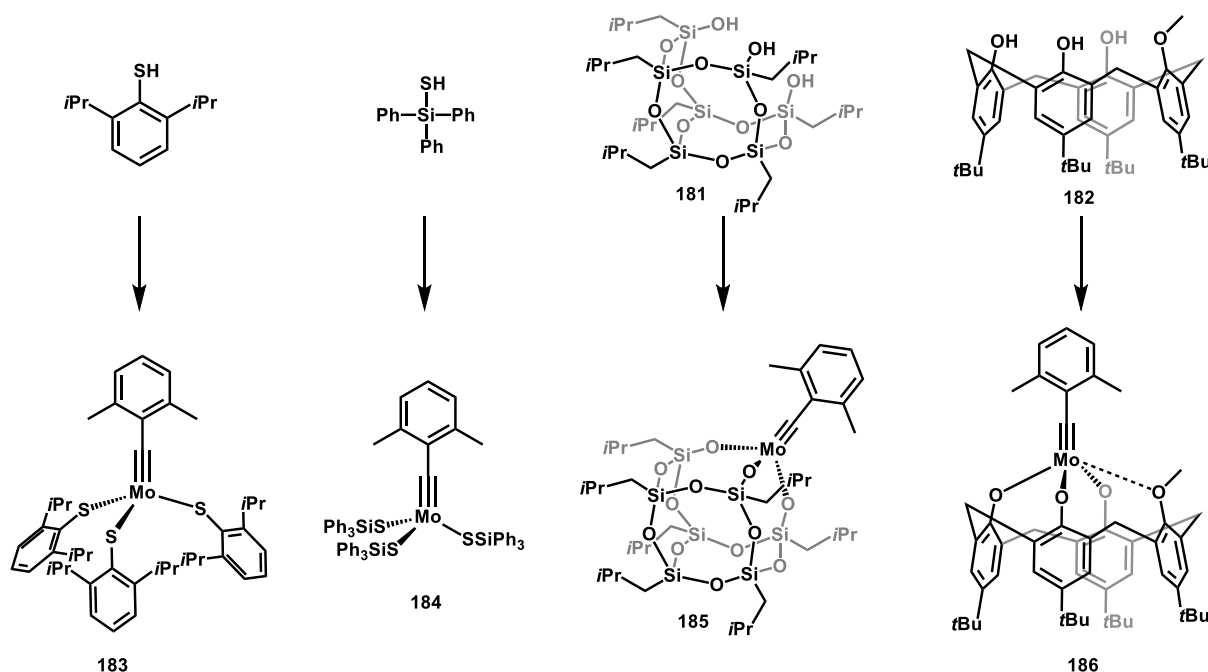
To shed light on the problem, the species resulting from an *in situ* complexation of the carbon tethered ligand **7d** and the trisamido complex **40b** was investigated. The NMR study, carried out in cooperation with Dr. M. Leutzsch, revealed two major organometallic components (*scheme 74*). Importantly, the NMR spectra are virtually identical to the spectra shown in the original publication.^[70b]

**Scheme 74:** New structures proposed for the constitution of the species formed in the mixture of **40b** and **7d**.

Besides some free ligands (aniline and triphenol **7d**) the mixture contained two closely related species, which both comprised an alkylidyne unit. In contrary to previous suggestions, the triphenol ligand does not bind in a tripodal manner. The 2D ^1H - ^{15}N HMBC clearly shows an amido ligand to remain bound to the metal. The ^1H NMR data further displays signals consistent with the triphenol ligand arranged in a bidentate manner with a freely pendent third phenol. The two complexes are believed to be isomers, however, the exact difference in terms of their conformation is difficult to determine. The major species **179** shows a NOE cross peak between a proton on an *iso*-propyl residue *ortho* to the phenolate and a proton on the alkylidyne unit. This interaction is absent in the minor species **180**, implying a change in the orientation of the alkylidyne unit with respect to the bidentate ligand.

Anyway, the important point is the heteroleptic nature of the formed complexes – a fact which had not been noticed in the original publications. The finding might help to explain small differences in the functional group tolerance of these systems compared to molybdenum alkylidyne complexes with silanolate ligands. For example, the latter do not tolerate substrates comprising aldehydes, whereas the former readily convert them. It could be speculated that the heteroleptic ligand sphere tempers the Lewis acidity of the molybdenum and prevents it from engaging in destructive ‘Wittig-type’ reactivity with aldehydes.

Four additional ligands were briefly screened (*scheme 75*). Motivated by the success of catecholthiolate carbene complexes in alkene metathesis, an attempt was made at replacing the oxygen in phenolate or silanolate molybdenum alkylidyne complexes with sulfur.^[181] Complexes **183** and **184** could be obtained by combining the commercially available ligands 2,6-di(*iso*-propyl)-thiophenol or triphenylsilanethiol with the alkoxide precursor complex **18b**.



Scheme 75: Miscellaneous ligand designs resulting in complexes which were not active in alkyne metathesis.

The structure of both complexes could be confirmed *via* NMR analysis, although the samples were not entirely pure. The ^{13}C NMR shifts of the alkylidyne carbons (**183**: $\delta = 320$ ppm; **184**: $\delta = 332$ ppm) did not fall into the range defined for active alkyne metathesis catalysts.^[78] Even more indicative were the recorded ^{95}Mo NMR shifts (**183**: $\delta = 1275$ ppm; **184**: $\delta = 1377$ ppm), which were far from the range usually observed for molybdenum alkylidynes with silanolate or alkoxide ligands. Accordingly, no reactivity was observed, when the complexes were submitted to the standard benchmark reaction.

Schaubach had previously investigated calyx[4]arenes and silsesquioxanes as multidentate ligands in alkyne metathesis.^[118] The partially-condensed T_7 polyoctahedral silsesquioxanes (POSS) **181** had failed to give a structurally defined complex. A new attempt was made with $[(t\text{BuO})_3\text{Mo}\equiv\text{C}-\text{Ar}]$ (**18**) as the precursor expecting the mild protonolysis to be a superior complexation method. Indeed, an initial control of the crude product through NMR spectroscopy indicated the desired structure to have formed. However, since the complex was unreactive in alkyne metathesis the approach was not further investigated. Potentially, changing the organic substituents at the silicon atoms could change the outcome. *Schaubach* had reported metathesis activity for an *in situ* created mixture with a derivative carrying phenyl residues at this position.

A structurally defined molybdenum nitrido complex had been obtained with a mono-methylate tetra hydroxyl calyx[4]arene.^[182] Yet, the resulting complex had been too stable to function as competent catalyst.^[118] The corresponding molybdenum alkylidyne complex **186** was synthesized and characterized by NMR spectroscopy and high resolution mass spectrometry. A ^{95}Mo NMR shift could not be detected, likely due to the asymmetrical ligand sphere around the molybdenum. Ultimately, **186** failed to catalyze the benchmarking reaction. A possible reason is the obstruction of the fourth equatorial coordination site by the methyl ether.

1.3.9 Outlook

The air-stable complex **139•Py** and its slimmer congener **140** have been demonstrated to be highly active catalysts for alkyne metathesis and are expected to be enabling tools for synthetic organic chemists.

Both have already found application in the total synthesis of natural products (*figure 33*).

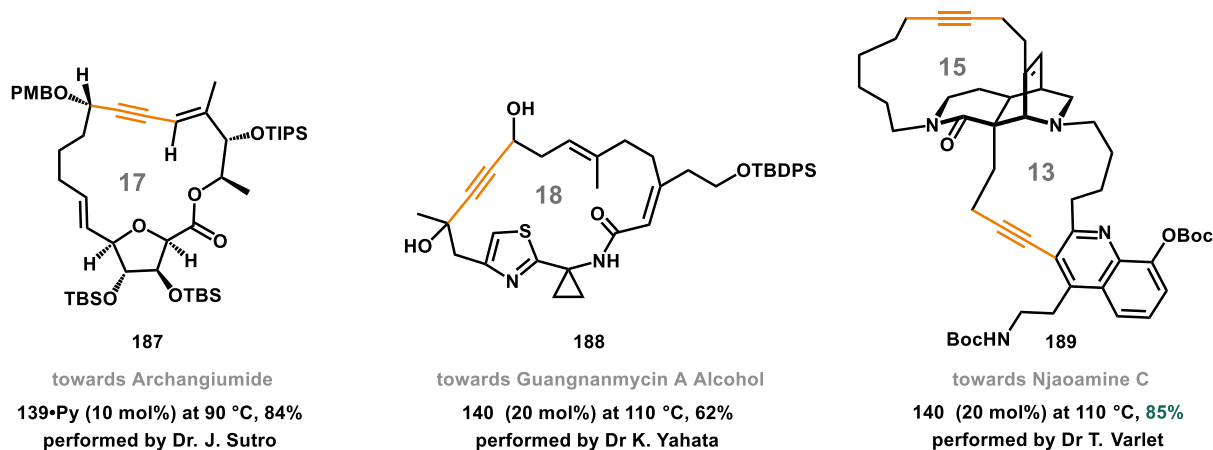


Figure 33: Application of the new catalysts in the total synthesis of natural products.

While Dr. *J. Sutro* was able to form the depicted macrocycle **187** on the way towards Archangiumide using air-stable catalyst **139•Py** with ease,^[144] exceptionally challenging RCAM reactions required the ethyl variant **140** to effect ring closure.^[75c, 120a] Especially the double ring closing alkyne metathesis (dRCAM) in the synthesis of Njaoamine C, conducted by Dr. *T. Varlet*, served as a reminder that sterically encumbered alkynes (**189**) might clash with the larger residues at the silanolate ligands in the air-stable complex. As a consequence, future efforts might target a stabilized catalyst with a slimmer ‘fence’ surrounding the molybdenum alkylidyne unit.

B. Breustedt has already started work in this direction with the synthesis of **190•Py** based on the same general design (*figure 34*).^[171]

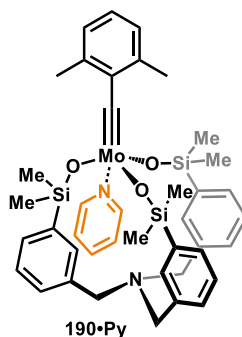
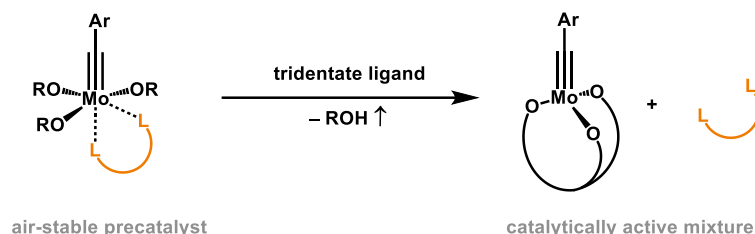


Figure 34: Slimmer catalyst based on the same general design.

A conceptually different approach might be rednering a molybdenum alkylidyne precatalyst air-stable and employing it in *in situ* complexations with the various ligands already available. The tactic would take into account that not all ligands are suitable for all substrates, as

demonstrated in the dRCAM discussed above. Utilizing bidentate donor ligands for the stabilization might be admissible, when using tridentate ligands for the *in situ* formation of the catalytic species. The complexation with a tripodal ligand precludes reassociation of both binding sites of the stabilizing ligand, in theory, allowing the tridentate ligand to supplant the bidentate ligand. However, for the approach to be viable, the bidentate ligand needs to be considerably more labile than the phenanthroline previously used.^[31b, 183]



Scheme 76: Future direction for air-stable alkyne metathesis catalysts.

Another way for potentially improving the stability even further would be to attach the additional stabilizing ligand to the rest of the ligand sphere. The goal could be accomplished with a tetradentate ligand, or by attaching the labile ligand to the benzyldiyne unit, or by using the tether of a tripodal ligand itself as a stabilizing element (figure 35).

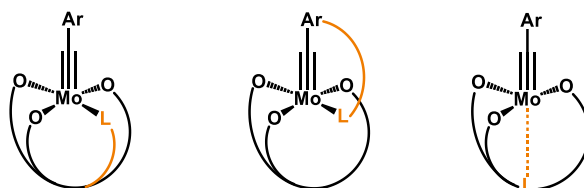


Figure 35: Possibilities for tethering an additional stabilizing neutral ligand.

The phenolate complex **118** could serve as a prototype for this design. The octahedral coordination of the molybdenum in the solid-state renders it especially robust as revealed by a cursory investigation of its stability on the bench. In solution, however, the nitrogen tether and the additional phenol ligand are dissociated from the metal center. Even so, the reactivity in alkyne metathesis would have to be improved significantly.

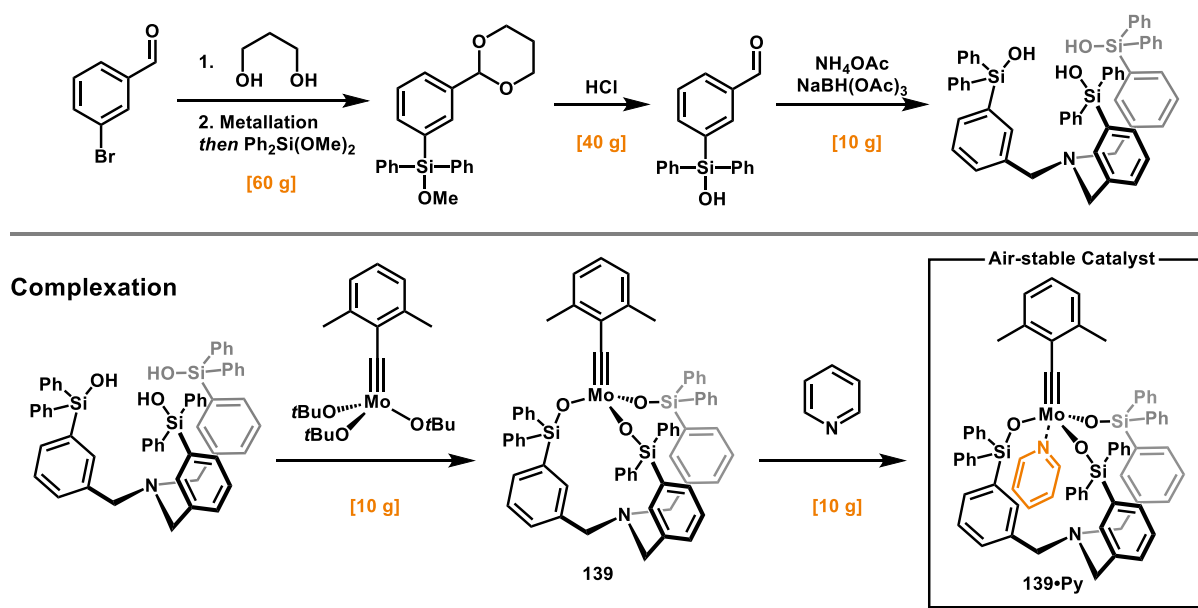
Further directions for future alkyne metathesis research include the pursuit of catalysts based on other transition metals such as ruthenium or vanadium alkylidyne.

I.4 Summary

Alkyne metathesis has become a strategic transformation in natural product synthesis over the course of the last two decades. The group of *Fürstner* has repeatedly proven its enabling features and versatility by conquering numerous challenging macrocyclic targets. Catalyst development has gone hand-in-hand with tackling evermore ambitious natural products; however, the Achilles' heel of alkyne metathesis catalysts has always been their stability, which is unsurprising considering that they comprise an early transition metal in its highest oxidation state. While significant progress had been made, an air-stable catalyst that does not require preactivation remained elusive.

The presented work addressed this issue, which is deemed crucial in making alkyne metathesis accessible to the wider chemical community. A new catalyst was designed seeking maximal stability whilst maintaining the chemical virtues of its predecessors. The blueprint drew on lessons learned from 25 years of catalyst development and included four main features: firstly, a sterically demanding alkyldiyne unit was chosen to ensure stability in the bulk material. Secondly, a tripodal ligand scaffold, which was selected from two initial designs, with a focus on an improved balance between preorganization of the ligand and adequate flexibility.

Ligand Synthesis



Scheme 77: Scalable synthesis of the air-stable alkyne metathesis catalyst **139•Py**.

Thirdly, silanolates were selected as ancillary ligands as they synergize exceedingly well with molybdenum alkyldynes. The enhanced flexibility in the new ligand framework allowed for bulky aryl substituents at the silanolates which shield the metal center. This leads to improved stability in the solid-state, while not overly impacting catalytic activity. Lastly, a stabilizing yet labile external ligand had to be found. After extensive screening, the choice fell on simple

pyridine, which binds tightly to the molybdenum in the solid-state, but can spontaneously dissociate in toluene at ambient temperature, revealing the active catalyst.

The catalyst could be prepared on multigram scale and was extensively characterized by crystallographic and spectroscopic means, including ^{95}Mo NMR.

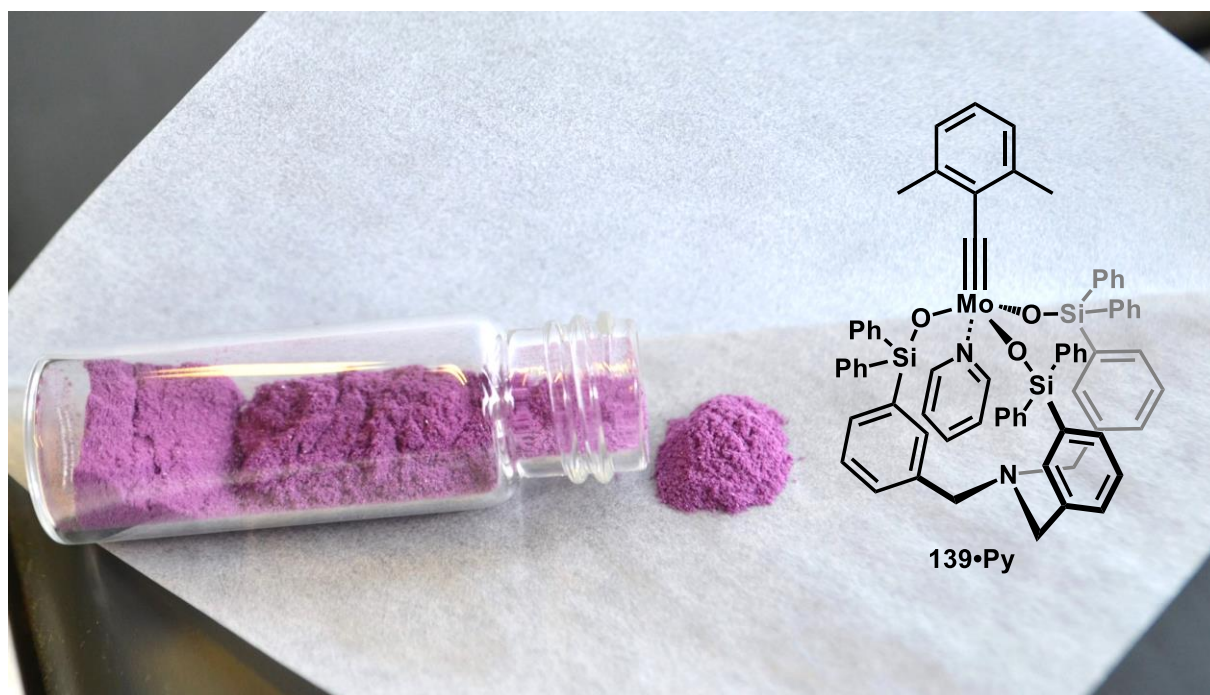
Additionally, a few derivatives could be accessed changing some features mentioned above to prove their importance for stability or activity of the catalyst. For example, variable temperature NMR was employed to analyze the equilibrium between the free complex and adducts with different stabilizing ligands. For pyridine, broad signals were detected at 298 K indicating a fluxional coordination. At 233 K, sharp signals indicated the adduct to be the only present species, whereas at 323 K free pyridine and the active catalyst were visible. Conveniently, the equilibrium can be easily tracked by a characteristic color change from lilac (adduct) to orange (free complex). Other pyridines, phosphines or tertiary amines proved either too labile or too tightly bound.

The catalysts activity was carefully benchmarked in a standardized homometathesis reaction against a library of catalysts from previous generations. The new catalyst showed excellent performance, reaching equilibrium within 60 min at ambient temperature.

Most importantly the stability of the catalyst when stored under air was investigated. Previous generations of catalysts decomposed within hours when subjected to the same conditions. The novel catalyst showed no significant degradation after eight months. More importantly the 'aged' sample was able to catalyze the benchmarking reaction with unchanged rate and efficiency. Lifetimes on the shelf of this order of magnitude are unprecedented for molybdenum alkylidyne and are believed to be key on the path for commercializing an alkyne metathesis catalyst. The stability of the new catalyst allows it to be routinely weighed and handled in air without the need for a glovebox.

The catalysts enabling properties were demonstrated by its application to numerous challenging substrates. The functional group tolerance is impressive: protic groups such as primary and secondary aliphatic, benzylic, propargylic alcohols, phenols, anilines, and secondary amines pose no problem anymore. Further, the catalyst stays operative in the presence of potentially coordinating heterocycles: a pyridine, pyrimidine, quinoline, thiophene, *N*-alkyl piperidine, and thiazole were tolerated. Several RCAM reactions on intermediates from previous natural product synthesis campaigns were performed and shown to give high yields, with the key difference being that the new catalyst neither needs preactivation nor a glovebox for handling and storage.

The enhanced stability allows also non-experts to harness the power of alkyne metathesis and is expected to foster more regular use of this enabling transformation in general.



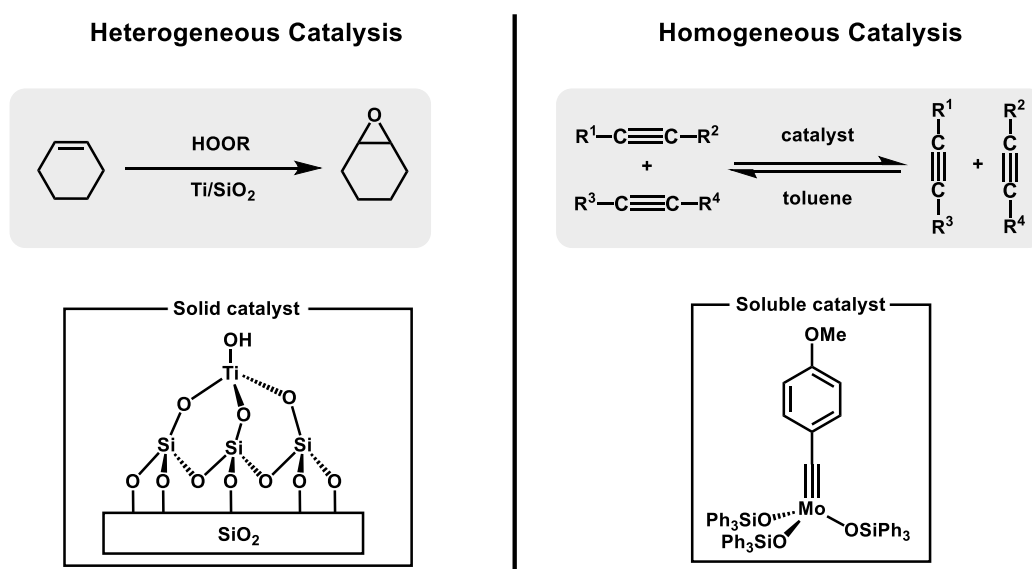
2 Tripodal Tris(silanolate) Ligands in Coordination Chemistry and Catalysis

2.1 Introduction

2.1.1 Silanolate Ligands in Coordination Chemistry and Catalysis

Silica (SiO_2) is a material of fundamental importance in heterogeneous catalysis.^[184] Composed of corner-sharing tetrahedral SiO_4 units, silica can adopt numerous different morphologies with high specific surface areas. This property, in combination with its thermal stability and a high absorption capacity, makes silica an ideal support material for active metal sites.^[185] Traditionally, silica has been viewed as a chemically inert structural component, solely responsible for metal dispersion and fixation, and occasionally selectivity through pore size.^[186] In recent years, however, the ‘non-innocent’ properties of silica supports have increasingly moved into the focus.^[187] Fully hydrated silica surfaces are essentially covered with silanol groups, that can actively participate in catalysis or act as ligands for metal ions in the traditional coordination chemistry sense, creating *single-site* catalysts.^[188]

Compared to the ubiquity of silica and derived supporting structures in heterogeneous catalysis, in homogeneous catalysis metal catalysts with ancillary silanolate ligands are relatively rare.^[108] Alkyne metathesis catalysts, as discussed in the first part of the thesis, are one of the few examples.^[31b] *Scheme 78* shows one of the respective catalysts along with a representative for a *single-site* heterogeneous catalyst supported by silica.^[189]



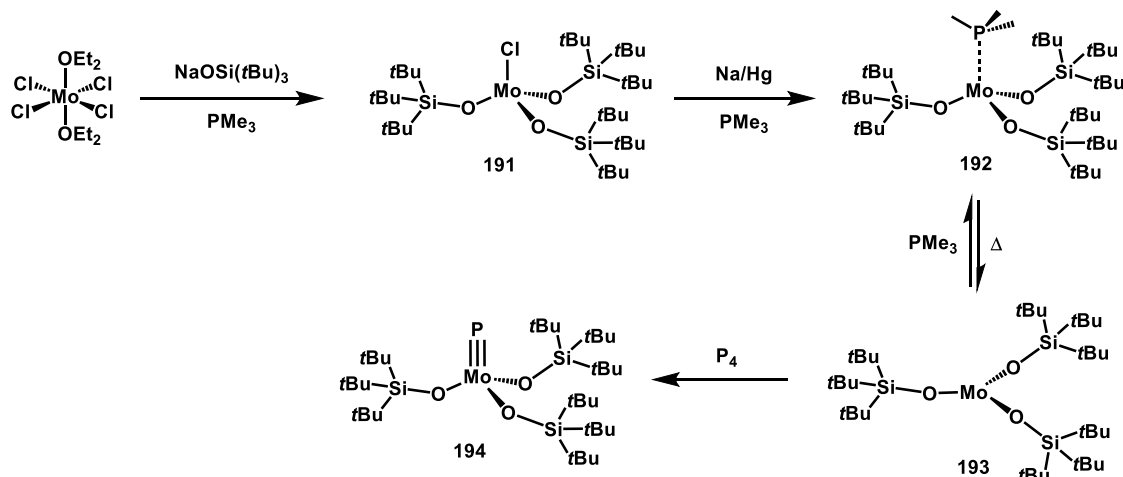
Scheme 78: Examples for silanolates in heterogeneous and homogeneous catalysis.

In the following, some precedents for the use of molecular silanolate ligands in coordination chemistry and catalysis are briefly reviewed. The focus is on complexes comprising ligands derived from monosilanols [$\text{R}_3\text{Si}(\text{OH})$] rather than from silanediols [$\text{R}_2\text{Si}(\text{OH})_2$] or silanetriols

[RSi(OH)₃]. Multidentate silanolate ligands such as silsesquioxanes will be discussed in the next chapter.

In principle, silanolate ligands are closely related to alkoxides. However, the ligands based on the heavier homolog of carbon exhibit some notable differences, which influence their interaction with the bonded metals. Generally, silanols are more acidic than their carbon-based counterparts. The increased acidity is attributed to hyperconjugation (silicon α -effect).^[190] Furthermore, silicon is considerably more electropositive than carbon on the Pauling scale (Si: 1.90; C: 2.55). This, in combination with the larger covalent radius of silicon, results in longer average bond lengths for silanolates (Si–O (1.631 Å); C–O (1.426 Å)).^[191] The dependency of the donor properties of silanolate ligands on the Si–O–M angle has already been discussed in *chapter 1.1.3.2*. However, the way the general concept acts out in a specific case seems to be difficult to predict, as demonstrated by the reversal of the initial assessment in the case of silanolate supported molybdenum alkylidynes.^[61] Often, silanolate ligands are weaker donor ligands than the corresponding aliphatic alkoxides. Their properties can be further tuned by choosing appropriate substituents on the silicon atom.^[192] In the case of carbon substituents, the on average longer bond lengths (Si–C(*sp*³) (1.863 Å); C(*sp*³)–C(*sp*³) (1.530 Å)) leads to steric bulk that is slightly further removed from the bonded metal, which can be taken advantage of for stabilizing low-coordinate complexes.^[193]

Wolczanski and coworkers pioneered this strategy and isolated a series of low-valent early transition metal complexes (Ti^{III}, V^{III}, Nb^{III}, Mo^{III}, W^{III}, Ta^{III}).^[194] The compounds could be obtained in monomeric form with the aid of the sterically highly demanding *silox* ligand (*t*Bu₃SiO). Despite the extensive shielding, the complexes remained reactive and some were even capable of activating hydrocarbons.^[195] A prominent example for the success of silanolate ligands in isolating low-coordinate species is molybdenum (III) complex **193**.^[196] The famous propensity of group six transition metals for forming stable metal-metal triple bonds renders the isolation of monomeric complexes challenging. Previously, only one example of a trigonal planar molybdenum (III) complex had been reported by Cummins (see *chapter 1.1.2*).^[51]

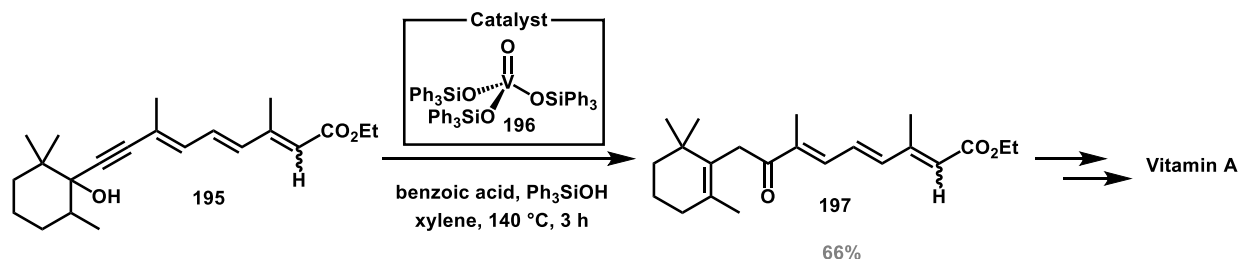


Scheme 79: Synthesis of molybdenum (III) complex **193** and its reaction with phosphorus.

The *Wolczanski* group showed that the chlorido complex **191** could be reduced in the presence of trimethylphosphine; the resulting adduct **192** was labile under vacuum when heated, releasing the monomeric molybdenum (III) complex **193**. Although not capable of splitting dinitrogen (unlike its famous cousin **3**), the complex readily reacted with white phosphorus to give phosphide **194**.

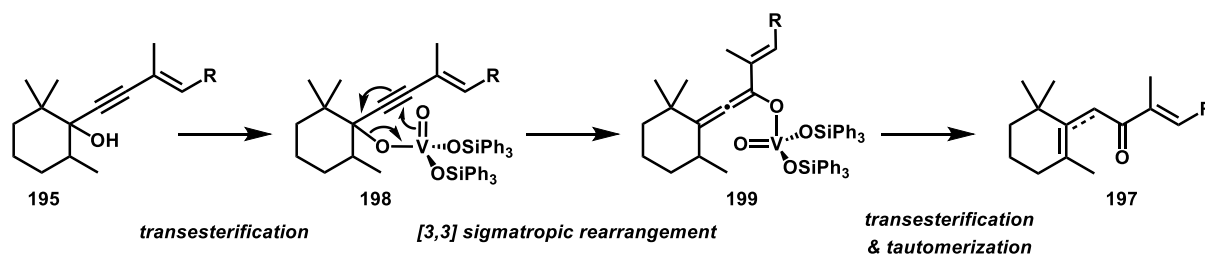
The coordination chemistry of silanolate ligands is not limited to low-valent early transition metals. Rather, complexes with silanolate ligands are known for practically all metals and metalloids of the periodic table.^[193b, 197] These complexes are of relevance as model systems for silica-supported heterogeneous catalysts or as molecular precursors for the synthesis of metal/silicate structures.^[198] In contrast, reports on the direct use of such molecular silanolate supported metal complexes in homogeneous catalysis are rare.

One of the few examples was disclosed by Hoffmann-La Roche during the 1970s for the industrial synthesis of Vitamin A.^[199] A key step in the route was a tris(triphenylsilyl) vanadate complex **196** catalyzed Meyer-Schuster rearrangement of the propargylic alcohol **195** into the β,γ -unsaturated ketone **197** (scheme 80).



Scheme 80: Tris(triphenylsilyl) vanadate **196** catalyzed rearrangement in the synthesis of Vitamin A developed by Hoffmann-La Roche.

The reaction was postulated to involve a transesterification of the propargylic alcohol with the silanolate complex **196**. The resulting vanadate ester **198** then undergoes a [3,3]-sigmatropic rearrangement to afford the allenyl vanadate ester **199**. Subsequent transesterification with excess triphenylsilanol followed by an isomerization gives the β,γ -unsaturated ketone **197** (scheme 81).^[200]



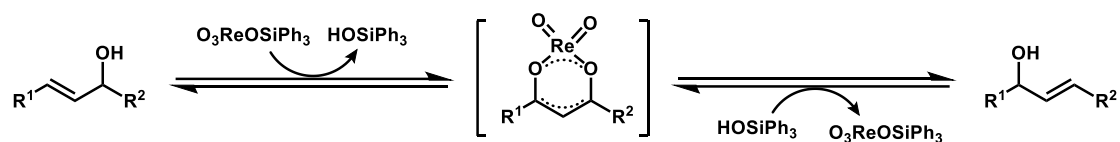
Scheme 81: Proposed mechanism for the Meyer-Schuster-type rearrangement.

Commercially available alkyl vanadates were considerably less effective in catalyzing the transformation, highlighting the critical role of the silanolates as ancillary ligands.^[200a] Introducing electron-withdrawing groups on the triarylsilanolates entailed a rate acceleration, indicating that the poor σ -donating properties of silanolates are essential in rendering the

vanadium sufficiently Lewis acidic for the rearrangement to proceed. Another pivotal quality of tris(triarylsilyl) vanadate catalysts is their excellent thermal stability, which allows them to endure the harsh reaction conditions. In this aspect, they are somewhat reminiscent of heterogeneous catalysts.

Later, *Trost* and coworkers showed that the allenyl vanadate esters of the type **199** can be intercepted with electrophiles such as aldehydes or imines to give aldol-type products.^[201] The original discovery was followed by a series of papers expanding the methodology to electrophilic halide sources, π -allylpalladium species, trifluoromethyl reagents, and diaryliodonium salts.^[202] The “sigmatropic functionalization” enjoyed some success in the organic synthesis community, resulting in the tris(triphenylsilyl) vanadate complex **196** becoming one of the few commercially available catalysts with silanolate ligands.

While silanolates occasionally crop up in other transformations involving homogeneous metal catalysis for organic synthesis, their role is often limited to acting as a convenient leaving group. An example of this is the use of catalytic triphenylsilyl perrhenate in the 1,3-rearrangement of allylic alcohols (*scheme 82*).^[203]



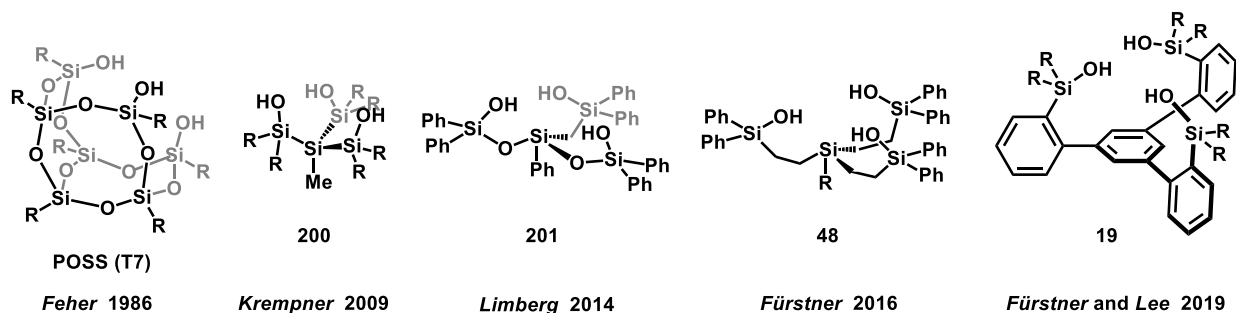
Scheme 82: Bystander role of the silanolate ligand in the 1,3-rearrangement of allylic alcohols.

To conclude, silanolate ligands are capable of stabilizing a wide variety of metals in different oxidation states and with different coordination numbers. The properties of the ligands can be fine-tuned through different substitution patterns and they impart a distinct electronic influence on the metal center. Astonishingly, the potential of the resulting complexes in homogeneous catalysis for organic synthesis remains largely unexplored.^[108]

2.1.2 Tridentate Tris(silanolate) Ligands

Tridentate tris(silanol) ligands are a special class in silanolate coordination chemistry. Their ability to bind metal centers in a facial, tripodal manner is the closest imitation of a silica surface possible with molecular ligands. This concept of mimicking surface-sites of silica-supported metal catalysts with tridentate tris(silanol) ligands was introduced by *Feher* and coworkers in 1986.^[204] The idea was rooted in the inherent difficulty of characterizing specific surface-sites in heterogeneous systems due to their often irregular structures. As a result, the mechanisms of many transformations that take place over heterogeneous catalysts are unknown, and reaction optimizations must rely on cumbersome empirical screening campaigns.

Feher proposed metal complexes of partially condensed polyhedral oligomeric silsesquioxanes (POSS) as easier to observe and characterize molecular models to study the transformations taking place on silica surfaces. Ligands of this type (**T7**, *scheme 83*) were first reported by *Brown* and can be prepared through the controlled hydrolysis of monosubstituted trichlorosilanes.^[205]

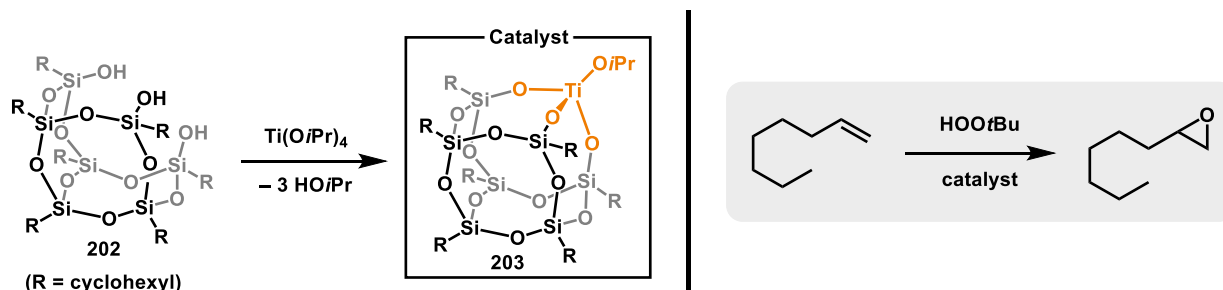


Scheme 83: Selected tridentate tris(silanol) ligands from the literature.

Over the years, other tridentate tris(silanol) ligands have been introduced with a similar goal, for example, by the groups of *Krempner* or *Limberg* (*scheme 83*).^[206] Complexes with a series of metals (Zr^{IV} , Ti^{IV} , Zn^{II} , Cu^I , Al^{III}) have been reported, but generally these ligands do not bind in a tripodal fashion and bridged complexes with several metal centers were obtained.^[198b, 207] For this reason, silsesquioxanes continue to dominate the field.^[208] The most common method for the formation of metallasilsesquioxanes is combining isolated partially condensed structures such as **T7** or the corresponding alkali metal salts with appropriate metal precursors. The alternative route involves constructing the polyhedral structure around a central metal, but in this case the speciation is harder to control.^[209]

A large number of complexes with ligands of type **T7** have been made encompassing transition and main group metals as well as lanthanides and actinides.^[208-209, 210] Besides binding to the metal in a tripodal manner (as shown in *scheme 84*), the complexation with partially condensed silsesquioxanes can also result in the formation a dimeric structure with two ‘cubes’ being bridged by two metals.^[211] Monomeric species such as **203** proved to be useful models

for industrially relevant titanium/silicate epoxidation catalysts. The complex is not limited to being an easier to study molecular mimic of a surface-site, but is also a competent catalyst in its own right.^[212] Valuable insights could be gained by comparing the performance of the complex with other models corresponding to different conceivable surface-sites and by probing the steric environment or the fourth ligand.^[210b]



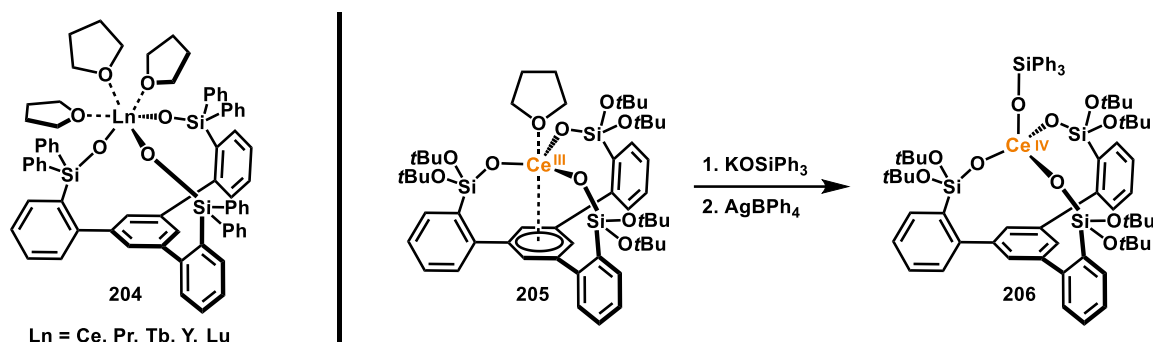
Scheme 84: An example for the formation of a well-defined metallasilsesquioxane and its use in catalysis.

The underlying concept has been applied to numerous cases, but there are also limitations to the approach.^[210b] The targeted synthesis of well-defined POSS can be challenging and depends strongly on the nature of the organic residues. Not all structures can be easily accessed with all residues, making specific variations arduous. The analogy to surface-sites is also far from perfect, since metallasilsesquioxanes in solution are subject to processes such as dimerization that are not possible in heterogeneous systems.^[213] Significant advances in solid-state spectroscopy techniques, especially solid-state NMR (ssNMR), have made it easier to directly characterize surface-sites.^[214] For these reasons, the interest in metallasilsesquioxanes as model systems has waned in recent years, but their popularity as precursor compounds or homogeneous catalysts remains unbroken.^[208]

Other tridentate tris(silanol) ligands were directly designed for homogeneous catalysis. The group of *Fürstner* introduced two generations of tripodal ligands for application in alkyne metathesis (*scheme 83* and *chapter 1.1.3.3*).^[73, 76] The second generation **19** was simultaneously disclosed by *Lee* and coworkers.^[77] A notable difference of these ligands from the previously discussed systems is their reliance on a carbon based scaffold, avoiding Si–O and Si–Si bonds. This reduces the risk of detrimental condensation reactions that put the integrity of the catalysts in jeopardy. Also, secondary coordination effects by the siloxane oxygen atoms are precluded, reducing the risk of dimerizations frequently observed with partially condensed POSS. However, the first generation of ligands **48** (and **49**) from the *Fürstner* group proved too flexible to form monomeric complexes with molybdenum alkylidyne. The second generation **19**, on the other hand, was highly efficient in coordinating to the molybdenum center in the desired tripodal manner.^[74, 76]

Recently and in parallel to the work discussed in the second part of the thesis, the ‘canopy ligands’ **19** have enjoyed increasing success in the field of actinide and lanthanide redox chemistry. Seminal work by the groups of *Cui* and *Mazzanti* showed the ligands to be uniquely

positioned to support trivalent rare-earth metal ions and facilitate the oxidation to an even higher oxidation state in the case cerium (*scheme 85*).^[215]



Scheme 85: Lanthanide complexes with tripodal tris(silanolate) ligands and redox chemistry of a Ce complex.

The disclosure was followed by a series of publications from the group of *Mazzanti* focusing on the same topic.^[216] The ‘canopy ligands’ were identified as suitable ligands due to their rigid tripodal form, which prevents ligand redistribution. Additionally, silanolates themselves are redox inactive and do not participate in reductive decomposition events. The arene tether, on the other hand, is far from redox innocent and can act as a supporting ligand (*scheme 85*). Note that the coordination geometry depends on the electronic properties of the silanolate ligands: the stronger electron donor ligands in **204** lead to an octahedral coordination with three solvent molecules, while the less electron-donating ligands in **205** cause the metal center to interact with the arene and adopt a trigonal bipyramidal geometry. This change is reflected in the oxidation potential of the lanthanide (III) complexes, making the corresponding ion in oxidation state IV more accessible from **204**. The oxidation of **205** was facilitated by the addition of an external carbon-substituted silanolate ligand (e.g., –OSiPh₃).^[216c]

The ‘canopy ligands’ were also used in uranium coordination chemistry for preparing complexes with the metal in oxidation states below III.^[216a] These extremely rare cations were stabilized by δ -bonding interactions with the arene anchor and engaged in electron transfer reactions. Overall, these burgeoning efforts demonstrate the ‘canopy ligands’ to be of use beyond their original purpose. They appear to be remarkably versatile in binding metal cations with different coordination geometries and ion radii.

Unrelated to the efforts concerning f-block metals, the laboratory of *Fürstner* investigated molybdenum nitrido complexes with the tripodal tris(silanolate) ligands **19**.^[217] In contrast to the corresponding tungsten nitrido complexes, the molybdenum species were shown to be monomeric in nature. However, the complexes failed react with alkynes precluding them from acting as the envisioned precursors for alkyne metathesis catalysts.

2.2 Motivation and Aim

The second part of this thesis strove to explore the coordination chemistry of tridentate tris(silanol) ligands more thoroughly with potential applications in catalysis in mind. This work is focused on investigating the ability of the relatively new class of ‘canopy ligands’ for forming complexes with transition metals and main group elements.

The motivation for the project stemmed from the scarcity of silanolate supported complexes in homogeneous catalysis and the contrast of the ubiquity of silica in heterogeneous catalysis (*vide supra*).^[108, 187] While ample strategies exist for grafting molecular metal catalysts on silica, thereby creating defined, *single-site* heterogeneous catalysts, the reverse approach has received little attention.^[112b] Using molecular silanolate ligands to support active metal sites in homogeneous catalysis could potentially leverage their thermal stability and unique electronic properties.

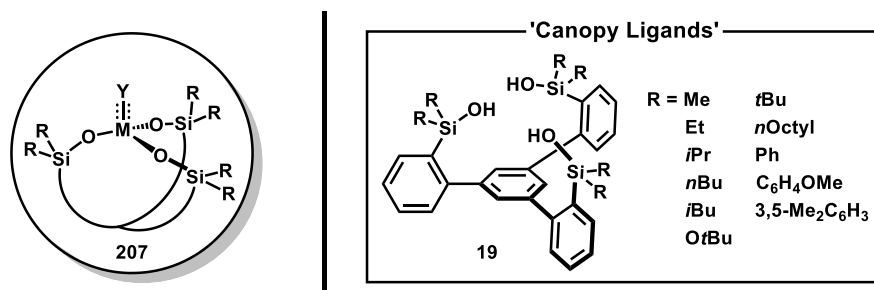


Figure 36: General blueprint of the targeted complexes and the variety of ‘canopy ligands’ available.

Complexes of a general structure **207** were targeted using the ‘canopy ligands’ **19** (figure 36). The ligand design contains an all sp^2 -hybridized arene scaffold and three silanol groups with varying substituents on the silicon atoms. While quite an assortment of different ligands of this general design are known, their coordination chemistry has so far only been explored for molybdenum and tungsten.^[76, 132] In parallel to the presented investigation, additional complexes of lanthanides and actinides with the ‘canopy ligands’ were published (*vide supra*).^[215b, 216a, c] Hence, further efforts focused on the remaining sections of the periodic table. The ‘canopy ligands’ were chosen over the other available tridentate ligands because of their useful preorganization. This property bodes well for the formation of monomeric complexes rather than the multi-nuclear bridged complexes commonly observed with partially condensed POSS or more flexible ligands. The tunable steric bulk of the ‘canopy ligands’ helps to prevent dimerization processes, which are potentially detrimental and, for example, not possible on silica surfaces. Furthermore, the ligands are easily accessible in three steps from commercial starting materials on a multi-gram scale.

The main interest in the project was not to provide new model compounds for heterogeneous catalysts, since the *Fürstner* laboratory has little expertise in this regard. Rather, the focus was on exploring (1) which cation sizes can be supported by the ligands, (2) the coordination

geometries accessible, (3) which types of apical ligands can be incorporated, and (4) how the tripodal tris(silanolate) ligands influence the properties of the central metal.

The overarching goal was to use the information gathered to find applications for the novel complexes in homogeneous catalysis. It was hypothesized that the *single-sites* of heterogeneous systems could be emulated with the tripodal chelating ligands, resulting in similarly robust catalysts in the homogeneous realm. Simultaneously, by providing a well-defined site with an easily tunable ligand environment, complexes of the general type **207** may offer a way to overcome one of the archetypically shortcomings of heterogeneous catalysis: selectivity.^[184] The envisioned complexes could potentially combine some of the favorable properties from the often disparate fields of homogeneous and heterogeneous catalysis.

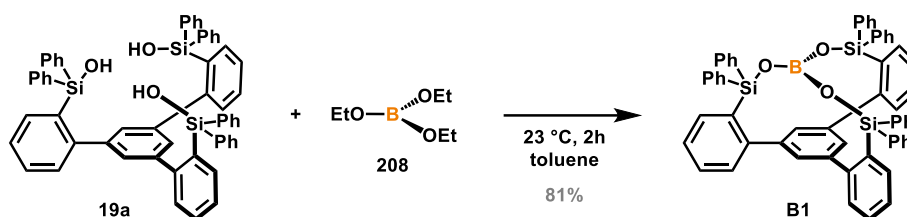
2.3 Results

2.3.1 Main Group Complexes with ‘Canopy Ligands’

The project commenced with the investigation of elements from group 13 of the periodic table. Thus far, only complexes with *d*-block and *f*-block metals had been made. A first objective was to test if cations with a small ionic radius would be coordinated in a tripodal fashion by the ligands. Furthermore, the Lewis acidity of the formed complexes was of particular interest, since boron/aluminum/gallium silicate sites are commonly implicated as active sites in zeolite catalysts.^[218]

2.3.1.1 Boron

The boron cation has one of the smallest crystal radii (0.20 Å)^[219] in the periodic table, making it a perfect test case for investigating the adaptability of the ‘canopy ligands’. Gratifyingly, the corresponding complex **B1** could be obtained by simply stirring a solution of the ligand **19a** with triethyl borate **208** at ambient temperature (*scheme 86*). The by-product of the protonolysis (ethanol) could be removed together with the solvent under high vacuum.

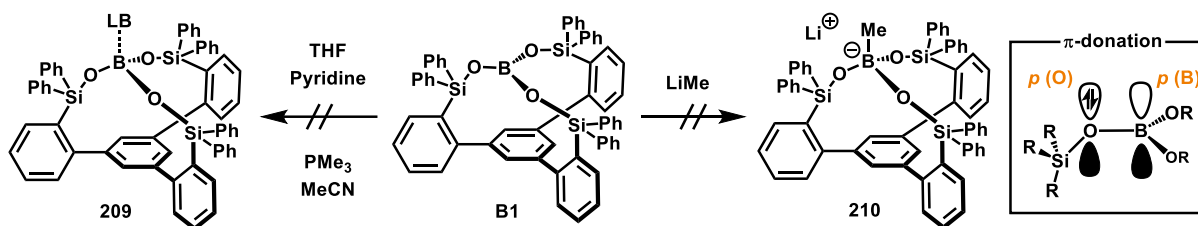


*Scheme 86: Synthesis of the boron complex **B1** carrying Ph groups on silicon.*

The recorded NMR spectra showed signals corresponding to a species in which the C_3 -symmetry of the ligand is retained. All signals were shifted in comparison to the free silanol ligand and the SiO–H peak was notably absent, but no ^{11}B signal could be detected. High resolution mass spectrometry indicated the desired product had formed, but additional confirmation was pursued.

Multiple attempts at crystallizing **B1** failed due to the peculiar solubility behavior of the complex. While the reaction mixture during the synthesis is a clear toluene solution, the isolated compound cannot be redissolved in the same solvent. NMR characterization in deuterated dichloromethane was possible, but even after filtration, solutions of the complex became turbid again within minutes. The same phenomenon was observed for solutions in tetrahydrofuran and diethyl ether. Presumably, some sort of aggregation takes place involving the ten arene rings present in **B1**, which are available for intermolecular π - π -interactions. Several attempts at changing the solubility properties of the complex were undertaken with Lewis bases. Astonishingly however, **B1** failed to form adducts with pyridine, trimethylphosphine, and acetonitrile (*scheme 87*). Contrary to expectations, the silyl

orthoboric ester does not act as a Lewis acid. Efforts to react **B1** with the hard nucleophile methyl lithium were also unsuccessful, revealing the boron complex to be non-electrophilic.



Scheme 87: The peculiar reluctance of **B1** to react as a Lewis acid or electrophile.

The surprising behavior was observed in a similar system by *Beckett* and coworkers. They had reported the incorporation of triorganosilyl groups in orthoboric esters to generally increase the Lewis acidity of the obtained complexes relative to organic esters.^[220] The reason for this seems to be the reduced π -donor ability of silanolates due to backbonding into the low lying σ^* (C–Si) from the lone-pairs at the oxygen. However, when increasing the steric bulk around the orthoborate ester a sharp reduction in Lewis acidity is observed.^[221] Likely, this is also the explanation for the counterintuitive behavior of **B1**.

Next, the boron complex **B1** was examined *via* ssNMR spectroscopy to obtain unambiguous confirmation for the proposed structure. In addition, it would test if the complex is suitable as a model for trigonal planar boron silicate sites in, for example, zeolites.

In cooperation with Dr. *C. Farés*, the ^{11}B chemical shift of **B1** could be detected at 11.5 ppm with magic-angle-spinning (MAS) (*figure 37*).

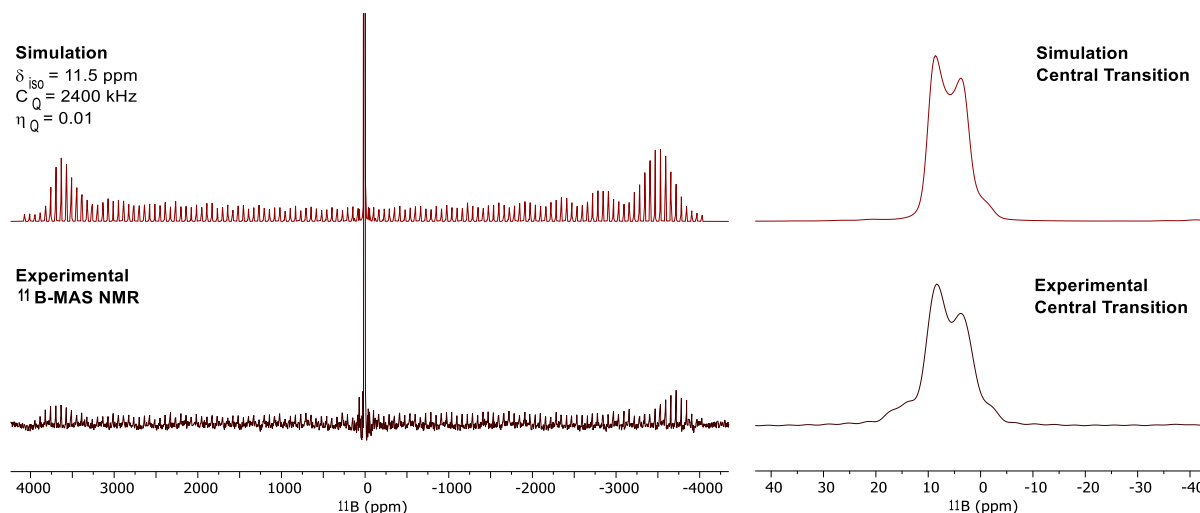


Figure 37: Experimental ssNMR spectrum of **B1** (bottom) and the simulation (top) of spectra for a trigonal planar boron species.

^{11}B is a spin-3/2 nucleus and the NMR signal is dominated by quadrupolar interactions. Accordingly, a large nuclear quadrupole coupling constant (C_Q) is expected. The high axial symmetry of trigonal planar boron compounds, such as **B1**, should result in a small anisotropy (η_Q = asymmetry parameter). A simulation of the ssNMR spectrum using parameters expected

for a trigonal planar boron complex showed excellent overlap with the experimental spectrum (figure 37, top).

The data was further corroborated with the ssNMR spectrum of the literature known complex tris(triphenylsilyl)borane **211** carrying monodentate silanolate ligands.^[222]

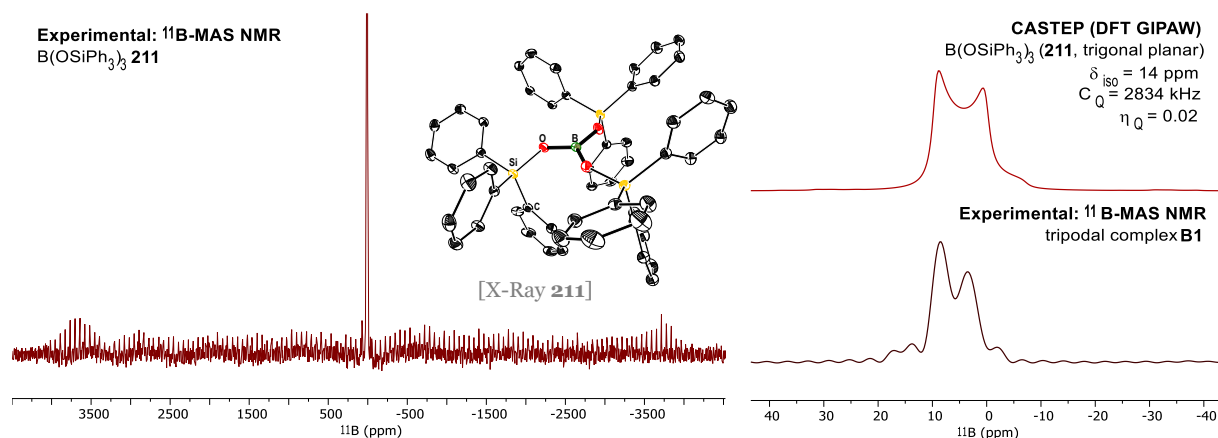
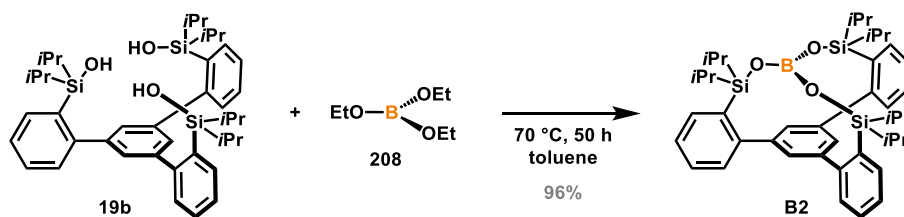


Figure 38: Experimental ssNMR spectrum of **211** (left), DFT based simulation of the ssNMR spectrum of **211** based on the solid-state structure (right, top) and comparison to the central transition of the ssNMR spectrum of **B1** (right, bottom).

The experimental spectrum of **211** exhibits the same characteristics as the spectrum of complex **B1** with the tripodal ligand. A DFT simulated spectrum of **211** based on the available solid-state structure showed a good match and is also very similar to the spectrum for **B1**. It is therefore safe to assume that boron in **B1** is indeed in a trigonal planar coordination environment, as proposed.

A comparison of the values obtained from the simulation of the ssNMR spectra of **B1** ($\delta_{\text{iso}} = 11.5$ ppm, $C_Q = 2.4$ MHz, $\eta_Q = 0.01$) with values measured for trigonal planar boron sites in zeolites ($\delta_{\text{iso}} = 9.8$ - 10.7 ppm, $C_Q = 2.3$ - 2.6 MHz, $\eta_Q = 0.1$) finds them in good agreement.^[218a] Although not the focus of the presented work, this finding indicates the ‘canopy ligands’ can be used to generate adequate spectroscopic model compounds for metal sites in heterogeneous systems.^[223]

Since crystallization attempts for **B1** had not borne fruit, an additional derivative was prepared. Complex **B2** carries *iso*-propyl groups on silicon with the goal of preventing the aggregation observed for **B1**. The complex was obtained in high yield *via* the same protonolysis route as employed before (scheme 88). Unlike with **B1**, heating and prolonged reaction times were required to achieve full conversion.



Scheme 88: Synthesis of the boron complex **B2** carrying *iPr* groups on silicon.

Presumably, the more sterically demanding branched alkyl groups in ligand **19b** cause a higher energetic barrier for the complexation with the tripodal ligand. Complex **B2** was soluble in toluene, dichloromethane, and even pentane and showed no signs of aggregation. The complex could be fully characterized and, contrary to **B1**, a solution state ^{11}B chemical shift was detected in the expected range ($\delta = 12.5$ ppm). Colorless crystals suitable for single-crystal X-ray diffraction were grown from a saturated pentane solution at 4 °C (*figure 39*).

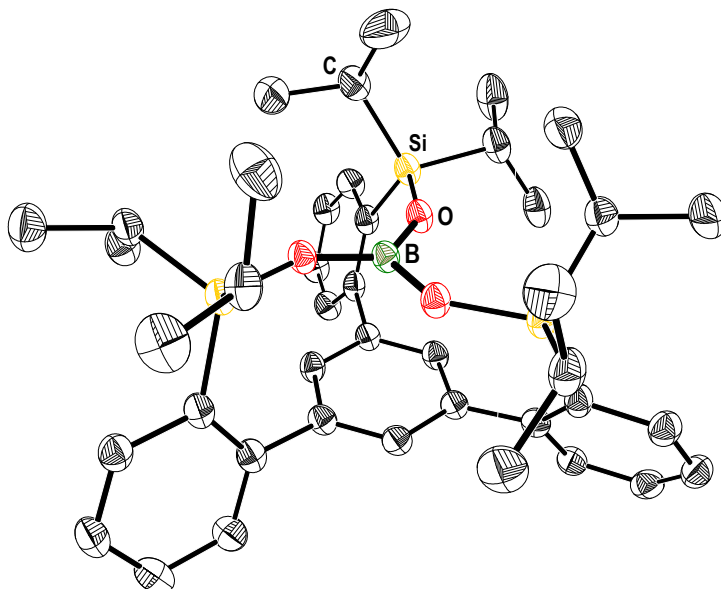


Figure 39: Structure of complex **B2** in the solid-state; all H-atoms were omitted for clarity.

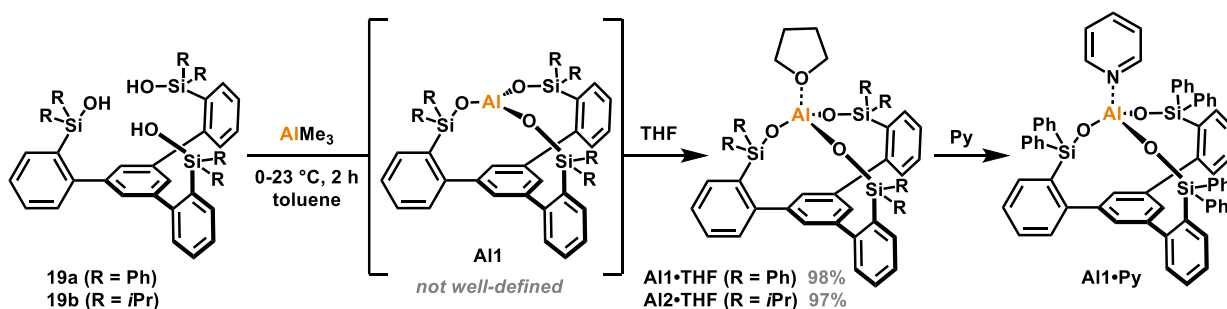
The central boron atom is coordinated in a trigonal planar fashion by three silanolates with close-to-ideal O–B–O angles (119.9°, 119.7°, and 120.4°). Strikingly, the silicon atoms sit in the same plane as the boron and the three coordinating oxygen atoms. The oxygen-boron bond lengths are in the expected range (1.368 Å, 1.369 Å, and 1.359 Å) and similar to those of orthoborate esters with fluorinated alcohols.^[224] The *iso*-propyl groups are closely packed around the metal center, effectively shielding it. In line with this and the previously described results for **B1**, the complex **B2** did not form an adduct with pyridine.

In summary, the ‘canopy ligands’ can form complexes with trivalent boron, although prolonged heating is required to assemble the more sterically demanding ligand **19b** in a tripodal fashion around the small boron cation. The complex **B1** exhibited an ssNMR spectrum equivalent to trigonal planar boron sites in heterogeneous materials and can therefore likely be considered as a model compound. Both **B1** and **B2** did not react as Lewis acids or even electrophiles, precluding them from acting as Lewis acid catalysts.^[225] Reducing the steric bulk around the metal center by employing ‘slimmer’ versions of the ‘canopy ligands’ might ‘switch on’ its Lewis acidic properties.

2.3.1.2 Aluminum

The heavier homolog from group 13, aluminum, was examined next. With an ionic radius of 0.39 Å (for CN 4)^[226] the cation is considerably larger than boron and of a similar size to molybdenum (VI) (0.41 Å for CN 4)^[226], the complexes of which had been the original ‘canopy catalysts’.

The complexation was achieved with trimethylaluminum as the metal source. Methane bubbles evolving from the protonolysis reaction with the alkyl ligands could be visually observed in larger scale reactions. Attempts at isolating the presumably highly Lewis acidic species **Al1** without an additional apical ligand yielded a sparingly soluble material. NMR analysis revealed it to be ill-defined. The addition of tetrahydrofuran to the colorless powder resulted in the almost quantitative formation of the adduct **Al1•THF**. In further syntheses, simply using tetrahydrofuran as a co-solvent in the complexation reaction allowed the respective complexes to be isolated in excellent yields (*scheme 89*).



Scheme 89: Synthesis of aluminum complexes with ‘canopy ligands’ with variable neutral apical ligands.

The neutral ligand is labile and can be exchanged with an excess of another ligand or a stronger Lewis base, as exemplified for **Al1•THF** with pyridine. This property augurs well for the use of the aluminum complexes as Lewis acid catalysts, since it allows a potential substrate to bind to the metal center.

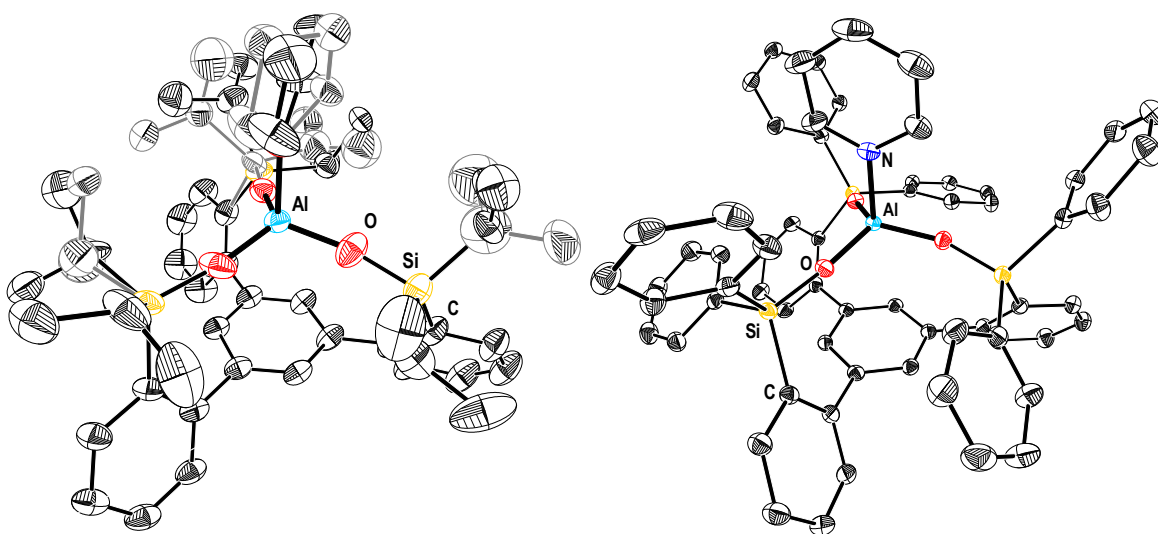


Figure 40: Structures of complexes **Al2•THF** and **Al1•Py** in the solid-state; disordered parts are shown in grey and all H-atoms and solvent molecules were omitted for clarity.

Crystals suitable for single-crystal X-ray diffraction could be grown of complexes **Al2•THF** and **Al1•Py**, confirming the proposed tripodal binding mode of the tridentate tris(silanolate) ligands (*figure 40*). Both structures are fundamentally similar with a distorted tetrahedral coordination around the aluminum atom and a weakly bound ligand in the apical position. In **Al2•THF**, the bond strength is reflected in the interatomic distances between each of the four oxygen atoms and the central metal. The bond lengths for the three tethered ligands are considerably shorter than the bond to the datively bonded oxygen of the tetrahydrofuran (approx. 1.70 Å vs. 1.90 Å respectively). This results in the distorted tetrahedral coordination with the metal center only marginally lifted above the plane defined by the three covalently bonded ligands. In the case of **Al1•Py**, the deflection is somewhat greater in accordance with pyridine being the stronger Lewis base.

The Si–O–Al angles are close to linear (for **Al2•THF**: 167.3°, 167.1°, and 171.4°) in stark contrast to the bend angles observed for **B1** (140.1°, 139.3°, and 147.9°). The observation highlights the adaptability of the ‘canopy ligands’ enabling them to accommodate different metal cations.

As observed for other complexes with the ‘canopy ligands’ the residues on silicon are arranged in a tight ‘fence’ around the metal center. In the case of aluminum, there remains enough room for a neutral apical ligand (or a potential small substrate) to coordinate to the metal.

The strikingly different behavior of the aluminum-based complexes compared to their boron congeners is evidently related to the increased Lewis acidity of aluminum. While **B1** did not react with Lewis bases, **Al1•THF** can only be isolated as a Lewis base adduct. Although it is difficult to generalize trends in Lewis acidity, aluminum complexes have been repeatedly classified as stronger Lewis acids on scales based on computational and experimental methods.^[227] The Lewis acidity of the present aluminum complexes was determined with the Gutmann-Beckett method and compared to the literature known complex tris(triphenylsilanolate) aluminum **212** (*table 7*).^[228]

Table 7: ³¹P chemical shifts and calculated AN for the complexes using the Gutmann-Beckett method.^[221, 229]

Complex	³¹ P chemical shift	AN
Al1	69.62 ppm	63.25
Al2	67.02 ppm	57.50
Al(OSiPh ₃) ₃ (212)	72.57 ppm	69.77
Al(C ₆ F ₅) ₃	—	75.6 ^[227a]
Al(OC(C ₆ F ₅) ₃) ₃	—	72.7 ^[227a]

The aluminum complexes formed stable adducts with triethylphosphine oxide, replacing the tetrahydrofuran quantitatively, as judged *via* ¹H NMR. The examined aluminum silanolate complexes exhibited lower acceptor numbers (AN) than aluminum centers coordinated by

highly electron-deficient perfluorinated aryl or alkoxide ligands. However, they retain appreciable Lewis acidity with the aryl substituted silanolate ligands resulting in a higher AN compared to ligands substituted with more electron-releasing alkyl groups. The trend is the same as observed for molybdenum alkylidyne complexes (the Lewis acidity was inferred from the ^{95}Mo NMR shifts in their case).^[78]

Interestingly, the complex **212** carrying monodentate aryl substituted ligands showed a higher AN than the structurally very similar complex **Al1**, the only difference being the arene tether connecting the three anionic ligands in the tripodal version. Possibly, the geometric restrictions imposed on the silanolate ligands through the rigid scaffold interfere with back donation from the filled p -orbital at the oxygen to the empty low lying σ^* -antibonding orbital of a silicon carbon bond.^[108] Thereby, π -donation from the lone-pair of the oxygen into the sp^3 -orbital directed towards the apical ligand is upregulated causing a reduction in Lewis acidity. Some evidence for the contortion caused by the tripodal ligands is found in the O–Si–C(tethered arene) angles (**Al1**•Py: 111.6°, 110.8°, and 113.1°) which are somewhat different from the close-to-ideal tetrahedral angles found in **212**•THF (O–Si–C: all approx. 109°).^[228] Even more telling is perhaps the reversed orientation of the aryl rings on silicon which will be discussed in *chapter 2.3.3.3*.

In any case, the aluminum complexes exhibit the expected Lewis acidity, in contrast to **B1**, which does not interact with triethylphosphine oxide. This property allows them to be used as robust catalysts for organic synthesis, as will be discussed in *chapter 2.3.3*.

Al1•THF was also investigated *via* ^{27}Al ssNMR.⁴ Although it was possible to detect a signal with the help of MAS, the interpretation of the obtained spectrum was challenging (*figure 41*).

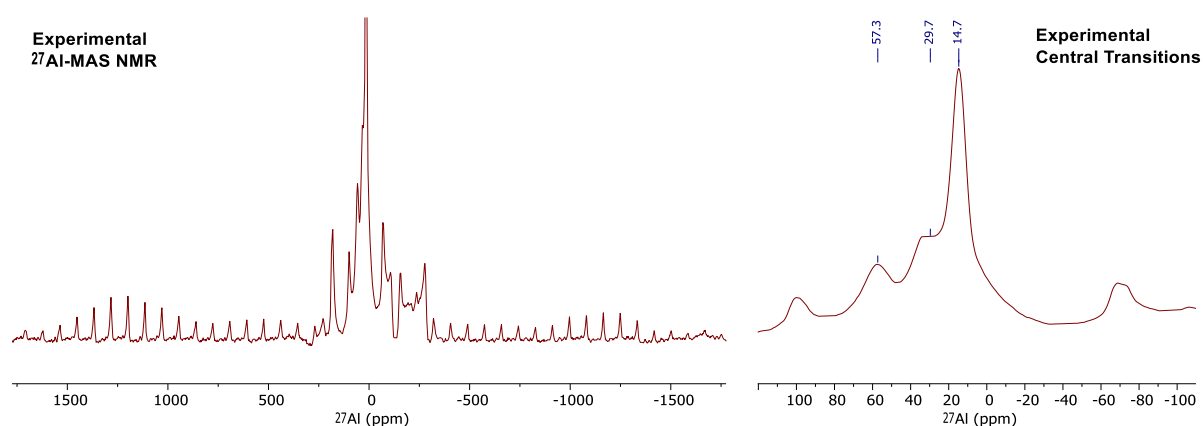


Figure 41: Experimental ^{27}Al ssNMR spectrum of complex **Al1**•THF.

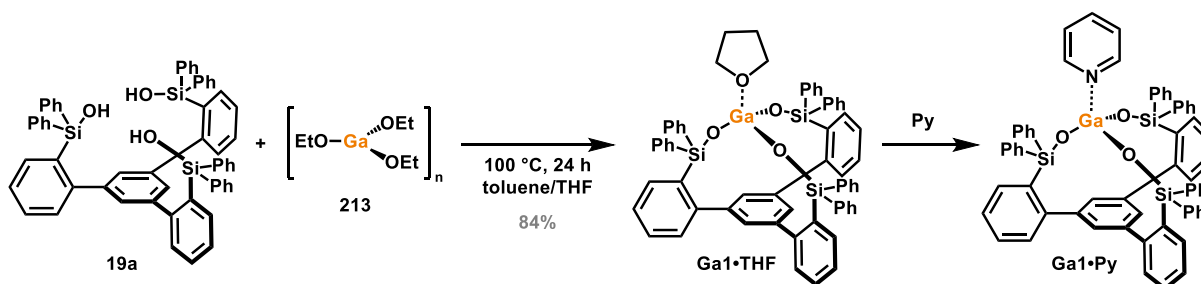
At least three central transitions could be identified in the ^{27}Al spectrum. The additional surrounding peaks were MAS rate dependent and therefore classified as spin echos. Inexplicably, the smallest of the three signals correlates the best with tetrahedral coordinated aluminum sites in heterogeneous catalysts and the solution state signal for the literature

⁴ The ssNMR measurement was carried out by Dr. C. Farés.

known complex **212•THF** (^{27}Al $\delta = 57.5$ ppm).^[228, 230] The other two dominant signals are more diagnostic of higher coordinated aluminum species. Since the structure of **Al1•THF** was irrefutably established through solution NMR spectroscopy, there are three plausible explanations for the other species. Either the sample decomposed before the measurement, which seems unlikely since **Al2•THF** is reasonably stable in air (*vide infra*), or in the solid-state there is some sort of aggregation. The last possibility is contamination of the sample, for example, with silica grease which can also contain some aluminum. The questions raised by the unusual ^{27}Al ssNMR spectra could not be clarified at this point.

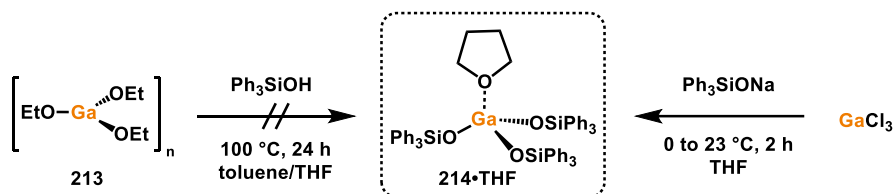
2.3.1.3 Gallium

Gallium was investigated next. Moving further down in group 13, the ionic radius increases (0.47 Å for CN 4)^[226]. The corresponding complex **Ga1•THF** could be synthesized from gallium (III) ethoxide **213**. Unlike the preparation of the boron congener, the synthesis of **Ga1•THF** required forcing conditions. Gallium (III) ethoxide is reported to adopt a polymeric structure in the solid-state and likely retains a multinuclear structure in solution, thus heating was required to induce the desired complexation (*scheme 90*).^[231]



Scheme 90: Synthesis of gallium complexes **Ga1** with variable neutral apical ligands.

Like for the aluminum congeners, the apical ligand could be exchanged without difficulty to afford **Ga1•Py**. Crystals of **Ga1•Py** suitable for single X-ray diffraction were grown from a concentrated dichloromethane solution. To further probe the subtle changes between the complexes comprising tripodal ligands and complexes with the equivalent monomeric silanolate ligands an effort was made to synthesize tris(triphenylsilanolate)gallium (**214•THF**) (*scheme 91*).



Scheme 91: Synthesis of **214•THF**.

The reaction starting from gallium (III) ethoxide failed to deliver the desired product with a monodentate silanol ligand. NMR analysis of the crude reaction mixture showed an ill-defined speciation that appeared to be oligomeric in nature. The result highlights the ability of the ‘canopy ligands’ in preventing this type of pit-fall. Resorting to salt-metathesis, the complex **214•THF** could be obtained as a tetrahydrofuran adduct. However, an impurity with broad NMR signals (possibly a polymeric version of **214**) could not be entirely removed from the crude material. Even so, colorless crystals suitable for X-ray diffraction were grown from a concentrated benzene solution (*figure 42*).

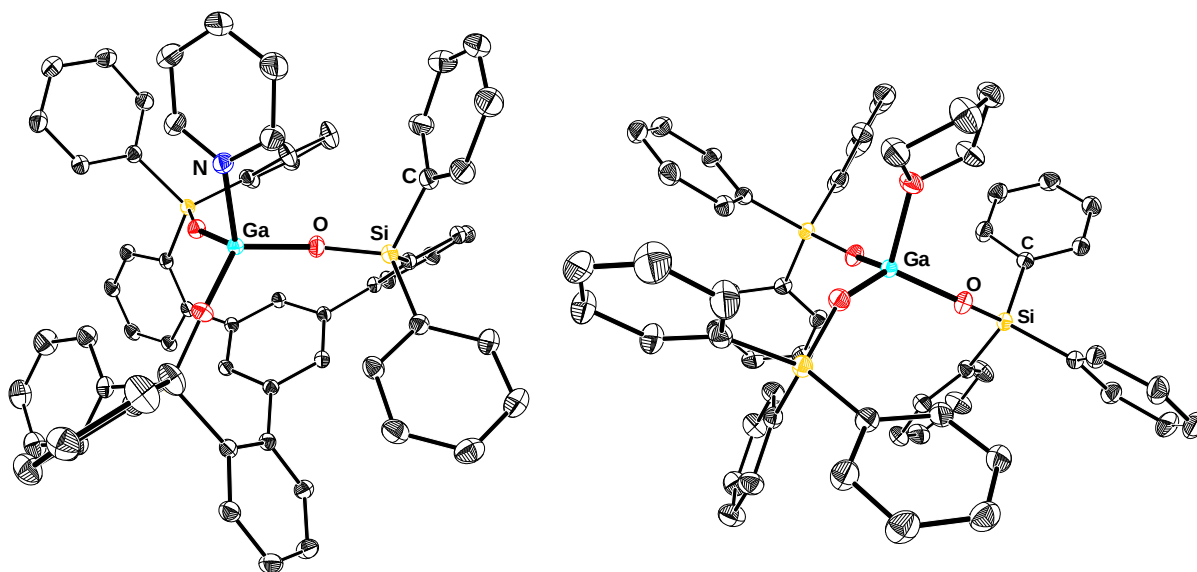


Figure 42: Structures of complexes **Ga1•Py** (left) and **214•THF** (right) in the solid-state; all H-atoms and solvent molecules were omitted for clarity.

The two structures are fundamentally similar with a distorted tetrahedral coordination geometry around the gallium metal and a weakly bound neutral ligand in the apical position. Upon closer inspection, small, but significant, differences can be found. On the one hand, the silanolate-metal angles are again notably straighter in **Ga1•Py** (Si–O–Ga: 158.6°, 171.5°, and 155.8°) than in the version with the untethered ligands (**214•THF**: Si–O–Ga 149.7°, 152.4°, and 140.6°). The same trend could be found in the corresponding aluminum complexes (**Al1•Py** and **Al2•THF** vs. **212•THF**) and previously published molybdenum alkylidyne complexes with the same ligand scaffold.^[61] In their case, the forced alteration in the silanolate angles had been implicated as the reason for the changed electronic structure of metal center and, by extension, the subtle differences in reactivity.^[61] Although the reasoning for the changes cannot be directly extrapolated – after all the *p*-block elements do not interact through *d*-orbitals – it is plausible to assume that the straighter bonds also have an effect in the present case.

The other distinct shift from **214•THF** to **Ga1•Py** is the orientation of the lateral phenyl substituents. While in **214•THF** one aryl ring for each ligand is orientated nearly straight downwards (as shown in *figure 42*), this is not possible in the tridentate scaffold. The phenyl substituents, which are connected by the central arene ring, are forced into a more contorted conformation (the same is observed for the aluminum complexes). As a result, the two other substituents reorientate themselves in a way, which has one of the phenyl groups pointing upward into the direction of the labile ligand. In short, the geometry restrictions imposed by the tripodal ligand change the binding angles of the silanolates as well as the arrangement of the substituents on silicon.

Intrigued by the question, if these subtle adjustments caused by the tether translate into reactivity changes, the Lewis acidity of the two gallium complexes (**Ga1** and **214**) was examined *via* the Gutman-Beckett method.

Table 8: ^{31}P chemical shifts and calculated AN for the complexes using the Gutmann-Beckett method.^[221, 229]

Complex	^{31}P chemical shift	AN
Ga1	72.87 ppm	70.43
214	75.36 ppm	75.94

Both complexes formed stable adducts with triethylphosphine oxide and the acceptor numbers (AN) could be calculated from the corresponding ^{31}P NMR shifts. Notably, the gallium complexes are more Lewis acidic than their aluminum-based cousins. This trend was previously observed in the corresponding trisphenolate complexes, but is not entirely obvious because gallium has an overall lower electronegativity and is also affected by the *d*-block contraction.^[232]

In any case, **214** carrying monodentate ligands exhibits a higher AN than complex **Ga1** equipped with a ‘canopy ligand’. The result confirms the trend observed with the aluminum complexes (**212** vs. **Al1**) and suggests that the tripodal tris(silanolate) ligands temper the Lewis acidity of group 13 elements. It is worth mentioning that this trend goes in the opposite direction to that observed for the molybdenum alkylidyne complexes.

Finally, **Ga1•THF** was examined *via* ^{71}Ga ssNMR.⁵ Although gallium containing materials have played a role as catalysts in industrially relevant reactions, there are fewer precedents for probing the corresponding sites with ssNMR than for boron and aluminum.^[218b, 233] The quadrupolar nature of ^{71}Ga makes the detection of signals challenging, in particular, due to the massive quadrupole broadening of the central transition. All the more important are reliable molecular models.^[198c]

A central transition for **Ga1•THF** could be detected by co-adding nine WURST-QCPMG (wideband uniform-rate smooth truncation – quadrupolar Carr-Purcell Maiboom-Gill) spectra with a sweep width of 5 MHz each. The quadrupolar coupling constant is several tens of MHz (in comparison for **B1**: $C_Q = 2.4$ MHz). The spectrum was simulated with parameters similar to those previously used for model complexes with tetracoordinated gallium.^[198c] The simulation emulates the general line shape of the recorded spectra well.

A comparison to spectra recorded for other model compounds by the group of *Copéret* shows good agreement in regard to the general peak shape, but the chemical shift is notably different. This might be caused by the more electron-deficient ancillary ligands used in these model complexes.^[198c]

⁵ The ssNMR measurement was carried out by Dr. C. Fares.

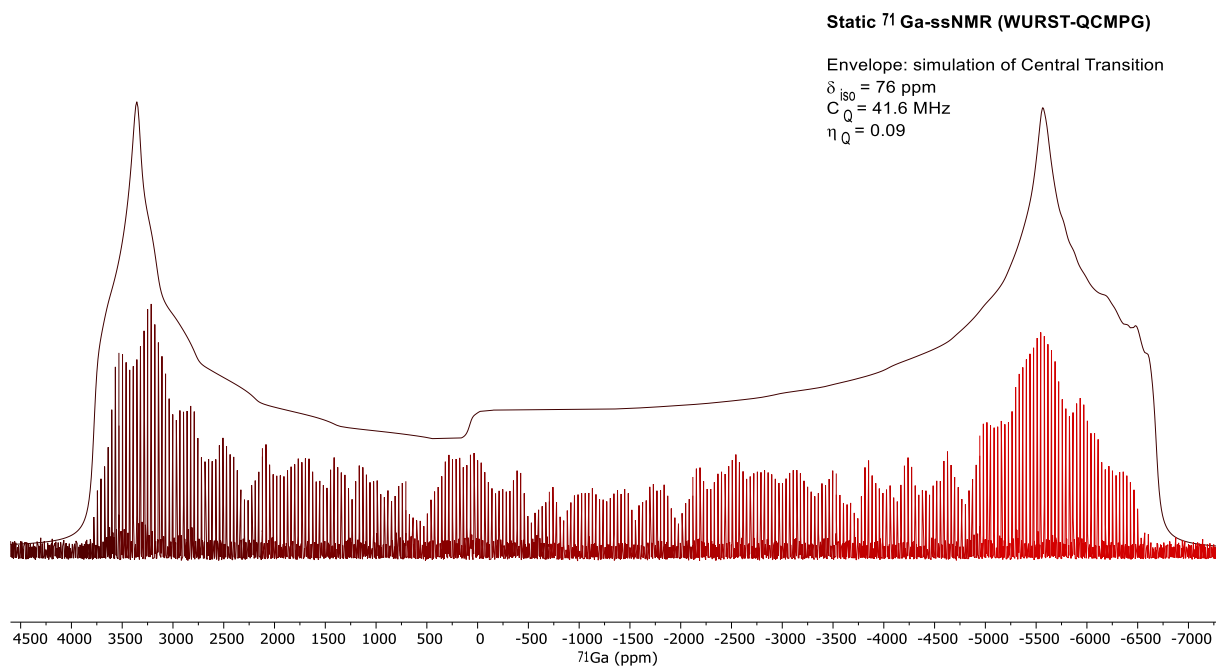
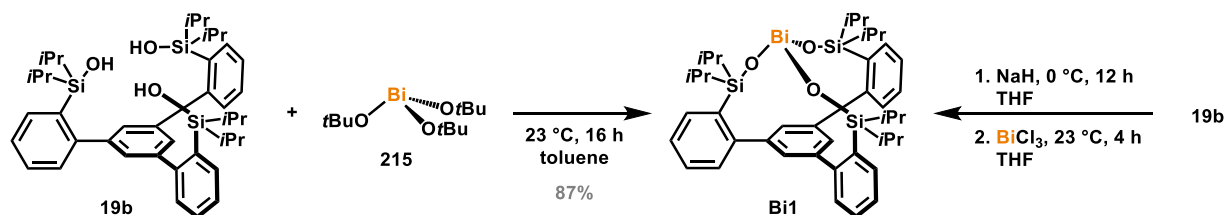


Figure 43: Central transition of the ^{71}Ga ssNMR spectrum of complex **Gal•THF** and an envelope simulation (continuous line); nine WURST-QCPMG spectra were co-added to give the shown spectrum (for further information see the experimental section).

2.3.1.4 Bismuth

The preceding chapters established that the ‘canopy ligands’ are capable of supporting trivalent *p*-block cations, including the exceptionally small boron (III) ion. To further challenge the adaptability of the ‘canopy ligands’, an exceptionally large cation was examined next. Bismuth (III) represents such a metal center with an ionic radius of 0.96 Å (for CN 5; no data has been reported for CN 3 or 4)^[226].

Complex **Bi1** was obtained through the protonolysis reaction of ligand **19b** with monomeric bismuth tris(*tert*-butoxide) (*scheme 92*).^[234]



Scheme 92: Synthesis of the bismuth complex **Bi1** carrying *i*Pr groups on silicon.

An alternative route to **Bi1** relies on the salt-metathesis of the tris(sodium) salt of **19b** and bismuth (III) chloride. However, in this case the product was contaminated with minor amounts of free ligand, likely a result of the insufficiently dry commercial bismuth (III) chloride. An attempt to synthesize a bismuth complex with ‘canopy ligand’ **19a** carrying phenyl groups on silicon resulted in the formation of a highly insoluble material, which could not be analyzed further. Similar observations had been made by *Hubert-Pfalzgraf* and coworkers when seeking to synthesize bismuth tris(triphenylsilanolate).^[235] Bismuth is known to form adducts with aryl groups through metal... π -arene interactions.^[236] It is possible that such intermolecular interactions with the many phenyl groups present in **19a** caused the formation of insoluble oligomers.

Vapor diffusion of the anti-solvent pentane into a concentrated solution of **Bi1** in diethyl ether afforded fine needle-shaped crystals. The interpretation of the X-ray diffraction data obtained from these crystals turned out to be challenging. The *iso*-propyl groups of the ligand were strongly disordered and the unit cell contained several of the complexes arranged in a pillar like formation. Despite the poor quality of the structural models, it was discernible that the bismuth cation interacts with the basal arene of the next molecule. These metal... π -arene interactions appear to cause **Bi1** to crystallize as fine needles of poor crystal quality.

Consequently, the crystallization was attempted with an aromatic solvent. It was hypothesized that utilizing an aromatic solvent would disrupt the metal... π -arene interactions and result in a different crystal habit. Indeed, colorless prisms could be grown from benzene, which resulted in structural data of excellent quality for **Bi1**·C₆H₆ (*figure 44*).

The threefold-coordination of the bismuth cation by the oxygen atoms of the tripodal ligand results in a trigonal pyramidal geometry with the metal residing well above the plane defined

by the anionic ligands ($\text{Bi}-\Delta(\text{OOO}) = 1.091 \text{ \AA}$). The bond angles for $\text{O}-\text{Bi}-\text{O}$ (94.3°) are closer to 90° than the ideal angle for the trigonal pyramidal geometry (109.5°). The orbitals in bismuth (III) generally do not hybridize and the bonds are formed exclusively by the perpendicular p -orbitals causing this peculiar geometry. In the case of **Bi1**• C_6H_6 , there is a fourth weakly bond ligand: a benzene ring.

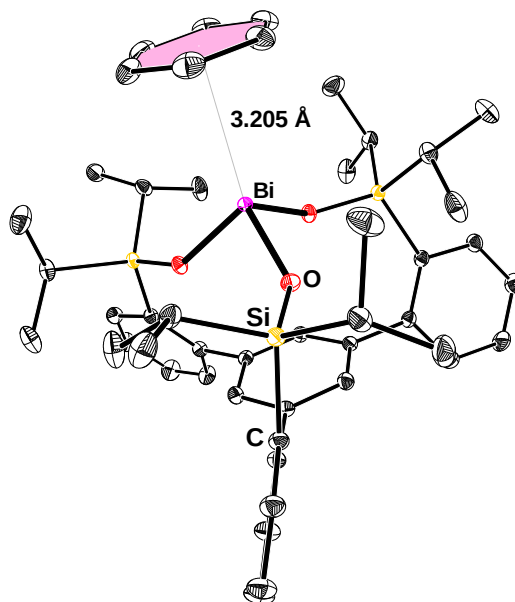


Figure 44: The structure of **Bi1** in the solid-state and coordination of a co-crystallized benzene molecule; all H-atoms were omitted for clarity.

The distance between the bismuth and the benzene centroid is $3.205 \text{ \AA}$ and closer to bismuth-arene π -interactions of bismuth (III) halides ($3.0 - 3.2 \text{ \AA}$) than those of triaryl bismuthines ($3.47 - 3.96 \text{ \AA}$). Computational analysis of such bonds indicate they are not typical directional donor – acceptor bonds. Rather, they are dominated by dispersion-type interactions between the exceptionally large cation and the π -system of the arene.^[236]

The unusual coordination geometry required of the ligand by the bismuth (III) cation is even more striking when considering that the same ligand is also able to support boron (III) in a trigonal planar coordination geometry. The $\text{Si}-\text{O}-\text{M}$ angles are even similar for both metals (**Bi1**• C_6H_6 : all 138.9° ; **B1**: 140.1° , 139.3° , and 147.9°). However, the complexes differ strongly in the directionality of the silanolate bonds with the bismuth residing $1.091 \text{ \AA}$ above the plane defined by the three oxygen atoms, whereas boron resides on the same level as the ligands. These two extremes emphasize the ability of ‘canopy ligands’ to adapt to the needs of widely different central metals.

A number of bismuth (III) compounds are good Lewis acids and have been applied in organic synthesis.^[237] However, when **Bi1** was subjected to the Gutmann-Beckett method, no adduct was formed with triethylphosphine oxide. It appears the silanolate ligands are not electron-deficient enough to render the antibonding σ^* ($\text{Bi}-\text{O}$) orbital accessible.

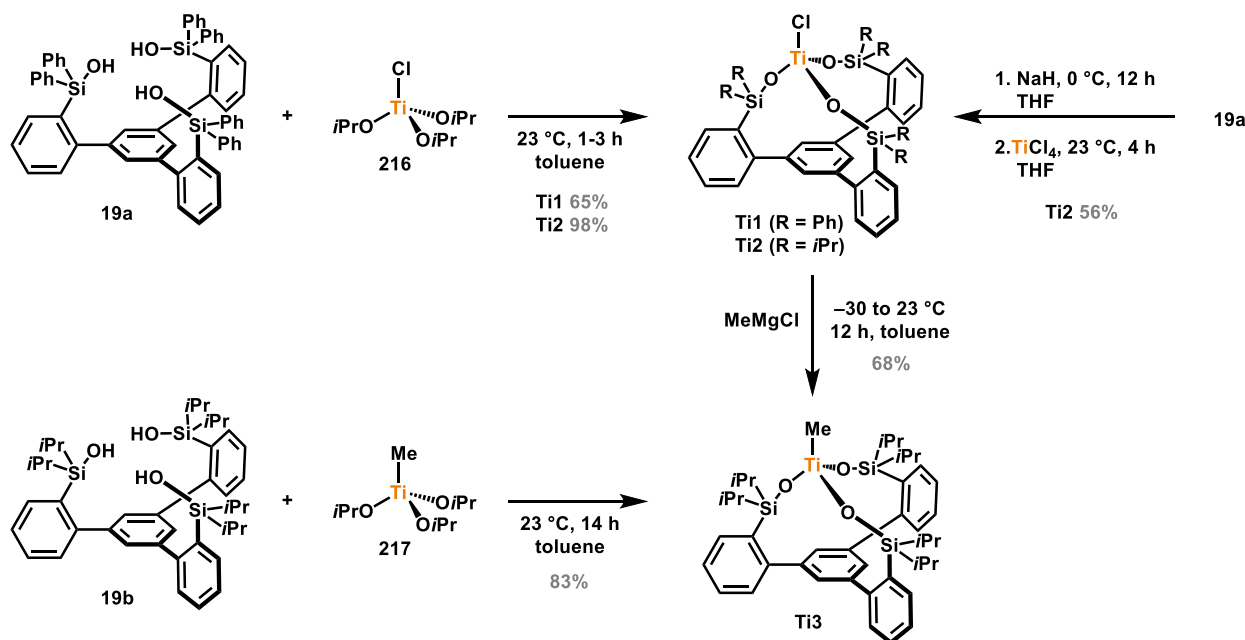
Nevertheless, in recent years *Cornella* and coworkers have reported some applications of bismuth complexes to organic synthesis that do not rely on their Lewis acidity. On the contrary, they tap into bismuth redox catalysis or *open-shell* bismuth intermediates. It is conceivable that complex **Bi1** could find use in this context.^[238]

2.3.2 Transition Metal Complexes with ‘Canopy Ligands’

After the coordination chemistry of the ‘canopy ligands’ with main group cations had been thoroughly explored, transition metal complexes were examined next. From this section of the periodic table, complexes of molybdenum and tungsten with apical alkylidyne or nitrido ligands as well as an yttrium complex had been previously discussed.^[36b, 76, 215a, 217] The aim was to expand the variety of transition metals, the type of oxidation states supported, and to test what kind of additional ligands could be incorporated into the complexes. Organic ligands were of special interest due to the potential similarity of such species to organometallic complexes grafted on silica surfaces.

2.3.2.1 Titanium

Starting with early transition metals, titanium from group four was examined first. Titanium in the oxidation state IV has an ionic radius of 0.42 Å (CN 4)^[226] and a number of monomeric, tetrahedral titanium complexes are commercially available. Titanium alkyl complexes have been shown to catalyze Ziegler-Natta polymerizations and titanium chloride or alkoxide complexes are commonly applied as Lewis acids, for example, in the Sharpless epoxidation.^[239] Simple protonolysis of the alkoxide precursor **216** with the canopy ligands **19a** or **19b** afforded the chlorido titanium complexes **Ti1** and **Ti2** in good yields (*scheme 93*).



Scheme 93: Synthesis of the titanium complexes **Ti1**, **Ti2**, and **Ti3**.

Complex **Ti2** could also be made *via* salt-metathesis using titanium(IV) tetrachloride as metal source. The inferior yield obtained serves to confirm mild protonolysis reactions as the preferred method of complexation. Reacting the titanium chloride complex **Ti2** with methyl magnesium chloride afforded the alkyl titanium complex **Ti3** in good yield. Alternatively, it

can be synthesized directly from commercial methyltitanium (IV) tris(*iso*-propoxide) in excellent yield.

Generally, stable alkyl complexes of early transition metals are rare due to their susceptibility for β -hydride elimination.^[240] Indeed, the addition of *n*-butyllithium to **Ti1** resulted in insoluble oligomeric material. Methyl derivatives (such as **Ti3**) or β -branched alkyl substituents are exempt from this and find applications as mild nucleophiles for the addition to carbonyls.^[241]

The crystal structures of a number of monomeric tetra-coordinated titanium silanolate complexes are known.^[212, 242] Surprisingly, to the best of the author's knowledge, no examples have been reported for complexes with either one methyl or chloride ligand. Pleasingly, it was possible to obtain crystals suitable for single crystal X-ray diffraction of complexes **Ti2** and **Ti3** (figure 45).

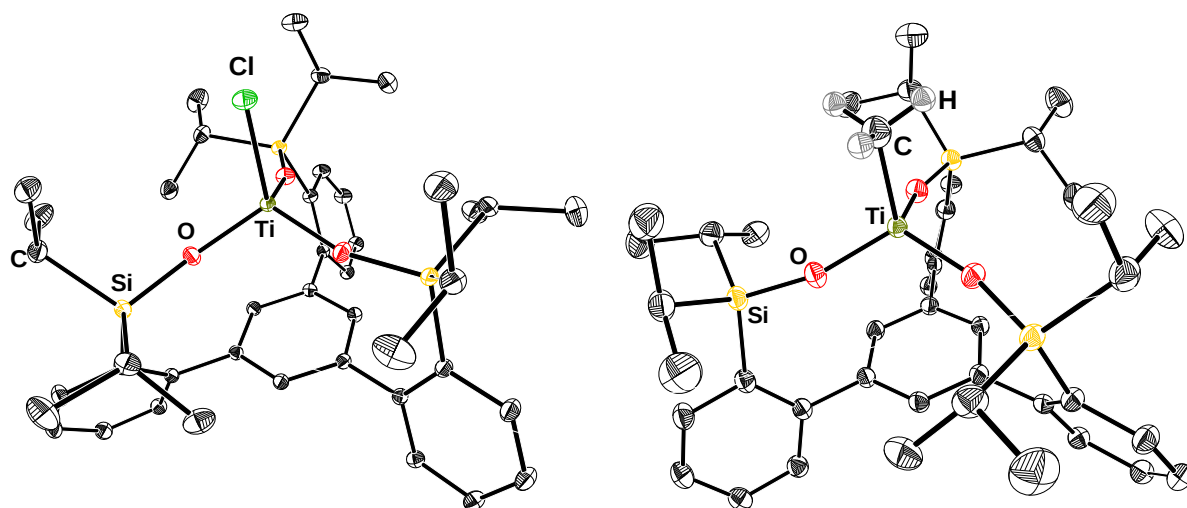
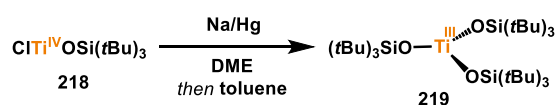


Figure 45: Solid-state structures of **Ti2** (left) and **Ti3** (right); all H-atoms were omitted for clarity, except those at the methyl group.

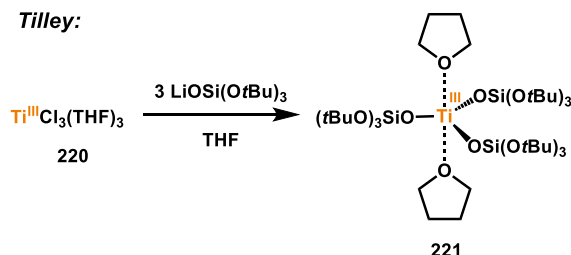
Both complexes are perfectly C_3 -symmetric around a central axis passing through the centroid of the basal arene ring, the central metal, and the apical ligand. In both cases, the titanium center is coordinated in a tetrahedral fashion with the geometry in **Ti2** ($\angle \text{O-M-O}$: 111.0°) being closer to an ideal tetrahedron than in **Ti3** ($\angle \text{O-M-O}$: 114.9°). The metal carbon bond (Ti-C: $2.062 \text{ \AA}$) in **Ti3** is considerably shorter than the metal halide bond in **Ti2** (Ti-Cl: $2.245 \text{ \AA}$), but falls into the range previously reported for titanium carbon bond lengths of complexes coordinated by three anionic oxygen ligands.^[243]

Bulky siloxy and silanolate ligands have been used by the groups of *Wolczanski* and *Tilley* to stabilize titanium (III) metal centers.^[244] Aside from these coordination chemistry efforts, titanium (III) species have played a role in organic synthesis.^[245] A prominent example is the anti-Markovnikov radical opening of epoxides with the *Nuget-RajanBabu* reagent.^[246] The highly reactive bis(cyclopentadienyl)titanium (III) chloride **223** is generated *in situ* through the one electron reduction of titanocene (IV) dichloride **222** with zinc (scheme 94).

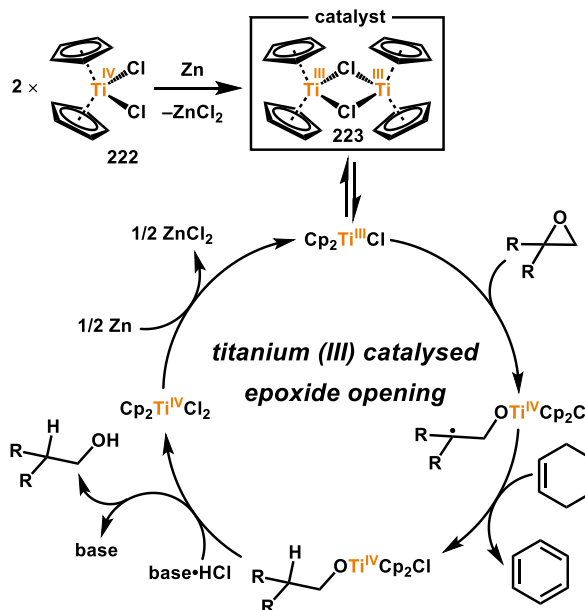
Wolczanski:



Tilley:



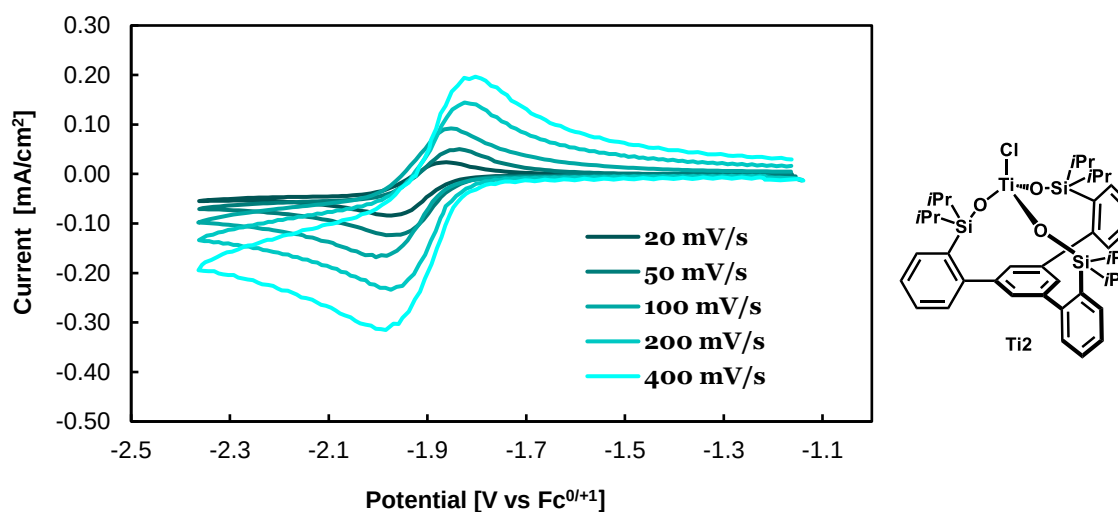
Nugent and RajanBabu:



Scheme 94: Synthesis of Ti(III) complexes **219** and **221** by Wolczanski and Tilley (left) and the catalytic radical opening of epoxides with the Nugent-RajanBabu reagent **223**.

Given this precedent, it was investigated whether **Ti2** could potentially serve as a catalyst in a titanium (III)/titanium (IV) redox cycle such as the one shown in *scheme 94*. It was hypothesized that the bulky tripodal ligand could help to stabilize the required titanium (III) species in a low coordinate state. This feat is quite difficult to achieve, as demonstrated by **219** and **221**; already the use of a slightly less sterically encumbered siloxy ligand results in the formation of a five coordinated species.

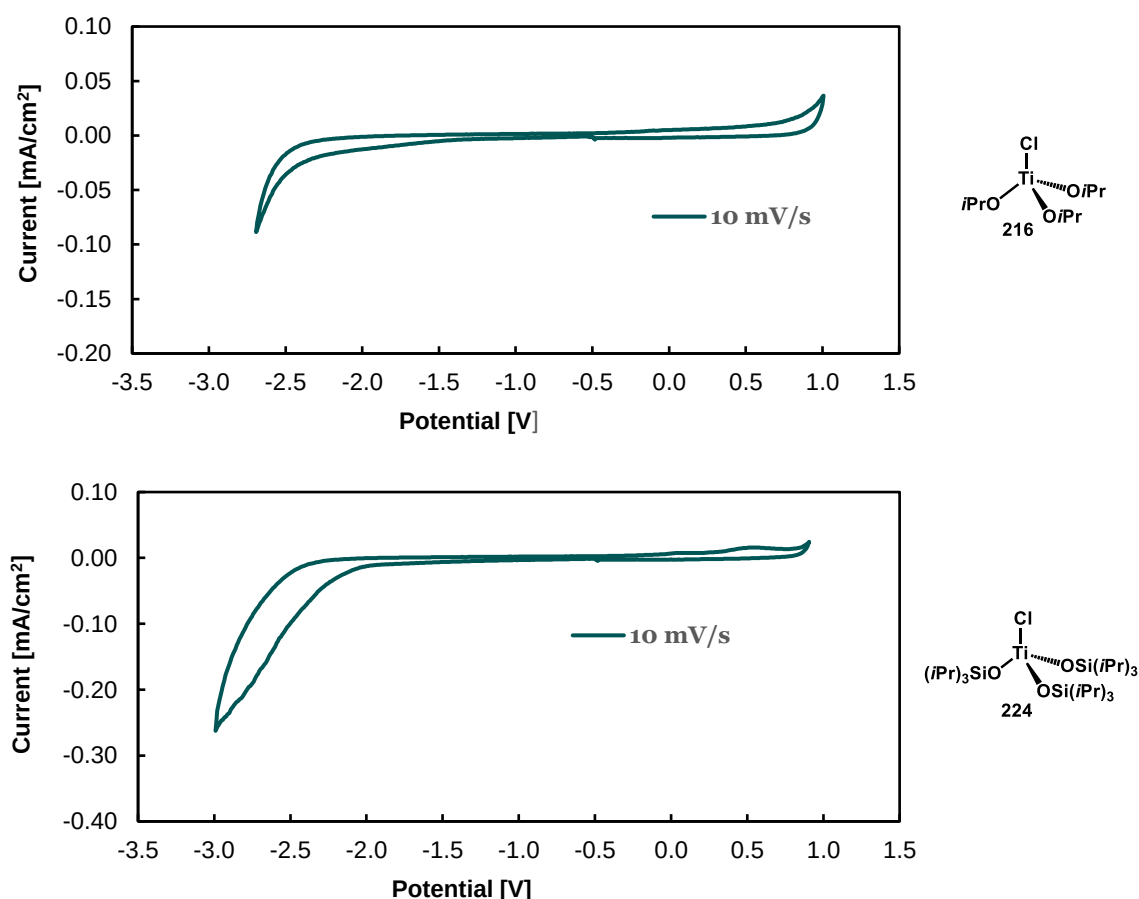
An initial attempt to reduce **Ti2** with zinc only returned unperturbed starting material. Hence, a more systematic approach was pursued by employing cyclic voltammetry to determine if a reduction of **Ti2** is feasible and reversible (*graph 13*).



Graph 13: Cyclo voltammogram of **Ti2** recorded in THF (1.0 mM analyte, 1.0 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte, $T = 298 \text{ K}$, stationary glassy carbon working electrode, with variable scan rates).

For **218**, Wolczanski and coworkers had observed an electrochemically irreversible reduction at -1.10 V (Ag/AgCl, 270 mV against $\text{Fc}^{0/+}$ in THF).^[244a] In contrast, **Ti2** showed a reversible reduction at approx. -2.0 V (graph 13).⁶ Further investigations demonstrated the peak potential of the oxidation wave to shift depending on the scan rate. Accordingly, the process must be classified as pseudo-reversible. This signals that not all the reduced titanium (III) species is reoxidized to titanium (IV) and there is a subsequent reaction step depleting the generated titanium (III) species. However, the rate of this reaction seems to be considerably slower for complex **Ti2** than for **219**, since no oxidation was observed during the reverse cyclic voltammetric sweep for the latter.

In order to further probe the disparity between the complex containing a tripodal tris(silanolate) ligand and complex **219** with monodentate ligands, cyclic voltammograms of two additional titanium (IV) chloride complexes with monodentate ligands were measured. Chloro tris(*iso*-propoxide) titanium (IV) **216** is commercially available and chloro tris(tri(*iso*-propyl)silanolate) titanium (IV) **224** could be synthesized from **216** through a protonolysis reaction with the respective silanol.



Graph 14: Cyclo voltammograms of **216** and **224** recorded in THF (0.5 mM analyte, 1.0 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte, $T = 298$ K, scan rate = 10 mV/s, stationary glassy carbon working electrode).

⁶ The cyclic voltammetry measurements were carried out together with Dr. A. Stamoulis.

Both complexes gave irreversible voltammetric responses with reductions at low voltages (*graph 14*). However, these are at the edge of the solvent window for tetrahydrofuran and should not be over-interpreted.

Remarkably, all three titanium complexes with monodentate ligands exhibit irreversible reductions, signaling fast subsequent reactions of the formed titanium (III) species. The nature of these reactions, whether it is simply the dissociation of a chloride anion or, for example, a dimerization, can only be speculated upon. No definitive conclusions can be drawn from the data. The group of *Daasbjerg* has studied the electrochemical reduction of titanocene (IV) dichloride **222**. At least for this complex, they have observed a quasi-reversible reduction similar to the voltammogram of **Ti2**.^[247]

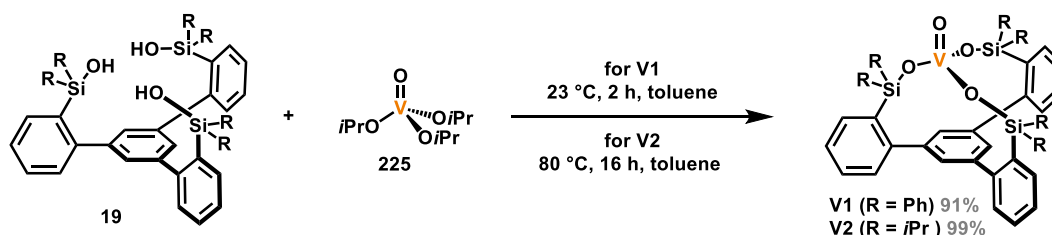
The tripodal ‘canopy ligand’ appears to aid the stabilization of a titanium (III) metal center. Yet, the potential required to reduce **Ti2** (approx. -2.0 V (V vs $\text{Fc}^{0/+}$)) is much lower than in the case of titanocene (IV) dichloride (approx. -1.2 V (V vs $\text{Fc}^{0/+}$)).^[247] A catalytic reaction involving **Ti2** as the source for a titanium (III) species would demand considerably harsher reducing agents than zinc or manganese. Such reagents would not be compatible with highly functionalized substrates making the whole process hardly attractive for organic synthesis.^[248] For this reason, no further efforts were undertaken towards using **Ti2** as a catalyst. Nevertheless, the cyclic voltammetry data indicates that it should be possible to reduce **Ti2** in a stoichiometric fashion to access a reasonably stable titanium (III) complex.

2.3.2.2 Vanadium

From group five of the periodic table, vanadium was selected for further investigations. The sixth most earth-abundant transition metal can adopt a range of formal oxidation states (+V to –III) and has found frequent application in catalysis.^[249] Oxidation reactions are the most common transformations and vanadium oxides supported by silica are of interest for industrial processes such as the oxidative dehydrogenation of alkanes or the conversion of methanol into formaldehyde.^[250] As a consequence, considerable efforts have been undertaken to make model compounds for oxo-vanadium sites on silica surfaces.^[251]

In line with this, the synthetic work commenced with the synthesis of two complexes containing vanadium in the oxidation state V (ionic radius 0.36 Å for CN 4)^[226] with an oxo ligand in the apical position (*scheme 95*).

The synthesis relied on the commercially available, monomeric oxo-vanadium (V) species **225** with alkoxide ligands, which was transformed into the corresponding complexes with ‘canopy ligands’ *via* protonolysis.



Scheme 95: Synthesis of oxo-vanadium complexes carrying ‘canopy ligands’.

In the case of the more sterically demanding *iso*-propyl groups on the silanolate ligands, a higher temperature and longer reaction time were necessary to achieve full conversion. **V1** and **V2** were obtained as yellowish solids and were soluble in most common organic solvents.

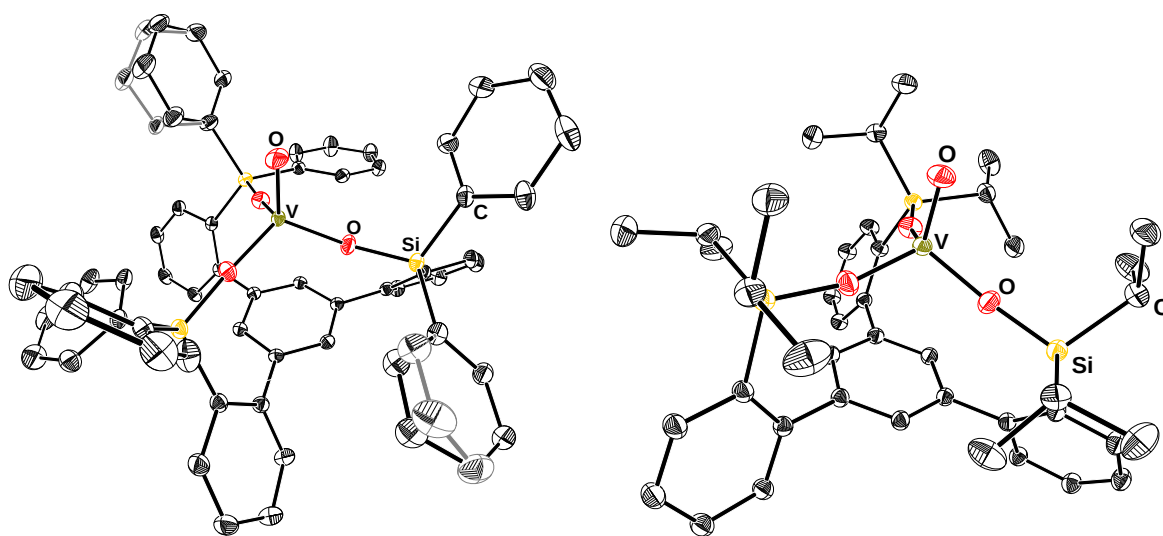


Figure 46: Solid-state structures of **V1** (left) and **V2** (right); disordered parts are shown in grey and all H-atoms were omitted for clarity.

Crystals of **V1** suitable for single crystal X-ray diffraction were grown from a concentrated diethyl ether/dichloromethane solution. Crystals of **V2** were obtained from a pentane solution during a subsequent experiment (see *scheme 100*), which involved the formation of **V2** as a side product.

The solid-state structures revealed the ligands to bind in the familiar tripodal manner with the vanadium overall being tetracoordinated by oxygen atoms. **V2** features a C_3 -symmetry around a central axis passing through the basal benzene, the metal center, and the apical oxo ligand similar to **Ti2** and **T3**. In both structures (**V1** and **V2**) the symmetry around the vanadium is nearly perfectly tetrahedral.

A comparison to the structure of the literature known complex tris(triphenylsilyl) vanadate **196**, which is the pendant to **V1** with monodentate silanolate ligands, is instructive.^[251a] The Si–O–V bond angles are considerably larger for the complexes with tridentate ligands (**196**: 146.5°, 161.8°, and 155.5° against 173.4°, 176.6°, and 172.4° in **V1**). These bond angles are suspected, as previously discussed, to have an influence on the electron density at the metal center. While the O–V bond lengths of the three silanolate ligands remain unaffected by the change in silanolate angles (**196**: 1.743 Å, 1.745 Å, and 1.739 Å against 1.745 Å, 1.746 Å, and 1.744 Å in **V1**), the double bond to the apical oxo ligand becomes somewhat elongated in the complexes with the tripodal ligands (V=O: 1.572(2) Å for **196**, 1.5880(9) Å for **V1**, and even 1.5937(9) Å for **V2**). The difference is small and it remains difficult to predict if the geometrically restricted silanolate ligands are better or worse π -donor ligands for a specific given metal. Nonetheless, the change in bond length for the apical ligand suggests that the tridentate ligands render the vanadium center less Lewis acidic.

To investigate this aspect further, the complexes were examined by solution state ^{51}V NMR spectroscopy. The spin $7/2$ nucleus ^{51}V is the major isotope in naturally occurring vanadium (99.75%) and exhibits a relatively small quadrupole moment, allowing sharp peaks to be observed through NMR.

Signals were detected for the two novel complexes carrying ‘canopy ligands’ as well as for the literature known complexes **225** and **196**, which were found to be in good agreement with previously reported data (*figure 47*).^[252]

The ^{51}V NMR spectra indicate that in the case of oxo-vanadium (V) complexes, silanolates are better donor ligands than alkoxides, as shown by the more up-field chemical shifts. The electron-donating ability is also clearly linked with the angles of the silanolate bonds. The more obtuse the Si–O–V angle is in each complex, the further the ^{51}V NMR signal is shifted upfield (mean values for $\angle\text{Si–O–V}$: **V1** 174.1°, **V2** 165.8°, **196** 154.6°). The group of *G. Guillemot* ascribed the correlation to the increased orbital overlap between the lone-pairs at the oxygen and the d -orbitals at the formally d^0 vanadium. They had been able to corroborate their observation with structural and spectroscopic data from other silica surface models.^[251b]

The trend for the donating properties of silanolate ligands in oxo-vanadium complexes moves in the opposite direction as the one described for molybdenum alkylidyne complexes by *Fürstner* and *Neese*.^[61] Apparently, the electronic effects of silanolate ligands, and more specifically the ‘canopy ligands’, cannot be easily generalized and depend on the metal center they are bound to. However, tethering the silanolate ligands together clearly has an effect regardless of whether the ligands act as good or less good electron-donors. The influence even seems to override other effects such as the more electron-releasing alkyl groups in **V2**.

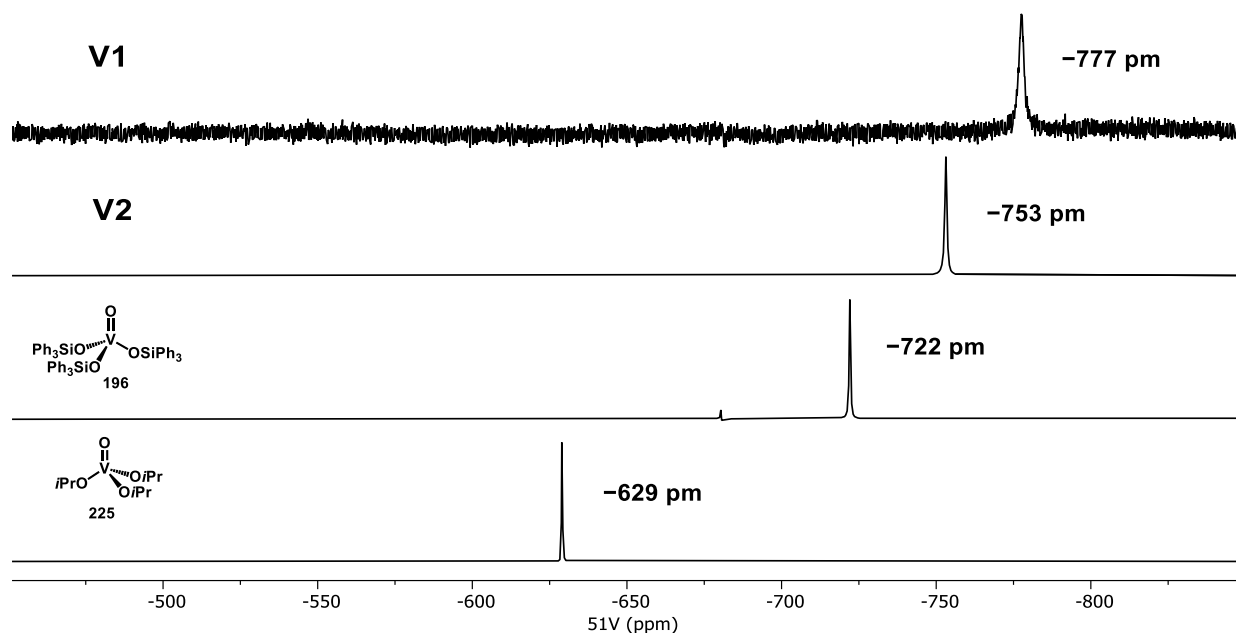


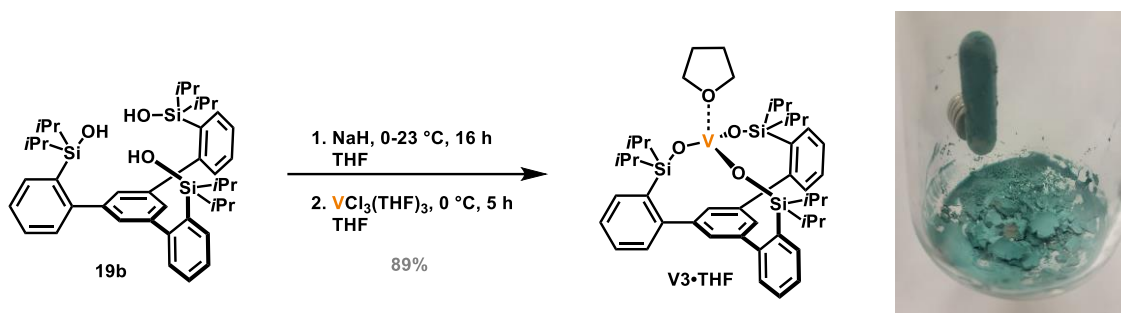
Figure 47: ^{51}V -NMR-spectra of vanadium complexes **V1**, **V2**, **196**, and **225**.

The recorded solution state ^{51}V -shifts were compared with literature ssNMR data obtained for silica-supported vanadium oxide catalysts. Signals with isotropic chemical shifts of -670 to -710 ppm are commonly attributed to tetracoordinated vanadium (V) sites, whereas square pyramidal V_2O_5 sites have distinct shifts in the region around -610 ppm.^[253] Although these values do not match particularly well with the data recorded for the complexes obtained with the ‘canopy ligands’, these could still have potential as model compounds due to the absence of surrounding siloxane bonds that can cause undesired aggregation in other model systems such as silsesquioxanes.^[251e]

So far, mainly transition metals in their highest oxidation state have been ligated with the ‘canopy ligands’. In order to investigate whether early transition metals can also be stabilized in low-oxidation states with the tripodal tris(silanolate) ligands, vanadium (III) was targeted next. Since no vanadium (III) alkoxide precursors are commercially available, a salt metathesis reaction was employed to synthesize **V3•THF** from the corresponding vanadium (III) chloride tetrahydrofuran adduct (*scheme 96*).

The vanadium precursor complex has a distinct pink color in the solid-state, which changes to red upon dissolution in tetrahydrofuran. Addition of the solution to the trisodium salt of **19b**

resulted in a rapid color change to deep purple and then, more slowly, to green. After the color had stabilized, the sodium chloride by-product was filtered off and volatiles were removed *in vacuo* to afford a turquoise powder.



Scheme 96: Synthesis of the vanadium (III) complex **V3•THF**, and a photograph of the solid material.

Due to the two unpaired electrons vanadium (III) complexes are paramagnetic and **V3•THF** showed no discernible features in the recorded NMR spectra. Elemental analysis of the solid material indicated a tetrahydrofuran to be bound to the metal center, which is not readily removed, since extended heating of **V3•THF** under vacuum did not entail a significant weight loss. However, high resolution mass spectrometry only detected the complex **V3** without a coordinating tetrahydrofuran. Possibly the neutral ligand is lost during the ionization process (in the case of **A11•THF** both the adduct and the complex without tetrahydrofuran could be detected in one measurement). Irrefutable proof for the proposed structure of **V3•THF** was obtained by recrystallization of the material from a saturated tetrahydrofuran solution layered with pentane at $-78\text{ }^\circ\text{C}$. X-ray diffraction of the obtained bluish crystals showed one tetrahydrofuran to be coordinated (*figure 48*).

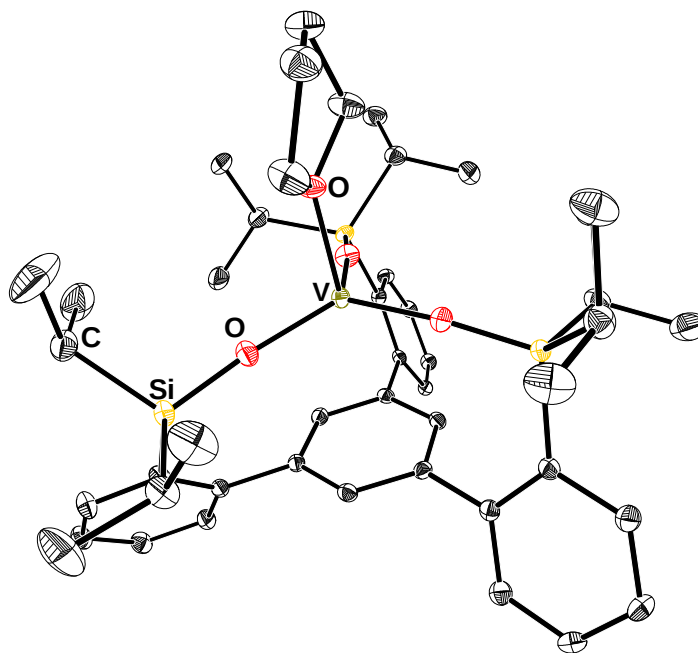


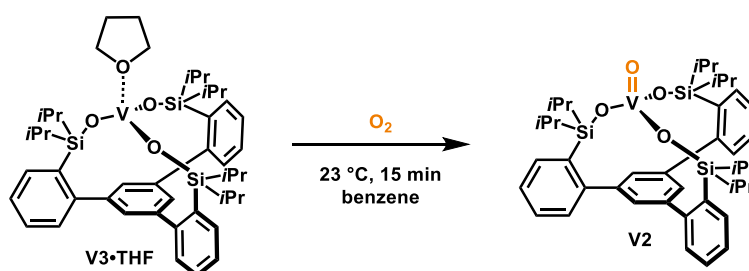
Figure 48: Structure of complex **V3** as a tetrahydrofuran adduct; all H-atoms were omitted for clarity.

The geometry around the vanadium is closer to trigonal planar ($\angle\text{O}-\text{V}-\text{O}$: 121.6° , 115.8° , and 119.4°) than to tetrahedral. The neutral tetrahydrofuran appears to exert little influence on the metal center, since the vanadium cation sits only marginally above the plane defined by the three anionic oxygen ligands ($\text{V}-\Delta\text{OOO}$: $0.192 \text{ \AA}$). The distance between the neutral donor ligand and the metal center is longer in **V3•THF** than for the equivalent aluminum complex ($\text{O}(\text{THF})-\text{M}$: $2.045 \text{ \AA}$ (**V3•THF**) against $1.902 \text{ \AA}$ (**Al2•THF**)). Again, the silanolate bond angles are remarkably straight due to the geometry imposed by the ligand scaffold ($\angle\text{Si}-\text{O}-\text{V}$: 173.2° , 171.4° , and 163.1°).

A direct comparison to a relevant complex with monodentate ligands is not possible because tris(triphenylsilanolate)vanadium (III) forms a bis-adduct with two tetrahydrofuran molecules and has a trigonal bipyramidal geometry.^[254] Although a tetrahydrofuran mono-adduct is known for tris(*tert*-butylsilanolate)vanadium (III) (**230**, see *scheme 99*) no crystal structure has been reported.^[194b] The only structural data for this complex stems from adducts with trialkyl phosphine oxides, which are closer to a tetrahedral geometry due to the stronger donor properties of the neutral ligands.^[255]

In summary, the ‘canopy ligand’ **19** can bind a low-valent early transition metal and stabilize it in a pseudo-trigonal planar conformation. Low-coordinated vanadium (III) complexes are highly reactive and have been shown to engage as electrophiles with, for example, chalcogens.^[256]

Consistent with this, complexes **V3•THF** could be quantitatively transformed into the corresponding vanadium (V) oxo complex **V2** by sparging a benzene solution with oxygen (*scheme 97*).

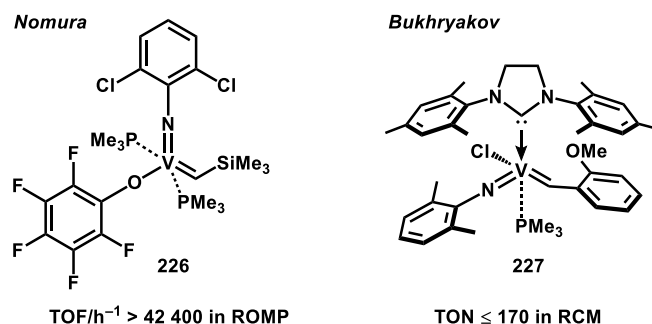


Scheme 97: Reaction of **V3•THF** with oxygen to give **V2**.

More interestingly, the d^2 vanadium metal with two unpaired electrons is a tantalizing partner for an alkylidene fragment. Vanadium alkylidene complexes have been investigated as alternatives to ruthenium-based alkene metathesis catalysts.^[257] The major motivation for this endeavor comes from the low cost associated with the first-row transition metal and its smaller environmental impact.

Nomura and coworkers developed vanadium alkylidene complexes as catalysts for ring-opening metathesis polymerization (ROMP) carrying arylimido ligands and fluorinated phenolates or alkoxides. The example **226** reached turnover frequencies (TOF) of over 40 000 per hour in the ROMP of norbornene.^[258] However, these catalysts are inactive towards

acyclic terminal olefines. In recent years, the group of *Bukhryakov* developed a separate set of catalysts carrying bulky NHC-ligands for ring-closing metathesis (RCM). The embodiment **227** was able to catalyze the ring-closure of simple substrates with turn over numbers (TON) of up to 170 (*scheme 98*; right).^[259]

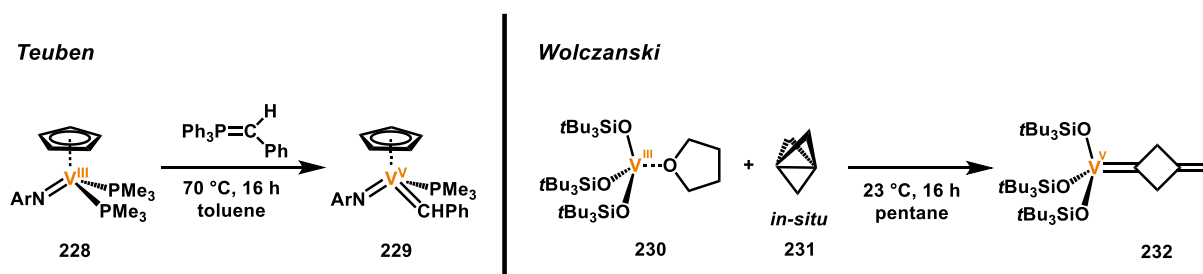


Scheme 98: Vanadium alkylidene catalysts for ROMP and RCM.

Although the performance of vanadium-based systems is still far from that of their ruthenium- or molybdenum-based counterparts, this serves as motivation to explore novel, unusual ligand environments for vanadium alkylidenes.

The alkylidene ligands in the vanadium complexes shown above are generated through α -hydrogen eliminations promoted by the coordination of an additional neutral ligand to dialkyl precursors. Examination of the solid-state structure of **V3•THF** cast doubt on the viability of this approach in the present case, as the coordination sphere is unlikely to accommodate two β -branched alkyl ligands. A more direct route was therefore sought to convert **V3•THF** into the corresponding vanadium alkylidene complex.

In 1994, *Teuben* and coworkers synthesized complex **229** through the transfer of an alkylidene fragment from a phosphonium ylide (*scheme 99*).^[260] However, **V3•THF** did not react with methylenetriphenylphosphorane. Other common methods of generating alkylidene complexes, such as reacting **V3•THF** with a diazo compound or 3,3-diphenylcyclopropene, also failed to afford the desired complex.^[261]

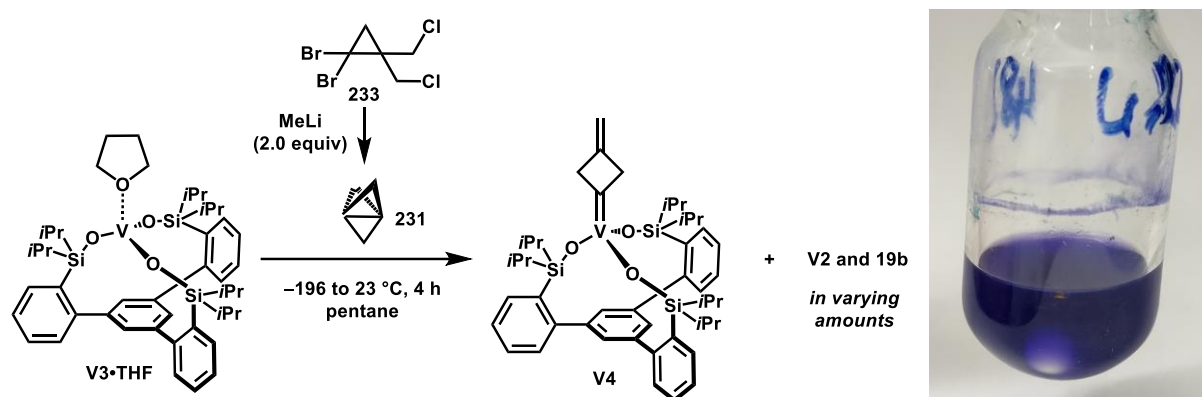


Scheme 99: Different ways to synthesize vanadium (V) alkylidenes from vanadium (III) complexes.

In 2021, the group of *Wolczanski* explored [1.1.1]-propellane **231** as an alkylidene precursor reagent.^[262] Destabilized through the ring strain of the three fused cyclopropanes, **231** reacts like a poised spring in the presence of a variety of metals. *Wolczanski* and coworkers were able to isolate alkylidene complexes with ruthenium and osmium and a year later with vanadium

starting from tris(*tert*-butylsilanolate) vanadium (III) **230**.^[263] However, the obtained complex **232** exhibited only minimal activity in the ROMP of norbornene, possibly due to excessive steric hindrance.

V3•THF offers a vanadium (III) metal center with the same tetracoordinated geometry as **230**, but a somewhat reduced steric bulk. This is made possible by the tripodal scaffold of the ‘canopy ligand’. Slimmer monodentate silanolate ligands than in **230** result in a change of coordination geometry (e.g., $[\text{V}(\text{OSiPh}_3)_3(\text{THF})_3]$).^[254] Taking advantage of this opportunity **V3•THF** was reacted with a solution of *in situ* generated [1.1.1]-propellane (**231**) to afford a deep blue material (*scheme 100*).



Scheme 100: Synthesis of the vanadium (V) alkylidene complex **V4**, and a photograph of the reaction solution.

The reaction could be followed visually because the turquoise starting material **V3•THF** is insoluble in pentane, whereas the blue product **V4** is highly soluble in this solvent. As soon as no solid remained, the reaction was deemed complete and the solvents were removed *in vacuo* along with excess [1.1.1]-propellane **231**.

NMR analysis of the obtained material revealed three diamagnetic species. The major set of signals could be assigned to the desired product with characteristic signals for the methylene protons of the alkylidene unit appearing at δ_{H} 5.74 ppm. The two other components arise from the decomposition of **V3•THF** and/or **V4** and were identified as the oxo-vanadium (V) complex **V2** and the free ligand **19b**. Both species were present in varying, minor amounts, but could never be fully removed. When leaving solutions of **V4** in benzene under argon atmosphere standing over longer periods of time (days) the ratio of **V2** increased, suggesting that **V4** is highly sensitive even to trace oxygen. It appears that the alkylidene ligand is weakly bonded and may be subject to dissociation at ambient temperature. Supporting this, the ^1H NMR signals of the alkylidene unit are broadened at 25 °C and become much sharper at -40 °C where the complex was characterized. The presence of **V2** could further be confirmed *via* single crystal X-ray diffraction (for the structure see *figure 46*).

Additional evidence for the alkylidene ligand in complex **V4** proved vexingly hard to come by. No ^{13}C NMR shift for the alkylidene carbon could be detected. Apparently, the signal is broadened by interactions with the ^{51}V quadrupole, in line with what has been previously

observed by *Wolczanski*.^[263] Also, high resolution mass spectrometry only detected a peak for the complex without the alkylidene fragment, supporting the notion that it is an adduct rather than a tightly covalently bonded fragment. ^{51}V NMR was of little help since the only discernible signal belonged to the impurity **V2**. Presumably, the signal for **V4** is broadened in the same way as the alkylidene signal in the ^{13}C NMR spectrum. *Wolczanski* and coworkers observed a signal for their complex **232** at -705 ppm with a large linewidth ($\nu_{1/2} \approx 200$ Hz).^[263] However, the peak is conspicuously located in the region of most oxo-vanadium silanolate complexes. It seems plausible that the presence of small amounts of the corresponding oxo complex (^{51}V NMR: -733 ppm)^[255] in the sample was overlooked and the signal was incorrectly assigned, in particular since the ^1H NMR signals would likely overlap. Fortunately, highly sensitive blue single crystals of **V4** could be obtained after multiple crystallization attempts (*figure 49*).

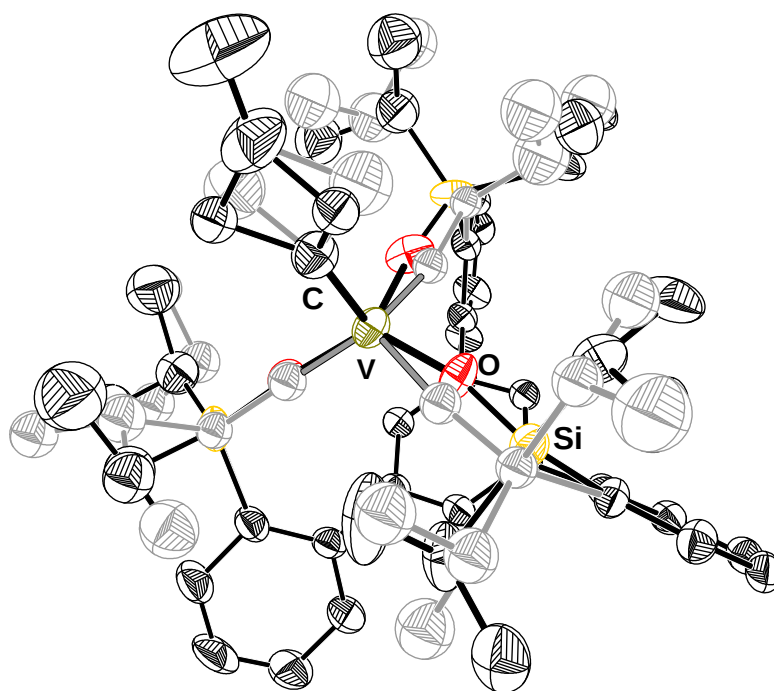


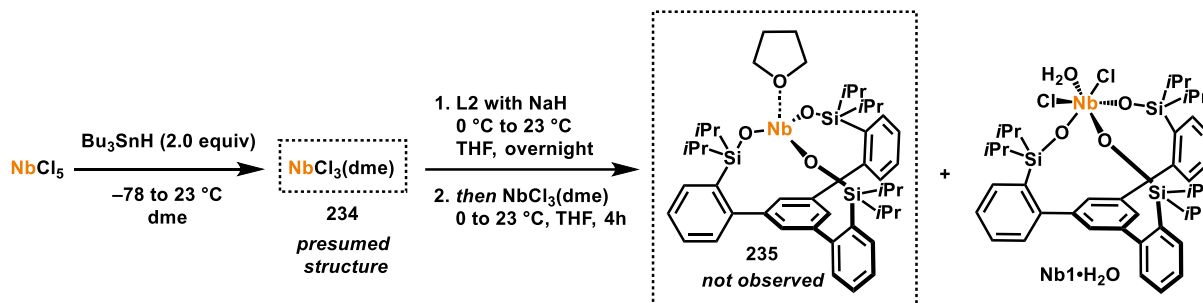
Figure 49: Solid-state structure of **V4**; disordered parts are shown in grey and all H-atoms were omitted for clarity.

Although the quality of the data obtained from the X-ray diffraction was only moderate, a structural model could be constructed. The *iso*-propyl groups are highly disordered. In comparison to **V3•THF** the binding of the alkylidene unit changes the geometry towards a more tetrahedral conformation ($\text{V}-\Delta\text{OOO}$: 0.399 Å). The O–V–O angles are markedly unequal ($\angle\text{O}-\text{V}-\text{O}$: 110.8° , 127.8° , and 108.4°), as previously observed for **232**.^[263] The carbon-vanadium distance ($\text{V}=\text{C}$: 1.858 Å) is similar to that of vanadium alkylidenes active in alkene metathesis.

Alas, the addition of excess norbornene to a solution of complex **V4** did not entail any signs of polymerization at ambient temperature. When raising the temperature to 50 °C, rapid decomposition of the vanadium alkylidene complex was observed. Hence, **V4** is not competent as a catalyst for alkene metathesis. Ostensibly, the steric hindrance around the metal-carbon bond is still too great with *iso*-propyl groups on the silanolate ligands. The same observation was previously made for related molybdenum alkylidyne complexes in alkyne metathesis.^[74] In summary, using the ‘canopy ligands’ complexes with vanadium in oxidation states III and V could be obtained, bearing varying apical ligands, namely an oxide, tetrahydrofuran or an alkylidene fragment.

2.3.2.3 Niobium

A brief attempt was made to extend the reach of the ‘canopy ligands’ to niobium complexes. Since low-valent early transition metals are of general interest for organic synthesis and catalysis, a complex containing niobium in oxidation state III was targeted.^[264]



Scheme 101: Attempted synthesis of a Nb (III) complex carrying a tripodal tris(silanolate) ligand **235** and the octahedral Nb (V) complex $\text{Nb1}\cdot\text{H}_2\text{O}$ observed instead.

The envisaged synthesis relied on a salt metathesis with the literature known niobium (III) chloride dimethoxyethane adduct **234** (scheme 101). Following the described procedure, a batch of bright yellow niobium (V) chloride was reduced to what was presumed to be **234**. The obtained material exhibited the red color reported and was not analyzed further due to the paramagnetic nature of the complex.^[265] An attempt at the subsequent salt metathesis reaction yielded a complex mixture. The analysis of the obtained material failed to produce any indication for the presence of the desired product **235**. The only identifiable species was $\text{Nb1}\cdot\text{H}_2\text{O}$ of which small crystals appeared in a NMR sample after two weeks.

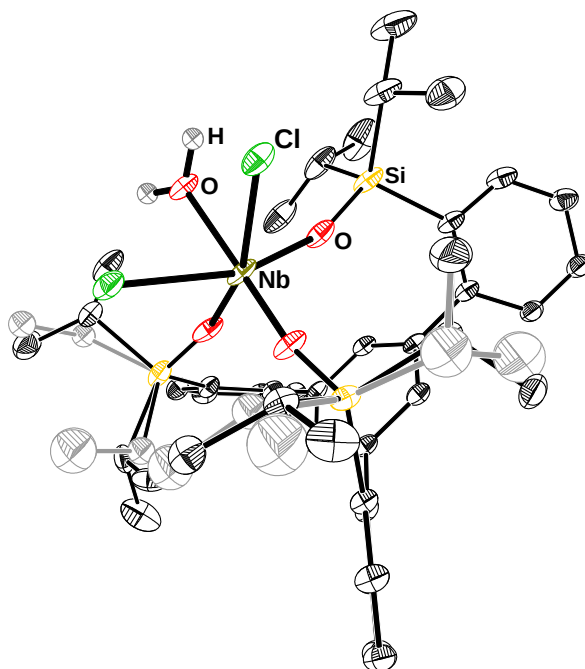


Figure 50: Solid-state structure of $\text{Nb1}\cdot\text{H}_2\text{O}$; disordered parts are shown in grey and all H-atoms were omitted for clarity, except those at the bonded water molecule.

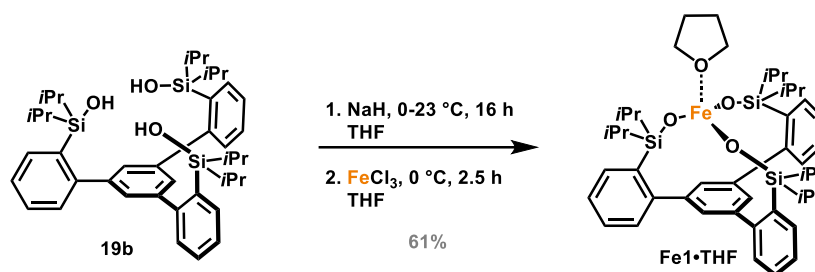
The structure of complex **Nb1•H₂O** is the only case during the presented investigation in which the central metal atom has an octahedral coordination geometry (*figure 50*). Together with the Cui's octahedral lanthanide complexes, it serves to highlight the variety of coordination geometries supported by 'canopy ligands'.^[215a]

Besides the tripodal tris(silanolate) ligand, there are two chloride atoms bound to niobium atom as well as an adventitious water molecule. Consequently, the metal center must be in oxidation state V instead of the targeted III, which put the constitution of the starting material in doubt. A reinvestigation of the presumed batch of **234** afforded several crystals from a concentrated tetrahydrofuran solution. Although the quality of the structural data obtained through X-ray diffraction was of mediocre quality, it was sufficient to show the crystals contained a mixture of niobium (IV) chloride and niobium (III) dimers. Apparently, not all the material had been successfully reduced to niobium (III) and the salt metathesis had been attempted with a mixture of different oxidation states, explaining the unclear result obtained. No further efforts were made to optimize the reduction conditions and reattempt a complexation. However, it seems highly plausible that further complexes of niobium with 'canopy ligands' can eventually be made.

2.3.2.4 Iron

Moving from left to right through the transition metals in the periodic table, high oxidation states become less common and therefore fewer opportunities arise for the tris-anionic ‘canopy ligands’. Iron, from the middle section of the transition metals, is known for its redox promiscuity and occurs in a range of oxidation states. Iron silicate materials possess intriguing catalytic properties, mainly in the field of oxidation chemistry or as Lewis acids.^[207a] A series of molecular models have been developed for iron silicate sites in different oxidation states (II and III are most common) by the groups of *Limberg*, *Tilley*, *Edelmann*, and others.^[266]

Iron in the oxidation state III was selected (ionic radius: 0.49 Å for CN 4) and the corresponding complex could be obtained in good yield *via* the salt metathesis route (*scheme 102*).



Scheme 102: Synthesis of the iron (III) complex **Fe1•THF**.

Fe1•THF is a paramagnetic yellow solid and did not show any assignable features in the NMR spectra. Elemental analysis indicated the complex to be a mono-tetrahydrofuran adduct, which is in agreement with reports on similar complexes.^[266b] High resolution mass spectrometry identified only the complex without the Lewis base, as was previously observed for several complexes. Pale-yellow crystals of **Fe1•THF** could be grown from a concentrated tetrahydrofuran solution over a week.

X-Ray diffraction revealed the iron cation to be coordinated in a distorted tetrahedral manner by the tripodal tris(silanolate)ligand and an apical tetrahydrofuran (*figure 51*). As expected, the dative bond to the neutral ligand is considerably longer (Fe–O(THF): 2.043 Å) than the bonds to the remaining three oxygen ligands (Fe–O: 1.818 Å, 1.793 Å, and 1.816 Å). As a consequence, the angles between the covalently bonded ligands are relatively large ($\angle\text{O–Fe–O}$: 121.1°, 113.2°, and 116.2°) and the iron sits only 0.326 Å above the plane defined by these three oxygen atoms.

When compared to the known mono-tetrahydrofuran adduct tris(*tert*-butylsilanolate) iron(III) the silanolate angles are less obtuse in the version with the tripodal ligand ($\angle\text{Si–O–Fe}$: monodentate: 176.9°, 179.8° and 172.7° against tripodal 173.4°, 161.6°, and 162.7°).^[267] The conformation is perhaps a consequence of the high steric bulk of tris(*tert*-butylsilanolate) ligands. This serves as a reminder that the trend towards more linear silanolate bonds in complexes carrying tripodal ligands (see *chapter 2.3.2.2*) is not necessarily a general

one. Rather, the ‘canopy ligands’ are remarkable in their ability to adapt to the needs of specific cations. Complex **Fe1•THF** shows this capability to extend beyond the early transition metals, which are the group most intensively investigated in conjunction with ‘canopy ligands’.

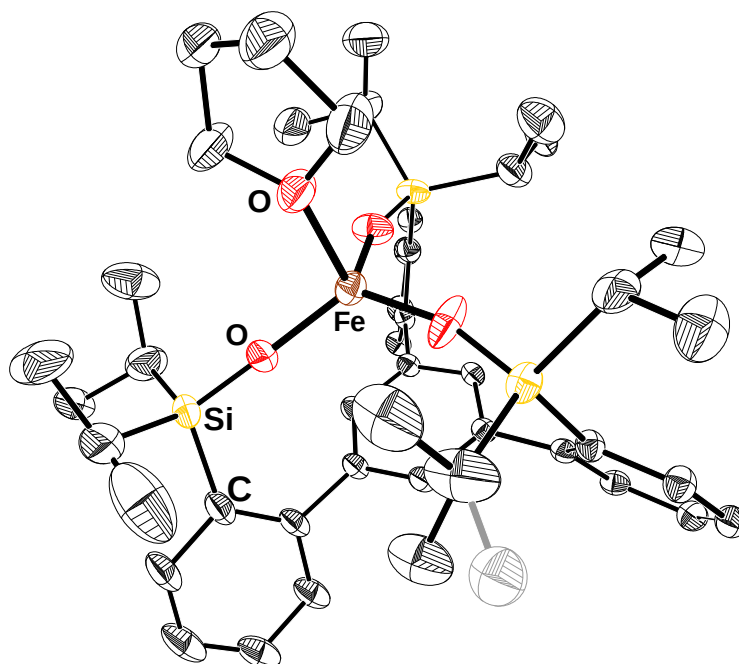


Figure 51: Solid-state structure of **Fe1•THF**; disordered parts are shown in grey and all H-atoms were omitted for clarity.

2.3.3 Robust Catalysts for the Cyclization of Citronellal to Isopulegol

The first part of the project was dedicated to extending the chemical space accessible with the ‘canopy ligands’ and proving their versatility in coordination chemistry. By sampling the periodic table, the broad applicability of the tripodal tris(silanol) ligands in forming complexes with all kinds of different cations was demonstrated. Complexes of the type **207** appear to be quite general and can possibly be synthesized with an even larger number of metal centers.

The underlying motivation for these exploratory efforts was the prospect of applying the complexes as catalysts in organic synthesis. The general design of the complexes was targeted at emulating *single-sites* in heterogeneous catalysis and thereby creating robust homogeneous catalysts. As indicated above, the reactivities of these complexes are expected to be as diverse as the metals contained therein. Thus, a test case was required to demonstrate the general concept.

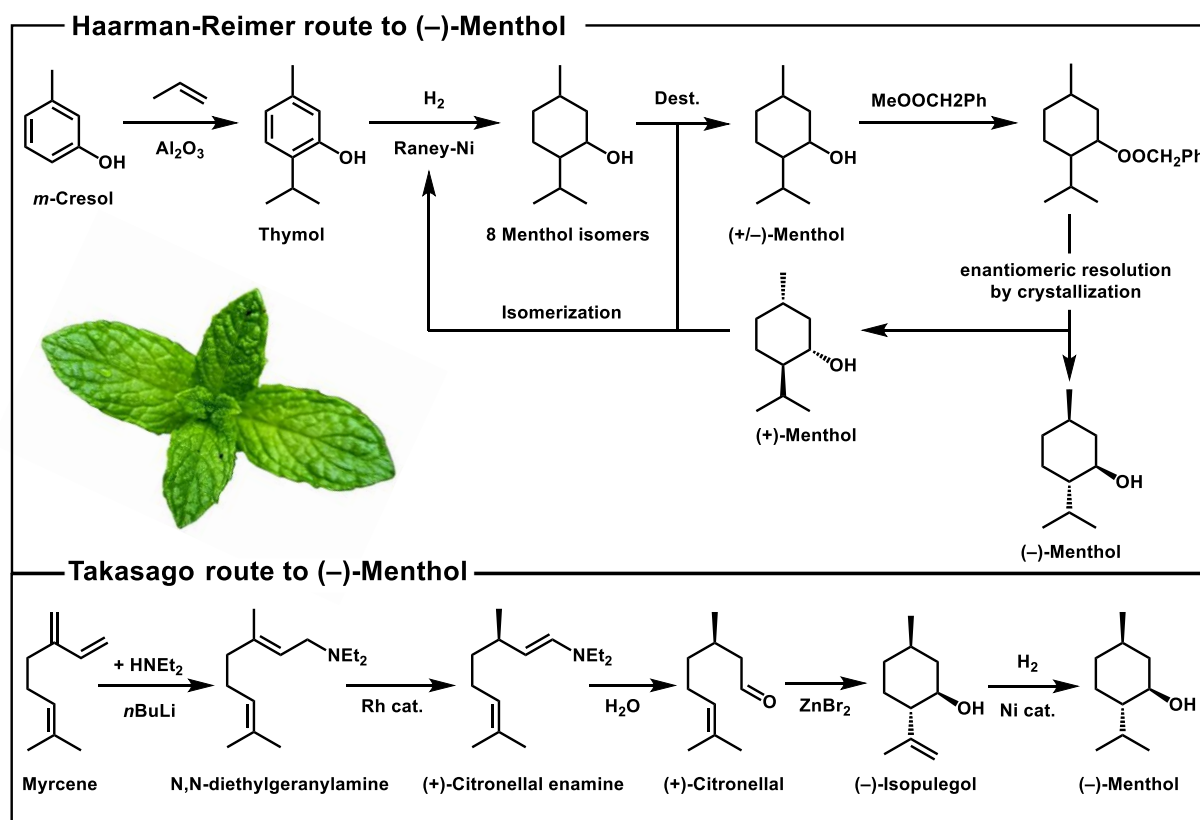
Lewis acid-catalyzed transformations are among the most common reaction types in organic synthesis.^[268] Contrary to their denomination as ‘catalytic’ some of the most iconic reactions actually require stoichiometric amounts of Lewis acids, a prominent example being Friedel-Crafts acylations. Great efforts have been undertaken to render such processes truly catalytic and solid acids have received increasing attention in the last decades.^[269] They are particularly favorable considering the growing sustainability demands. Solid Lewis acid catalysts are easily separated from the products and can often be recycled, reducing the environmental impact.

Silica supported metal sites are among the materials being investigated as solid acid catalysts.^[270] An example of a process that can be catalyzed by such materials is the cyclization of citronellal to isopulegol.^[271] The product is an important intermediate in the industrial synthesis of the aroma chemical (–)-menthol and is obtained through the acid-catalyzed intramolecular carbonyl-ene reaction of citronellal. For this particular process, the chemical industry continues to rely on homogeneous Lewis acid catalysts due to their superior selectivity. This highlights one of the general challenges of heterogeneous catalysis: the difficulty in tuning catalysts to attain specificity. On the other hand, the homogeneous catalysts are not without their own difficulties, which will be delineated in the next chapter. For these reasons, the cyclization of citronellal to isopulegol was chosen as a test case to demonstrate the utility of the novel complexes carrying ‘canopy ligands’ in catalysis.

2.3.3.1 Industrial Routes to (–)-Menthol

In terms of production volume (–)-menthol is among the most important chiral chemicals worldwide (estimated at 34 000 t/a).^[271-272] It is a popular flavor and fragrance compound responsible for the cooling sensation and characteristic odor of plants from the mint family.^[273] (–)-Menthol finds application in the cosmetic and medical sector as an ingredient in toothpaste, mouthwash, aftershave, and nonprescription medical products.^[274] Of the eight possible isomers arising from the characteristic monoterpene connectivity, only (–)-menthol has the desirable odor and fragrance properties; the enantiomer (+)-menthol produces a significantly less-pronounced cooling effect, and the other isomers have a distinct fragrance profile which has been described as unpleasantly earthy and musty.^[275]

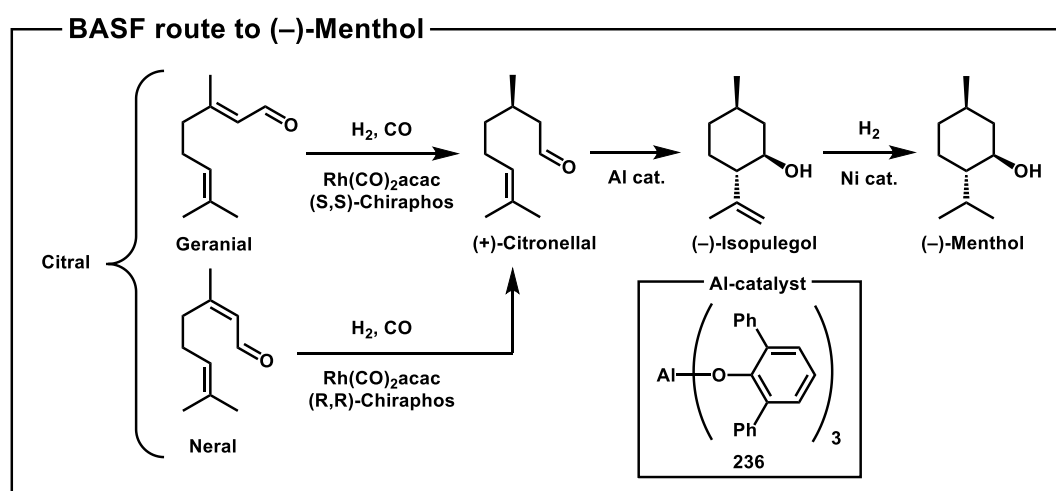
Historically, (–)-menthol was obtained from natural sources such as corn mint oil, but with ever-growing demand a majority of (–)-menthol is now produced synthetically.^[276] Currently, three major industrial processes for the synthesis of (–)-menthol are in operation. Symrise GmbH & Co. KG (formerly Haarmann & Reimer) relies on a non-selective synthesis and separates the resulting enantiomers by crystallization (*scheme 103, top*).^[275, 277]



Scheme 103: Haarman-Reimer and Takasago industrial routes to (–)-menthol; photograph of a mint leave.

A first asymmetric industrial synthesis of (–)-menthol was developed by the Japanese company Takasago in the 1980s.^[278] Their route starts with myrcene and involves the isomerization of diethylgeranylamine to (+)-citronellal enamine catalyzed by an enantiomerically pure rhodium-BINAP catalyst (*scheme 103, bottom*).^[279] The reaction was

developed with the help of the later Nobel laureate *R. Noyori* and has garnered much attention from industry and academia alike.^[280] The subsequent diastereoselective intramolecular carbonyl-ene reaction catalyzed by a Lewis Acid (e.g., zinc bromide) sets the remaining two of three stereocenters to give isopulegol (*table 9, entry 1-2*).^[281] This crucial intermediate contains all the stereoinformation and is transformed into the final product (–)-menthol by simple hydrogenation. Compared to the efforts directed at asymmetrically setting the first stereocenter, the cyclization step has received far less attention in academic research.^[282] Even so, due to problems with diastereoselectivity efforts have been directed at finding alternatives. Increasing concerns about the efficiency and environmental impact of traditional homogeneous Lewis acids (poor handling, high loadings, recycling) have provided additional motivation.^[268, 283]



Scheme 104: BASF industrial route to (–)-menthol.

In 2012, BASF entered the market with a process build on their large-scale production of citral (*scheme 104*).^[284] The two double-bond isomers neral and geranial (together citral) are hydrogenated with chiral rhodium catalysts (using (R,R)-Chiraphos and (S,S)-Chiraphos respectively) to give (+)-citronellal, the same intermediate utilized in the Takasago process.^[282] The following cyclization step is catalyzed by tris(2,6-diphenylphenoxy)aluminum **236** with exquisite selectivity for the desired diastereomer isopulegol.^[285] The original discovery was made by chemists at Takasago in the early 2000s, but the catalyst seems to find application in both companies.^[286] However, the excellent performance of the aluminum complex appears to be limited to a small temperature window. While the stereoselectivity for isopulegol over its three possible isomers iso-isopulegol, neo-isopulegol and neo-iso-isopulegol remains >99% independent of the temperature, the overall yield drops from 95% at 0 °C to 48% at 50 °C (*entry 3-5*).^[286a] In recent years, efforts have been undertaken to develop derivatives of this system that can tolerate slightly higher reaction temperatures (40 °C), but the required ligands are far more complicated to produce.^[287]

A second issue appears to be the recycling of the catalyst.^[288] Separation of the product from the catalyst by distillation is not possible without decomposition of the aluminum complex. The current state-of-the-art seems to be the recovery of the (relatively) expensive phenol ligand by hydrolysis of the complex. Accordingly, the aluminum catalyst must be generated anew for each batch from pyrophoric and difficult to handle alkyl aluminum reagents (e.g. triethylaluminum). Attempts at addressing this challenge with heterogeneous catalysts have been reported: a number of acidic materials promote the cyclization, but the diastereoselectivity is generally lower than in homogeneous catalysis.^[289] Among the catalysts shown to be effective for the transformation are silicate materials such as aluminosilicate (*entry* 6) and traditional Lewis acids grafted on silica surfaces.^[290] The highest selectivity for isopulegol (93%) with a heterogeneous catalyst was achieved by *Chuah* and coworkers with zeolite Zr-beta-100 (*entry* 7), but they observed reduced activity upon recycling of the zeolite.^[291]

Table 9: Overview of selected catalysts for the cyclization of citronellal to isopulegol.

Citronellal

Isopulegol

Iso-Isopulegol

Neo-Isopulegol

Neo-Iso-Isopulegol

Catalysts

236

237 (R = Ph)
237 (R = 1-naphthyl)

Entry	Catalyst	T [°C]	Yield [%] (isopulegols)	Selectivity [%] (±)-isopulegol
1	ZnBr ₂ ^a	5-10	70	94 ^[281]
2	ZnBr ₂	110	—	86 ^[286a]
3	236	0	95	99 ^[286a]
4	236	25	63	99 ^[286a]
5	236	50	48	99 ^[286a]
6	SiO ₂ /Al ₂ O ₃	90	96	65 ^[290b]
7	Zr-beta-100	80	92	93 ^[291]
8	Al(OSiPh ₃) ₃	0-25	>99	76 ^[292]
9	Al(OSi(1-naphthyl) ₃) ₃	0-25	>99	97 ^[292]

^astoichiometric ZnBr₂.

^astoichiometric ZnBr₂.

During the development of the BASF route to (–)-menthol in the 2000s, Symrise patented catalysts for the cyclization of citronellal to isopulegol based on *in situ* generated aluminum silanolate complexes. Tris(triphenylsilanolate) aluminum **212** gives excellent yields of the isopulegols, albeit with only moderate diastereoselectivity (*entry* 8).^[293] The author observed an increased temperature stability and described an experiment in which the catalyst could be reused through removal of the product by distillation. In accordance with observations made with the sterically encumbered 2,6-diphenylphenol ligands, increasing the steric hindrance by substituting the silanolates with 1-naphthyl groups (**237**) improved the diastereoselectivity for

isopulegol (entry 9). However, it remains unclear if the described process was ever applied in an industrial setting.^[271]

Therefore, there continues to be a demand for a robust catalyst for the cyclization of citronellal to isopulegol. The catalyst should meet following criteria: it should give (1) a high overall yield of the isopulegols and (2) high diastereoselectivity for (–)-isopulegol. Additionally, it should be (3) stable at temperatures above 25 °C and (4) reusable through separation of the product from the catalyst by distillation.

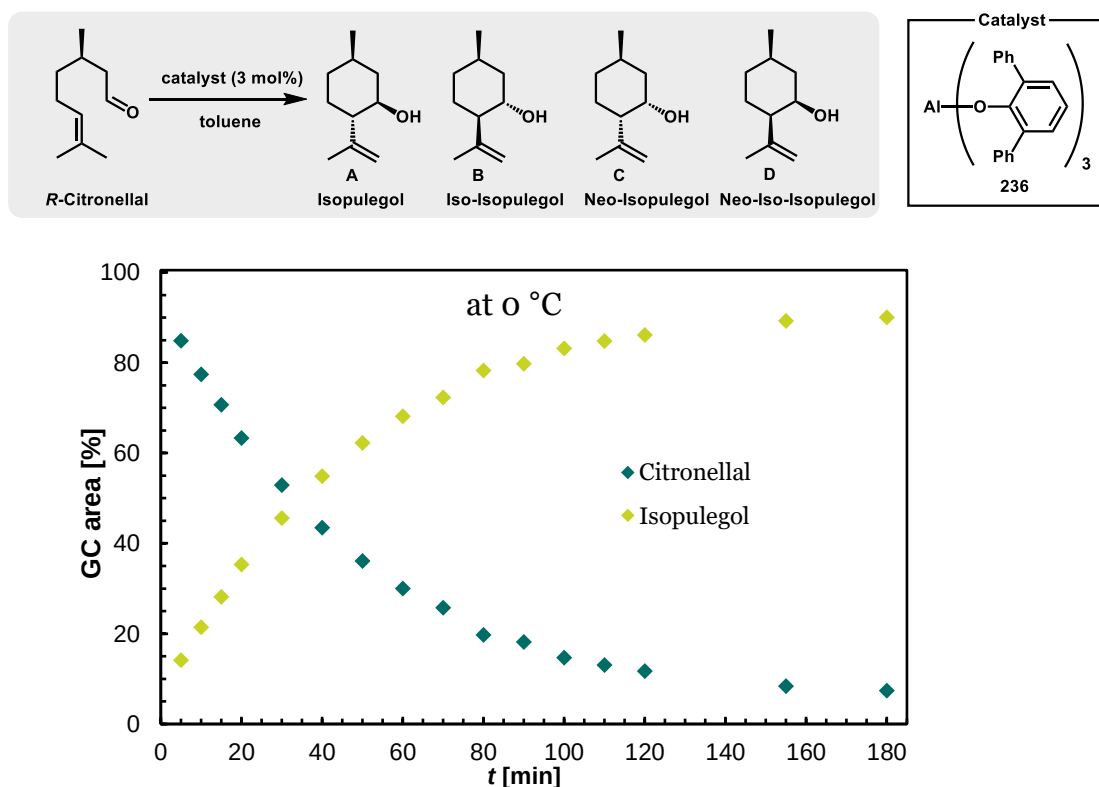
In light of the encouraging prior work with silanolates by Symrise, the reaction was seen as a promising test case for trying out complexes such as **Al₁•THF** in catalysis.

2.3.3.2 Decomposition Pathway of the Industrial Catalyst System

Due to the scarcity of peer-reviewed literature on the catalyst prevalently employed by the chemical industry, the investigation was started by probing the temperature stability of the **236** system.^[294]

Complex **236**, first reported by *Yamamoto* and coworkers, is usually generated *in situ* from alkyl aluminum reagents and the respective phenol ligand.^[295] The complex has not been isolated and the available structural information stems from adducts formed with dimethylformamide or other carbonyl compounds.^[296] Reactions that rely on the **236** system as catalysts are mostly carried out at temperatures below 0 °C.

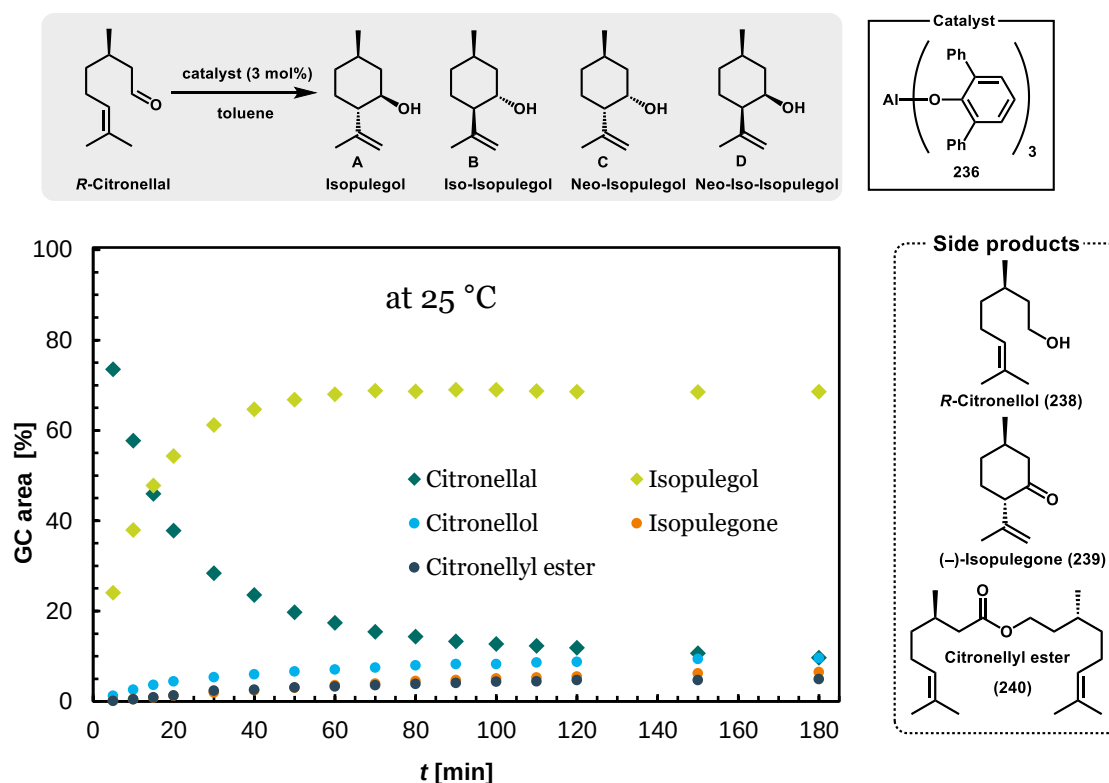
In the present case, the cyclization reached full conversion with high chemo- and diastereoselectivity for isopulegol when the substrate was added to the catalyst solution at 0 °C. However, the reaction provided erratic results when the temperature of the catalyst solution was raised to 25 °C prior to the addition of the substrate.



Graph 15: Consumption of *R*-citronellal and generation of product isopulegol in toluene using complex **236** as catalyst (3 mol%) as monitored by GC at 0 °C.

Tracing the reaction with gas chromatography (GC) showed steady conversion of citronellal to the desired product at 0 °C with >90% conversion reached after ca. 160 min (*graph 15*). Only trace amounts (<1%) of the other isopulegol isomers were detected, confirming the excellent diastereoselectivity conferred onto the reaction by **236**.

At 25 °C, fast initial conversion was observed after which the product formation stalled at 65% (after ca. 60 min). At this point, the original catalyst system appears to be inactive; however, the levels of citronellal continued to decline although at a slower rate (*graph 16*).



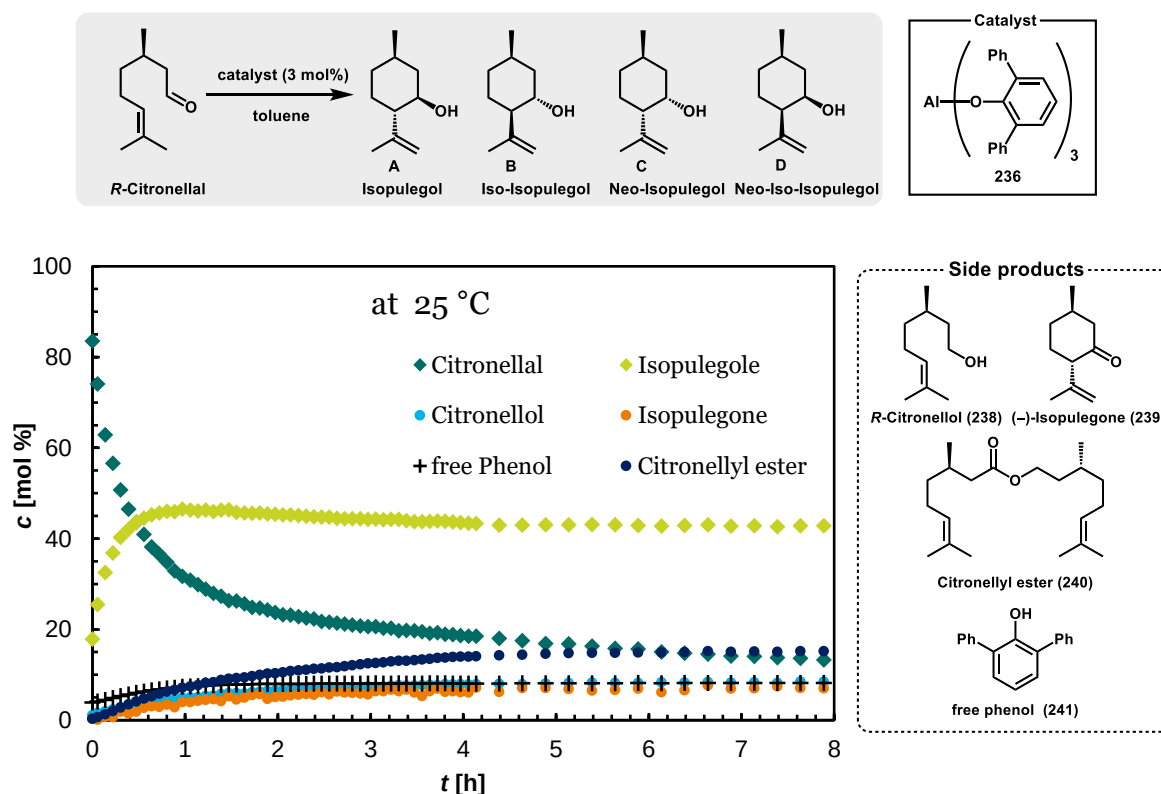
Graph 16: Consumption of *R*-citronellal and generation of product isopulegol as well as side products (citronellol, isopulegone, and citronellyl ester) in toluene using complex **236** as catalyst (3 mol%) as monitored by GC at 25 °C.

Closer inspection of the GC trace revealed three major side products: citronellol (**238**), isopulegone (**239**), and citronellyl ester **240**, which were further confirmed to be present by analysis of the NMR spectra of the crude product mixture. The formation of these three side products continued to deplete the remaining levels of citronellal after the desired reaction had stopped, indicating that they arise at least partially from processes promoted by different catalytic species.

Citronellyl ester **240** has already been described as a side product of the cyclization by *Itoh* and coworkers and was speculated to arise from a Tishchenko reaction.^[294, 297] Different additives were reported to suppress this pathway (ethylglyoxylate, citronellic acid or other organic acids).^[285] However, the use of additives is suboptimal for the subsequent purification. Citronellol **238** was briefly mentioned by *Chuah* and coworkers as the major product when the cyclization was attempted in 2-propanol with an aluminum containing zeolite.^[291] To the best of the author's knowledge, isopulegone **239** has not been previously observed as a side product. It appears likely that these species originate from mechanistically related pathways: presumably, citronellol and isopulegone arise *via* Meerwein-Ponndorf-Verley/Oppenauer-type hydride shuttling between the starting material citronellal and the product isopulegol,

whilst citronellyl ester **240** emanates from a Tishchenko reaction of citronellal. All three reactions are known to be catalyzed by aluminum alkoxide complexes.^[298] Against this background, a tentative decomposition pathway for the **236** catalyst system would involve the replacement of one, two or three of the phenolate ligands by the product isopulegol. The formed alkoxide species could generate isopulegone and citronellol *via* a hydride transfer as well as catalyze the Tishchenko reaction of citronellal. Indeed, while monitoring the cyclization reaction with NMR at 25 °C increasing amounts of free 2,6-diphenyl phenol **241** could be detected (*graph 17*). When all the phenolate ligands are replaced, the resulting species ceases to be active for catalyzing the desired cyclization reaction. While higher conversions could sometimes be achieved when repeating the experiment, the overall picture at ambient temperature was that of an unreliable catalyst.

A robust temperature-stable catalyst for the conversion of citronellal into isopulegol requires a design that prevents the dissociation of the sterically demanding ligands from the metal center.



Graph 17: Consumption of *R*-citronellal and generation of product isopulegol as well as side products (citronellol, isopulegone, and citronellyl ester) and free phenol **241** in [*D*₈]-toluene using complex **236** as catalyst (3 mol%) as monitored by ¹H NMR spectroscopy at 25 °C.

2.3.3.3 Complexes with ‘Canopy Ligands’ as Temperature Stable Catalysts

The findings outlined above suggested that side reactions might be blocked by avoiding ligand dissociation; taking advantage of the chelate effect with the tridentate ‘canopy ligands’ seemed a promising strategy. The tether would prevent the product from displacing the three anionic ligands.

An even more straightforward approach would be to utilize literature known aluminum complexes with tridentate tris(phenolate) ligands.^[299] Prominent among them are amine-tethered tris(phenolate) complexes used, for example, by the *Kleij* group for the synthesis of cyclic carbonates from epoxides and CO₂.^[300] However, complex **242•THF** showed significantly reduced activity in the cyclization of citronellal to isopulegol when compared to the standard catalyst from industry (*table 10, entry 1 vs. 2*). An acceptor number determined for **242•THF** via the Gutmann-Beckett method (AN = 48.2) suggests the Lewis acidity of the aluminum center to be tempered through the coordinating nitrogen tether.^[301] Since aluminum is prone to interact with any Lewis base, the ‘canopy ligands’ with their all hydrocarbon tether are supposedly a more auspicious choice. Additionally, silanolates as ancillary ligands show good temperature stability and exert significant steric bulk, which is of high importance for the desired diastereoselectivity.

From the various complexes with ‘canopy ligands’ that can potentially be classified as Lewis acids (**Al1•THF**, **Ga1•THF**, **Ti1**, **V3•THF**, and **Fe1•THF**), the aluminum-containing complexes were selected. There is ample encouraging prior art with aluminum and the metal is earth abundant and inexpensive.

Next, the performance of the tridentate complexes as catalysts for the cyclization of citronellal to isopulegol was investigated (*table 10*). Comparison is made with respect to the two major catalyst systems mentioned in the patent literature and to a complex bearing a tridentate tris(phenolate) ligand.^[286a, 293] All reactions were conducted in toluene with the citronellal being metered into the respective catalyst solution at the indicated temperatures.

The **236** system was generated *in situ* as described by *Yamamoto* and coworkers.^[302] Addition of the substrate at 0 °C, followed by slowly warming the reaction mixture to ambient temperature gave isopulegol with outstanding selectivity (*table 10, entry 1*). However, raising the temperature of the catalyst solution to 25 °C before the addition gave erratic results with changing conversions which were accompanied by the formation of side products (*vide supra*). The aluminum complex **242•THF** endowed with an amine-tethered tris(phenolate) ligand showed considerably reduced activity under the same conditions and only moderate selectivity for isopulegol (*entry 2*). While the drop in selectivity might be caused by the less sterically imposing methyl substituent adjacent to the phenolic O atom, the low conversion of starting material implied that a more sterically demanding congener of this system was unlikely to prove especially viable.

Complex **212•THF** comprising three monodentate silanolate ligands gave excellent conversion with the same moderate diastereoselectivity as reported before (*entry 3*).^[292] Gratifyingly, upon changing to the tethered analog (**Al1•THF**) the cyclization proceeded with the same conversion and an increased selectivity for the desired isopulegol (*entry 4*). The shift in selectivity from **212•THF** to **Al1•THF** indicates the benefits of the tripodal ligand to extend beyond the intended increased stability. Subtle conformational differences observed in the solid-state structures appear to persist (to some degree) in solution and have an influence on the selectivity for the desired isomer.

Table 10: Results of the cyclization of citronellal to isopulegol with different catalysts.

Entry	Catalyst	T [°C]	Time	Conversion [%] ^a	Selectivity A/B/C/D [%] ^b
1	236^c	0 to 25	18 h	>99	99/0/1/0
2	242•THF	0 to 25	18 h	8	77/3/19/1
3	212•THF	0 to 25	18 h	97	77/2/20/2
4	Al1•THF	0 to 25	18 h	96	82/3/15/0
5	243^c	0 to 25	4 d	97	83/2/15/0
6	Al2•THF	0 to 25	5 d	80	93/1/4/2
7	Al2•THF	25 to 45	24 h	94	93/1/4/2
8	Al2•THF	25 to 100	2 h	99	91/2/4/3

Catalysts

^abased on the area%(GC) of citronellal; ^bratio based on area% (GC) of isopulegol and its isomers; ^c*in situ* formation.

Figure 52 shows relevant parts of the solid-state structures of **212•THF** (left)^[228] and **Al1•Py** (right) with only one silanolate ligand depicted for each complex. It becomes clear that the orientation of the lateral phenyl substituents is reversed in the version with the tripodal ligand. Whereas one aryl ring is orientated straight downward in **212•THF** with the Si–C bond nearly parallel to the Al–O(THF) bond, the tether in **Al1•Py** prevents this conformation. Quite the opposite, one aryl ring is orientated practically straight upward (as shown in figure 52) in proximity to the apical ligand. It is important to note, that during catalysis the substrate for the cyclization reaction must be bound at the position of the labile ligand. It stands to reason,

that the observed increase in diastereoselectivity for the complex carrying a ‘canopy ligand’ could be caused by the described rearrangement of the steric bulk around the metal center.

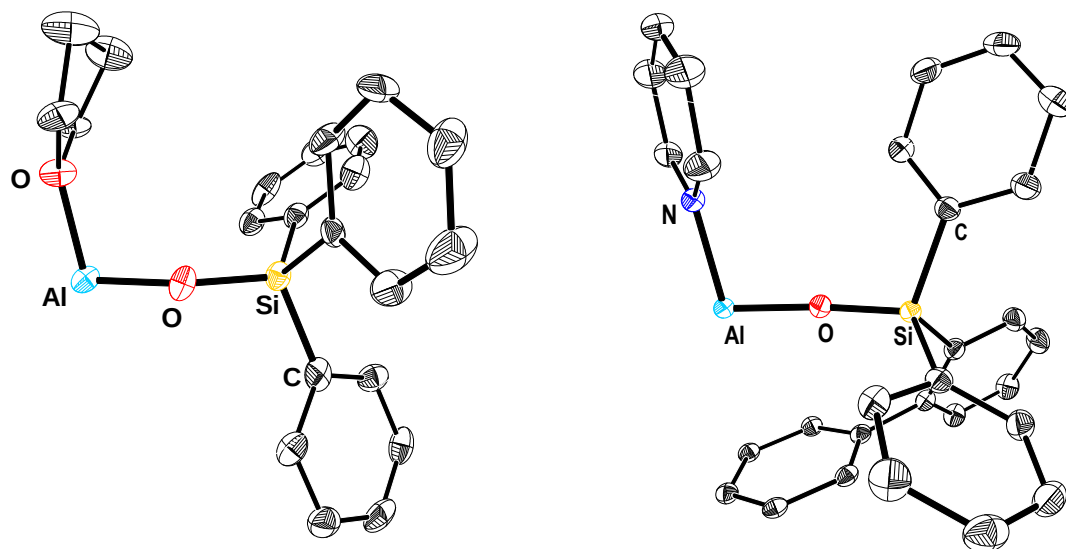
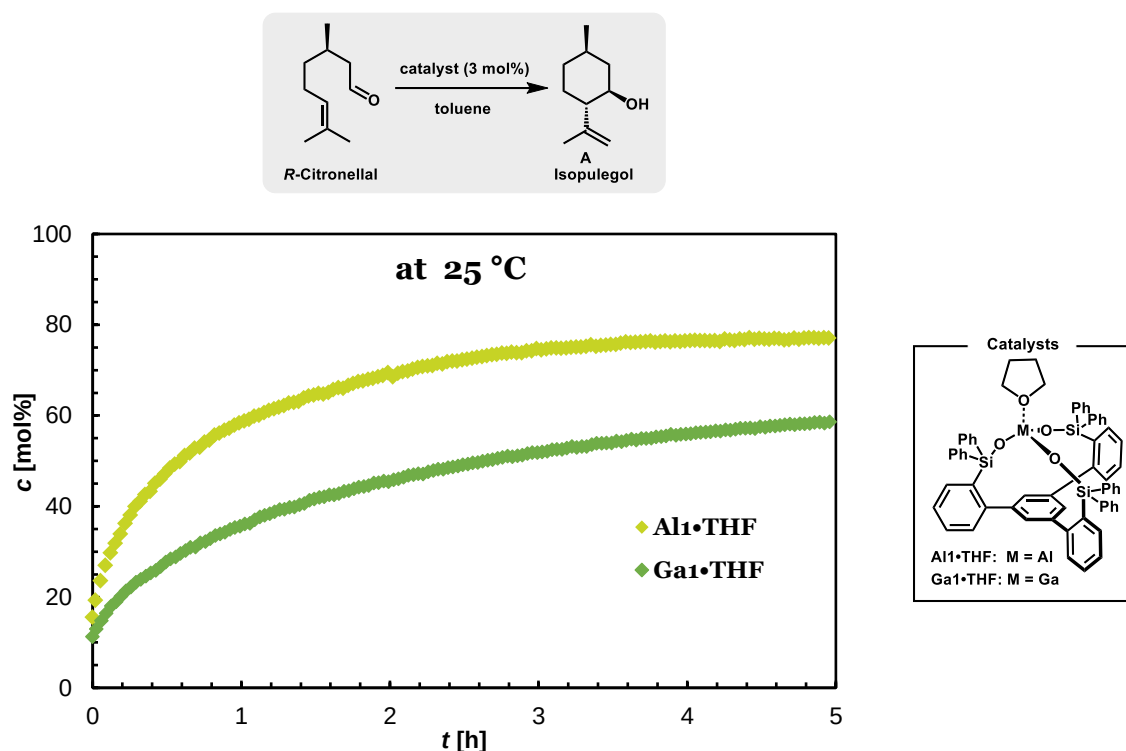


Figure 52: Truncated solid-state structures of **212•THF** (left)^[228] and **Al1•Py** (right); only one silanolate ligand is shown for each complex in order to highlight the change in conformation resulting from the tether; all H-atoms and solvent molecules were omitted for clarity.

Expanding on the notion of tightening the cavity around the metal center, *iso*-propyl groups on the silanolate ligands should exert an even greater steric influence. To this end, complex **243** was generated *in situ* with commercially available tris(*iso*-propyl)silanol and trimethylaluminum. Indeed, the reaction proceeded with increased selectivity for isopulegol in comparison to **212•THF** (*entry* 5). Once more, switching to the corresponding analog with a tripodal ligand (**Al2•THF**) entailed a significant increase in diastereoselectivity (*entry* 6). However, there is a penalty to be paid in terms of activity for increasing the steric bulk of the ligand. When started at 0 °C and then continued at ambient temperature the cyclization took five days to reach 80% conversion. Fortunately, raising the temperature to 45 °C increased the rate significantly (*entry* 7). When the reaction was conducted at 100 °C full conversion was reached in less than 2 h with only a minor decrease in selectivity (*entry* 8); this vindicates the hypothesis that the use of a chelating silanolate ligand yields a more robust catalyst.

The related gallium-based complex **Ga1•THF** was briefly considered as an alternative catalyst for the transformation. As shown above, it possesses an intrinsically higher Lewis acidity (*chapter 2.3.1.3*) and could potentially accelerate the reaction.

The complex **Ga1•THF** was benchmarked against the aluminum-based catalyst **Al1•THF** in the cyclization reaction. The generation of the product isopulegol was traced by NMR at ambient temperature (*graph 18*).



Graph 18: Generation of the product isopulegol in the cyclization reaction of *R*-citronellal in [*D*₈]-toluene using either complex **Al1•THF** or **Ga1•THF** as catalyst (3 mol%) as monitored by ¹H NMR spectroscopy at 25 °C.

Al1•THF produced a faster initial rate than the gallium-based catalyst. Lewis acidity does not seem to be the deciding factor for the reaction rate. Nevertheless, **Ga1•THF** is a competent catalyst for the reaction reaching 93% conversion of the starting material after 18 h with a selectivity for the desired product isomer of 78%. The diastereoselectivity is lower than with the aluminum congener. The reason for this can likely be found in the somewhat wider cavity in **Ga1•THF** resulting from the larger cation.

Table 11: Comparison of the catalysts at elevated temperatures.

Entry	Catalyst	T [°C]	Time	Conversion [%] ^a	Yield A [%] ^b
1	236^c	60	2 h	68	50
2	243^c	60	2 h	60	19
3	Al2•THF	100	2 h	>99	93

^abased on the area%(GC) of citronellal; ^bdetermined with cyclohexanol as an internal standard; ^c*in situ* formation.

To emphasize the robust performance of the aluminum complex **Al2•THF** at elevated temperatures a comparison was made by determining the absolute yield of isopulegol in

reactions using an internal standard (*table 11*). The experiments shed light not only on the selectivity for isopulegol over the other isomers, but also on the overall chemoselectivity of the reaction.

At 60 °C the **236** system commonly employed in industry did not lead to full conversion and gave only 50% of the desired product along with significant amounts of the three side products (*table 11, entry 1*). Monodentate silanolate ligands also failed to guarantee the stability of the catalyst at elevated temperatures (*entry 2*). In contrast, **Al2•THF** catalyzed the cyclization of citronellal to isopulegol at 100 °C with good diastereoselectivity and excellent chemoselectivity (*entry 3*). A yield of 93% (isopulegol) was obtained and none of the side products were observed. The tridentate ligand design appears to effectively prevent the decomposition of **Al2** through ligand exchange with the product.

In addition, the ‘canopy ligand’ brings about an improved overall stability: no decomposition was detected when a toluene solution of **Al2•THF** was heated to 100 °C for 24 h and the complex could be stored on the bench for >1 month.

To provide a more stringent test for the qualities of **Al2•THF** a cycling experiment was performed. The set-up is also meant to provide an outlook towards a different (maybe more efficient) industrial process for the production of isopulegol.^[292] The reaction was performed in a flask equipped with a distillation apparatus on an 11 mmol scale (approx. tenfold increase compared to previous reactions). Citronellal was added to a solution of catalyst **Al2•THF** in Dowtherm™ A (a commercial high boiling solvent consisting of a mixture of biphenyl and biphenyl ether) at 100 °C and the reaction was allowed to proceed for 2 h. Full conversion of the starting material was observed and vacuum was applied to the apparatus. The product isopulegol was distilled from the reaction mixture into a receiving flask. The use of a high boiling solvent such as Dowtherm™ A allows for the separation of the product from the catalyst without having to reisolate the complex; this reveals the potential for a ‘continuous’ process which would minimize solvent and catalyst use. After removal of the product from the reaction mixture, a second batch of citronellal was added. The cycle was repeated a total of five times with the results listed in *table 12*.

Table 12: Results of the cycling experiment; photography of the reaction set-up.

Cycle	Yield Isopulegol [%] ^a
1	94
2	94
3	91
4	94
5	95

^a determined through qNMR with 1,2-dichlorethane.



Even after prolonged heating to 100 °C no reduction in the activity of **Al2** was observed. Moreover, none of the side products, which would indicate a degradation of the catalyst, were detected. The catalyst with a tripodal tris(silanolate) ligand can therefore be considered not only temperature stable, but reusable.

This quality might be used to imagine an alternative to the current process employed by industry for the cyclization of citronellal to isopulegol, based on the described cycling experiment. Such a process would not merely reduce the volume of solvents used, since the product can be separated from the catalyst solution by distillation, but also remove the need for handling dangerous alkyl aluminum reagents to form the catalytic species in each batch. Moreover, reusing the catalyst would entirely avoid tedious recovery procedures for the ligand. While at first glance a reaction temperature of 100 °C is more energy intensive, there is an argument to be made for operating the process at higher temperatures. The **236** system is most effective in a temperature range between 0 – 25 °C, which from a chemical engineering perspective can be more challenging to maintain due to varying external factors (weather, seasons etc.) than, for example, constant 100 °C.^[303] The high temperature could also be used for the subsequent distillation, which is the preferred purification method for fragrance compounds.

While **Al2•THF** does not exceed the exquisite diastereoselectivity of the **236** system, the presented catalyst surpasses the **236** system in terms of stability and chemoselectivity above 25 °C. In a sense, the complex combines the advantage of homogeneous catalysts (selectivity) with the benefits of heterogeneous catalysts (robustness and stability). In contrary to the latter, the general design of the ‘canopy ligands’ allows for precise modifications around the metal center in a simple and straightforward manner. Results from Symrise indicate that the diastereoselectivity could potentially be increased by further tuning the substituents on the silanolate ligands.^[293] This possibility notwithstanding, the current example is judged sufficient to prove the broader concept: complexes of the general type **207** equipped with tripodal tris(silanolate) ligands can be successfully applied in catalysis.

2.3.4 Outlook

The work presented on the coordination chemistry of the ‘canopy ligands’ can only be considered preliminary and much remains to be explored. There is no doubt that more metals in different oxidation states could be complexed using the tripodal tris(silanolate) ligands. So far, trigonal planar, tetrahedral, trigonal bipyramidal, and octahedral coordination geometries were shown to be attainable.^[215b] A future goal could be to add a square planar complex to this list. It is worth noting that this is a geometry more usually associated with late transition metal complexes, which have thus far not been explored in the context of the ‘canopy ligands’.

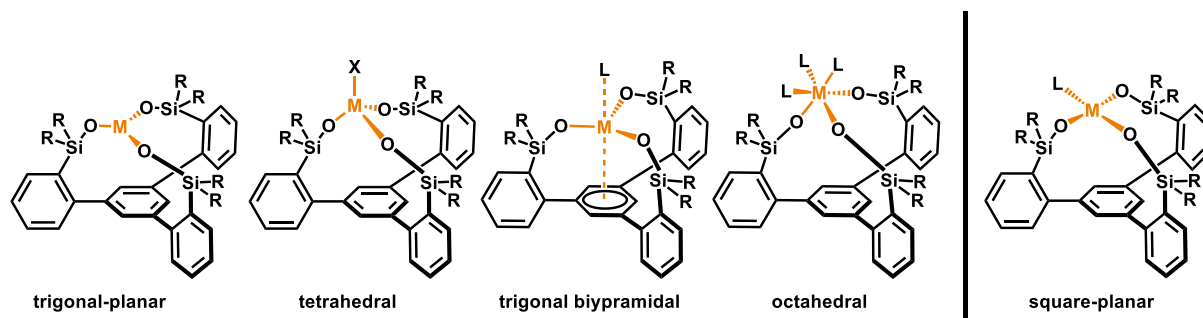


Figure 53: Coordination geometries supported by the ‘canopy ligands’ and a possible future extension of the list.

The successful application of one of the newly synthesized complexes as a catalyst in the high-temperature cyclization of citronellal to isopulegol opens the door to a whole range of Lewis acid catalyzed transformations. In the future, it could be worthwhile to investigate other reactions that require particularly robust catalysts. Beyond that, processes that demand tunable steric bulk around the metal center for controlling the selectivity may be of interest. A candidate might be *exo/endo*-selective Diels-Alder reactions.^[304] Yamamoto and coworkers showed that bulky Lewis acids can be used to control the selectivity.^[302] It has been proposed that the shape of the cavity around the metal center influences which transition state is favored (shallow: *exo*; tight and narrow: *endo*).^[305]

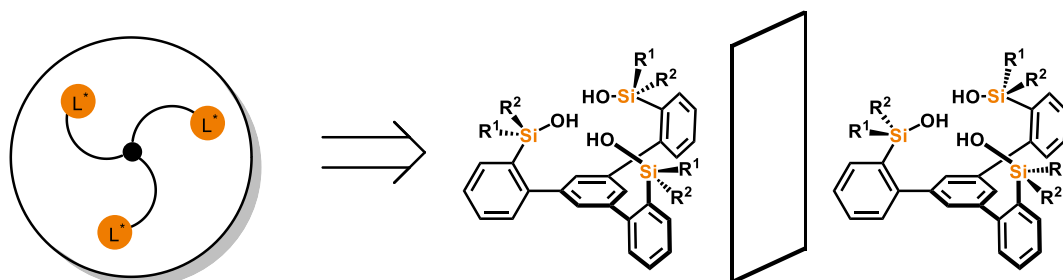
Table 13: *Exo/endo* selectivity in Diels-Alder reactions using aluminum-based Lewis acids.

Complexes			
Entry	Complex	mol%	<i>Exo/endo</i>
1	236	150	96:4 ^[302]
2	AlMe₃	—	63:37 ^[302]
3	Al1•THF	6	50:50

In an exploratory experiment, complex **Al1•THF** was used to catalyze the Diels-Alder reaction of cyclopentadiene and a simple dienophile (*table 13*). The selectivity was compared to the results obtained with a Lewis acid comprising sizeable steric bulk (*entry 1*) and trimethylaluminum (*entry 2*). While there is exactly no selectivity with the aluminum complex equipped with a ‘canopy ligand’ (*entry 3*), this result is notably different from the other two outcomes. By deliberately changing the substituents on the silanolate ligands, it might be possible to tilt the selectivity in one way or the other.

A more ambitious endeavor would be to render the ‘canopy ligands’ chiral and apply them to enantioselective transformations. Stereogenic silanols have moved into the focus of organic chemists in recent years and methods for their synthesis are becoming available.^[306] Introducing three Si-chiral stereocenters in a ‘canopy ligand’ would result in a C_3 -symmetrical chiral ligand (*scheme 105*). Molecules of this type have been discussed for applications in asymmetric catalysis.^[307] Chiral C_3 -symmetrical ligands might offer an alternative to the privileged C_2 -symmetric ligands that have dominated the field. Based on symmetry considerations the former are speculated to be more effective in conferring enantioselectivity on reactions with metal intermediates with an octahedral coordination geometry.^[308]

C_3 -symmetrical chiral ligands

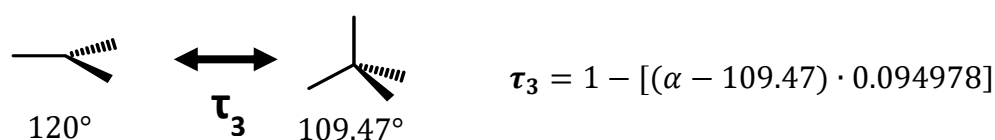


Scheme 105: Possible future application of ‘canopy ligands’ as C_3 -symmetrical chiral ligands

2.4 Summary

In the second part of this thesis, the coordination chemistry of a specific class of tridentate tris(silanolate) ligands was explored. The so-called ‘canopy ligands’ are characterized by their preorganization into a tripodal shape, allowing for facile and high yielding complexation reactions. At the same time, the ligands are malleable enough to be able to adapt to many different central metals, coordination geometries, and oxidation states. This analysis is supported by the preparation of numerous novel complexes comprising ‘canopy ligands’. In addition to the two previously known transition metals, complexes with three other transition metals as well as three main group metals and one metalloid are reported. In parallel, the groups of *Cui* and *Mazzanti* further expanded the collection by adding complexes with lanthanides and actinides.^[215]

The ‘canopy ligands’ are able to ligate to vastly different cation sizes, from boron (III) to bismuth (III).^[226] Metals in the oxidation states III to VI have been supported with the ligands. It was shown that all kinds of different additional ligands can be incorporated into metal complexes with ‘canopy ligands’: neutral Lewis bases (tetrahydrofuran, pyridine), halides (chloride), oxides, nitridos,^[217] but also organic ligands (alkyl, alkylidene, and alkylidyne fragments)^[76] and a weakly coordinated arene. The tripodal tris(silanolate) ligands also permit different coordination environments. Although most of the new complexes lie somewhere on the spectrum between trigonal planar and tetrahedral geometries, there are also examples for trigonal bipyramidal and octahedral complexes. To better illustrate the continuum between the ideal geometries for trigonal planar and tetrahedral, in which many of the novel complexes fall, a new geometry index was defined in cooperation with Dr. R. Goddard (equation 1).

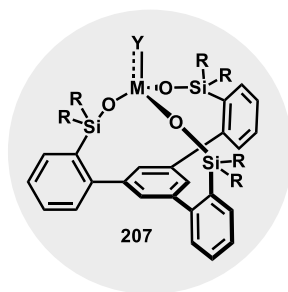


Equation 1: Definition of the geometry index τ_3 indicating if the coordination geometry of a given complex is closer to the ideal angles for trigonal planar or tetrahedral coordination environments.

The geometry index τ_3 indicates if the average O–M–O angle (α) in a given complex with a ‘canopy ligand’ is closer to the ideal angle for a trigonal planar complex ($\tau_3 = 0$) or for a tetrahedral complex ($\tau_3 = 1$). Table 14 provides an overview of selected bond lengths, angles, and calculated τ_3 values for several of the newly reported complexes. This is meant to highlight the large structural space accessible for coordination compounds comprising ‘canopy ligands’. The presented studies also investigated the geometric constraints imposed on the silanolate ligands by the tripodal scaffold, as well as the resulting effect on the ligands electronic influence on the central metal. The obtained picture is ambiguous and the outcome appears to depend heavily on the bound metal cation.

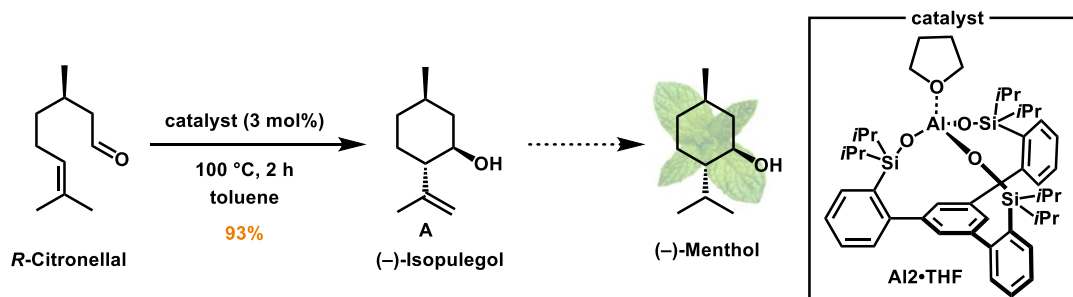
Summary

Table 14: Selected bond lengths, angles, and calculated τ_3 values for the solid-state structures of a series of newly synthesized complexes comprising ‘canopy ligands’.



Entry	M	Y	R	$\angle \text{O-M-O} [^\circ]$			$\angle \text{Si-O-M} [^\circ]$			M-Y [Å]	O-M [Å]			τ_3	M- $\Delta(\text{C}_6)$ [Å]	M- $\Delta(\text{OOO})$ [Å]
B2	B ^{III}	—	iPr	119.9	119.7	120.4	140.1	139.3	147.9	—	1.368	1.369	1.359	0.00	2.935	0.015
Al1	Al ^{III}	N (Py)	Ph	115.7	117.4	114.4	171.5	164.5	160.1	1.9719	1.7058	1.7090	1.7102	0.40	3.465	0.361
Al2	Al ^{III}	O (THF)	iPr	114.9	118.5	115.9	167.3	167.1	171.4	1.902	1.696	1.702	1.697	0.38	3.390	0.325
Ga1	Ga ^{III}	N (Py)	Ph	120.1	113.0	113.2	158.6	171.5	155.8	2.0164	1.7753	1.7755	1.7837	0.43	3.496	0.383
Bi1	Bi ^{III}	C ₆ H ₆	iPr	94.3	94.3	94.3	138.9	138.9	138.9	3.205	2.0482	2.0482	2.0482	—	4.017	1.091
Ti2	Ti ^{IV}	Cl	iPr	111.0	111.0	111.0	162.8	162.8	162.8	2.2451	1.7711	1.7711	1.7711	0.86	3.614	0.544
Ti3	Ti ^{IV}	Me	iPr	114.1	114.1	114.1	162.8	162.8	162.8	2.062	1.7864	1.7865	1.7865	0.56	3.511	0.443
V1	V ^V	O	Ph	111.7	109.1	109.0	173.4	176.6	172.4	1.5883	1.7452	1.7463	1.7437	0.95	3.543	0.567
V2	V ^V	O	iPr	109.9	109.9	109.9	165.8	165.8	165.8	1.5917	1.7454	1.7454	1.7454	0.96	3.576	0.570
V3	V ^{III}	O (THF)	iPr	121.6	115.8	119.4	173.2	171.4	163.1	2.0454	1.8378	1.8314	1.8339	0.10	3.220	0.192
V4	V ^V	C (C ₄ H ₆)	iPr	106.5	127.9	110.8	173.9	166.1	170.9	1.8566	1.793	1.736	1.821	0.47	3.377	0.399
Fe1	Fe ^{III}	O (THF)	iPr	121.13	113.2	116.2	173.4	161.6	162.7	2.043	1.818	1.793	1.816	0.30	3.375	0.326

Examining selected complexes through heteronuclear (solid-state and solution) NMR spectroscopy showed some of them to be adequate molecular models for metal sites in heterogeneous catalysts based on silica. For other complexes, the correlation between their spectroscopic signature and that of corresponding surface sites was less obvious. Nevertheless, the complexes synthesized with tripodal tris(silanolate) ligands could be valuable tools for research groups specialized in elucidating reaction mechanisms in heterogeneous catalysis. The potential of the novel complexes for homogenous catalysis was demonstrated by the cyclization reaction of citronellal to isopulegol as the key step of the industrial route to (–)-menthol. Close inspection of a previously reported aluminum catalyst featuring monodentate phenolate ligands revealed it to suffer from poor stability at high temperatures, giving rise to side products. Moreover, the insufficient temperature stability of these systems made the separation of product and catalyst tedious and recycling of the later essentially impossible. In contrast, the complex **Al₂•THF** endowed with three silanolate ligands tethered together by an arene ring showed excellent stability at 100 °C under the reaction conditions (*scheme 106*). It catalyzes the reaction with good diastereoselectivity and excellent chemoselectivity. The improved stability renders a separation of product and catalyst *via* distillation possible. A cycling experiment with no loss of activity and selectivity over five cycles underlined its robust performance.



Scheme 106: A high-temperature stable catalyst for the cyclization of citronellal to isopulegol.

These exploratory studies with the highly enabling ‘canopy ligands’ provide the basis for potential future applications of the obtained metal complexes in homogeneous catalysis. The unique properties of silanolates and the tridentate chelating nature of the ligands are expected to be powerful assets in developing robust and selective catalysts for organic synthesis.

3 Experimental Section

3.1 General

General laboratory techniques

Unless stated otherwise, all reactions were carried out in glassware that had previously been heated in high vacuum with a Bunsen burner, cooled to ambient temperature, and then filled with argon. The cannulas and syringes used to transfer reagents and solutions were carefully flushed with argon before use. Manipulations of air- and moisture-sensitive substances were carried out using standard Schlenk techniques under argon overpressure.

The solvents were purified by distillation over the drying agents indicated and were transferred under argon: tetrahydrofuran (magnesium/anthracene), toluene (NaAlEt₄), dichloromethane (CaH₂), 1,2-dimethoxyethane (CaH₂), acetonitrile (CaH₂), diethyl ether (Na/K), and *n*-pentane (Na/K). Pyridine was dried by an absorption purification system based on molecular sieves (3 Å). Dowtherm™ A (mixture of biphenyl and biphenyl ether) was degassed by sparging with argon for 1 h and dried over molecular sieves (3 Å). Deuterated solvents were stored over molecular sieves (3 Å) for a minimum of five days prior to use.

The molecular sieves used in this investigation were dried for 24 h at 150 °C (sand bath) under vacuum (10⁻³ mbar) prior to use and were stored and transferred under argon atmosphere.

All commercially available compounds (abcr, Sigma-Aldrich, TCI, Strem) were used as received, unless stated otherwise. Known compounds were prepared according to the literature: **122**^[104a], **242**^[309], **212•THF**^[228], **215**^[234], **196**^[251a], and **211**^[222]. Ligands for **S2** and **S3** were graciously provided by *Daniel Rütter*.^[217] Ligand **117** was prepared by Dr. *L. Martínez-Rodríguez* as described in the literature.^[310] Substrates for alkyne metathesis reactions were prepared as described in the literature.^[73, 107, 118, 311] Starting materials for the intermediates of natural product syntheses were provided by Dr. *D. Dalling*, Dr. *C. Mathes*, Dr. *O. Larionov*, Dr. *K. Gebauer* and Dr. *S. Spohr*.^[66a, 79b, c, 102c, 146b]

Flash chromatography was carried out on silica gel (Merck, type 9385, 230 - 400 mesh, 60 Å pore diameter) as stationary phase. Reaction control was performed on ready-to-use films for thin-layer chromatography (40 × 80 mm, Polygram® SIL G/UV254). Detection was achieved under UV-light (254 nm) and by staining with either acidic p-anisaldehyde, cerium ammonium molybdate, or basic potassium permanganate solution.

Nuclear magnetic resonance spectroscopy (NMR)

Spectra were acquired on Bruker AvanceIII 300, 400, 500 MHz or an Avance Neo 600 MHz NMR (equipped with a Bruker BBO CryoProbe) spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to tetramethylsilane (TMS), coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the

TMS scale (CDCl_3 : $\delta_{\text{C}} = 77.16$ ppm; residual ^1H : $\delta_{\text{H}} = 7.26$ ppm; CD_2Cl_2 : $\delta_{\text{C}} = 53.84$ ppm; residual ^1H : $\delta_{\text{H}} = 5.32$ ppm; C_6D_6 : $\delta_{\text{C}} = 128.06$ ppm, residual ^1H : $\delta_{\text{H}} = 7.16$ ppm; $[\text{D}_8]$ -toluene: $\delta_{\text{C}} = 20.60$ ppm; residual ^1H : $\delta_{\text{H}} = 2.09$ ppm).^[312] ^{29}Si NMR spectra were acquired with a polarization transfer pulse sequence (refocussed INEPT) and broadband proton decoupling. ^{95}Mo NMR spectra were acquired with the aring pulse sequence to minimize acoustic ringing from the NMR probe. The $\pi/2$ pulse was calibrated for a 2 M Na_2MoO_4 in D_2O and had a typical length of 22.5 μs at a power of 85 W.

^{95}Mo , ^{29}Si , ^{51}V , and ^{31}P chemical shifts were referenced indirectly to the ^1H chemical shift of the solvent according to IUPAC recommendations using the *xiref* macro in Bruker Topspin. ^{29}Si chemical shifts are reported relative to TMS ($\delta = 0$ ppm; $\Xi = 19.867187\%$), ^{31}P chemical shifts are reported relative to H_3PO_4 ($\delta = 0$ ppm; $\Xi = 40.480742\%$), ^{51}V chemical shifts are reported relative to VOCl_3 ($\delta = 0$ ppm; $\Xi = 26.302948\%$), and ^{95}Mo chemical shifts are reported relative to Na_2MoO_4 ($\delta = 0$ ppm; $\Xi = 6.516926\%$). The multiplicities of the signals are described by the following abbreviations: s: singlet, d: doublet, t: triplet, q: quartet, pent: quintet, sept: septet, m: multiplet, bs: broad signal.

Gas Chromatography (GC)

GC was measured on an Agilent Technologies GC 7890B system with a FID detector and a DB-Waxetr (30 m $\times$ 0.25 mm $\times$ 0.25 μm) column using hydrogen as a carrier gas. As a chiral stationary phase a BGB-174/BGB-1701 (30 m $\times$ 0.25 mm $\times$ 0.25 μm) column was used. GC-MS was measured on a Shimadzu GCMS-QP2010 Ultra and on a Finnigan SSQ 7000 Quadrupole MS instrument.

Infrared spectroscopy (IR)

IR spectra were measured on a Spectrum One (Perkin-Elmer) spectrometer at ambient temperature and are given in wavenumbers ($\tilde{\nu}$) in cm^{-1} . Samples were prepared as a neat film or film by evaporation of a solution in CDCl_3 prior to direct application on the ATR unit.

Mass spectrometry (MS)

High-resolution mass spectra (HRMS) were measured with a Finnigan MAT 95 spectrometer (EI) or a Bruker APEX III FT-ICR-MS (ESI). All values are given in mass units per elementary charge (m/z).

Cyclic voltammetry (CV)

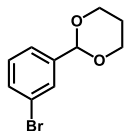
Cyclic voltammograms were collected using a 3-electrode cell consisting of a 3 mm glassy carbon working electrode, platinum wire as the counter electrode, and a bare silver wire as a pseudoreference electrode in an argon-filled glovebox. Sublimed ferrocene was added as the internal reference.

Elemental analysis: H. Kolbe, Mülheim an der Ruhr.

3.2 Preparative Procedures

3.2.1 Ligands

Compound **125a**

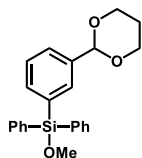


A 100 mL, two-necked round bottom flask equipped with a Dean-Stark apparatus (reflux condenser and distilling trap filled with toluene) and connected to a vacuum/argon manifold was charged with 5-bromobenzaldehyde (6.85 g, 37.0 mmol), toluene (50 mL) and propan-1,3-diol (2.94 mL, 40.7 mmol). *p*-Toluenesulfonic acid (211 mg, 1.11 mmol) was added and the solution was stirred at reflux temperature overnight. After cooling to ambient temperature, the organic layer was washed with an aqueous solution of sodium bicarbonate (2 × 50 mL) and brine (1 × 50 mL). The organic phase was dried over magnesium sulfate and filtered, and the solvents were evaporated. The residue was purified by flash chromatography on silica (hexane/ethyl acetate, 19:1 to 9:1) to give the title compound as a yellow liquid (7.25 g, 81%).

¹H NMR (400 MHz, CDCl₃): δ 7.67 (t, *J* = 1.8 Hz, 1H), 7.50 – 7.36 (m, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 5.46 (s, 1H), 4.26 (ddd, *J* = 12.0, 5.0, 1.5 Hz, 2H), 4.03 – 3.90 (m, 2H), 2.21 (dtt, *J* = 13.6, 12.4, 5.0 Hz, 1H), 1.45 (ddt, *J* = 13.6, 2.6, 1.3 Hz, 1H).

The spectroscopic data was found to be in agreement with the data reported in the literature.^[313]

Compound **126a**



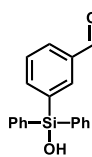
A 100 mL Schlenk flask was charged with compound **125a** (7.25 g, 29.8 mmol) and tetrahydrofuran (30 mL). The solution was cooled to 0 °C before a solution of isopropylmagnesium chloride lithium chloride complex (1.25 M in tetrahydrofuran, 9.18 mL, 11.9 mmol) was added dropwise. After stirring for 5 min, a solution of *n*-butyllithium (1.6 M in hexane, 14.6 mL, 23.9 mmol) was added dropwise and the resulting grey suspension was stirred for 1 h at 0 °C.

A 250 mL, two-necked round bottom flask equipped with a pressure equilibrating dropping funnel and connected to a vacuum/argon manifold was charged with dimethoxydiphenylsilane (13.5 mL, 59.6 mmol) and tetrahydrofuran (25 mL). The resulting solution was cooled to 0 °C. The Grignard reagent was transferred into the dropping funnel with a LDPE tube and argon overpressure and then slowly added to the dimethoxydiphenylsilane solution at 0 °C. Once the addition was complete, the mixture was allowed to reach ambient temperature and stirring was continued overnight. The reaction was carefully quenched by the addition of an saturated aqueous solution of ammonium chloride (100 mL). The layers were separated and the aqueous phase was extracted with ethyl acetate (3 × 75 mL). The combined organic layers were dried over magnesium sulfate and filtered, and the solvents were evaporated. The residue was

purified by flash chromatography on silica (hexane/ethyl acetate, 9:1) to give the title compound as a colorless oil (9.58 g, 85%).

¹H NMR (400 MHz, CDCl₃): δ 7.76 (ddt, *J* = 1.7, 1.1, 0.6 Hz, 1H), 7.67 – 7.61 (m, 6H), 7.49 – 7.36 (m, 7H), 5.50 (s, 1H), 4.26 (ddt, *J* = 10.5, 5.1, 1.5 Hz, 2H), 4.02 – 3.91 (m, 2H), 3.64 (s, 3H), 2.23 (ddt, *J* = 13.5, 12.4, 5.0 Hz, 1H), 1.43 (ddt, *J* = 13.5, 2.7, 1.4 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃): δ 138.3, 136.1, 135.61, 135.56, 134.0, 133.9, 133.1, 130.2, 128.1, 128.0, 128.0, 127.9, 101.9, 67.5, 52.0, 25.9. **²⁹Si NMR** (60 MHz, CDCl₃): δ –11.3. **IR** (film): $\tilde{\nu}$ 2965, 1835, 1737, 1589, 1428, 1371, 1237, 1102, 1081, 995, 770, 738, 698, 504. **HRMS** (EI) calc. for C₂₃H₂₄O₃SiNa [M + Na]⁺: 399.13869; found: 399.13871.

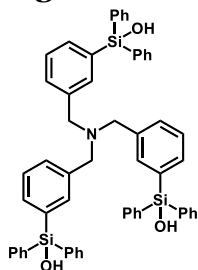
Compound 127a



A 500 mL, one-neck round bottom flask equipped with a 100 mL dropping funnel was charged in air with compound **126a** (9.58 g, 24.53 mmol) and tetrahydrofuran (245 mL). The solution was cooled to 0 °C before hydrochloric acid (6 M in water, 62 mL, 0.37 mol) was added *via* the dropping funnel over 10 min. The mixture was warmed to ambient temperature and stirred for 1 h. The solution was carefully neutralized with an aqueous solution of sodium bicarbonate and extracted with dichloromethane (3 × 150 mL). The combined organic layers were dried over sodium sulfate and filtered, and the solvents were evaporated. The residue was purified by flash chromatography on silica (toluene/ethyl acetate, 10:1) to give the title compound as a colorless solid (6.88 g, 92%).

¹H NMR (400 MHz, CDCl₃): δ 9.97 (s, 1H), 8.18 – 8.12 (m, 1H), 7.92 (ddt, *J* = 17.4, 7.3, 1.4 Hz, 2H), 7.66 – 7.60 (m, 4H), 7.58 – 7.52 (m, 1H), 7.51 – 7.44 (m, 2H), 7.44 – 7.37 (m, 4H), 2.83 (bs, 1H). **¹³C NMR** (101 MHz, CDCl₃): δ 192.9, 141.1, 137.00, 136.96, 135.8, 135.1, 134.4, 130.9, 130.6, 128.7, 128.3. **²⁹Si NMR** (60 MHz, CDCl₃): δ –13.4. **IR** (film): $\tilde{\nu}$ 3414 (b), 3070, 3051, 1736, 1696, 1587, 1428, 1372, 1240, 1114, 1044, 862, 697, 645, 505, 457. **HRMS** (ESI) calc. for C₁₉H₁₆O₂SiNa [M + Na]⁺: 327.08118; found: 327.08071.

Ligand 116a

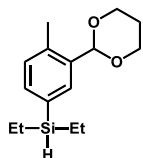


A 500 mL, two-necked round bottom flask connected to a vacuum/argon manifold was charged with compound **127a** (8.20 g, 26.9 mmol), tetrahydrofuran (270 mL) and ammonium acetate (642 mg, 8.33 mmol). Sodium trisacetoxyborohydride (9.10 g, 42.9 mmol) was added in portions and the resulting suspension was stirred for 24 h. The solution was neutralized with an aqueous solution of sodium bicarbonate and extracted with ethyl acetate (3 × 200 mL). The combined organic layers were dried over magnesium sulfate and filtered, and the solvents were evaporated. The residue was purified by flash chromatography on silica (dichloromethane/methanol, 99:1 to 98:2) to give a mixture of siloxane dimers/oligomers and ligand **116a** as a colorless powder.

A 500 mL, one-necked flask was charged in air with this crude material and tetrahydrofuran (400 mL). An aqueous solution of sodium hydroxide (2 M, 400 mL) was added and the mixture was stirred overnight. The layers were separated and the aqueous layer was extracted with ethyl acetate (3 × 300 mL). The combined organic phases were washed with brine (300 mL), dried over magnesium sulfate and filtered. The solvents were evaporated to give the title compound as a colorless powder (4.75 g, 60%).

¹H NMR (600 MHz, CDCl₃): δ 8.29 (t, *J* = 1.5 Hz, 3H), 7.51 – 7.45 (m, 12H), 7.39 – 7.32 (m, 9H), 7.29 (dt, *J* = 7.7, 1.6 Hz, 3H), 7.22 (dddd, *J* = 7.5, 6.5, 2.4, 0.7 Hz, 15H), 4.74 (s, 3H), 3.61 (s, 6H). **¹³C NMR** (151 MHz, CDCl₃): δ 139.9, 135.4, 135.3, 135.1, 135.0, 133.5, 130.5, 130.0, 128.0, 127.6, 57.8. **²⁹Si NMR** (119 MHz, CDCl₃): δ –13.5. **IR** (film): $\tilde{\nu}$ 3290 (b), 3048, 1428, 1117, 828, 791, 740, 712, 699, 541, 509. **HRMS** (ESI) calc. for C₅₇H₅₀NO₃Si₃ [M – H][–] : 880.31041; found: 880.31091.

Compound 13ob



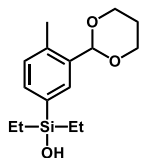
A 50 mL Schlenk flask was charged with compound **125b** (4.00 g, 15.6 mmol) and tetrahydrofuran (30 mL). The solution was cooled to 0 °C and a solution of isopropylmagnesium chloride lithium chloride complex (1.25 M in tetrahydrofuran, 4.78 mL, 6.22 mmol) was added dropwise. After stirring for 5 min, a solution of *n*-butyllithium (1.6 M in hexane, 7.78 mL, 12.4 mmol) was added dropwise and the resulting grey suspension was stirred for 1 h at 0 °C.

A 250 mL, two necked round bottom flask equipped with a pressure equilibrating dropping funnel and connected to a vacuum/argon manifold was charged with Et₂SiH₂ (6.01 mL, 46.7 mmol) and tetrahydrofuran (20 mL). The resulting solution was cooled to 0 °C. The Grignard reagent was transferred into the dropping funnel with a LDPE tube and argon overpressure and then slowly added to the cooled diethylsilane solution. Once the addition was complete, the mixture was allowed to warm to ambient temperature and stirring was continued overnight. The reaction was carefully quenched with an aqueous, saturated solution of ammonium chloride (40 mL). The layers were separated and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over magnesium sulfate and filtered, and the solvents were evaporated. The residue was purified by flash chromatography on silica (hexane/ethyl acetate, 12:1) to give the title compound as a colorless oil (3.88 g, 94%).

¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, *J* = 1.3 Hz, 1H), 7.39 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 5.61 (s, 1H), 4.29 (ddt, *J* = 10.5, 5.0, 1.4 Hz, 2H), 4.20 (p, *J* = 3.4 Hz, 1H), 4.02 – 3.96 (m, 2H), 2.41 (s, 3H), 2.27 (qt, *J* = 13.5, 5.0 Hz, 1H), 1.45 (dtt, *J* = 13.4, 2.6, 1.4 Hz, 1H), 1.01 (t, *J* = 7.8 Hz, 6H), 0.84 (td, *J* = 8.3, 3.3 Hz, 4H). **¹³C NMR** (101 MHz, CDCl₃): δ 136.9, 135.9, 135.0, 132.5, 132.1, 130.0, 100.6, 77.2, 77.0, 76.8, 67.5, 25.8, 18.9, 8.2, 3.5. **²⁹Si NMR**

(60 MHz, CDCl₃): δ -5.1. **IR** (film): $\tilde{\nu}$ 2954, 2872, 2102, 1377, 1235, 1149, 1106, 998, 967, 895, 801, 712, 687, 478. **HRMS** (EI) calc. for C₁₅H₂₄O₂Si [M]⁺: 264.15401; found: 264.15419.

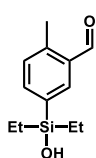
Compound 131b



A 50 mL, one-necked round bottom flask was charged in air with compound **130b** (3.87 g, 14.7 mmol) and dichloromethane (30 mL). The solution was cooled to 0 °C before *m*-chloroperoxybenzoic acid (77% *w/w*, 3.62 g, 16.1 mmol) was added in portions. After stirring at ambient temperature for 5 h, the mixture was transferred into a separation funnel and was washed with a saturated aqueous solution of sodium bicarbonate (2 × 60 mL) and aqueous sodium hydroxide (1 M, 60 mL). The organic layer was dried over magnesium sulfate and filtered, and the solvents were evaporated to give the title compound as a colorless liquid (3.84 g, 92%).

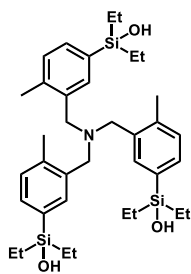
¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J* = 1.3 Hz, 1H), 7.42 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.16 (dt, *J* = 7.4, 0.7 Hz, 1H), 5.61 (s, 1H), 4.28 (ddt, *J* = 10.4, 5.0, 1.4 Hz, 2H), 3.99 (dddd, *J* = 12.6, 10.5, 2.6, 1.5 Hz, 2H), 2.41 (d, *J* = 0.6 Hz, 3H), 2.36 – 2.17 (m, 1H), 1.74 (bs, 1H), 1.45 (dtt, *J* = 13.5, 2.6, 1.3 Hz, 1H), 1.03 – 0.94 (m, 6H), 0.91 – 0.76 (m, 4H). **¹³C NMR** (101 MHz, CDCl₃): δ 137.5, 136.0, 134.4, 134.1, 131.1, 130.2, 100.7, 67.7, 25.9, 19.1, 6.7, 6.5. **IR** (film): $\tilde{\nu}$ 3433 (b), 2956, 2874, 1460, 1378, 1236, 1149, 1107, 1010, 897, 821, 719, 480. **HRMS** (EI) calc. for C₁₅H₂₄O₃Si [M]⁺: 280.14892; found: 280.14896.

Compound 132b



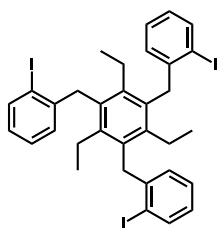
A 250 mL, one-neck round bottom flask equipped with a 50 mL dropping funnel was charged in air with compound **131b** (3.87 g, 13.8 mmol) and tetrahydrofuran (120 mL). The solution was cooled to 0 °C before hydrochloric acid (12 M in water, 17.0 mL, 207 mmol) was added *via* the dropping funnel over 10 min. After 20 min at 0 °C, the solution was carefully neutralized with a saturated aqueous solution of sodium bicarbonate and the aqueous phase was extracted with dichloromethane (3 × 100 mL). The combined organic layers were dried over sodium sulfate and filtered, and the solvents were evaporated to give the title compound as a colorless liquid (2.72 g, 89%). Compound **132b** is prone to siloxane formation and was immediately used in the subsequent step.

¹H NMR (400 MHz, CDCl₃): δ 10.29 (s, 1H), 7.98 (d, *J* = 1.4 Hz, 1H), 7.68 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 2.68 (d, *J* = 0.7 Hz, 3H), 1.94 (s (br), 1H), 1.05 – 0.96 (m, 6H), 0.93 – 0.82 (m, 4H). **¹³C NMR** (101 MHz, CDCl₃): δ 193.4, 142.1, 138.9, 137.8, 135.4, 133.8, 131.5, 19.9, 6.7, 6.6. **IR** (film): $\tilde{\nu}$ 3390, 2956, 2876, 1698, 1684, 1594, 1202, 1110, 1091, 1008, 899, 828, 725. **HRMS** (ESI) calc. for C₁₂H₁₈O₂SiNa [M + Na]⁺: 245.09683; found: 245.09693.

Ligand 134b

A 250 mL, two-necked round bottom flask connected to a vacuum/argon manifold was charged with compound **132b** (2.72 g, 12.2 mmol), tetrahydrofuran (100 mL) and ammonium acetate (304 mg, 3.95 mmol). Sodium triacetoxyborohydride (3.81 g, 18.0 mmol) was added in portions and the resulting suspension was stirred for 24 h. Additional sodium triacetoxyborohydride (1.00 g, 4.72 mmol) was then added and stirring continued for an additional 48 h. For work up, the solution was cooled to 0 °C and carefully neutralized with an aqueous solution of sodium bicarbonate. The mixture was concentrated *via* rotary evaporation until 50 mL remained and was then extracted with *tert*-butyl methyl ether (3 × 50 mL). The combined organic layers were washed with an aqueous solution of sodium hydroxide (1 M, 40 mL), dried over magnesium sulfate and filtered, and the solvents were evaporated. The residue was purified by flash chromatography on silica (hexane/ethyl acetate, 5:1 to 4:1) to give the title compound as a colorless powder (873 mg, 35%).

¹H NMR (600 MHz, CDCl₃): δ 8.31 (s, 3H), 7.20 (dd, *J* = 7.4, 1.0 Hz, 3H), 7.08 (d, *J* = 7.4 Hz, 3H), 4.28 (s, 3H), 3.64 (s, 6H), 2.25 (s, 9H), 0.87 (t, *J* = 7.9 Hz, 18H), 0.71 (m, 12H). **¹³C NMR** (151 MHz, CDCl₃): δ 137.7, 137.3, 134.7, 134.1, 131.3, 129.4, 55.0, 19.4, 6.7, 6.7. **²⁹Si NMR** (119 MHz, CDCl₃): δ 7.5. **¹⁵N NMR** (61 MHz): δ -338. **IR** (film): $\tilde{\nu}$ 3312 (b), 2955, 2912, 2876, 2801, 1460, 1359, 1236, 1086, 1009, 967, 819, 727. **HRMS** (ESI) calc. for C₃₆H₅₆NO₃Si₃ [M - H]⁻: 634.35736; found: 634.35773.

Compound 123⁷

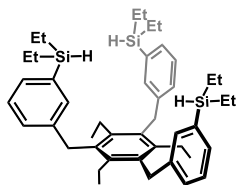
A 250 mL, two-necked flask equipped with an argon manifold was charged with silane **122** (2.31 g, 3.56 mmol) and dichloromethane (150 mL). The solution was cooled to -20 °C and iodine monochloride (0.56 mL, 11.0 mmol) was added dropwise. After stirring at -20 °C for 10 min, a saturated aqueous solution of sodium thiosulfate (70 mL) was added and the mixture was allowed to warm to ambient temperature. The layers were separated and the organic layer was washed with saturated aqueous solutions of sodium thiosulfate (3 × 70 mL) and brine (2 × 70 mL). The organic layer was dried over magnesium sulfate, filtered, and the solvents were removed *via* rotary evaporation. The title compound **123** was obtained as a beige solid (2.30 g, 2.84 mmol, 80%).

¹H NMR (400 MHz, CDCl₃) δ 7.49 (dt, *J* = 7.8, 1.4 Hz, 3H), 7.37 (s, 3H), 7.02 (t, *J* = 7.8 Hz, 3H), 6.90 (dt, *J* = 7.8, 1.3 Hz, 3H), 4.09 (s, 6H), 2.37 (q, *J* = 7.5 Hz, 6H), 1.09 (t, *J* = 7.5 Hz, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.7, 141.6, 137.0, 134.9, 133.3, 130.3, 126.8, 94.8, 34.0,

⁷ The synthesis of compound **123** was already reported in the author's master's thesis.

23.7, 15.2. **IR** (film): $\tilde{\nu}$ 2963, 2927, 2897, 2869, 1588, 1561, 1486, 1470, 1427, 1415, 1375, 1063, 935, 907, 769, 733, 680, 655. **HRMS** (EI) calc. for $C_{33}H_{33}I_3$ [M]: 809.97164; found: 809.97137.

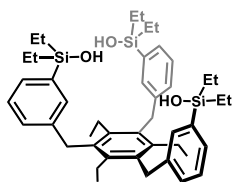
Compound S1



A 100 mL, two-necked flask equipped with an argon manifold was charged with **123** (300 mg, 0.37 mmol) and diethyl ether (21 mL). The resulting mixture was cooled to $-125\text{ }^{\circ}\text{C}$ using a bath of *n*-pentane and liquid nitrogen. A solution of *tert*-butyllithium (1.7 M in *n*-pentane, 1.33 mL, 2.26 mmol) was added dropwise and the mixture was allowed to warm to ambient temperature. After stirring for 1 h, the mixture was cooled to $-125\text{ }^{\circ}\text{C}$ before diethylsilane (0.29 mL, 2.22 mmol) was added dropwise. The mixture was then allowed to warm to ambient temperature and stirring was continued overnight. The reaction was carefully quenched by the addition of ethanol (3 mL) and water (30 mL) at $0\text{ }^{\circ}\text{C}$. The layers were separated and the aqueous layer was extracted with ethyl acetate ($3 \times 20\text{ mL}$). The combined organic layers were dried over magnesium sulfate, filtered, and the solvents removed under reduced pressure (rotary evaporation). The residue was purified by flash chromatography on silica gel (*n*-pentane / dichloromethane 30:1) to give **S1** (193 mg, 75%) as a white solid.⁸

¹H NMR (600 MHz, CDCl_3) δ 7.30 (dt, $J = 7.3, 1.2\text{ Hz}$, 3H), 7.27 (dt, $J = 1.6, 0.7\text{ Hz}$, 3H), 7.20 (td, $J = 7.4, 0.6\text{ Hz}$, 3H), 6.93 (ddd, $J = 7.7, 2.1, 1.2\text{ Hz}$, 3H), 4.16 (p, $J = 3.3\text{ Hz}$, 3H), 4.14 (s, 6H), 2.44 (q, $J = 7.5\text{ Hz}$, 6H), 1.12 (t, $J = 7.5\text{ Hz}$, 9H), 1.01 – 0.91 (m, 18H), 0.84 – 0.74 (m, 12H). **¹³C NMR** (151 MHz, CDCl_3) δ 141.5, 140.5, 135.5, 134.5, 134.1, 132.1, 128.5, 128.0, 34.7, 23.8, 15.3, 8.3, 3.6. **²⁹Si NMR** (119 MHz, CDCl_3): δ -5.3. **IR** (film): $\tilde{\nu}$ 2956, 2932, 2911, 2873, 2107, 1458, 1408, 1117, 1013, 972, 808, 774, 705. **HRMS** (APPIpos) calc. for $C_{45}H_{66}Si_3$ [M]⁺: 690.44668; found: 690.44615.

Ligand 115b



A 250 mL, one-necked round bottom flask was charged in air with compound **S1** (853 mg, 1.23 mmol), dichloromethane (70 mL) and an aqueous buffer solution (25 mL, 0.5 M NaHCO_3 , pH = 8). The solution was cooled to $0\text{ }^{\circ}\text{C}$ before *m*-chloroperoxybenzoic acid (77% *w/w*, 1.00 g, 4.07 mmol) was added in portions. After stirring at ambient temperature for 1.5 h, the mixture was transferred into a separation funnel and was washed with a saturated aqueous solution of sodium bicarbonate ($3 \times 50\text{ mL}$). The organic layer was dried over magnesium sulfate and filtered, and the solvents were evaporated under reduced pressure (rotary evaporation). The

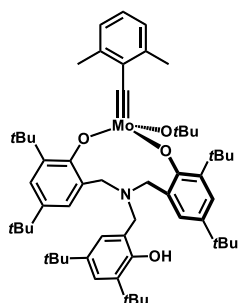
⁸ The crude product of the reaction is already very pure. In subsequent batches it was directly oxidized without further purification.

residue was purified by flash chromatography on silica gel (*n*-pentane/MTBE 7:3) to give **115b** (237 mg, 26%) as a white solid.

¹H NMR (600 MHz, CDCl₃) δ 7.29 (m, 6H), 7.23 (ddd, *J* = 5.8, 3.0, 1.9 Hz, 3H), 7.18 (dt, *J* = 2.0, 0.9 Hz, 3H), 4.16 (s, 6H), 3.31 (s, 2H), 2.47 (q, *J* = 7.5 Hz, 6H), 1.19 (t, *J* = 7.5 Hz, 9H), 0.87 (m, 18H), 0.71 (m, 12H). **¹³C NMR** (151 MHz, CDCl₃) δ 141.45, 140.32, 137.55, 134.04, 132.66, 130.90, 129.60, 127.79, 34.89, 23.83, 15.24, 6.64, 6.39. **²⁹Si NMR** (119 MHz, CDCl₃): δ 7.3. **IR** (film): $\tilde{\nu}$ 2956, 2874, 1715, 1459, 1117, 1008, 907, 826, 777, 726, 678, 647, 615, 438. **HRMS** (ESI) calc. for C₄₅H₆₆O₃Si₃Na [M + Na]⁺ : 761.42120; found: 761.42159.

3.2.2 Molybdenum Alkylidyne Complexes

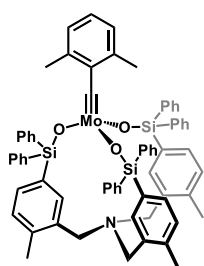
Complex 118



A 100 mL Schlenk flask was charged with ligand **117** (310 mg, 0.46 mmol) which was azeotropically dried with benzene (2×3 mL) to remove residual water. Toluene (35 mL) was added and a solution of the alkylidyne complex **18b** (200 mg, 0.46 mmol) in toluene (6 mL) was added dropwise to the solution. After stirring for 5 h, all volatile materials were removed *in vacuo* to give the title complex as a brown/red powder (420 mg, 94%). Red crystals suitable for single-crystal X-ray diffraction were grown from a concentrated solution in benzene.

^1H NMR (600 MHz, C_6D_6): δ 7.48 (d, $J = 2.4$ Hz, 2H), 7.00 (d, $J = 2.4$ Hz, 1H), 6.97 (d, $J = 2.5$ Hz, 2H), 6.70 (d, $J = 7.4$ Hz, 2H), 6.64 (dd, $J = 8.2, 6.7$ Hz, 1H), 6.28 (s, 1H), 5.47 (s, 1H), 5.01 (d, $J = 13.5$ Hz, 2H), 3.31 (s, 2H), 3.17 (d, $J = 13.6$ Hz, 2H), 2.48 (s, 6H), 1.69 (s, 9H), 1.54 (s, 18H), 1.44 (s, 18H), 1.24 (s, 9H), 1.09 (s, 9H). **^{13}C NMR** (151 MHz, C_6D_6): δ 292.7, 160.2, 149.9, 143.6, 142.7, 142.5, 138.9, 137.9, 137.2, 133.0, 129.3, 128.6, 128.2, 128.1, 127.9, 125.7, 124.4, 124.1, 123.9, 123.7, 120.4, 81.5, 69.5, 58.4, 35.5, 34.3, 34.1, 33.9, 33.2, 32.2, 31.8, 31.0, 30.8, 21.4, 20.3. **^{15}N NMR** (61 MHz, C_6D_6): δ -323.8. **^{95}Mo NMR** (26 MHz, C_6D_6): δ 349. **IR** (neat): $\tilde{\nu}$ 2951, 2900, 2867, 1477, 1444, 1414, 1359, 1286, 1264, 1238, 1204, 1169, 1149, 947, 915, 870, 841, 774, 751, 732, 695, 588, 574, 547, 527, 483, 466. **HRMS** (ESI) calc. for $\text{C}_{58}\text{H}_{85}\text{MoNO}_4\text{Na}[\text{M} + \text{Na}]^+$: 980.54249; found: 980.54168.

Complex 139b

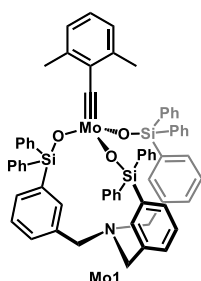


A 250 mL Schlenk flask was charged with ligand **116b** (855 mg, 0.93 mmol), which was azeotropically dried with benzene (2×4 mL) to remove any residual water. The compound was suspended in toluene (90 mL) and a solution of the alkylidyne complex **18b** (400 mg, 0.93 mmol) in toluene (10 mL) was added dropwise. After stirring for 1.5 h, all volatile materials were removed *in vacuo* to give the title complex as a yellow powder (1.04 g, 98%). Orange crystals suitable for single-crystal X-ray diffraction were grown from a concentrated solution in benzene.

^1H NMR (600 MHz, $[\text{D}_8]$ -toluene): δ 8.84 (s, 3H), 7.69 (m, 12H), 7.34 (dd, $J = 7.5, 1.0$ Hz, 3H), 7.14 (tt, $J = 7.1, 1.4$ Hz, 6H), 7.04 (t, $J = 7.6$ Hz, 12H), 6.93 (d, $J = 7.5$ Hz, 3H), 6.55 (m, 3H), 3.45 (s, 6H), 2.13 (s, 6H), 2.06 (s, 9H). **^{13}C NMR** (151 MHz, $[\text{D}_8]$ -toluene): δ 309.6, 145.6, 139.3, 138.3, 137.6, 136.5, 135.5, 134.6, 133.8, 133.2, 129.95, 129.89, 128.1, 127.9, 126.3, 54.4, 20.5, 19.4. **^{29}Si NMR** (119 MHz, $[\text{D}_8]$ -toluene): δ -10.1. **^{15}N NMR** (61 MHz): δ -333. **^{95}Mo NMR** (26 MHz, $[\text{D}_8]$ -toluene, 60 $^\circ\text{C}$): δ 495. **IR** (neat): $\tilde{\nu}$ 1427, 1192, 1113, 1094, 1023,

926, 892, 816, 740, 730, 695, 648, 561, 495, 422. **HRMS** (ESI) calc. for $C_{69}H_{63}MoNO_3Si_3Na$ $[M + Na]^+$: 1158.30620; found: 1158.30562. **Elemental analysis** (%) calc. for $C_{69}H_{63}MoNO_3Si_3$: C 73.05, H 5.60, Mo 8.46, Si 7.43; found: C 72.85, H 5.54, Mo 8.28, Si 7.23.

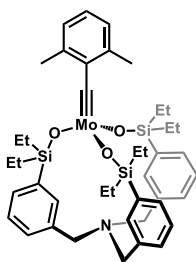
Complex 139a



A 50 mL Schlenk flask was charged with ligand **116a** (204 mg, 0.23 mmol), which was azeotropically dried with benzene (3×1.5 mL) to remove residual water. The compound was suspended in toluene (30 mL) and a solution of the alkylidyne complex **18b** (100 mg, 0.93 mmol) in toluene (8 mL) was added dropwise. After stirring for 3.5 h, all volatile materials were removed *in vacuo* to give the title complex as a yellow powder (238 mg, 94%).

1H NMR (600 MHz, $[D_8]$ -toluene): δ 8.76 (s, 3H), 7.71 – 7.62 (m, 12H), 7.40 (dt, J = 7.4, 1.3 Hz, 3H), 7.20 – 7.12 (m, 6H), 7.07 (td, J = 7.4, 0.6 Hz, 3H), 7.05 – 6.99 (m, 15H), 6.58 – 6.54 (m, 2H), 6.54 – 6.50 (m, 1H), 3.39 (s, 6H), 2.09 (s, 6H). **^{13}C NMR** (151 MHz, $[D_8]$ -toluene): δ 309.6, 145.7, 140.6, 139.4, 136.8, 136.4, 135.6, 135.0, 133.7, 130.6, 130.0, 128.1, 127.7, 126.4, 128.11, 58.1, 20.6. **^{29}Si NMR** (119 MHz, $[D_8]$ -toluene): δ -10.3. **^{95}Mo NMR** (26 MHz, $[D_8]$ -toluene, 60 °C): δ 499. **IR** (neat): $\tilde{\nu}$ 3045, 1428, 1406, 1114, 1020, 981, 915, 770, 741, 697, 540, 509, 488, 452. **HRMS** (ESI) calc. for $C_{66}H_{58}MoNO_3Si_3$ $[M + H]^+$: 1094.27731; found: 1094.27686.

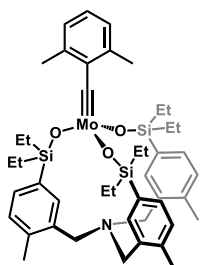
Complex 140a



A 100 mL Schlenk flask was charged with ligand **134a** (339 mg, 0.52 mmol, 90% purity), which was azeotropically dried with benzene (2×2 mL) to remove residual water. The compound was dissolved in toluene (50 mL) and a solution of the alkylidyne complex **18b** (222 mg, 0.51 mmol) in toluene (6 mL) was added dropwise. After stirring for 1 h, all volatile materials were removed *in vacuo* to give a brown residue. This residue was dissolved in

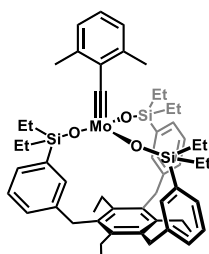
dichloromethane (3 mL) and an excess of pentane (50 mL) was added. The title complex precipitated from the solution after 3 d at -78 °C as a yellow powder and was collected by filtration (336 mg, 81%).

1H NMR (600 MHz, $[D_8]$ -toluene): δ 8.45 (s, 3H), 7.26 (dt, J = 7.3, 1.3 Hz, 3H), 7.15 (td, J = 7.4, 0.6 Hz, 3H), 7.03 – 6.99 (m, 3H), 6.85 (d, J = 7.5 Hz, 2H), 6.72 (t, J = 7.5 Hz, 1H), 3.39 (s, 6H), 2.85 (s, 6H), 1.06 – 1.00 (m, 18H), 1.01 – 0.93 (m, 6H), 0.92 – 0.84 (m, 6H). **^{13}C NMR** (151 MHz, $[D_8]$ -toluene): δ 305.7, 145.8, 140.4, 138.6, 138.0, 134.6, 131.7, 130.0, 127.6, 126.9, 127.8, 58.1, 20.8, 8.4, 7.1. **^{29}Si NMR** (119 MHz, $[D_8]$ -toluene): δ 12.1. **^{95}Mo NMR** (26 MHz, $[D_8]$ -toluene, 60 °C): δ 454. **IR** (neat): $\tilde{\nu}$ 2952, 2873, 1457, 1407, 1233, 1113, 981, 868, 768, 723, 665, 450, 420. **HRMS** (ESI) calc. for $C_{42}H_{58}MoNO_3Si_3$ $[M + H]^+$: 806.27731; found: 806.27657.

Complex 140b

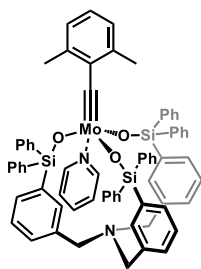
A 100 mL Schlenk flask was charged with ligand **134b** (300 mg, 0.47 mmol), which was azeotropically dried with benzene (2×2 mL) to remove residual water. The compound was suspended in toluene (45 mL) and a solution of the alkylidyne complex **18b** (204 mg, 0.47 mmol) in toluene (8 mL) was added dropwise. After stirring for 3.5 h, all volatile materials were removed *in vacuo* to give a brown residue. The crude material was repeatedly triturated with pentane and then dried under high vacuum to give the toluene-free complex **140b** as a yellow powder (399 mg, 99%).

^1H NMR (600 MHz, $[\text{D}_8]$ -toluene): δ 8.60 (s, 3H), 7.22 (dd, $J = 7.3, 1.1$ Hz, 3H), 7.01 (d, $J = 7.3$ Hz, 3H), 6.88 – 6.84 (m, 2H), 6.72 (t, $J = 7.5$ Hz, 1H), 3.52 (s, 6H), 2.85 (s, 6H), 2.07 (s, 9H), 1.04 – 1.00 (m, 18H), 1.00 – 0.91 (m, 6H), 0.92 – 0.82 (m, 6H). **^{13}C NMR** (151 MHz, $[\text{D}_8]$ -toluene): δ 305.7, 145.8, 138.5, 138.1, 137.0, 135.1, 134.1, 131.3, 129.8, 127.6, 126.9, 54.7, 20.8, 19.4, 8.3, 7.1. **^{29}Si NMR** (119 MHz, $[\text{D}_8]$ -toluene): δ 12.2. **^{95}Mo NMR** (26 MHz, $[\text{D}_8]$ -toluene, 60 °C): δ 451. **IR** (neat): $\tilde{\nu}$ 2951, 2910, 2873, 1457, 1374, 1233, 1193, 1094, 1013, 910, 892, 816, 765, 726, 705, 679, 550, 427. **HRMS** (ESI) calc. for $\text{C}_{45}\text{H}_{64}\text{MoNO}_3\text{Si}_3$ $[\text{M} + \text{H}]^+$: 848.32426; found: 848.32437. **Elemental analysis** (%) calc. for $\text{C}_{45}\text{H}_{63}\text{MoNO}_3\text{Si}_3$: C 63.87, H 7.50, N 1.66, Mo 11.34, Si 9.96; found: C 62.46, H 7.65, N 1.59, Mo 10.87, Si 9.11.

Complex 138

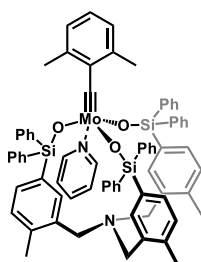
A 50 mL Schlenk flask was charged with ligand **115b** (158 mg, 0.21 mmol), which was azeotropically dried with benzene (3×2 mL) to remove any residual water. The compound was dissolved in toluene (30 mL) and a solution of the alkylidyne complex **18b** (92 mg, 0.21 mmol) in toluene (7 mL) was added dropwise. After stirring for 3.5 h, all volatile materials were removed *in vacuo* to give the crude product. The material was extracted with dichloromethane (2×1 mL). Addition of the solution to an excess of pentane (45 mL) gave the title complex **138** (102 mg, 50%) as a yellow powder.

^1H NMR (600 MHz, $[\text{D}_8]$ -toluene): δ 7.48 (s, 3H), 7.32 – 7.24 (m, 6H), 7.24 – 7.19 (m, 3H), 6.84 (d, $J = 7.5$ Hz, 2H), 6.77 – 6.67 (m, 1H), 4.19 (s, 6H), 2.76 (s, 6H), 2.58 (q, $J = 7.5$ Hz, 6H), 1.08 (t, $J = 7.5$ Hz, 9H), 1.00 – 0.90 (m, 24H), 0.90 – 0.82 (m, 6H). **^{13}C NMR** (151 MHz, $[\text{D}_8]$ -toluene): δ 299.2, 145.5, 141.8, 140.9, 138.5, 137.7, 137.5, 134.0, 132.4, 130.8, 130.4, 127.9, 127.6, 127.0, 35.7, 24.1, 21.3, 15.0, 8.1, 7.0. **^{29}Si NMR** (119 MHz, $[\text{D}_8]$ -toluene): δ 11.8. **^{95}Mo NMR** (26 MHz, $[\text{D}_8]$ -toluene, 25 °C): δ 402. **IR** (neat): $\tilde{\nu}$ 2952, 2922, 2864, 1715, 1592, 1461, 1375, 1114, 1014, 994, 880, 820, 788, 766, 757, 719, 703, 669, 662, 644, 512, 504. **HRMS** (ESI) calc. for $\text{C}_{54}\text{H}_{73}\text{MoO}_3\text{Si}_3$ $[\text{M} + \text{H}]^+$: 951.39161; found: 951.39247.

Adducts:**Adduct 139a•Py**

A 25 mL Schlenk flask was charged with complex **139a** (835 mg, 0.76 mol) and dichloromethane (15 mL). Pyridine (80 μ L, 0.99 mmol) was added to the orange solution, causing an immediate color change to dark purple. After stirring for 1 h, all volatile materials were removed *in vacuo* to give a purple powder, which was washed with pentane (2 $\times$ 6 mL) and dried in vacuum to yield the title adduct (787 mg, 88%). Purple crystals suitable for single-crystal X-ray diffraction were grown from a dichloromethane/pentane solution by slow evaporation of the solvents.

^1H NMR (600 MHz, $[\text{D}_8]$ -toluene, 253 K): δ 9.68 (s, 1H), 9.02 (s, 2H), 7.99 (dd, J = 6.3, 1.4 Hz, 2H), 7.95 – 7.90 (m, 4H), 7.69 (d, J = 7.3 Hz, 1H), 7.55 – 7.51 (m, 4H), 7.48 (dt, J = 7.3, 1.3 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.20 – 7.13 (m, 8H), 7.10 – 7.05 (m, 5H), 6.99 (t, J = 7.8 Hz, 4H), 6.93 – 6.85 (m, 6H), 6.82 (d, J = 7.8 Hz, 2H), 6.75 – 6.70 (m, 5H), 6.04 (tt, J = 7.7, 1.6 Hz, 1H), 5.40 – 5.34 (m, 2H), 3.61 (d, J = 13.8 Hz, 2H), 3.53 (d, J = 13.8 Hz, 2H), 3.36 (s, 2H), 2.72 (s, 6H). **^{13}C NMR** (151 MHz, $[\text{D}_8]$ -toluene, 253 K): δ 301.3, 150.8, 143.0, 142.8, 141.0, 140.0, 138.9, 138.6, 138.4, 137.4, 137.2, 137.0, 136.6, 135.6, 135.5, 134.4, 134.0, 133.8, 130.2, 129.3, 129.2, 129.0, 128.9, 128.5, 127.9, 127.7, 127.38, 127.36, 127.3, 124.4, 26.8, 58.2, 57.7, 21.2. **^{29}Si NMR** (119 MHz, $[\text{D}_8]$ -toluene, 253 K): δ –18.2, –18.0. **^{15}N NMR** ($[\text{2D } ^1\text{H}-^{15}\text{N}$ HMBC], 61 MHz, $[\text{D}_8]$ -toluene, 253 K): δ –113.9 (N-pyridine); signal of benzylamine not detected. **IR** (film): $\tilde{\nu}$ 3044, 1605, 1446, 1427, 1404, 1361, 1108, 1033, 1024, 1011, 997, 922, 855, 773, 740, 696, 637, 540, 506, 486, 445, 426. **Elemental analysis** (%) calc. for $\text{C}_{71}\text{H}_{62}\text{MoN}_2\text{O}_3\text{Si}_3$: C 72.79, H 5.33, N 2.39; found: C 72.42, H 5.58, N 2.34.

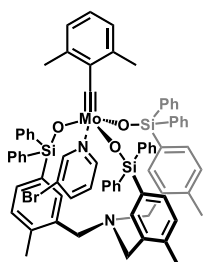
Adduct 139b•Py

A 10 mL Schlenk flask was charged with complex **139b** (98 mg, 87 μ mol) and dichloromethane (2 mL). Pyridine (11 μ L, 0.13 mmol) was added to the orange solution, causing an immediate color change to dark purple. After stirring for 2 h, all volatile materials were removed *in vacuo* to give a purple powder which was washed with pentane (3 $\times$ 1.5 mL) and dried in vacuum to yield adduct **139b•Py** (81 mg, 77%). Purple crystals suitable for single-crystal X-ray diffraction were grown from a dichloromethane/pentane solution by slow evaporation of the solvents.

^1H NMR (600 MHz, $[\text{D}_8]$ -toluene/ CD_2Cl_2 , 253 K): δ 9.61 (s, 1H), 8.93 (s, 2H), 7.92 – 7.81 (m, 2H), 7.78 – 7.63 (m, 4H), 7.45 (d, J = 7.4 Hz, 1H), 7.38 – 7.31 (m, 4H), 7.15 (d, J = 7.9 Hz, 2H), 7.09 (dt, J = 7.7, 1.6 Hz, 2H), 7.05 – 6.99 (m, 3H), 6.96 – 6.87 (m, 6H), 6.84 (t, J = 7.7 Hz, 6H), 6.73 – 6.68 (m, 6H), 6.65 (dd, J = 8.1, 7.0 Hz, 1H), 6.37 (tt, J = 7.7, 1.6 Hz, 1H), 5.78 – 5.62 (m,

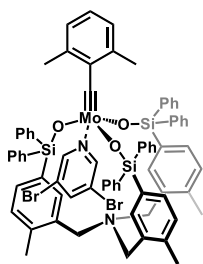
2H), 3.68 (d, $J = 14.9$ Hz, 2H), 3.58 (d, $J = 14.8$ Hz, 2H), 3.47 (s, 2H), 2.47 (s, 6H), 2.11 (s, 6H), 2.10 (s, 3H). **^{13}C NMR** (151 MHz, $[\text{D}_8]$ -toluene/ CD_2Cl_2 , 253 K): δ 301.1, 151.1, 142.72, 142.67, 138.7, 138.63, 138.60, 137.3, 137.21, 137.16, 137.1, 136.5, 135.7, 135.42, 135.43, 135.39, 135.38, 134.5, 133.7, 133.3, 132.7, 129.52, 129.48, 129.1, 128.8, 128.6, 128.5, 127.7, 127.5, 127.3, 126.6, 124.3, 20.9, 55.0, 54.7, 19.7, 19.2. **^{29}Si NMR** (119 MHz, $[\text{D}_8]$ -toluene/ CD_2Cl_2 , 253 K): δ -18.8, -17.7. **^{15}N NMR** ($[\text{2D } ^1\text{H}-^{15}\text{N}$ HMBC], 61 MHz, $[\text{D}_8]$ -toluene/ CD_2Cl_2 , 253 K): δ -113.2 (N-pyridine); signal of benzylamine not detected. **IR** (neat): $\tilde{\nu}$ 1427, 1110, 1024, 997, 926, 88, 817, 742, 694, 645, 560, 485, 421. **HRMS** (ESI) calc. for $\text{C}_{74}\text{H}_{68}\text{MoN}_2\text{O}_3\text{Si}_3$ $[\text{M}]^+$: 1214.35863; found: 1214.35929.

3-Bromopyridine Adduct **139•A**



A 10 mL Schlenk flask was charged with complex **139b** (49 mg, 43 μmol) and dichloromethane (1.5 mL). 3-Bromopyridine (7 μL , 73 μmol) was added to the orange solution, causing an immediate color change to dark purple. After 15 min, pentane (7 mL) was added and the solution was cooled to -78 $^\circ\text{C}$. The supernatant solution was separated from the precipitate by transfer into a new Schlenk flask using a filter-capped LDPE tube and argon overpressure. The solvents were removed in a constant stream of argon. The resulting purple solid was washed with pentane (3×1.5 mL) at 0 $^\circ\text{C}$ and dried in a gentle stream of argon to give the title adduct (48 mg, 85%).

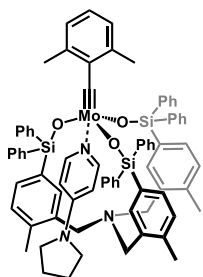
^1H NMR (600 MHz, $[\text{D}_8]$ -toluene, 233 K): δ 9.76 (s, 1H), 9.11 (s, 2H), 8.09 (s, 1H), 8.01 (d, $J = 5.4$ Hz, 1H), 7.94 – 7.90 (m, 4H), 7.60 (d, $J = 7.7$ Hz, 1H), 7.59 (dd, $J = 8.2, 1.4$ Hz, 4H), 7.37 (d, $J = 7.4$ Hz, 2H), 7.27 – 7.22 (m, 4H), 7.19 – 7.10 (m, 4H), 7.09 (d, $J = 7.5$ Hz, 1H), 7.03 (t, $J = 7.6$ Hz, 4H), 6.99 – 6.93 (m, 8H), 6.84 (t, $J = 7.6$ Hz, 4H), 6.76 (d, $J = 7.7$ Hz, 2H), 6.71 – 6.66 (m, 1H), 6.13 (dt, $J = 8.2, 2.3$ Hz, 1H), 5.20 (dd, $J = 8.2, 5.4$ Hz, 1H), 3.70 (d, $J = 15.0$ Hz, 2H), 3.54 (d, $J = 15.0$ Hz, 2H), 3.42 (s, 2H), 2.59 (s, 6H), 2.09 (s, 6H), 2.08 (s, 3H). **^{13}C NMR** (151 MHz, $[\text{D}_8]$ -toluene, 233 K): δ 301.9, 151.9, 150.0, 143.0, 142.3, 140.2, 139.7, 138.6, 138.5, 138.4, 137.2, 137.1, 136.4, 135.9, 135.53, 135.47, 135.4, 135.0, 134.6, 133.5, 133.4, 133.0, 129.7, 129.6, 129.3, 129.0, 128.7, 127.8, 127.8, 127.7, 127.3, 126.7, 125.2, 125.1, 124.9, 120.6, 54.83, 54.77, 21.0, 19.7, 19.3. **^{29}Si NMR** (119 MHz, $[\text{D}_8]$ -toluene, 233 K): δ -17.3, -17.1. **^{15}N NMR** ($[\text{2D } ^1\text{H}-^{15}\text{N}$ HMBC], 61 MHz, $[\text{D}_8]$ -toluene, 233 K): δ -108.0 (N-pyridine); signal of benzylamine not detected.

3,5-Dibromo-pyridine Adduct 139•b

A 10 mL Schlenk flask was charged with complex **139b** (75 mg, 66 μ mol) and dichloromethane (1.5 mL). 3,5-Dibromopyridine (23 mg, 99 μ mol) was added to the orange solution, causing an immediate color change to dark red. After stirring for 1 h, pentane (5 mL) was added. The supernatant solution was separated from the precipitate by transfer into a new Schlenk flask using a filter-capped LDPE tube and argon overpressure. The solvents were

removed in a constant stream of argon. The resulting purple solid was washed with pentane (3 $\times$ 2 mL) at 0 $^{\circ}$ C and dried in a gentle stream of argon to give the title adduct (75 mg, 83%).

^1H NMR (600 MHz, $[\text{D}_8]$ -toluene, 228 K): δ 9.70 (s, 1H), 9.08 (s, 2H), 8.20 (s, 2H), 7.91 (d, J = 6.9 Hz, 4H), 7.64 – 7.54 (m, 6H), 7.39 (d, J = 7.2 Hz, 2H), 7.34 (d, J = 6.8 Hz, 4H), 7.18 – 7.11 (m, 4H), 7.09 (d, J = 7.2 Hz, 1H), 7.05 – 7.01 (m, 4H), 7.99 – 6.96 (m, 7H), 6.92 (t, J = 7.0 Hz, 4H), 6.72 (d, J = 7.6 Hz, 2H), 6.67 – 6.58 (m, 1H), 6.29 (s, 1H), 3.69 (d, J = 14.8 Hz, 2H), 3.52 (d, J = 14.8 Hz, 2H), 3.40 (s, 2H), 2.54 (s, 6H), 2.10 (s, 6H), 2.08 (s, 3H). **^{13}C NMR** (151 MHz, $[\text{D}_8]$ -toluene, 228 K): δ 302.7, 150.8, 143.1, 141.9, 141.8, 138.5, 138.21, 138.20, 137.5, 137.1, 136.9, 136.5, 135.9, 135.4, 135.3, 135.2, 134.5, 134.4, 133.363, 133.360, 133.4, 133.1, 129.8, 129.6, 129.3, 129.1, 129.0, 128.7, 127.9, 127.9, 127.7, 127.3, 126.7, 120.8, 54.8, 54.7, 20.8, 19.7, 19.4. **^{29}Si NMR** (119 MHz, $[\text{D}_8]$ -toluene, 228 K): δ -16.6, -17.0.

4-Pyrrolidinopyridine Adduct 139•C

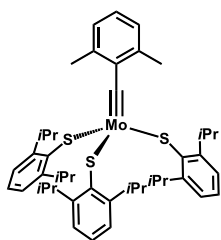
A 10 mL Schlenk flask was charged with complex **139b** (76 mg, 67 μ mol) and dichloromethane (1.5 mL). 4-Pyrrolidino-pyridine (15 mg, 0.1 mmol) was added to the orange solution, causing an immediate color change to dark purple. After stirring for 3 h, all volatile materials were removed *in vacuo*. The purple powder was washed with pentane (2 $\times$ 2 mL) to give the title adduct (71 mg, 55 μ mol, 83%) containing traces of free 4-pyrrolidinopyridine and hydrolyzed ligand. The purity of the sample was only ca. 93% (NMR).

^1H NMR (600 MHz, $[\text{D}_8]$ -toluene, 273 K): δ 9.80 (s, 1H), 9.16 (s, 2H), 7.94 (dd, J = 8.1, 1.4 Hz, 4H), 7.66 (d, J = 6.8 Hz, 2H), 7.64 – 7.58 (m, 5H), 7.41 (dd, J = 7.2, 1.0 Hz, 2H), 7.35 (dd, J = 8.0, 1.4 Hz, 4H), 7.15 – 7.08 (m, 2H), 7.08 (d, J = 7.5 Hz, 3H), 7.03 (td, J = 7.1, 1.7 Hz, 6H), 7.01 – 6.96 (m, 4H), 6.84 – 6.80 (m, 4H), 6.78 – 6.74 (m, 4H), 6.74 – 6.71 (m, 1H), 4.74 – 4.69 (m, 2H), 3.74 (d, J = 14.5 Hz, 2H), 3.63 (d, J = 14.5 Hz, 2H), 3.51 (s, 2H), 2.72 (s, 6H), 2.21 – 2.18 (m, 4H), 2.15 (s, 6H), 2.12 (s, 3H), 1.26 – 1.23 (m, 4H). **^{13}C NMR** (151 MHz, $[\text{D}_8]$ -toluene, 273 K): δ 298.8, 161.1, 150.7, 143.0, 142.9, 139.5, 138.7, 138.6, 137.2, 136.9, 136.4, 136.21, 136.17, 136.1, 136.0, 135.8, 135.2, 134.6, 133.7, 133.0, 129.53, 129.46, 129.0, 128.0, 127.9, 127.6, 126.9, 126.6, 128.3, 106.4, 55.1, 54.6, 46.4, 25.1, 21.2, 19.8, 19.3. **^{29}Si NMR** (119 MHz, $[\text{D}_8]$ -toluene, 273 K): δ -19.4, -18.6. **^{15}N NMR** ($[\text{2D } ^1\text{H}-^{15}\text{N} \text{ HMBC}]$, 61 MHz,

[D₈]-toluene, 273 K): δ -290.6 (N-pyrrolidinyl), -147.7 (N-pyridine); signal of benzylamine unit not detected.

Miscellaneous Complexes

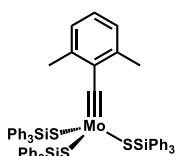
Complex 183



A 100 mL Schlenk flask was charged with 2,6-di(*iso*-propyl)thiophenol (279 mg, 1.44 mmol) and toluene (45 mL). A solution of the alkylidyne complex **18b** (206 mg, 0.48 mmol) in toluene (10 mL) was added dropwise. After stirring for 3 h, all volatile materials were removed *in vacuo* to give a yellow residue. The crude material was washed with pentane (2 × 3 mL) and dried under high vacuum. The title compound was obtained as a bright yellow powder (153 mg, 40%) containing some minor impurities.

¹H NMR (600 MHz, [D₈]-toluene): δ 7.07 – 7.04 (m, 3H), 7.00 (d, J = 7.1 Hz, 6H), 6.57 (t, J = 7.6 Hz, 1H), 6.45 (d, J = 7.6 Hz, 2H), 3.87 (hept, J = 6.8 Hz, 6H), 2.21 (s, 6H), 1.19 (d, J = 6.8 Hz, 36H). **¹³C NMR** (151 MHz, [D₈]-toluene): δ 320.2, 150.0, 144.0, 143.8, 139.3, 129.5, 128.8, 126.7, 123.5, 32.8, 23.7, 20.7. **⁹⁵Mo NMR** (26 MHz, [D₈]-toluene, 60 °C): δ 1275. **HRMS** (APPIpos) calc. for C₄₅H₆₀MoS₃ [M]⁺: 794.29057; found: 794.29026.

Complex 184

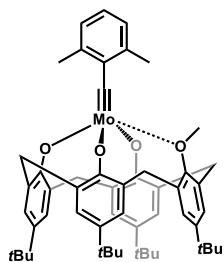


A 25 mL Schlenk flask was charged with triphenylsilanethiol (121 mg, 0.42 mmol) which was azeotropically dried with toluene (2 × 1.5 mL) to remove any residual water. The compound was dissolved in toluene (8 mL) and a solution of the alkylidyne complex **18b** (60 mg, 0.14 mmol) in toluene (6 mL) was added dropwise. After stirring for 2 h, all volatile materials were removed *in vacuo* to give a red viscous residue. The crude product was stripped with pentane (2 × 2 mL) to remove residual toluene and washed with diethyl ether (5 mL). The title compound was obtained as a dark red powder (58 mg, 38%) containing some minor impurities.

¹H NMR (600 MHz, [D₈]-toluene): δ 7.72 – 7.69 (m, 18H), 7.10 – 7.04 (m, 27H), 6.50 (t, J = 7.5 Hz, 1H), 6.30 (d, J = 7.6 Hz, 2H), 2.06 (s, 6H). **¹³C NMR** (151 MHz, [D₈]-toluene): δ 331.7, 145.6, 142.1, 136.5, 135.4, 130.2, 128.2, 128.1, 126.7, 22.0. **²⁹Si NMR** (119 MHz, [D₈]-toluene): δ -0.3. **⁹⁵Mo NMR** (26 MHz, [D₈]-toluene, 60 °C): δ 1378.

Complex 186

A 25 mL Schlenk flask was charged with ligand **182** (77 mg, 0.12 mmol) which was azeotropically dried with toluene (2 × 1 mL) to remove any residual water. The compound was dissolved in toluene (10 mL) and a solution of the alkylidyne complex **18b** (50 mg, 0.12 mmol)



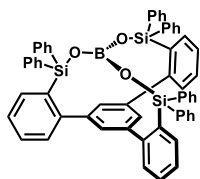
in toluene (6 mL) was added dropwise. After stirring for 2 h, all volatile materials were removed *in vacuo* to give a brown residue. The crude product was washed with pentane (3×1 mL) and dried under high vacuum.

The title compound was obtained as a brown powder (52 mg, 51%).

^1H NMR (600 MHz, $[\text{D}_8]$ -toluene): δ 7.24 (d, $J = 2.5$ Hz, 2H), 7.17 (d, $J = 2.5$ Hz, 2H), 7.09 (s, 2H), 6.99 (s, 2H), 6.90 – 6.86 (m, 2H), 6.81 (dd, $J = 8.0$, 7.0 Hz, 1H), 4.75 (d, $J = 12.3$ Hz, 2H), 4.49 (d, $J = 12.1$ Hz, 2H), 4.26 (s, 3H), 3.25 (d, $J = 12.1$ Hz, 2H), 3.25 (d, $J = 12.3$ Hz, 2H), 3.18 (s, 6H), 1.39 (s, 18H), 0.91 (s, 9H), 0.80 (s, 9H). **^{13}C NMR** (151 MHz, $[\text{D}_8]$ -toluene): δ 316.6, 156.7, 150.9, 150.7, 150.6, 146.1, 145.1, 143.5, 143.3, 136.0, 132.2, 131.4, 130.0, 129.8, 127.2, 126.7, 125.7, 125.5, 124.1, 74.6, 34.3, 34.1, 33.9, 33.6, 32.9, 32.0, 31.2, 30.7, 20.5. **IR** (neat): $\tilde{\nu}$ 2951, 2866, 1458, 1435, 1393, 1361, 1297, 1267, 1247, 1199, 1124, 987, 914, 871, 827, 803, 774, 755, 677, 601, 547, 431. **HRMS** (ESI) calc. for $\text{C}_{54}\text{H}_{65}\text{MoO}_4$ $[\text{M} + \text{H}]^+$: 875.39315; found: 875.39414.

3.2.3 Complexes Comprising ‘Canopy Ligands’

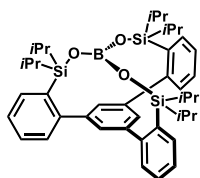
Complex B1



A 25 mL Schlenk flask was charged with ligand **19a** (98 mg, 0.13 mmol), which was azeotropically dried with benzene (2×1 mL) to remove residual water. The ligand was dissolved in toluene (6 mL) and triethyl borate (19 μ L, 0.13 mmol) was added dropwise. After 2 h, the flask was connected to a solvent trap and volatiles were removed *in vacuo*. The syrupy colorless residue was stripped with pentane (2×1.5 mL) under high vacuum to remove residual toluene. The powder was washed with pentane (3×1 mL) and dried under high vacuum to afford the title compound **B1** as a colorless solid (97 mg, 81%).

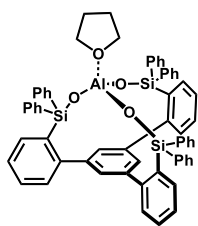
^1H NMR (600 MHz, CD_2Cl_2): δ 7.53 – 7.50 (m, 3H), 7.49 (dd, J = 8.0, 1.2 Hz, 12H), 7.39 – 7.31 (m, 6H), 7.27 – 7.22 (m, 6H), 7.13 – 7.08 (m, 15H), 7.00 (s, 3H). **^{13}C NMR** (151 MHz, CD_2Cl_2): 148.9, 144.0, 137.0, 137.0, 135.2, 135.1, 130.3, 129.8, 129.5, 128.5, 127.9, 126.4. **^{29}Si NMR** (119 MHz, CD_2Cl_2): δ –20.8. **IR** (film): $\tilde{\nu}$ 1428, 1361, 1320, 1259, 1110, 1087, 899, 857, 762, 736, 721, 699, 671, 659, 533, 514, 505, 482, 439. **HRMS** (ESI) calc. for $\text{C}_{60}\text{H}_{45}\text{O}_3\text{Si}_3\text{BNa}$ $[\text{M} + \text{Na}]^+$: 931.26618; found: 931.26576.

Complex B2



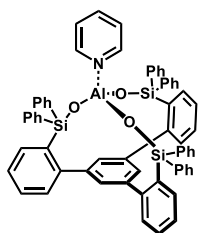
A 50 mL Schlenk flask was charged with ligand **19b** (200 mg, 0.29 mmol), which was azeotropically dried with benzene (2×1.5 mL) to remove residual water. The ligand was dissolved in toluene (14 mL) and triethyl borate (51 μ L, 0.30 mmol) was added dropwise. The solution was heated to 70 °C. After 50 h, the solution was allowed to cool to ambient temperature, the flask was connected to a solvent trap and volatiles were removed *in vacuo*. The crude material was recrystallized from a concentrated pentane (2.5 mL) solution by slowly cooling to –78 °C over 12 h. The title compound **B2** was collected by filtration (195 mg, 96%). Colorless crystals suitable for single-crystal X-ray diffraction were grown from a saturated pentane solution at 4 °C.

^1H NMR (600 MHz, CD_2Cl_2): δ 7.46 (dt, J = 7.5, 1.3 Hz, 3H), 7.43 – 7.38 (m, 6H), 7.35 (td, J = 7.4, 1.9 Hz, 3H), 7.26 (s, 3H), 1.23 – 1.12 (m, 6H), 0.96 (d, J = 7.5 Hz, 18H), 0.90 (d, J = 7.4 Hz, 18H). **^{13}C NMR** (151 MHz, CD_2Cl_2): 149.7, 141.9, 135.0, 134.8, 129.6, 128.8, 126.0, 18.2, 14.2. **^{29}Si NMR** (119 MHz, CD_2Cl_2): δ 0.1. **^{11}B NMR** (193 MHz, CD_2Cl_2): δ 12.5. **IR** (film): $\tilde{\nu}$ 2947, 2863, 1463, 1349, 1307, 1259, 1243, 1223, 1118, 1088, 994, 884, 839, 775, 762, 717, 691, 664, 652, 622, 612, 559, 511, 469. **HRMS** (ESI) calc. for $\text{C}_{42}\text{H}_{57}\text{O}_3\text{Si}_3\text{BNa}$ $[\text{M} + \text{Na}]^+$: 727.36008; found: 727.36005.

Complex Al1•THF

A 50 mL Schlenk flask was charged with ligand **19b** (1.00 g, 1.11 mmol), which was azeotropically dried with benzene (2×4 mL) to remove residual water. The ligand was dissolved in toluene (25 mL) and tetrahydrofuran (4.5 mL) and the solution was cooled to 0 °C. A solution of trimethyl aluminum (2 M in hexane, 0.56 mL, 1.13 mmol) was added dropwise. The reaction mixture was allowed to warm to ambient temperature. After 1 h, the flask was connected to a solvent trap and volatiles were removed *in vacuo*. The syrupy residue was stripped with pentane (2×4 mL) under high vacuum to remove residual toluene. The title compound **Al1•THF** was obtained as a colorless solid (1.08 g, 98%).

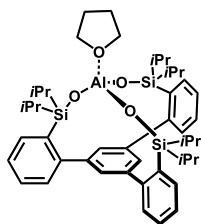
¹H NMR (600 MHz, CD₂Cl₂): δ 7.66 – 7.61 (m, 12H), 7.52 – 7.48 (m, 3H), 7.28 (td, J = 7.4, 1.5 Hz, 3H), 7.26 – 7.21 (m, 9H), 7.11 (t, J = 7.6 Hz, 12H), 6.92 – 6.88 (m, 3H), 6.85 (s, 3H), 3.50 – 3.27 (m, 4H), 1.27 – 1.07 (m, 4H). **¹³C NMR** (151 MHz, CD₂Cl₂): 149.7, 144.3, 140.5, 137.4, 137.1, 135.0, 129.54, 129.51, 129.2, 128.7, 127.8, 125.9, 72.1, 24.9. **²⁹Si NMR** (119 MHz, CD₂Cl₂): δ –25.2. **IR** (film): $\tilde{\nu}$ 3047, 1585, 1470, 1427, 1411, 1110, 1077, 1060, 1028, 998, 764, 742, 719, 698, 621, 510, 500, 466, 442, 408. **HRMS** (ESI) calc. for C₆₀H₄₅O₃Si₃AlNa [M + Na]⁺: 947.23841; found: 947.23853. (Complex without the labile tetrahydrofuran). **HRMS** (ESI) calc. for C₆₄H₅₃O₄Si₃AlNa [M + Na]⁺: 1019.29592; found: 1019.29641. (Complex with the labile tetrahydrofuran)

Complex Al1•Py

A 25 mL Schlenk flask was charged with complex **Al1•THF** (200 mg, 0.20 mmol) and dichloromethane (5 mL). Pyridine (0.16 mL, 2.01 mmol) was added. After 2 h, the flask was connected to a solvent trap and volatiles were removed *in vacuo*. The title compound **Al1•Py** was obtained as a colorless solid (198 mg, 98%).

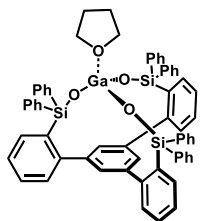
Colorless crystals suitable for single-crystal X-ray diffraction were grown from a dichloromethane solution by slow evaporation of the solvent.

¹H NMR (600 MHz, CD₂Cl₂): δ 7.94 – 7.91 (m, 2H), 7.63 – 7.58 (m, 13H), 7.56 – 7.52 (m, 3H), 7.29 (td, J = 7.4, 1.5 Hz, 3H), 7.26 (td, J = 7.4, 1.7 Hz, 3H), 7.24 – 7.19 (m, 6H), 7.12 – 7.02 (m, 12H), 6.95 – 6.91 (m, 3H), 6.93 (s, 3H), 6.90 – 6.83 (m, 2H). **¹³C NMR** (151 MHz, CD₂Cl₂): 149.8, 147.3, 144.3, 140.5, 137.5, 137.1, 135.0, 129.5, 129.5, 129.1, 128.8, 127.8, 125.9, 125.3. **²⁹Si NMR** (119 MHz, CD₂Cl₂): δ –25.5. **¹⁵N NMR** ([2D ¹H-¹⁵N HMBBC], 61 MHz, CD₂Cl₂): δ –135.9. **IR** (film): $\tilde{\nu}$ 1426, 1109, 1098, 1077, 1059, 1028, 746, 742, 718, 700, 510, 499, 469, 444. **HRMS** (APPI) calc. for C₆₅H₅₁NO₃Si₃Al [M + H]⁺: 1004.29866; found: 1004.29974.

Complex Al2•THF

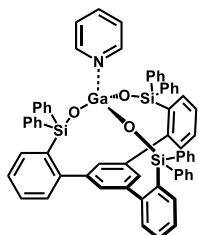
A 25 mL Schlenk flask was charged with ligand **19b** (300 mg, 0.43 mmol), which was azeotropically dried with benzene (2×2 mL) to remove residual water. The ligand was dissolved in toluene (7 mL) and tetrahydrofuran (1 mL) and the solution was cooled to 0 °C. A solution of trimethyl aluminum (2 M in hexane, 0.22 mL, 0.44 mmol) was added dropwise. The reaction mixture was allowed to warm to ambient temperature. After 1 h, the flask was connected to a solvent trap and volatiles were removed *in vacuo*. The syrupy residue was stripped with pentane (3 mL) under high vacuum to remove residual toluene. The title compound **Al2•THF** was obtained as a colorless solid (331 mg, 97%).

¹H NMR (600 MHz, CD₂Cl₂): δ 7.50 (ddd, $J = 7.3, 1.6, 0.6$ Hz, 3H), 7.31 (td, $J = 7.4, 1.6$ Hz, 3H), 7.27 (td, $J = 7.3, 1.5$ Hz, 3H), 7.20 (ddd, $J = 7.5, 1.5, 0.6$ Hz, 3H), 7.13 (s, 3H), 4.21 – 4.17 (m, 4H), 2.08 – 2.01 (m, 4H), 1.07 – 0.99 (m, 24H), 0.93 (d, $J = 6.5$ Hz, 18H). **¹³C NMR** (151 MHz, CD₂Cl₂): 150.3, 143.7, 137.7, 134.6, 130.0, 127.9, 127.5, 125.6, 72.2, 25.5, 18.9, 18.5, 16.1. **²⁹Si NMR** (119 MHz, CD₂Cl₂): δ –8.1. **IR** (film): $\tilde{\nu}$ 2941, 2861, 1463, 1124, 1068, 1051, 1011, 994, 883, 869, 761, 741, 719, 664, 609, 524, 465. **HRMS** (ESI) calc. for C₄₆H₆₆O₄Si₃Al [M + H]⁺: 793.4078; found: 793.4071.

Complex Ga1•THF

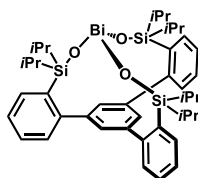
A 100 mL, two-necked flask equipped with a reflux condenser and an argon/vacuum manifold was charged with ligand **19a** (430 mg, 0.48 mmol) which was azeotropically dried with benzene (2×2 mL). The ligand was dissolved in toluene (34 mL) and tetrahydrofuran (34 mL) and triethoxy gallium (98 mg, 0.48 mmol) was added in one portion. The reaction mixture was heated to 100 °C. After 24 h, the reaction was allowed to cool to ambient temperature, the reflux condenser was removed, the flask connected to a solvent trap and volatiles were removed *in vacuo*. The residue was stripped with pentane (2×3 mL) under high vacuum to afford the title compound **Ga1•THF** as a beige solid (399 mg, 84%).

¹H NMR (600 MHz, CD₂Cl₂): δ 7.67 – 7.62 (m, 12H), 7.47 (ddd, $J = 7.3, 1.7, 0.6$ Hz, 3H), 7.26 (td, $J = 7.5, 1.5$ Hz, 3H), 7.24 – 7.21 (m, 9H), 7.15 – 7.10 (m, 12H), 6.84 (ddd, $J = 7.3, 1.5, 0.6$ Hz, 3H), 6.83 (s, 3H), 3.53 – 3.49 (m, 4H), 1.29 – 1.23 (m, 4H). **¹³C NMR** (151 MHz, CD₂Cl₂): 149.4, 144.4, 140.5, 137.5, 137.2, 134.9, 129.6, 129.5, 129.2, 128.7, 127.8, 126.0, 71.7, 25.0. **²⁹Si NMR** (119 MHz, CD₂Cl₂): δ –22.2. **IR** (film): $\tilde{\nu}$ 1427, 1261, 1109, 1065, 1041, 1023, 858, 802, 764, 738, 719, 699, 530, 509, 499, 458, 439. **HRMS** not detected (decomposition).

Complex Ga1•Py

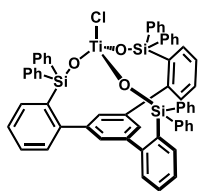
The pyridine adduct **Ga1•Py** was obtained in the form of colorless crystals from a concentrated solution of **Ga1•THF** in dichloromethane to which pyridine was added in excess. The NMR spectra showed an additional equivalent of pyridine to be present in the sample. This is in agreement with the structure obtained from single-crystal X-ray diffraction.

¹H NMR (600 MHz, CD₂Cl₂, 233 K): δ 8.00 – 7.95 (m, 2H), 7.68 (tt, *J* = 7.7, 1.6 Hz, 1H), 7.62 (dd, *J* = 8.0, 1.3 Hz, 12H), 7.47 (ddd, *J* = 7.3, 1.6, 0.5 Hz, 3H), 7.26 (td, *J* = 7.4, 1.4 Hz, 3H), 7.22 (td, *J* = 7.5, 1.6 Hz, 3H), 7.18 (t, *J* = 7.4 Hz, 6H), 7.04 (t, *J* = 7.2 Hz, 12H), 6.99 – 6.93 (m, 2H), 6.81 (ddd, *J* = 7.4, 1.4, 0.6 Hz, 3H), 6.79 (s, 3H). **¹³C NMR** (151 MHz, CD₂Cl₂, 233 K): 148.9, 146.4, 143.8, 141.8, 140.0, 137.2, 136.6, 134.3, 129.2, 129.0, 128.7, 128.2, 127.4, 125.6, 125.5. **²⁹Si NMR** (119 MHz, CD₂Cl₂, 233 K): δ –23.3. **¹⁵N NMR** ([2D ¹H-¹⁵N HMBC], 61 MHz, CD₂Cl₂, 233 K): δ –135.9. **IR** (film): $\tilde{\nu}$ 3064, 3048, 1615, 1584, 1454, 1427, 1410, 1306, 1235, 1184, 1123, 1108, 1065, 1044, 1017, 983, 900, 875, 764, 739, 719, 696, 651, 622, 532, 498, 450, 433, 406. **HRMS** (ESI) calc. for C₆₅H₅₀NO₃Si₃GaNa [M + Na]⁺: 1068.22464; found: 1068.22417.

Complex Bi1

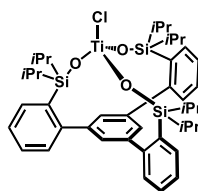
A 25 mL Schlenk flask was charged with ligand **19b** (350 mg, 0.50 mmol), which was azeotropically dried with benzene (2 × 2 mL) to remove residual water. The ligand was dissolved in toluene (20 mL) and a solution of bismuth (III) tris-*tert*-butoxide (215 mg, 0.50 mmol) in toluene (4 mL) was added dropwise. After 16 h, the flask was connected to a solvent trap and volatiles were removed *in vacuo*. The residue was washed with pentane (4 mL) and dried under high vacuum. The title compound **Bi1** was obtained as a colorless solid (402 mg, 87%). Colorless crystals of **Bi1•C₆H₆** suitable for single-crystal X-ray diffraction were grown from a concentrated benzene solution by slow evaporation of the solvent.

¹H NMR (600 MHz, [D₈]-Tol): 7.42 – 7.37 (m, 3H), 7.33 (s, 3H), 7.32 – 7.30 (m, 3H), 7.17 (td, *J* = 7.3, 1.6 Hz, 3H), 7.15 (td, *J* = 7.3, 1.7 Hz, 3H), 1.10 – 1.00 (m, 42H). **¹³C NMR** (151 MHz, [D₈]-Tol): 151.2, 142.7, 137.0, 133.9, 130.8, 128.7, 125.9, 19.0, 18.7, 16.1. **²⁹Si NMR** (119 MHz, [D₈]-Tol): δ 4.2. **IR** (film): $\tilde{\nu}$ 1428, 1361, 1320, 1259, 1110, 1087, 899, 857, 762, 736, 721, 699, 671, 659, 533, 514, 505, 482, 439. **HRMS** (ESI) calc. for C₄₂H₅₈O₃Si₃Bi [M + H]⁺: 903.34923; found: 903.34971.

Complex Ti1

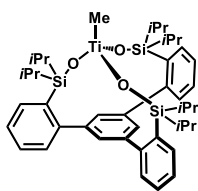
A 25 mL Schlenk flask was charged with ligand **19a** (300 mg, 0.33 mmol), which was azeotropically dried with benzene (3×1.5 mL) to remove residual water. Toluene (9 mL) was added and a solution of chlorotitanium triisopropoxide **216** (0.33 mL, 1.0 M in hexane, 0.33 mmol) was added dropwise. After 1 h, the flask was connected to a solvent trap and volatiles were removed *in vacuo*. The beige residue was dissolved in dichloromethane (2 mL) and the solution was added dropwise to an excess of cold pentane (25 mL) to afford the desired product as a white precipitate. The title compound **Ti1** was collected by filtration (213 mg, 65%).

^1H NMR (400 MHz, C_6D_6): δ 7.90 – 7.83 (m, 12H), 7.61 – 7.56 (m, 3H), 7.30 (s, 3H), 7.11 – 7.00 (m, 24H), 6.95 – 6.91 (m, 3H). **^{13}C NMR** (101 MHz, C_6D_6): δ 149.4, 144.6, 137.5, 136.8, 135.0, 134.5, 130.5, 130.2, 129.8, 129.4, 126.3. **^{29}Si NMR** (60 MHz, $[\text{D}_8]\text{-Tol}$): δ -10.9. **IR** (film): $\tilde{\nu}$ 3067, 1428, 1112, 1089, 1052, 922, 763, 740, 695, 622, 509, 496, 449, 410. **HRMS** (EI) calc. for $\text{C}_{60}\text{H}_{45}\text{ClO}_3\text{Si}_3$ $[\text{M}]^+$: 980.18391; found: 980.18434.

Complex Ti2

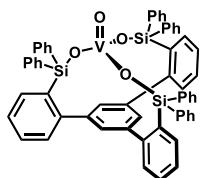
A 25 mL Schlenk flask was charged with ligand **19b** (200 mg, 0.29 mmol), which was azeotropically dried with benzene (2×1 mL) to remove residual water. Toluene (12 mL) was added and a solution of chlorotitanium triisopropoxide **216** (0.30 mL, 1.0 M in hexane, 0.30 mmol) was added dropwise. After 3 h, the flask was connected to a solvent trap and volatiles were removed *in vacuo*. The syrupy residue was stripped with pentane (2×1.5 mL) under high vacuum to remove residual toluene. The obtained colorless powder was dissolved in dichloromethane (1.6 mL) and the solution was added dropwise to an excess of cold pentane (25 mL) to afford the desired product as a white precipitate. The title compound **Ti2** was collected by filtration (220 mg, 98%). Colorless crystals suitable for single-crystal X-ray diffraction were grown from a dichloromethane/pentane solution by slow evaporation of the solvents.

^1H NMR (600 MHz, C_6D_6): δ 7.56 (s, 3H), 7.35 – 7.32 (m, 3H), 7.32 – 7.29 (m, 3H), 7.18 – 7.10 (m, 6H), 1.31 – 1.22 (m, 6H), 1.19 (d, $J = 7.1$ Hz, 18H), 1.11 (d, $J = 7.3$ Hz, 18H). **^{13}C NMR** (151 MHz, C_6D_6): δ 149.6, 144.2, 134.6, 134.5, 130.5, 129.2, 128.4, 126.5, 18.4, 18.0, 15.8. **^{29}Si NMR** (60 MHz, C_6D_6): δ 10.9. **IR** (film): $\tilde{\nu}$ 2945, 2864, 1461, 1122, 996, 905, 880, 759, 739, 723, 699, 651, 633, 542, 528, 462, 429, 420. **HRMS** (ESI) calc. for $\text{C}_{42}\text{H}_{57}\text{O}_3\text{Si}_3\text{Ti}$ $[\text{M} - \text{Cl}]^+$: 741.30895; found: 741.30906. (Only complex without Cl detected)

Complex Ti3

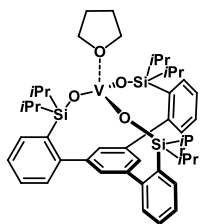
A 50 mL Schlenk flask was charged with ligand **19b** (400 mg, 0.57 mmol), which was azeotropically dried with benzene (2×2 mL) to remove residual water. Toluene (27 mL) was added and a solution of methyltitanium (IV) triisopropoxide **217** (0.57 mL, 1.0 M in hexane, 0.57 mmol) was added dropwise. After 14 h, the flask was connected to a solvent trap and volatiles were removed *in vacuo*. The syrupy residue was stripped with pentane (2×1.5 mL) under high vacuum to remove residual toluene. The colorless powder was washed with diethyl ether (2×0.8 mL) at 0 °C and dried under high vacuum to afford the title compound **Ti3** (361 mg, 83%). Colorless crystals suitable for single-crystal X-ray diffraction were grown from a dichloromethane/pentane solution by slow evaporation of the solvents.

¹H NMR (600 MHz, [D₈]-Tol): δ 7.43 (s, 3H), 7.41 – 7.34 (m, 3H), 7.23 – 7.19 (m, 3H), 7.17 – 7.12 (m, 6H), 1.27 – 1.19 (m, 6H), 1.22 (s, 3H) 1.15 (d, J = 7.2 Hz, 18H), 1.11 (d, J = 7.3 Hz, 18H). **¹³C NMR** (151 MHz, [D₈]-Tol): 149.7, 143.9, 135.0, 134.6, 130.7, 128.9, 128.3, 126.3, 50.0, 18.5, 18.1, 15.7. **²⁹Si NMR** (119 MHz, [D₈]-Tol): δ 5.3. **IR** (film): $\tilde{\nu}$ 2942, 2863, 1462, 1122, 1025, 917, 882, 773, 762, 739, 719, 694, 671, 653, 641, 518, 468. **HRMS** (APPI) calc. for C₄₃H₆₁O₃Si₃Ti [M + H]⁺: 757.34025; found: 757.33913.

Complex V1

A 50 mL Schlenk flask was charged with ligand **19a** (158 mg, 0.21 mmol), which was azeotropically dried with benzene (2×2 mL) to remove residual water. Toluene (10 mL) was added and vanadium (V) tris(iso-propoxide)-oxide **225** (50 μ L, 0.21 mmol) was added dropwise. After 2 h, the flask was connected to a solvent trap and volatiles were removed *in vacuo*. The syrupy light green residue was stripped with pentane (2×1.5 mL) under high vacuum to remove residual toluene. The light yellow powder was washed with pentane (3×1.5 mL) and dried under high vacuum to afford the title compound **V1** as a yellow solid (186 mg, 91%). Yellow crystals suitable for single-crystal X-ray diffraction were grown from a dichloromethane/diethyl ether solution by slow evaporation of the solvents.

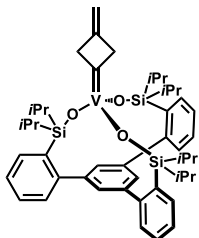
¹H NMR (600 MHz, [D₈]-Tol): δ 7.83 – 7.78 (m, 12H), 7.60 (dd, J = 7.2, 1.5 Hz, 3H), 7.17 (s, 3H), 7.10 – 6.99 (m, 24H), 6.92 – 6.88 (m, 3H). **¹³C NMR** (151 MHz, [D₈]-Tol): 149.8, 144.5, 137.5, 137.0, 135.1, 134.9, 130.3, 130.1, 130.0, 129.2, 128.3, 126.1. **²⁹Si NMR** ([2D ¹H-²⁹Si HMBC], 600 MHz, [D₈]-Tol): δ -7.2. **⁵¹V NMR** (158 MHz, [D₈]-Tol): δ -777. **IR** (film): $\tilde{\nu}$ 3047, 1583, 1557, 1469, 1427, 1410, 1263, 1113, 1053, 1006, 926, 912, 766, 743, 723, 697, 622, 594, 507, 454, 408. **HRMS** (ESI) calc. for C₆₀H₄₅O₄Si₃VNa [M + Na]⁺: 987.19574; found: 987.19645.

Complex V3•THF

A 100 mL Schlenk flask was charged with sodium hydride (60 mg, 2.51 mmol) and tetrahydrofuran (40 mL). The suspension was cooled to 0 °C and a solution of ligand **19b** (500 mg, 0.72 mmol) in tetrahydrofuran (6 mL) was added dropwise. The suspension was allowed to reach ambient temperature. After 16 h, the reaction mixture was cooled to 0 °C and a solution of vanadium (III) chloride-(tris-tetrahydrofuran) (268 mg, 0.72 mmol) in tetrahydrofuran (8 mL) was added dropwise. A rapid color change from purple to green was observed. After 5 h, the suspension was filtered *via* cannula into a new Schlenk flask and solvents were removed from the filtrate *in vacuo*. The green residue was washed with pentane (2 × 4 mL) and dried under high vacuum to afford the title compound **V3•THF** as a turquoise solid (474 mg, 89%). Blue crystals suitable for single-crystal X-ray diffraction were grown from a saturated tetrahydrofuran solution layered with pentane by cooling to –78 °C over 24 h.

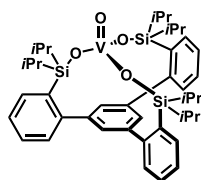
IR (film): $\tilde{\nu}$ 2961, 2863, 1463, 1409, 1259, 1086, 1015, 955, 917, 881, 793, 761, 719, 691, 662, 653, 613, 519, 506, 470. **HRMS** (ESI) calc. for $C_{42}H_{58}O_3Si_3V$ [$M - OC_4H_8 + H$]⁺: 745.31279; found: 745.31281. (Only the complex without the labile tetrahydrofuran could be detected)

Elemental analysis (%) calc. for $C_{46}H_{65}O_4Si_3V$: C 67.61, H 8.02, V 6.23, Si 10.31; found: C 67.39, H 7.99, V 6.21, Si 10.26.

Complex V4

A 25 mL Schlenk flask was charged with 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (150 mg, 0.51 mmol) and pentane (4 mL). The solution was cooled to –78 °C and methyl lithium (1.6 M in diethyl ether, 0.63 mL, 1.01 mmol) was added dropwise. The reaction mixture was stirred at –78 °C for 15 min, before it was allowed to warm to 0 °C, and stirred for another 1 h. The resulting cloudy solution of [1.1.1]-propellane in pentane was submitted to three freeze/pump/thaw cycles (using liquid nitrogen and high vacuum: 10^{–3} bar) with thawing temperatures not exceeding 0 °C.

A separate 25 mL Schlenk flask was charged with complex **V3•THF** (100 mg, 0.13 mmol) and connected to the flask containing the [1.1.1] propellane solution with a vacuum transfer bridge. All Schlenk tabs at the flasks were closed to prevent argon from condensing and the Schlenk flask containing the metal complex was cooled to –196 °C. The [1.1.1]-propellane solution was transferred into the cooled flask by applying gentle vacuum. The reaction mixture was allowed



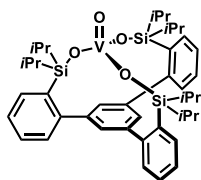
to reach ambient temperature and the system was again filled with argon. After 4 h, during which the reaction mixture adopted a deep blue color, the solution was filtered into a new Schlenk flask and volatiles were removed from the filtrate *in vacuo*. The title complex **V4** was obtained as a dark blue

powder (91 mg, 84%) containing some of the oxo-complex **V2** and free ligand **19b** ($\leq 5\%$). Blue crystals of **V4** and colorless crystals of **V2** suitable for single-crystal X-ray diffraction were grown from a pentane solution by slow evaporation of the solvent.

Complex V4 was found to be extremely sensitive to oxygen and to slowly decompose in solution to give V2, free ligand 19b, and unidentified paramagnetic species.

¹H NMR (600 MHz, [D₈]-Tol, 233 K): 7.47 (s, 3H), 7.45 – 7.42 (m, 3H), 7.31 – 7.28 (m, 3H), 7.18 – 7.11 (m, 6H), 5.74 (s, 4H), 4.59 (s, 2H), 1.33 – 1.25 (m, 6H), 1.16 (d, $J = 7.3$ Hz, 18H), 1.13 (d, $J = 7.4$ Hz, 18H). **¹³C NMR** (151 MHz, [D₈]-Tol, 233 K): 149.9, 143.9, 143.6, 135.0, 134.0, 130.6, 126.2, 105.7, 59.5, 18.3, 18.0, 15.8; (V=C not observed). **²⁹Si NMR** (119 MHz, [D₈]-Tol, 233 K): 11.6. Characteristic ions in **MS** (APPIpos): m/z 744 ([C₄₂H₅₇O₃Si₃V]⁺ $\triangleq$ **V3** or **V4** – C₅H₆), 761 ([C₄₂H₅₇O₃Si₃V]⁺ $\triangleq$ **V2**).

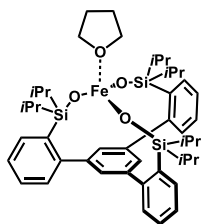
Complex V2



A 25 mL Schlenk flask was charged with ligand **19b** (100 mg, 0.14 mmol), which was azeotropically dried with benzene (2×1.5 mL) to remove residual water. Toluene (10 mL) was added and vanadium (V) tris(iso-propoxide)-oxide **225** (34 μ L, 0.14 mmol) was added dropwise. A reflux condenser

equipped with an argon manifold was mounted onto the Schlenk flask and the reaction mixture was heated to 80 °C. After 16 h, the heating was stopped, the reflux condenser replaced by a stopper and volatiles were removed *in vacuo*. The syrupy colorless residue was stripped with pentane (2×1.5 mL) under high vacuum to remove residual toluene. The title compound **V2** was obtained as a colorless solid (108 mg, 99%).

¹H NMR (600 MHz, [D₈]-Tol): δ 7.40 (s, 3H), 7.33 – 7.30 (m, 3H), 7.30 – 7.27 (m, 3H), 7.17 – 7.11 (m, 6H), 1.36 – 1.25 (m, 6H), 1.22 (d, $J = 7.2$ Hz, 18H), 1.11 (d, $J = 7.4$ Hz, 18H). **¹³C NMR** (151 MHz, [D₈]-Tol): 150.1, 144.1, 134.8, 134.3, 130.7, 129.0, 127.9, 126.3, 18.4, 18.1. **²⁹Si NMR** ([2D ¹H-²⁹Si HMBC], 600 MHz, [D₈]-Tol): δ 14.5. **⁵¹V NMR** (158 MHz, [D₈]-Tol): δ –753. **IR** (film): $\tilde{\nu}$ 2959, 2945, 2864, 1462, 1120, 995, 911, 879, 778, 762, 740, 720, 696, 669, 647, 628, 536, 478, 461, 417. **HRMS** (ESI) calc. for C₄₂H₅₇O₄Si₃VNa [M + Na]⁺: 783.28965; found: 783.28967.

Complex Fe1•THF

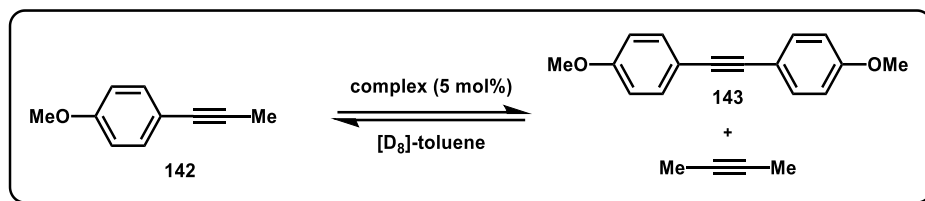
A 100 mL Schlenk flask was charged with sodium hydride (60 mg, 2.51 mmol) and tetrahydrofuran (50 mL). The suspension was cooled to 0 °C and a solution of ligand **19b** (500 mg, 0.72 mmol) in tetrahydrofuran (10 mL) was added dropwise. The suspension was allowed to reach ambient temperature. After 16 h, the ligand solution was cooled to –30 °C and a solution of iron (III) chloride (116 mg, 0.72 mmol) in tetrahydrofuran (6 mL) was added dropwise. The resulting orange suspension was allowed to warm to ambient temperature. After 2.5 h, the suspension was filtered *via* cannula into a new Schlenk flask and the filtrate was concentrated *in vacuo* until approx. 4 mL were remaining. The solution was slowly cooled to –78 °C over 22 h to afford the desired product as a yellow precipitate. Filtration, concentrating the filtrate *in vacuo* until approx. 1.5 mL were remaining and again slow cooling to –78 °C afforded a second crop. The title compound **Fe1•THF** was collected by filtration (360 mg, 61%).

Yellow crystals suitable for single-crystal X-ray diffraction were grown from a saturated tetrahydrofuran solution at ambient temperature over a week.

IR (film): $\tilde{\nu}$ 2939, 2888, 2860, 1463, 1122, 956, 881, 760, 739, 718, 664, 653, 622, 592, 517, 471. **HRMS** (ESI) calc. for $C_{42}H_{58}O_3Si_3Fe$ $[M - OC_4H_8 + H]^+$: 750.30376; found: 750.30357. (Only the complex without the labile tetrahydrofuran could be detected) **Elemental analysis**: (%) calc. for $C_{46}H_{65}O_4Si_3Fe$: C 67.20, H 7.97, Fe 6.79, Si 10.25; found: C 66.99, H 7.94, Fe 6.77, Si 10.28.

3.3 Experimental Procedures: Alkyne Metathesis

Alkyne Metathesis Benchmark Reaction



A flame-dried *J. Young* NMR tube filled with argon was charged with a stock solution of the respective complex (6.0 mM in $[D_8]$ -toluene, 0.5 mL, 3.0 μ mol, 5 mol%) and a 1H NMR spectrum recorded at 25 $^{\circ}C$. A solution of 1-methoxy-4-(prop-1-yn-1-yl)benzene **142** (0.6 M in $[D_8]$ -toluene, 100 μ L, 60.0 μ mol) was then added and the conversion of the substrate to tolane **143** and but-2-yne was monitored by 1H NMR spectroscopy at 25 $^{\circ}C$ (unless otherwise specified). The delay between the addition and the first NMR measurement amounts to 1 – 2 min due to sample loading and shimming.

Benchmark Experiment of Catalyst **40b** (at 25 $^{\circ}C$)

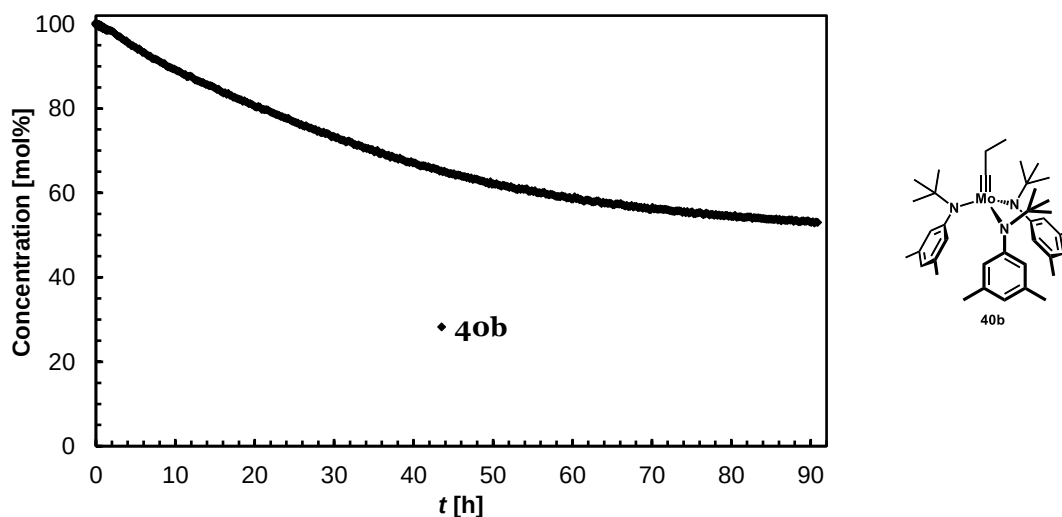


Figure S 1: Consumption of **142** in a benchmark experiment using complex **40b** as the catalyst (5 mol%) in $[D_8]$ -toluene; as monitored by 1H NMR spectroscopy at 25 $^{\circ}C$.

Benchmark Experiment of Catalyst **138** (at 25 °C)

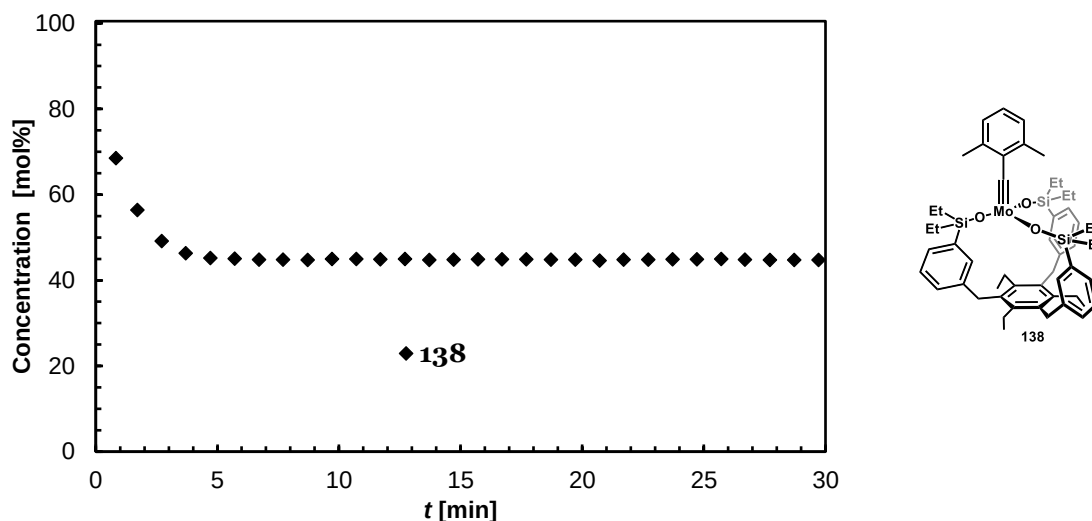


Figure S 2: Consumption of **142** in a benchmark experiment using complex **138** as the catalyst (5 mol%) in $[D_8]$ -toluene; as monitored by 1H NMR spectroscopy at 25 °C.

Benchmark Experiment Using a Zhang-type Catalyst Prepared *in situ* from the Molybdenum Alkylidyne **40b** and the Tris-Phenol Ligand **7d**

A stock solution of the catalytically active mixture was prepared by premixing molybdenum alkylidyne **40b** (6.0 mg, 9 μ mol) and ligand **7d** (4.2 mg, 9 μ mol) in $CDCl_3$ (1.5 mL) in a Schlenk flask. The solution was stirred for 30 min. A flame-dried *J. Young* NMR tube filled with argon was charged with an aliquot of the stock solution (6.0 mM in $CDCl_3$, 0.5 mL, 3.0 μ mol, 5 mol%), which was then cooled to -50 °C. A solution of 1-methoxy-4-(prop-1-yn-1-yl)benzene **142** (0.6 M in $[D_8]$ -toluene, 100 μ L, 60.0 μ mol) was added and the tube was transferred into the precooled NMR spectrometer. The temperature of the sample was then raised from 253 K to 273 K and later to 298 K as no conversion was observed at the lower temperatures (see figure S3).

The lack of reactivity at low temperature stands in marked contrast to the excellent performance of the new catalysts at 0 °C and even -20 °C, resulting in equilibration within minutes.

Note: $CDCl_3/[D_8]$ -toluene was chosen as the solvent system for this and the following benchmarking experiment. This medium is described in the literature as suitable, even though CCl_4 was recommended as optimal. Not only is CCl_4 less adequate for the NMR experiments, but this chemical is hepatotoxic and potentially carcinogenic. Therefore CCl_4 is regulated under Regulation (EC) No 1005/2009 of the European Parliament and of the

Council on substances that deplete the ozone layer (OJ L 286, 31.10.2009, p. 1) which prohibits its use except as an intermediate, industrial processing agent and laboratory agent.

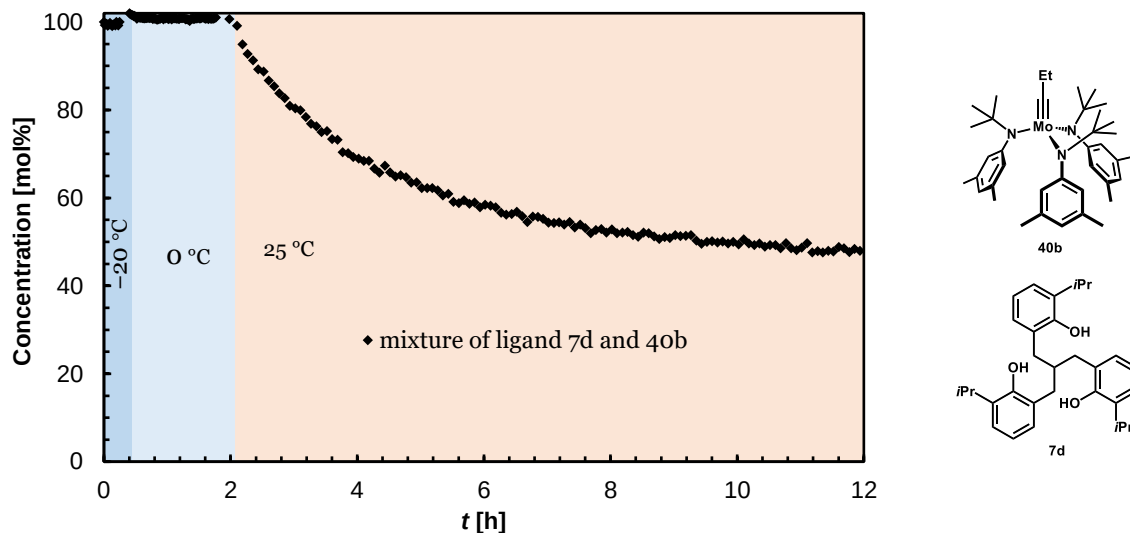
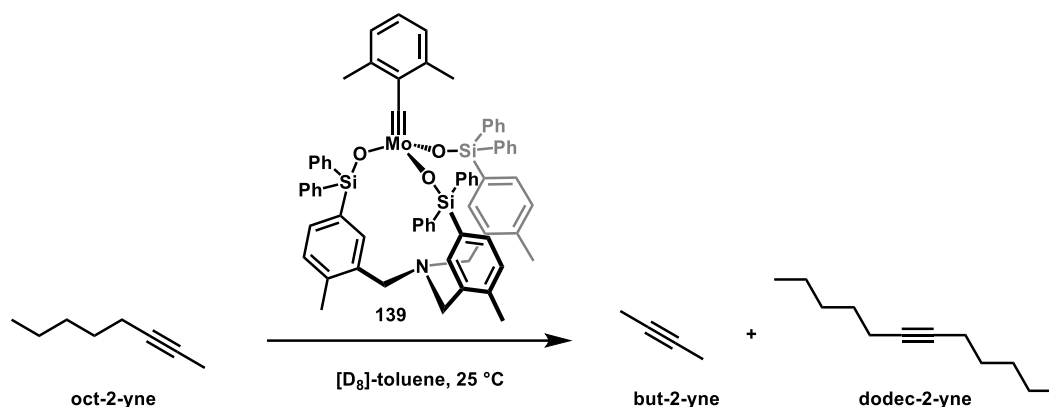


Figure S 3: Conversion-time diagram for alkyne **142** in the benchmark experiment using a mixture of ligand **7b** and molybdenum alkylidyne **40b** (5 mol% each) as catalyst in a mixture of deuterated chloroform and $[D_8]$ -toluene, as monitored by 1H NMR spectroscopy at 253 K, 273 K and 298 K.

Side Reaction: Polymerization



A flame-dried *J. Young* NMR tube filled with argon was charged with a stock solution of the complex **139** (6.0 mM in $[D_8]$ -toluene, 0.5 mL, 3.0 μ mol, 5 mol%) and a 1H NMR spectrum recorded at 25 °C. A solution of oct-2-yne (0.6 M in $[D_8]$ -toluene, 100 μ L, 60.0 μ mol) was then added and the conversion of this substrate to dodec-6-yne and but-2-yne was monitored by 1H NMR spectroscopy at 25 °C. The initial equilibrium was reached upon the first scan and the sample was further monitored for 70 h. Polymerization of but-2-yne as well as oct-2-yne and dodec-6-yne slowly lowered the concentration of these monomers in solution. After 70 h, the material in the NMR tube had converted into a gel.

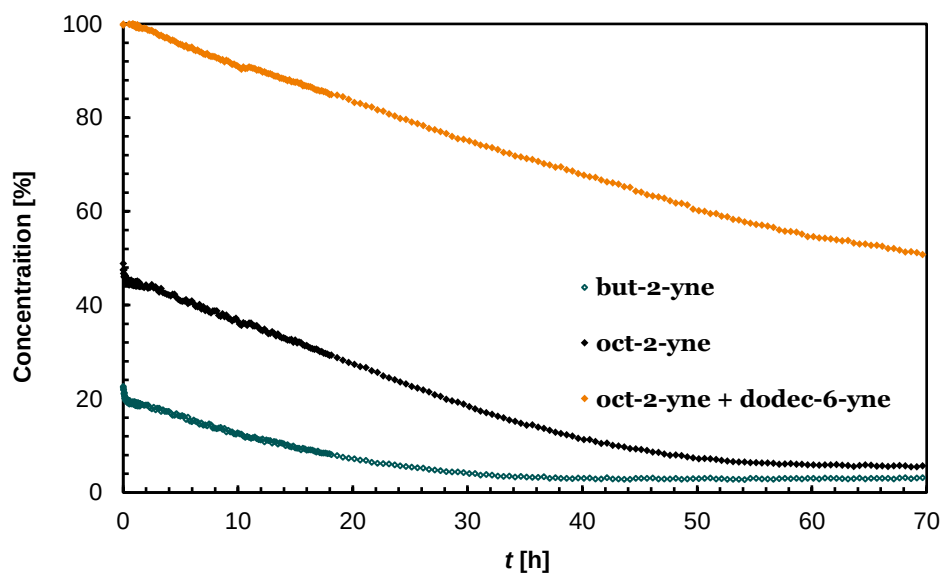


Figure S 4: Conversion-time diagram for oct-2-yne in the presence of complex **139** (5 mol%) in $[D_8]$ -toluene, as monitored by 1H NMR spectroscopy at 25 °C.

Pyridine Scavenger Strategy

A flame-dried *J. Young* NMR tube filled with argon was charged with a stock solution of adduct **139•Py** (6.6 mM in $[D_8]$ -toluene, 0.5 mL, 3.0 μ mol) and a 1H NMR spectrum was recorded at 25 °C. A solution of triphenylborane (0.06 M in $[D_8]$ -toluene, 50 μ L, 3.0 μ mol) was then added, causing a color change from purple to orange (see inserted photographs), along with a characteristic change of the 1H NMR spectrum recorded at 25 °C.

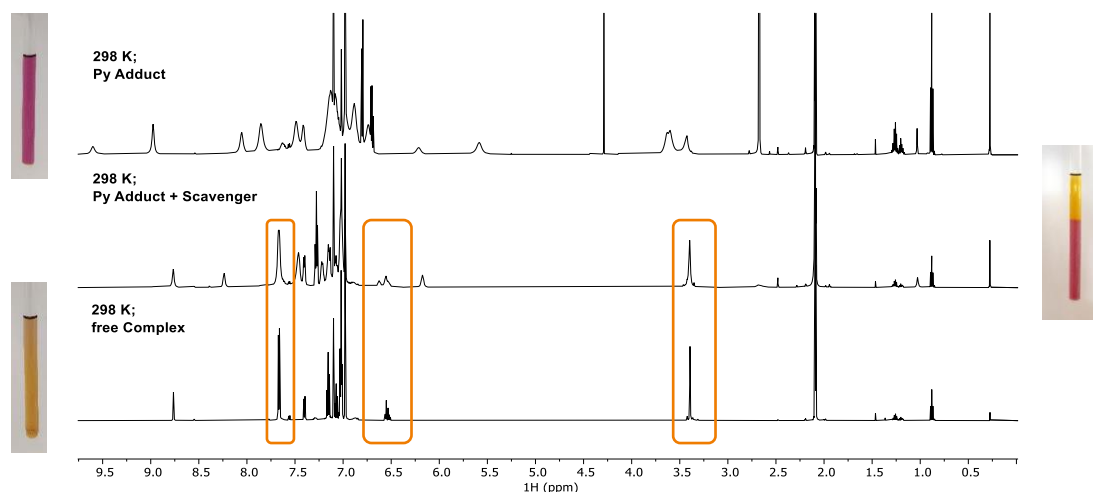
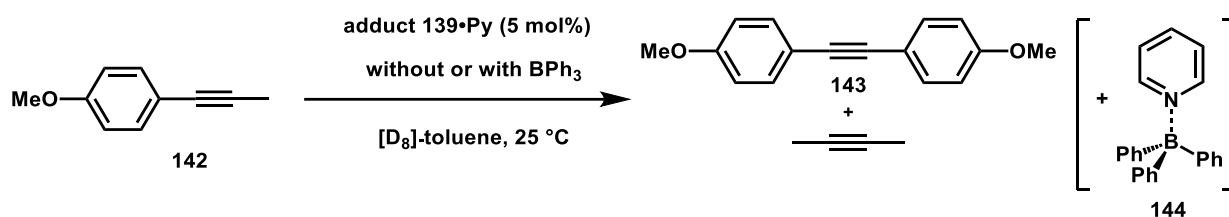


Figure S 5: 1H -NMR spectra of solutions of **139•Py**, **139•Py** after the addition of BPh_3 and the unligated complex **139** in $[D_8]$ -toluene and photographs of the pertinent samples.

Benchmarking Experiment for Adduct **139•Py** with/without Pyridine Scavenger (at 25 °C)



A flame-dried *J. Young* NMR tube filled with argon was charged with a stock solution of adduct **139•Py** (6.0 mM in $[D_8]$ -toluene, 0.45 mL, 3.0 μ mol, 5 mol%). A solution of triphenylborane (0.06 M in $[D_8]$ -toluene, 50 μ L, 3.0 μ mol) was added, followed by a solution of alkyne **142** (0.6 M in $[D_8]$ -toluene, 100 μ L, 60.0 μ mol). The conversion of the substrate to tolane **143** was monitored by 1H NMR spectroscopy at 25 °C.

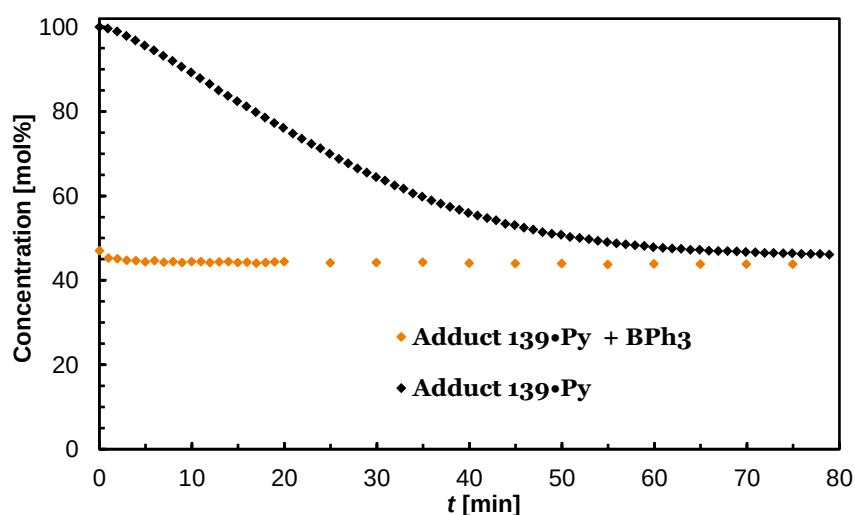
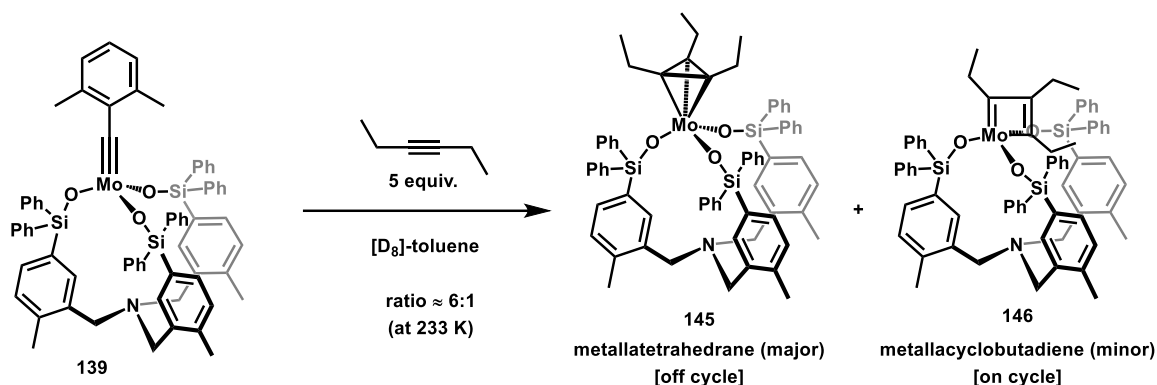


Figure S 6: Conversion-time diagram for alkyne **142** in the benchmark experiment using adduct **139•Py** (5 mol%) as catalyst in $[D_8]$ -toluene with or without the addition of BPh_3 as a pyridine scavenger at 25 °C.

Reactive Intermediates



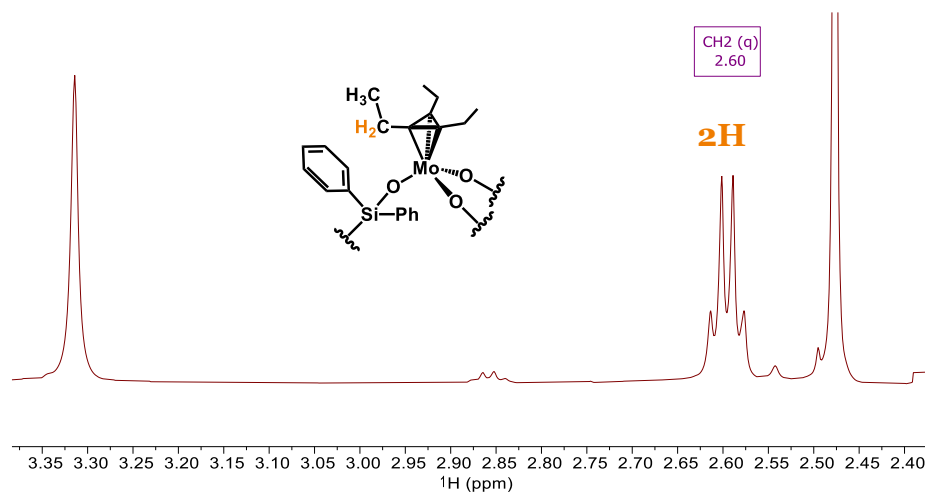
A flame-dried *J. Young* NMR tube filled with argon was charged with a stock solution of complex **139b** (20 mM in $[D_8]$ -toluene, 0.6 mL, 12 μ mol) and a 1H NMR spectrum recorded at 298 K. Hex-3-yne (7 μ L, 61 μ mol) was added and the *J. Young* NMR tube was inverted three times to ensure mixing, before a first 1H NMR spectrum was recorded. A variable-temperature NMR study was conducted from 298 K to 233 K.

The major product **145** could be characterized as metallatetrahedrane and all peaks were assigned. In contrast to what had been observed for the metallatetrahedrane derived from the canopy catalyst **8a**,^[74] however, the protons of the methylene groups of the ethyl substituents at the metallatetrahedrane unit are not diastereotopic in this case.

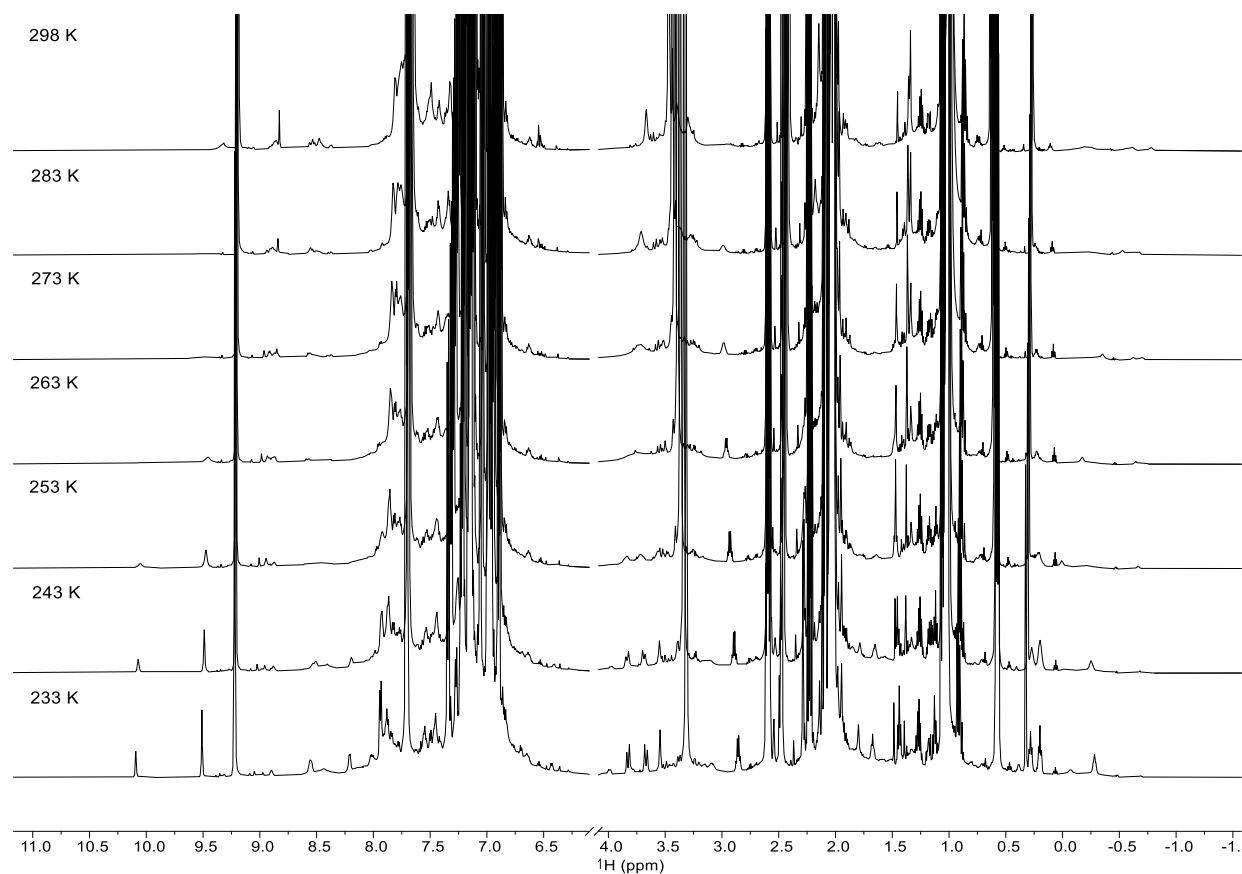
1H NMR (600 MHz, $[D_8]$ -toluene, 233 K): δ 9.22 (s, 3H), 7.71 (d, J = 6.8 Hz, 12H), 7.34 (d, J = 7.4 Hz, 3H), 7.22 (t, J = 7.4 Hz, 6H), 7.16 (d, J = 7.5 Hz, 12H), 6.96 (d, J = 7.4 Hz, 3H), 3.31 (s, 6H), 2.60 (q, J = 7.3 Hz, 6H), 2.01 (s, 9H), 0.58 (t, J = 7.5 Hz, 9H). **^{13}C NMR** (151 MHz, $[D_8]$ -toluene, 233 K): δ 138.4, 136.9, 137.6, 137.4, 135.6, 135.3, 135.1, 132.8, 129.5, 129.3, 82.6, 53.8, 20.3, 19.6, 14.9. **^{29}Si NMR** (119 MHz, $[D_8]$ -toluene, 233 K): δ -11.2.

The minor product **146** showed broad signals at higher temperatures. Due to the low concentration and lower symmetry not all signals could be unambiguously assigned, but all characteristic signals support the structure assignment as metallacyclobutadiene complex.^[74] This assignment is also consistent with the fact that this complex undergoes exchange with free hex-3-yne even at 233 K, whereas exchange for the metallatetrahedrane is only observed at 298 K.

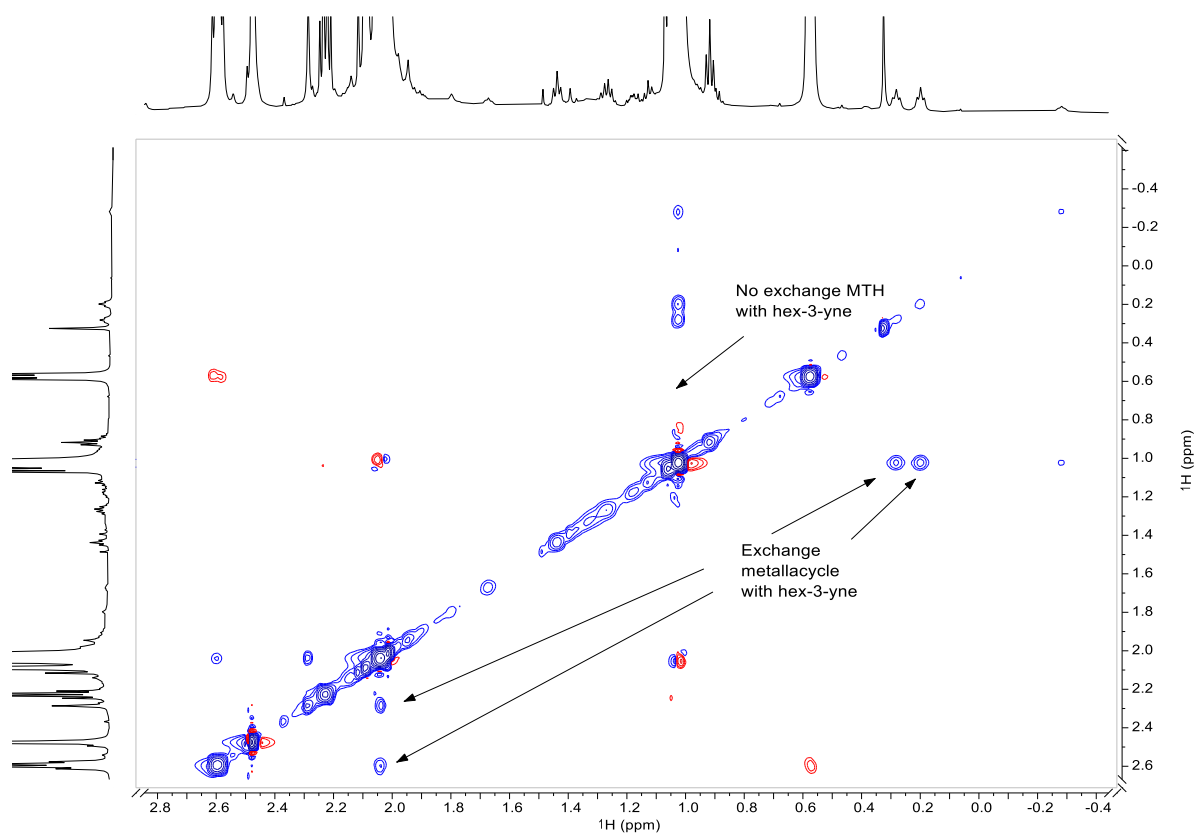
¹H NMR of the reaction mixture, 600 MHz, [D₈]-toluene, 233 K



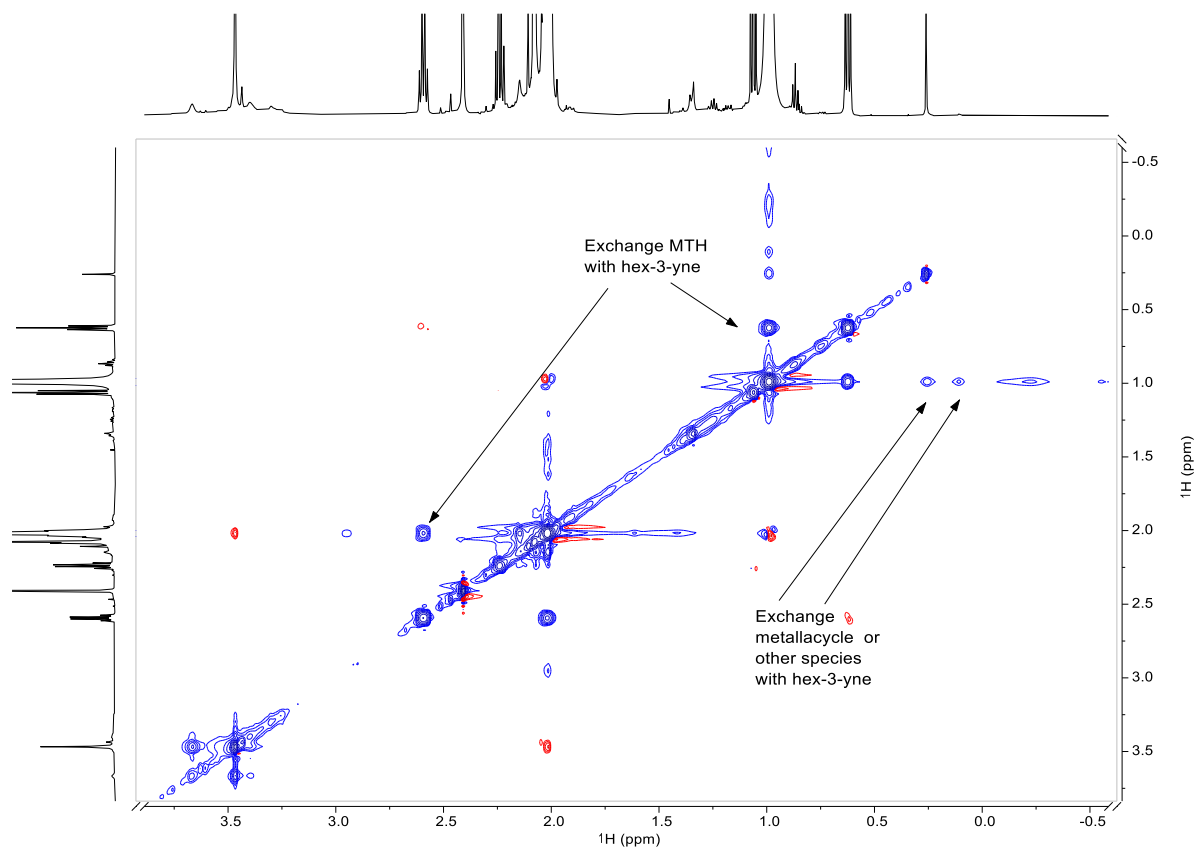
¹H NMR of the reaction mixture, 600 MHz, [D₈]-toluene, 298-233 K



^1H - ^1H ROESY of the reaction mixture, 600 MHz, $[\text{D}_8]$ -toluene, 233 K

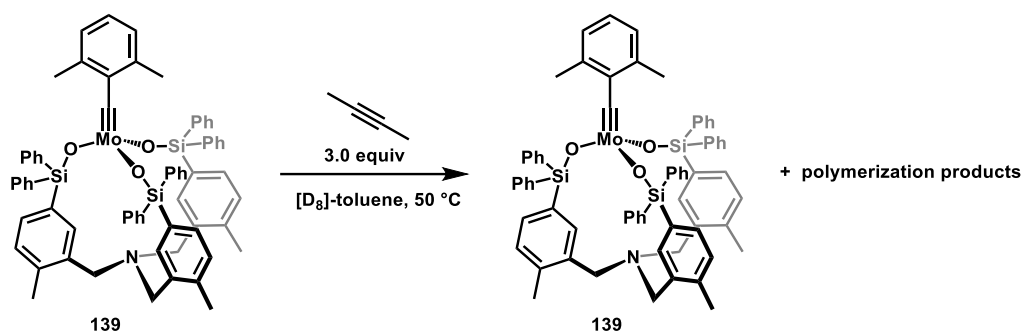


^1H - ^1H ROESY of the reaction mixture, 600 MHz, $[\text{D}_8]$ -toluene, 298 K

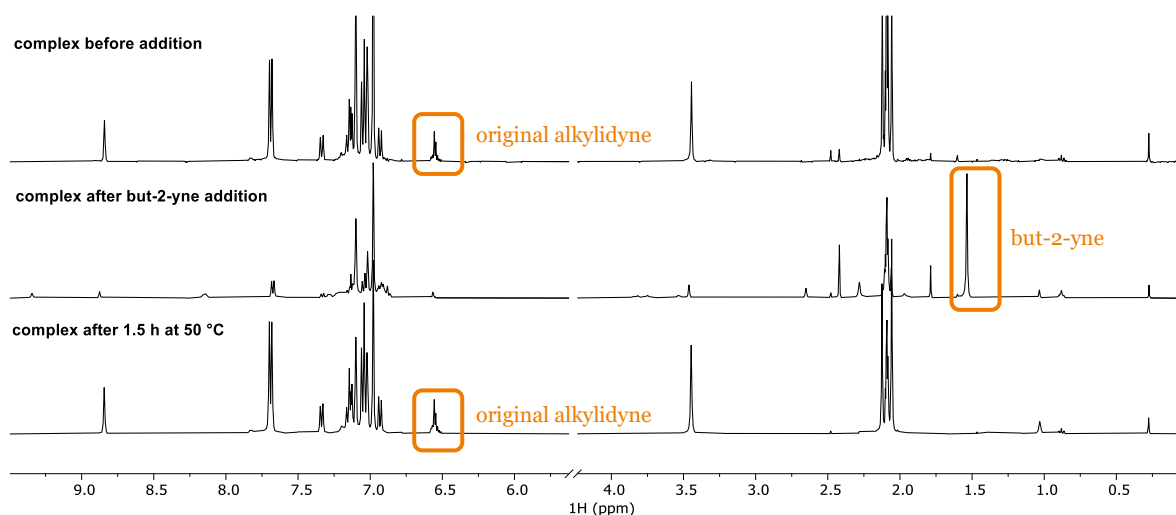


Stability Studies

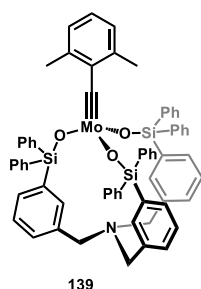
Stability in the Presence of But-2-yne



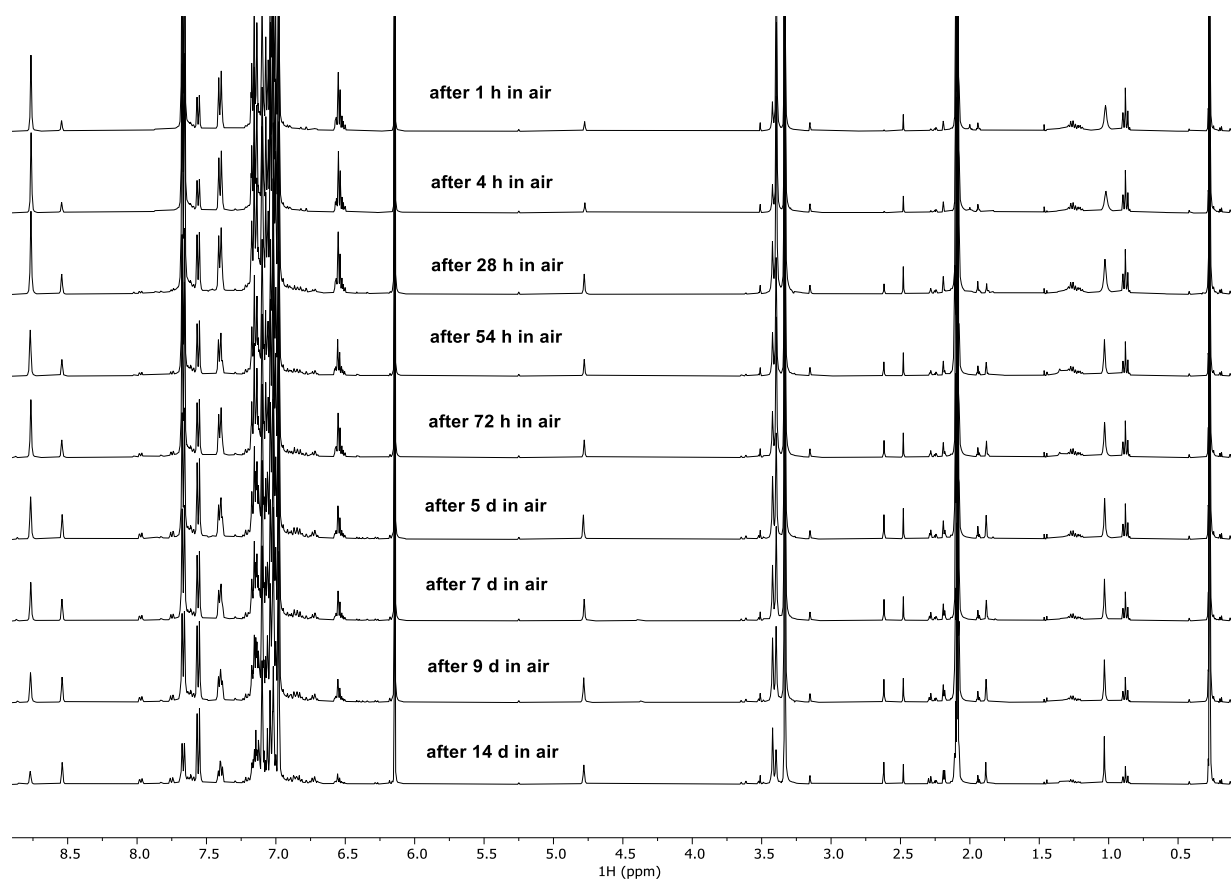
A flame-dried *J. Young* NMR tube filled with argon was charged with a stock solution of the complex **139** (18 mM in $[D_8]$ -toluene, 0.5 mL, 9 μ mol). An aliquot of a stock solution of but-2-yne (0.06 M in $[D_8]$ -toluene, 450 μ L, 27 μ mol) was added and the reactivity of complex **139** monitored by 1H NMR spectroscopy at 50 °C.



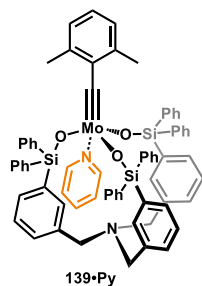
Upon addition of the but-2-yne, the signals of **139** instantly disappear and excess free but-2-yne is detected. Subsequently, the signal of but-2-yne became broad likely due to polymerization. After 1.5 h, no signal for but-2-yne could be observed any longer and the catalyst had returned to its original state.

Stability of Powdered Pyridine-free Complex **139 in Air**

A sample of complex **139a** was placed in a vial open to air, which was kept on the bench. At the indicated time intervals, aliquots of this batch (5 mg) were dissolved in [D₈]-toluene (0.5 mL) in a Schlenk flask and transferred into a flame-dried *J. Young* NMR tube filled with argon. The degree of decomposition was assessed by ¹H NMR spectroscopy at 25 °C.

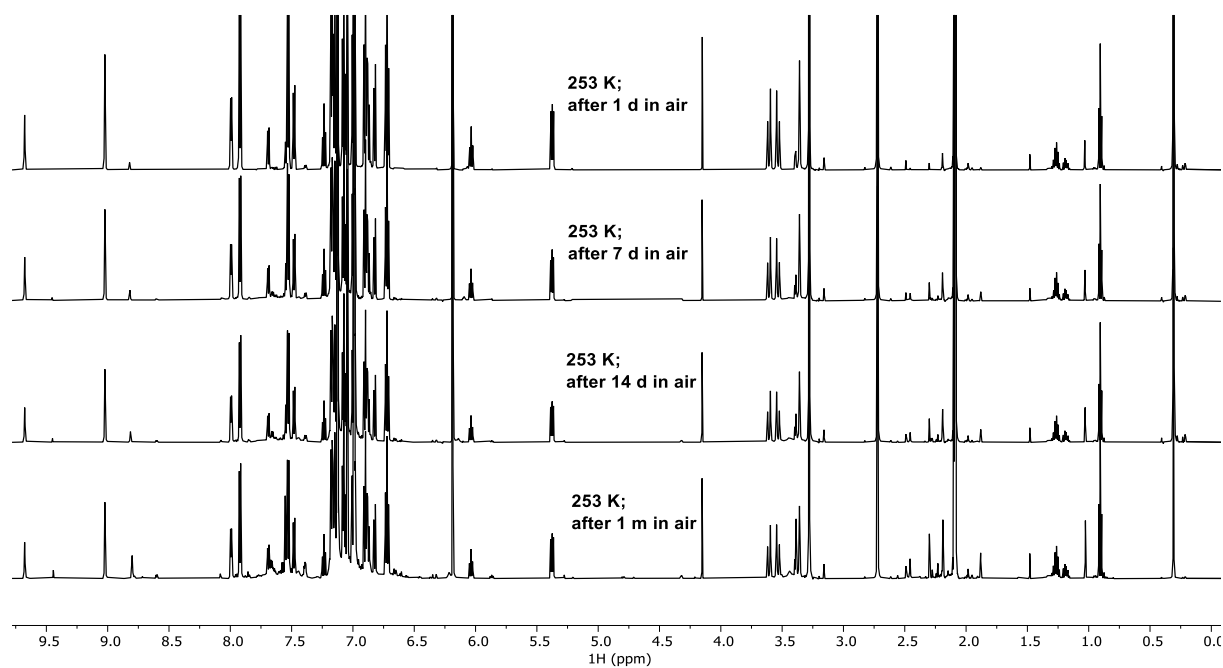
¹H NMR of complex **139a, 400 MHz, [D₈]-toluene, 25 °C**

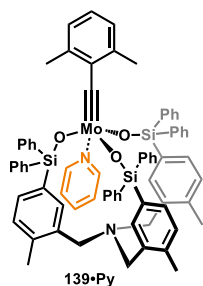
Stability of Adduct **139•Py** in Powder Form in Air



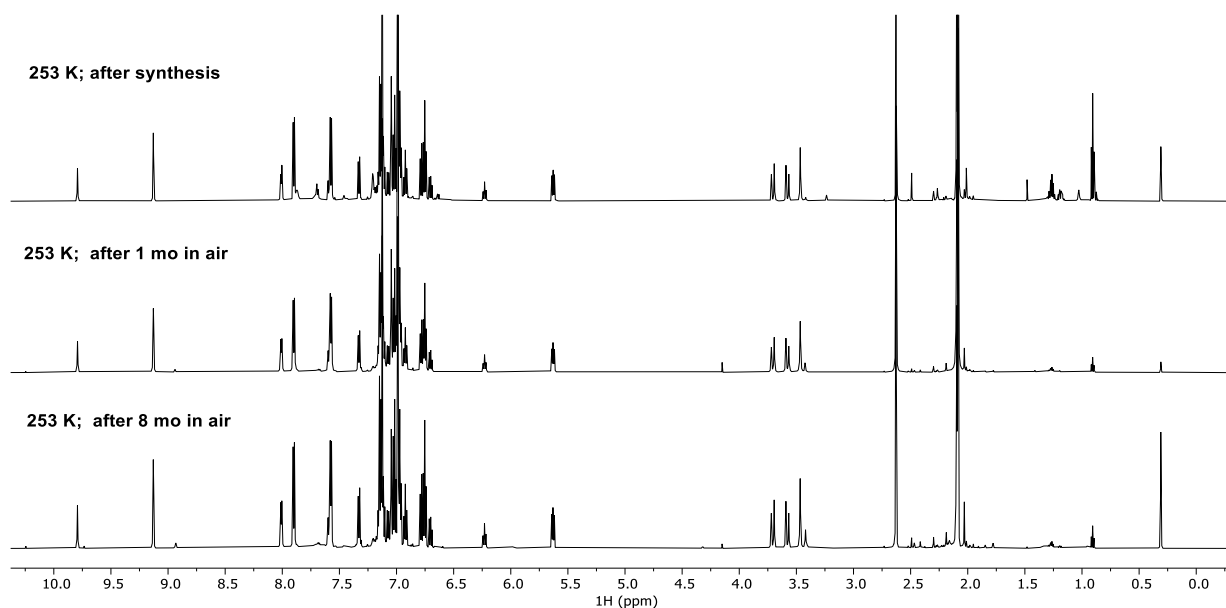
A sample of complex **139a•Py** in powder form was placed in a vial open to air, which was kept on the bench. At the indicated time intervals, aliquots of this batch (5 mg) were dissolved in $[D_8]$ -toluene (0.5 mL) in a Schlenk flask and transferred into a flame-dried *J. Young* NMR tube filled with argon. The degree of decomposition was assessed by 1H NMR spectroscopy at 25 °C.

1H NMR of adduct **139a•Py**, 400 MHz, $[D_8]$ -toluene, 253 K



Stability of Adduct $139\bullet\text{Py}$ in Crystalline Form in Air

A batch of crystalline adduct **139b•Py** was placed in a vial under air at ambient temperature and kept on the bench. At the indicated time intervals, aliquots of this batch (5 mg) were dissolved in $[\text{D}_8]$ -toluene (0.5 mL) in a Schlenk flask and the solution was transferred into a flame-dried *J. Young* NMR tube filled with argon. The stability was assessed by ^1H NMR spectroscopy at 253 K.

 ^1H NMR of adduct $139\text{b}\bullet\text{Py}$, 400 MHz, $[\text{D}_8]$ -toluene, 253 K

Additionally, the activity of the aged catalyst samples was tested in the standard benchmark experiment described above (*figure S7*).

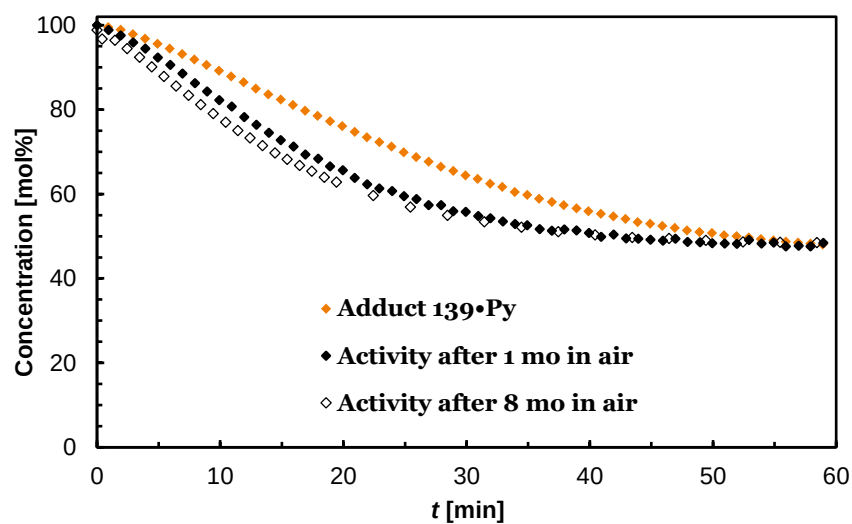
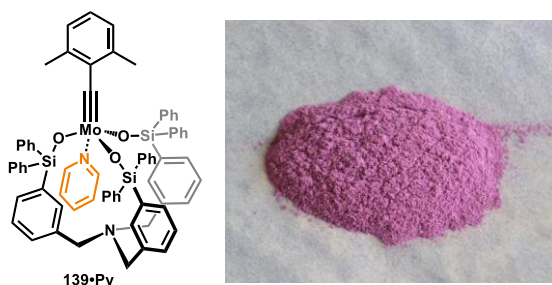
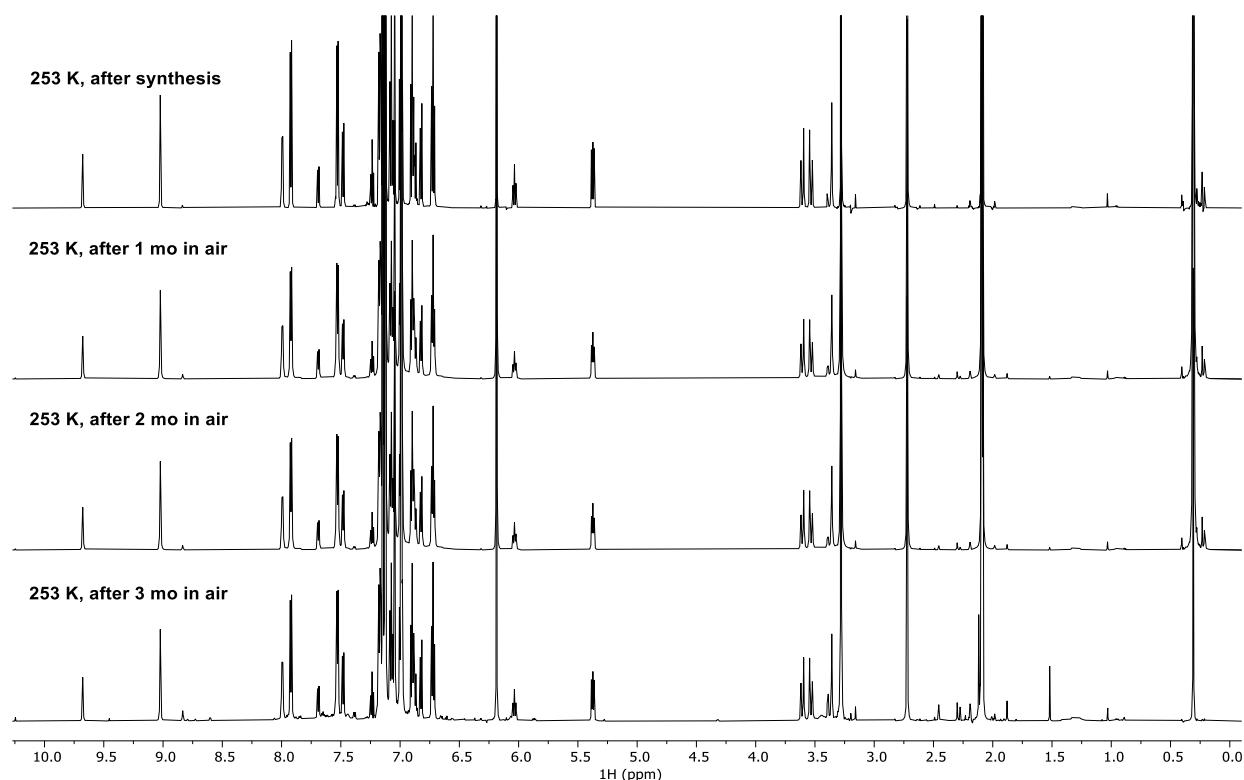


Figure S 7: Conversion-time diagrams for alkyne **142** in the benchmark experiment using samples of crystalline adduct **139•Py** (5 mol%) in $[D_8]$ -toluene as catalyst as monitored by 1H NMR spectroscopy at 25 °C. The samples were either freshly prepared, or had been stored in air for 1 month or 8 months.

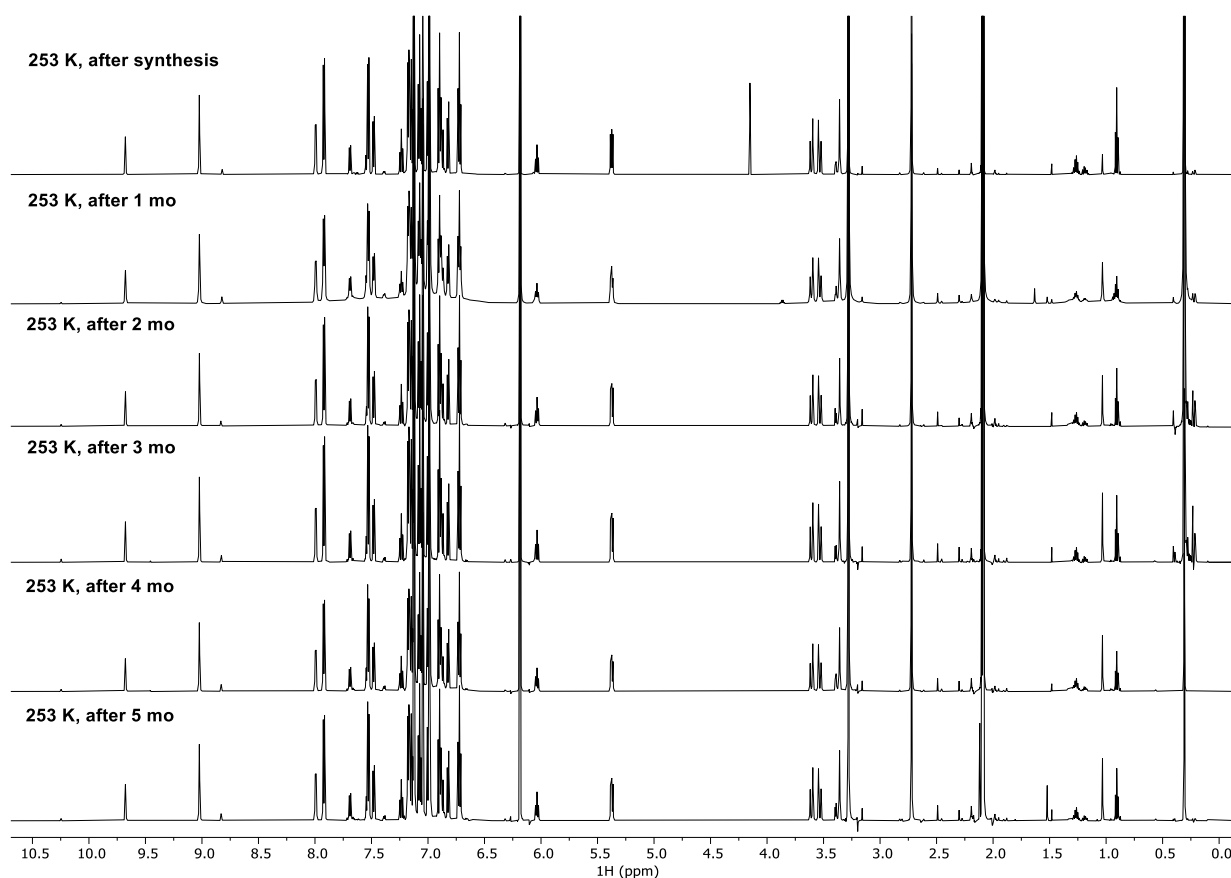
Stability of Adduct $139\cdot\text{Py}$ as a Powder under Optimal Storage Conditions

A batch of adduct **139·Py** in powder form was placed in an open vial which was stored at ambient temperature in an air-filled desiccator over silica orange gel (activated at 150 °C in the oven) as the drying agent. At the indicated time intervals, the vial was taken out of the desiccator and aliquots of the sample (5 mg) were dissolved in $[\text{D}_8]$ -toluene (0.5 mL) and the solution transferred into a flame-dried *J. Young* NMR tube filled with argon. The stability was assessed by ^1H NMR spectroscopy at 253 K. The storage vial was again placed in the desiccator.

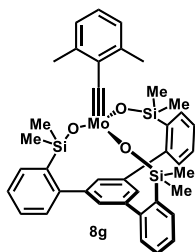
 ^1H NMR of adduct $139\cdot\text{Py}$ Stored in a Desiccator, 400 MHz, $[\text{D}_8]$ -toluene, 253 K

A second batch of adduct **139•Py** in powder form was placed in a vial which was briefly flushed with argon, closed with a non-air-tight screw cap, and stored at $-20\text{ }^{\circ}\text{C}$. At the indicated time intervals the vial was removed from the freezer, allowed to reach ambient temperature and opened in air. Aliquots of the sample (5 mg) were dissolved in $[\text{D}_8]$ -toluene (0.5 mL) and the solution transferred into a flame-dried *J. Young* NMR tube filled with argon. The stability was assessed by ^1H NMR spectroscopy at 253 K. The storage vial was again flushed with argon, closed with the screw cap, and stored at $-20\text{ }^{\circ}\text{C}$.

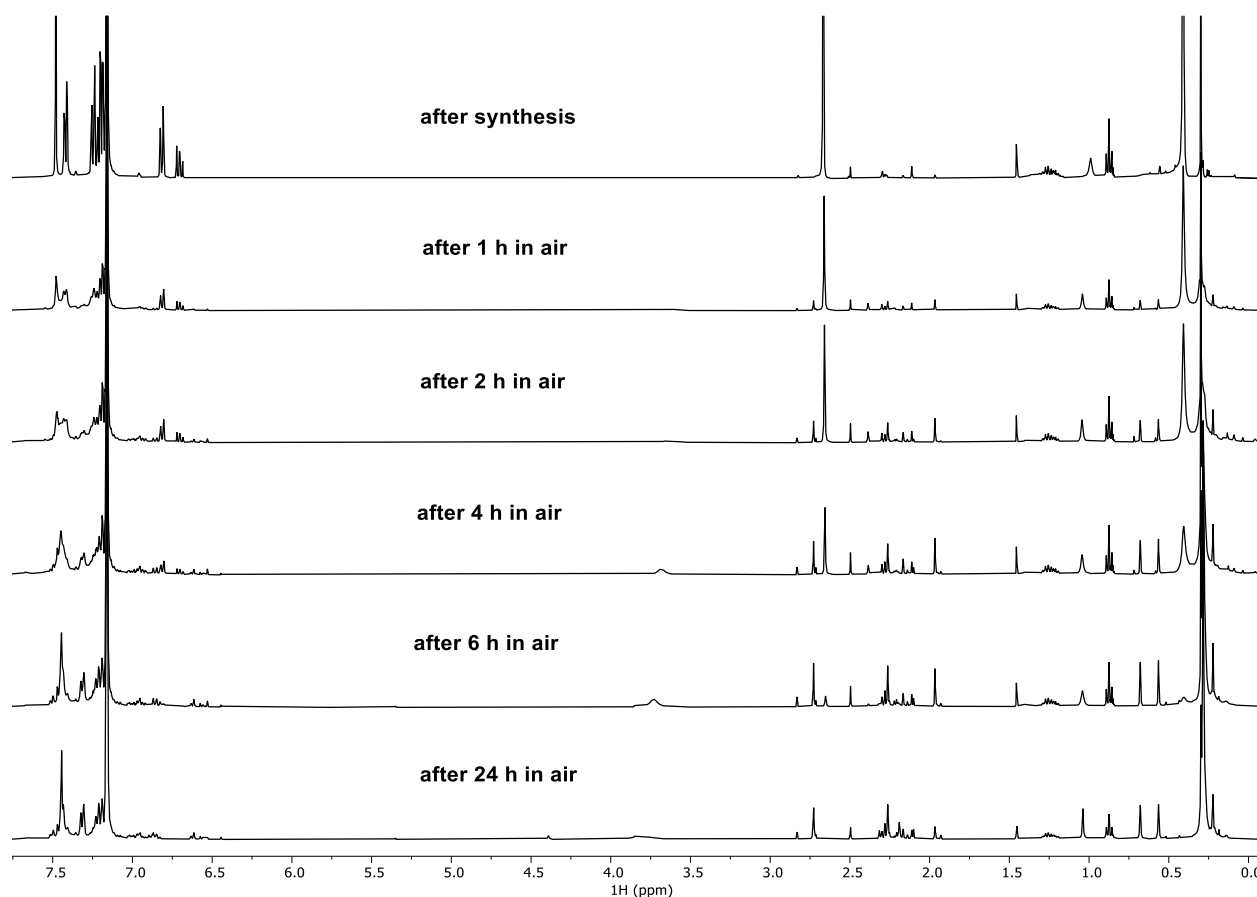
^1H NMR Spectra of adduct **139•Py stored in a freezer, 600 MHz, $[\text{D}_8]$ -toluene, 253 K**

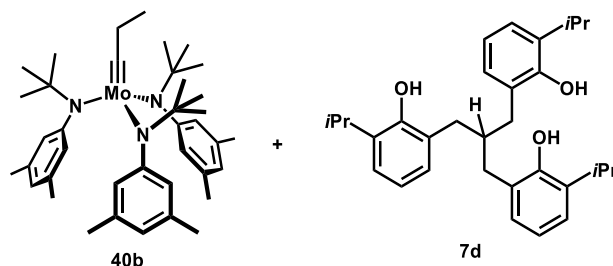


Elemental analysis of a sample taken from the catalyst batch after 4 months gave the following results: **Elemental analysis** (%) calc. for $\text{C}_{71}\text{H}_{62}\text{MoN}_2\text{O}_3\text{Si}_3$: C 72.79, H 5.33, N 2.39; found: C 72.42, H 5.51, N 2.31.

Stability of Adduct **8g as a Powder in Air**

A sample of complex **8g** was placed in a vial open to air, which was kept on the bench. At the indicated time intervals, aliquots of this batch (7 mg) were dissolved in [D₆]-benzene (0.55 mL) in a Schlenk flask and transferred into a flame-dried *J. Young* NMR tube filled with argon. The degree of decomposition was assessed by ¹H NMR spectroscopy at 25 °C.

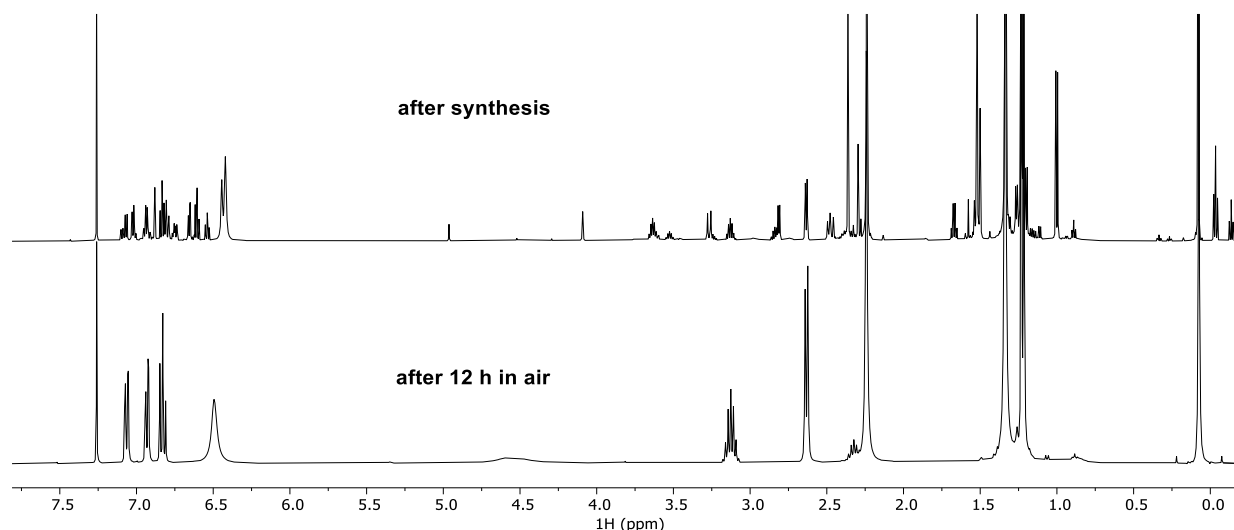
¹H NMR of complex **8g, 400 MHz, [D₆]-benzene, 25 °C**

Stability of a Zhang Type System (**40b** + **7d**) in Air

A 5 mL Schlenk flask was charged with molybdenum alkylidyne **40b** (10 mg, 15 μ mol) and deuterated chloroform (1.0 mL). Ligand **7d** (6.9 mg, 15 μ mol) was added and the resulting solution was stirred for 30 min. One half of the solution (0.5 mL) was transferred into a flame-dried *J. Young* NMR tube filled with argon and analyzed by NMR spectroscopy. The ^1H NMR (see below) showed several components. A more detailed analysis is given in *chapter 3.5*. Importantly, the ^1H NMR and HMBC spectra were virtually identical to the corresponding spectra depicted in the Supporting Information of ref.^[70b]

Solvents were removed from the other half of the solution to give a brown viscous residue, which was exposed to air. After 12 h, the residue was dissolved in deuterated chloroform (0.5 mL) in a Schlenk flask and transferred into a flame-dried *J. Young* NMR tube filled with argon. The degree of decomposition was assessed by ^1H NMR spectroscopy at 25 $^\circ\text{C}$.

^1H NMR of a mixture of ligand **7d and molybdenum alkylidyne **40b**, 600 and 400 MHz, CDCl_3 , 25 $^\circ\text{C}$**

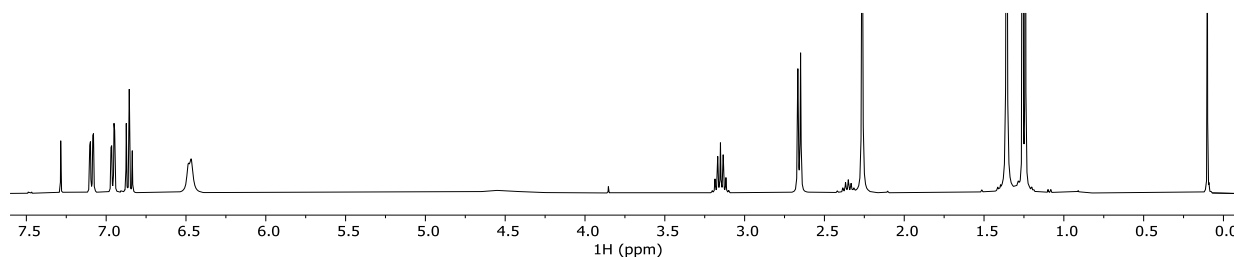


To confirm this conclusion, a small amount of alkyne **142** (ca. 3 mg) was added to the solution, but no metathesis reaction was observed by ^1H NMR, showing that all catalytic activity was lost.

Alternative Set-Up: A sample of molybdenum alkylidyne **4ob** was placed in a vial open to air, which was kept on the bench. After 2 h, an aliquot of this “aged” batch (1.9 mg, 2.9 μmol) was dissolved in deuterated chloroform (0.5 mL) in a Schlenk flask and ligand **7d** (1.2 mg, 2.9 μmol) was added. After stirring for 30 min, the solution was transferred into a flame-dried *J. Young* NMR tube filled with argon. No signs of complex formation were observed but only signals of the free ligand and unbound $\text{HN}[(\text{Ar})(\text{tBu})]_3$ derived from **4od** were detected (see below), implying that alkylidyne **4od** must have been fully decomposed before **7d** was introduced.

To confirm this conclusion, a small amount of alkyne **142** (ca. 3 mg) was added to the solution, but no metathesis reaction was observed by ^1H NMR, showing that all catalytic activity was lost.

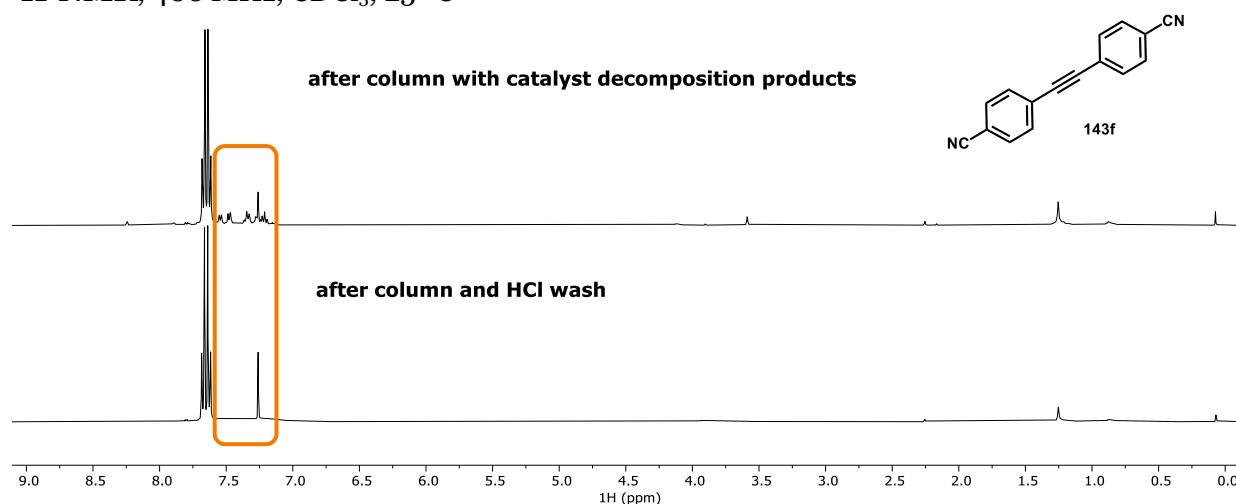
^1H NMR of a mixture of ligand **7d and molybdenum alkylidyne **4ob** after exposure to air, 400 MHz, CDCl_3 , 25 $^\circ\text{C}$**



Assisted Ligand Removal

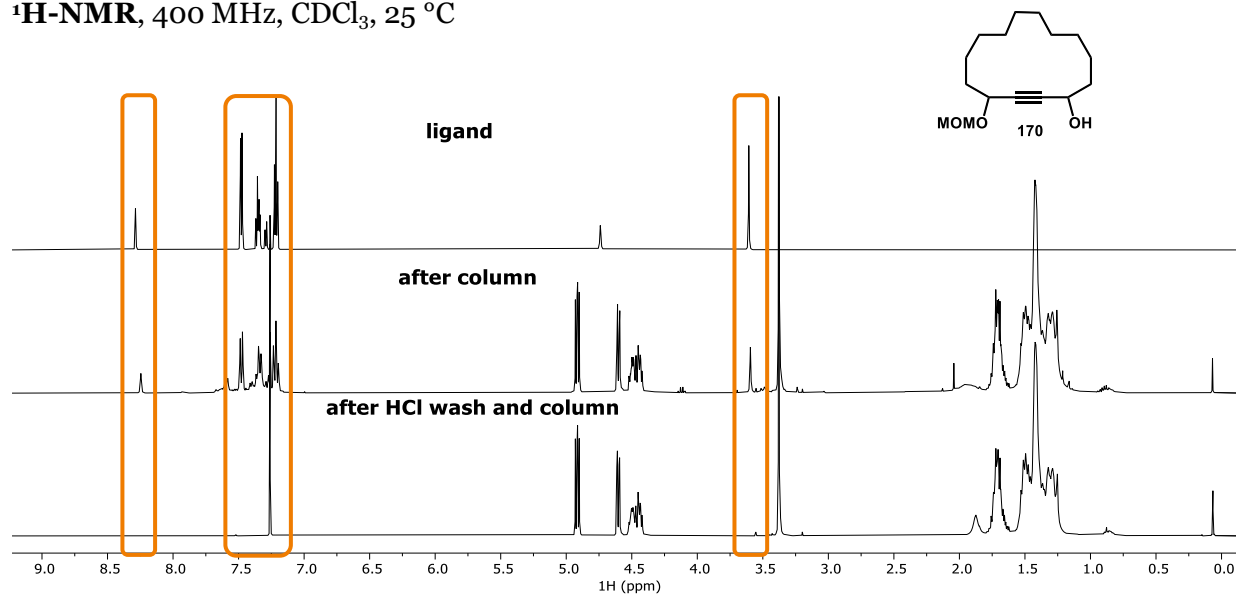
Advantage was taken of the heteroatom in the ligand backbone in order to separate products that proved to be copolar with catalyst debris formed upon work up. In a first example (compound **143f**) it sufficed to dissolve the material isolated after flash column chromatography in ethyl acetate and to wash this solution three times with aqueous HCl (3 M).

¹H-NMR, 400 MHz, CDCl₃, 25 °C



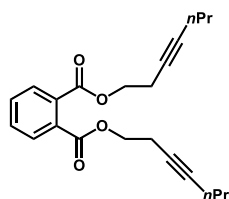
In a second example (compound **170**), the crude material was washed with aqueous HCl (3 M) prior to flash column chromatography in order to fully remove the catalyst decomposition products.

¹H-NMR, 400 MHz, CDCl₃, 25 °C



New Substrates

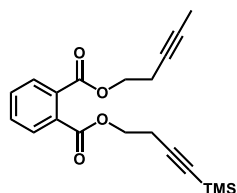
Diyne 172b



A 250 mL, one-necked flask was charged in air with phthalolyl chloride (2.00 mL, 13.8 mmol) and dichloromethane (70 mL). The solution was cooled to 0 °C before 3-hetyn-1-ol (3.36 mL, 27.6 mmol), pyridine (2.23 mL, 27.6 mmol) and 4-(dimethylamino)-pyridine (17 mg, 0.14 mmol) were added. The mixture was stirred at ambient temperature for 7 h. Water (50 mL) was added, the aqueous layer was extracted with dichloromethane (3 × 25 mL), the combined organic phases were washed with aqueous hydrogen chloride (1 M, 50 mL) and an a saturated aqueous solution of the sodium bicarbonate (70 mL). The organic layer was dried over magnesium sulfate and filtered, and the solvents were evaporated. The residue was purified by flash chromatography on silica gel (hexane/ethyl acetate, 9:1) to give the title compound as a colorless oil (3.50 g, 72%).

¹H NMR (400 MHz, CDCl₃): δ 7.74 (dd, *J* = 5.7, 3.3 Hz, 2H), 7.54 (dd, *J* = 5.7, 3.3 Hz, 2H), 4.38 (t, *J* = 7.2 Hz, 4H), 2.61 (tt, *J* = 7.2, 2.4 Hz, 4H), 2.13 (tt, *J* = 7.0, 2.4 Hz, 4H), 1.50 (h, *J* = 7.3 Hz, 4H), 0.96 (t, *J* = 7.4 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃): δ 167.4, 132.1, 131.2, 129.1, 82.3, 75.5, 64.1, 22.4, 20.9, 19.3, 13.6. **IR** (film): $\tilde{\nu}$ 2962, 2933, 1724, 1456, 1382, 1340, 1268, 1120, 1079, 1061, 1039, 100, 970, 742, 704. **HRMS** (ESI) calc. for C₂₂H₂₆O₄Na [M + Na]⁺ : 377.17233; found: 377.17237.

Diyne 172c



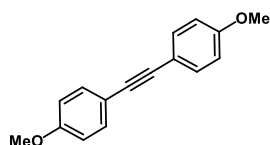
A 25 mL Schlenk flask was charged with diisopropylamine (0.12 mL, 0.84 mmol) and tetrahydrofuran (2 mL). The solution was cooled to −78 °C before a solution of *n*-butyllithium (1.6 M in hexane, 0.48 mL, 0.77 mL) was added. After 5 min, a solution of (but-3-yn-1-yl) (pent-3-yn-1-yl) phthalate (200 mg, 0.70 mmol) in tetrahydrofuran (2 mL) was added, causing a color change to yellow. After 15 min at −78 °C, a solution of trimethylchlorosilane (0.11 mL, 0.84 mL) in tetrahydrofuran (2 mL) was introduced and stirring was continued for 15 min at −78 °C. The mixture was allowed to warm to 0 °C and stirred at this temperature for 1 h. The reaction was quenched with a saturated solution of ammonium chloride (6 mL), the layers were separated, and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine (20 mL), dried over magnesium sulfate and filtered, and the solvents were evaporated. The residue was purified by flash chromatography on silica gel (hexane/ethyl acetate, 10:1) to give the title compound as a colorless oil (134 mg, 54%).

¹H NMR (400 MHz, CDCl₃): δ 7.78 – 7.71 (m, 2H), 7.58 – 7.51 (m, 2H), 4.40 (t, *J* = 7.2 Hz, 2H), 4.37 (t, *J* = 7.0 Hz, 2H), 2.68 (t, *J* = 7.2 Hz, 2H), 2.58 (ddq, *J* = 9.6, 7.2, 2.6 Hz, 2H), 1.79

(t, $J = 2.6$ Hz, 3H), 0.15 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3): δ 167.3, 167.3, 132.1, 132.0, 131.3, 131.2, 129.2, 102.1, 86.9, 77.6, 74.7, 64.1, 63.4, 20.4, 19.3, 3.6, 0.1. IR (film): $\tilde{\nu}$ 2960, 2179, 1728, 1449, 1384, 1336, 1273, 1124, 1081, 1061, 1039, 971, 843, 760, 744, 703, 642. HRMS (ESI) calc. for $\text{C}_{20}\text{H}_{24}\text{O}_4\text{SiNa} [\text{M} + \text{Na}]^+$: 379.13361; found: 379.13342.

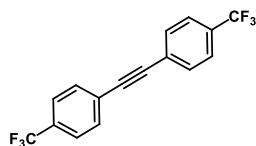
Alkyne Metathesis Reactions

Representative Procedure for Alkyne Homo-Metathesis. Compound 143a



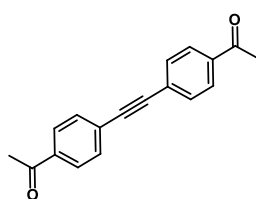
A 10 mL Schlenk flask was charged with 1-(4-methoxyphenyl)-1-propyne (**21**, 37 mg, 0.25 mmol), powdered molecular sieves (250 mg, 5 Å) and toluene (1.25 mL). Adduct **139•Py** (6 mg, 5 μmol , 2 mol%) was weight out in air and added in one portion to the mixture. After stirring for 12 h at ambient temperature, the reaction was quenched with ethanol (1 mL) and the mixture was filtered through a short pad of Celite® which was carefully rinsed with ethyl acetate (20 mL) and dichloromethane (10 mL). The combined filtrates were evaporated and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate, 70:1 to 50:1) to give the title compound as a colorless solid (27 mg, 91%). ^1H NMR (400 MHz, CDCl_3): δ 7.45 (d, $J = 8.8$ Hz, 4H), 6.87 (d, $J = 8.8$ Hz, 4H), 3.82 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 159.5, 133.0, 115.9, 114.1, 88.1, 55.4. The spectroscopic data was in agreement with the literature.^[314]

Compound 143b

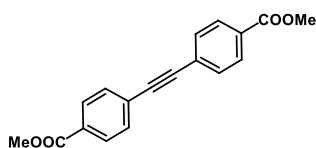


Prepared analogously with adduct **139•Py** as the catalyst (6 mg, 5 μmol , 2 mol%) at 50 °C. Purified by flash chromatography (hexane) to give the title compound as a colorless solid (35 mg, 89%). ^1H NMR (400 MHz, CDCl_3): δ 7.70 – 7.59 (m, 8H). ^{13}C NMR (101 MHz, CDCl_3): δ 131.6, 131.1, 130.8, 130.5, 130.2, 128.0, 126.5, 125.6, 125.5, 125.4, 125.3, 122.6, 119.9, 90.3. The spectroscopic data was in agreement with the literature.^[74]

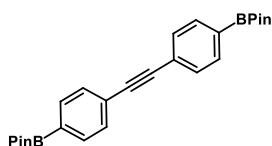
Compound 143c



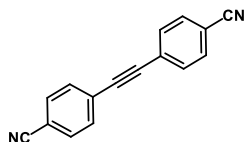
Prepared analogously with adduct **139•Py** as the catalyst (6 mg, 5 μmol , 2 mol%) at 50 °C. Purified by flash chromatography (hexane/ethyl acetate, 8:2 to 1:1) to give the title compound as a colorless solid (28 mg, 85%). ^1H NMR (300 MHz, CDCl_3): δ 7.95 (d, $J = 8.0$ Hz, 4H), 7.63 (d, $J = 8.1$ Hz, 4H), 2.61 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 197.1, 136.6, 131.6, 128.1, 127.5, 91.5, 26.5. The spectroscopic data was in agreement with the literature.^[31b]

Compound 143d

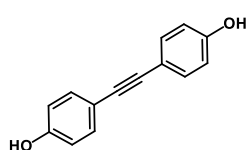
Prepared analogously with adduct **139•Py** as the catalyst (6 mg, 5 μ mol, 2 mol%) at 50 °C. Purified by flash chromatography (hexane/dichloromethane, 1:1) to give the title compound as a colorless solid (36 mg, 99%). **¹H NMR** (400 MHz, CDCl₃): δ 8.04 (d, J = 8.5 Hz, 4H), 7.60 (d, J = 8.6 Hz, 4H), 3.93 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃): δ 166.6, 131.8, 130.1, 129.7, 127.5, 91.5, 52.4. The spectroscopic data was in agreement with the literature.^[43a]

Compound 143e

Prepared analogously with adduct **139•Py** as the catalyst (6 mg, 5 μ mol, 2 mol%) at 50 °C. Purified by flash chromatography (hexane/dichloromethane, 10:1 to 8:2) to give the title compound as a colorless solid (38 mg, 71%). **¹H NMR** (400 MHz, CDCl₃): δ 7.79 (d, J = 8.2 Hz, 4H), 7.53 (d, J = 8.2 Hz, 4H), 1.35 (s, 24H). **¹³C NMR** (101 MHz, CDCl₃): δ 134.7, 131.0, 126.0, 91.0, 84.1, 25.0. **IR** (film): $\tilde{\nu}$ 2975, 1608, 1399, 1356, 1322, 1273, 1263, 1166, 1141, 1088, 1018, 962, 909, 859, 836, 739, 670, 652. **HRMS** (ESI) calc. for C₂₆H₃₂B₂O₄Na [M + Na]⁺: 453.23794; found: 453.23815. The spectroscopic data was in agreement with the literature.^[315]

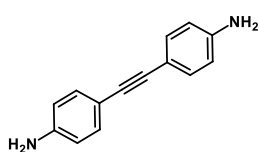
Compound 143f

Prepared analogously with adduct **139•Py** as the catalyst (15 mg, 13 μ mol, 5 mol%) at 50 °C. Purified by flash chromatography (hexane/ethyl acetate 12:1 to 3:2 to 1:1) to give crude product containing the co-polar ligand. To remove the impurity, the crude product was dissolved in ethyl acetate (30 mL) and the organic layer washed with aqueous hydrogen chloride (3 $\times$ 10 mL, 3 M). The organic layer was dried over magnesium sulfate and filtered, and the solvents were evaporated to give the title compound as a colorless solid (26 mg, 91%). **¹H NMR** (400 MHz, CDCl₃): δ 7.67 (d, J = 8.6 Hz, 4H), 7.63 (d, J = 8.7 Hz, 4H). **¹³C NMR** (101 MHz, CDCl₃): δ 132.4, 132.3, 127.2, 118.4, 112.6, 91.7. The spectroscopic data was in agreement with the literature.^[96c]

Compound 143g

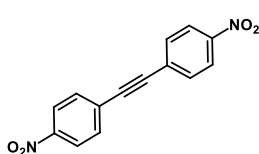
Prepared analogously with adduct **139•Py** as the catalyst (15 mg, 13 μ mol, 5 mol%) at 50 °C. Purified by flash chromatography (hexane/ethyl acetate, 8:2 to 1:1) to give the title compound as a red solid (36 mg, 98%). **¹H NMR** (400 MHz, CD₃CN): δ 7.35 (d, J = 8.8 Hz, 4H), 7.27 (bs, 2H), 6.81 (d, J = 8.7 Hz, 4H). **¹³C NMR** (101 MHz, CD₃CN): δ 157.8, 133.7, 116.3, 115.6, 88.3. The spectroscopic data was in agreement with the literature.^[73]

Compound 143h



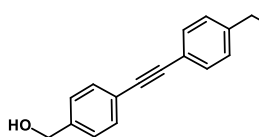
Prepared analogously with complex **140** as the catalyst (10 mg, 13 μ mol, 5 mol%) at 110 °C. Purified by flash chromatography (hexane/ethyl acetate, 3:1 to 1:1) to give the title compound as an orange solid (24 mg, 71%). **¹H NMR** (400 MHz, CDCl₃): δ 7.30 (d, J = 8.6 Hz, 4H), 6.62 (d, J = 8.5 Hz, 4H), 3.77 (s, 4H). **¹³C NMR** (101 MHz, CDCl₃): δ 146.3, 132.8, 114.9, 113.5, 87.9. The spectroscopic data was in agreement with the literature.^[73]

Compound 143i



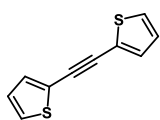
Prepared analogously with complex **140** as the catalyst (15 mg, 17 μ mol, 7 mol%) at 110 °C. Purified by flash chromatography (hexane/ethyl acetate, 4:1) to give the title compound as a yellow solid (15 mg, 45%). **¹H NMR** (400 MHz, CDCl₃): δ 8.26 (d, J = 8.9 Hz, 4H), 7.72 (d, J = 8.8 Hz, 4H). **¹³C NMR** (101 MHz, CDCl₃): δ 147.8, 132.8, 129.0, 123.9, 92.1. **HRMS** (EI) calc. for C₁₄H₈N₂O₄ [M]⁺: 268.04786; found: 258.04825. The spectroscopic data was in agreement with the literature.^[316]

Compound 147



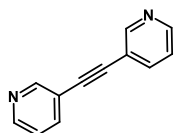
Prepared analogously with adduct **139•Py** as the catalyst (15 mg, 13 μ mol, 5 mol%) at 50 °C. Purified by flash chromatography (dichloromethane/methanol 98:2) to give the title compound as a colorless solid (24 mg, 81%). **¹H NMR** (400 MHz, [D₆]-DMSO): δ 7.50 (d, J = 8.2 Hz, 4H), 7.36 (d, J = 8.1 Hz, 4H), 5.28 (t, J = 5.7 Hz, 2H), 4.53 (d, J = 5.7 Hz, 4H). **¹³C NMR** (101 MHz, [D₆]-DMSO): δ 143.3, 131.1, 126.6, 120.5, 89.0, 62.5. The spectroscopic data was in agreement with the literature.^[317]

Compound 148



Prepared analogously with adduct **139•Py** as the catalyst (6 mg, 5 μ mol, 2 mol%) at 50 °C. Purified by flash chromatography (hexane/dichloromethane, 100:1) to give the title compound as a colorless solid (21 mg, 88%). **¹H NMR** (400 MHz, CDCl₃): δ 7.31 (dd, J = 5.2, 1.2 Hz, 2H), 7.28 (dd, J = 3.7, 1.2 Hz, 2H), 7.01 (dd, J = 5.2, 3.6 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃): δ 132.3, 127.8, 127.3, 123.1, 86.3. The spectroscopic data was in agreement with the literature.^[31b]

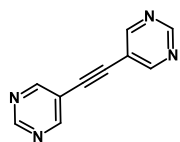
Compound 149



Prepared analogously with adduct **139•Py** as the catalyst (6 mg, 5 μ mol, 2 mol%) at 90 °C. Purified by flash chromatography (hexane/ethyl acetate, 3:2 to 1:1) to give the title compound as a yellowish solid (20 mg, 89%). **¹H NMR**

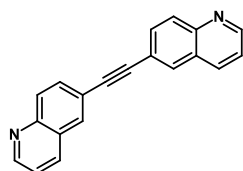
(400 MHz, CDCl_3): δ 8.78 (dd, $J = 2.2, 0.9$ Hz, 2H), 8.58 (dd, $J = 4.9, 1.7$ Hz, 2H), 7.83 (dt, $J = 7.9, 1.9$ Hz, 2H), 7.31 (ddd, $J = 7.9, 4.9, 0.9$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 152.5, 149.2, 138.7, 123.2, 119.9, 89.3. The spectroscopic data was in agreement with the literature.^[31b]

Compound 151



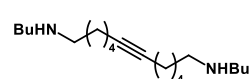
Prepared analogously with adduct **139•Py** as the catalyst (6 mg, 5 μmol , 2 mol%) at 100 °C. Purified by flash chromatography (dichloromethane/methanol, 95:5) to give the title compound as a colorless solid (10 mg, 44%). ^1H NMR (400 MHz, CDCl_3): δ 9.21 (s, 2H), 8.91 (s, 4H). ^{13}C NMR (101 MHz, CDCl_3): δ 159.0, 157.7, 118.7, 89.2. The spectroscopic data was in agreement with the literature.^[318]

Compound 140



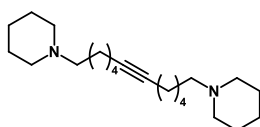
Prepared analogously with adduct **139•Py** as the catalyst (6 mg, 5 μmol , 2 mol%) at 50 °C. Purified by flash chromatography (dichloromethane/methanol, 99:1 to 98:2) to give the title compound as a colorless solid (28 mg, 80%). ^1H NMR (400 MHz, CDCl_3): δ 8.97 – 8.91 (m, 2H), 8.16 (dd, $J = 8.4, 1.7$ Hz, 2H), 8.13 – 8.04 (m, 4H), 7.86 (dd, $J = 8.7, 1.9$ Hz, 2H), 7.44 (dd, $J = 8.3, 4.2$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 151.3, 147.9, 135.9, 132.3, 131.5, 129.9, 128.2, 122.0, 121.4, 90.4. HRMS (EI) calc. for $\text{C}_{20}\text{H}_{12}\text{N}_2$ $[\text{M}]^+$: 280.09950; found: 280.09974. The spectroscopic data was in agreement with the literature.^[319]

Compound 155



Prepared analogously with adduct **139•Py** as the catalyst (15 mg, 13 μmol , 5 mol%) at 50 °C. Purified by flash chromatography (dichloromethane/methanol, 99:1 to 95:5 with 2% triethylamine) to give the title compound as a brown oil (31 mg, 80%). ^1H NMR (400 MHz, CD_2Cl_2): δ 2.64 – 2.47 (m, 8H), 2.20 – 2.06 (m, 4H), 1.71 (bs, 2H), 1.55 – 1.29 (m, 20H), 0.90 (t, $J = 7.3$ Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 80.4, 50.3, 50.1, 32.7, 30.1, 29.5, 27.0, 20.9, 19.0, 14.2. HRMS (ESI) calc. for $\text{C}_{20}\text{H}_{41}\text{N}_2$ $[\text{M} + \text{H}]^+$: 309.32643; found: 309.32658. The spectroscopic data was in agreement with the literature.^[74]

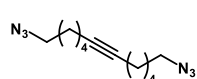
Compound 153



Prepared analogously with adduct **139•Py** as the catalyst (6 mg, 5 μmol , 2 mol%) at 50 °C. Purified by flash chromatography (hexane/ethyl acetate, 3:1 with trimethylamine 5%) to give the title compound as a yellow oil (35 mg, 80%). ^1H NMR (400 MHz, CDCl_3): δ 2.37 (d, $J = 14.1$ Hz, 8H), 2.27 (dd,

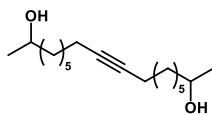
$J = 9.2, 6.5$ Hz, 4H), 2.18 – 2.09 (m, 4H), 1.57 (p, $J = 5.6$ Hz, 8H), 1.53 – 1.29 (m, 16H). ^{13}C NMR (101 MHz, CDCl_3): δ 80.3, 59.6, 54.8, 29.2, 27.1, 26.6, 26.1, 24.6, 18.8. The spectroscopic data was in agreement with the literature.^[73]

Compound 154



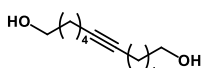
Prepared analogously with adduct **139•Py** as the catalyst (6 mg, 5 μmol , 2 mol%) at 50 °C. Purified by flash chromatography (hexane/ethyl acetate, 50:1) to give the title compound as a clear oil (24 mg, 77%). ^1H NMR (400 MHz, CDCl_3): δ 3.27 (t, $J = 6.9$ Hz, 4H), 2.16 (td, $J = 5.9, 2.0$ Hz, 4H), 1.68 – 1.56 (m, 4H), 1.55 – 1.40 (m, 8H). ^{13}C NMR (101 MHz, CDCl_3): δ 80.2, 51.5, 28.7, 28.5, 26.0, 18.7. The spectroscopic data was in agreement with the literature.^[73]

Compound 50



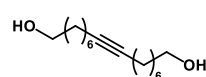
Prepared analogously with adduct **139•Py** as the catalyst (15 mg, 13 μmol , 5 mol%) at 50 °C. Purified by flash chromatography (dichloromethane/methanol, 98:2 to 90:10) to give the title compound as a yellow oil (29 mg, 82%). ^1H NMR (400 MHz, CDCl_3): δ 3.82 – 3.72 (m, 2H), 2.17 – 2.08 (m, 4H), 1.62 (s(br), 2H), 1.52 – 1.24 (m, 20H), 1.17 (d, $J = 6.2$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 80.4, 68.2, 39.4, 29.3, 29.2, 28.9, 25.8, 23.6, 23.6, 18.8. The spectroscopic data was in agreement with the literature.^[73]

Compound 156a



Prepared analogously with adduct **139•Py** as the catalyst (15 mg, 13 μmol , 5 mol%) at 50 °C using 4 Å molecular sieves (250 mg) instead of 5 Å molecular sieves. Purified by flash chromatography (hexane/ethyl acetate, 1:1) to give the title compound as a colorless solid (16 mg, 65%). ^1H NMR (400 MHz, CDCl_3): δ 3.64 (t, $J = 6.4$ Hz, 4H), 2.23 – 2.11 (m, 4H), 1.69 (s, 2H), 1.63 – 1.39 (m, 12H). ^{13}C NMR (101 MHz, CDCl_3): δ 80.3, 63.0, 32.4, 28.9, 25.1, 18.8. HRMS (ESI) calc. for $\text{C}_{12}\text{H}_{23}\text{O}_2$ $[\text{M} + \text{H}]^+$: 199.16962; found: 199.16956. The spectroscopic data was found to be in agreement with the data reported in the literature.^[320]

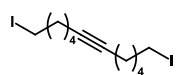
Compound 156b



Prepared analogously with adduct **139•Py** as the catalyst (15 mg, 13 μmol , 5 mol%) at 50 °C. Purified by flash chromatography (hexane/ethyl acetate, 2:3) to give the title compound as a colorless solid (25 mg, 79%). ^1H NMR (400 MHz, CDCl_3): δ 3.63 (t, $J = 6.6$ Hz, 4H), 2.18 – 2.09 (m, 4H), 1.62 – 1.28 (m, 22H). ^{13}C NMR (101 MHz, CDCl_3): δ 80.4, 63.1, 32.9, 29.15, 29.09, 28.9, 25.8, 18.8. HRMS (ESI) calc. for $\text{C}_{16}\text{H}_{30}\text{O}_2\text{Na}$

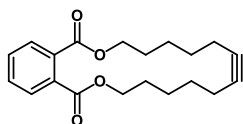
[M + Na]⁺: 277.21387; found: 277.21381. The spectroscopic data was in agreement with the literature.^[73]

Compound 152



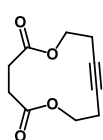
A 10 mL Schlenk flask was charged with 8-iodooct-2-yne (59 mg, 0.25 mmol), powdered molecular sieves (250 mg, 5Å) and toluene (1.15 mL). Adduct **139•Py** (6 mg, 5 μmol, 2 mol%) was weight out in air and added in one portion. A stock solution of triphenylborane (0.01 M in toluene, 0.5 mL, 5 μmol, 2 mol%) was added and the mixture was stirred for 1 h at ambient temperature. The reaction was quenched with ethanol (1 mL) and the mixture was filtered through a short pad of Celite® which was carefully rinsed with ethyl acetate (20 mL) and dichloromethane (10 mL). The solvents were evaporated and the residue was purified by flash chromatography on silica (hexane/ethyl acetate, 95:5) to give the title compound as a yellow oil (48 mg, 82%). ¹H NMR (400 MHz, CDCl₃): δ 3.20 (t, *J* = 7.0 Hz, 4H), 2.16 (ddt, *J* = 5.1, 3.5, 2.0 Hz, 4H), 1.92 – 1.78 (m, 4H), 1.58 – 1.43 (m, 8H). ¹³C NMR (101 MHz, CDCl₃): δ 80.2, 33.2, 29.8, 28.1, 18.7, 7.0. The spectroscopic data was in agreement with the literature.^[74]

Representative Procedure for Ring Closing Alkyne Metathesis. Compound 167.

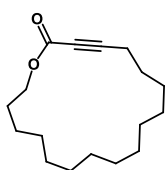


A 100 mL Schlenk flask was charged with di(oct-6-yn-1-yl) phthalate (38 mg, 0.10 mmol), powdered molecular sieves (250 mg, 5Å) and toluene (50 mL). Adduct **139•Py** (6 mg, 5 μmol, 5 mol%) was weight out in air and added in one portion, and the mixture was stirred for 12 h at ambient temperature. The reaction was quenched with ethanol (5 mL) and the mixture was filtered through a short pad of Celite® which was carefully rinsed with ethyl acetate (20 mL) and dichloromethane (10 mL). The solvents were evaporated and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate, 10:1) to give the title compound as a yellow oil (30 mg, 91%). ¹H NMR (400 MHz, CDCl₃): δ 7.73 (dd, *J* = 5.7, 3.3 Hz, 2H), 7.53 (dd, *J* = 5.7, 3.3 Hz, 2H), 4.35 (t, *J* = 6.0 Hz, 4H), 2.23 – 2.15 (m, 4H), 1.78 (dq, *J* = 9.2, 5.8 Hz, 4H), 1.63 – 1.44 (m, 8H). ¹³C NMR (101 MHz, CDCl₃): δ 168.0, 132.4, 131.1, 129.0, 80.7, 66.5, 28.5, 28.1, 26.0, 18.7. The spectroscopic data was in agreement with the literature.^[31b]

Compound 165

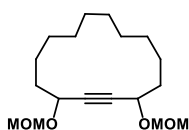


Prepared analogously with adduct **139•Py** as the catalyst (2 mg, 2 μmol, 2 mol%) at 50 °C. Purified by flash chromatography (hexane/ethyl acetate, 9:1) to give the title compound as a colorless oil (19 mg, 97%). ¹H NMR (400 MHz, CDCl₃): δ 4.31 – 4.22 (m, 4H), 2.69 (s, 4H), 2.51 – 2.42 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 171.9, 78.9, 61.5, 30.1, 19.8. The spectroscopic data was in agreement with the literature.^[31b]

Compound 168

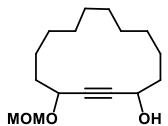
Prepared analogously with adduct **139•Py** as the catalyst (8.5 mg, 7 μ mol, 10 mol%) at reflux over 2 h. Purified by flash chromatography (hexane/ethyl acetate, 30:1) to give the title compound as a colorless solid (26 mg, 98%).

^1H NMR (400 MHz, CDCl_3): δ 4.27 – 4.18 (m, 2H), 2.41 (dd, J = 6.7, 4.8 Hz, 2H), 1.72 – 1.61 (m, 2H), 1.55 – 1.25 (m, 22H). **^{13}C NMR** (101 MHz, CDCl_3): δ 154.2, 89.1, 74.0, 65.7, 28.6, 28.3, 28.1, 27.74, 27.72, 27.2, 27.1, 26.8, 26.7, 26.5, 18.6. The spectroscopic data was in agreement with the literature.^[66b]

Compound 169

Prepared analogously with complex **140** as the catalyst (17 mg, 20 μ mol, 20 mol%) at reflux over 4 h. The complex was dissolved in a separate Schlenk

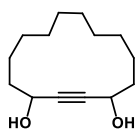
flask in toluene (1 mL) and the solution added dropwise to the solution of the diyne at 110 $^{\circ}\text{C}$. The crude product was purified by flash chromatography (hexane/ethyl acetate, 10:1 to 7:3) to give the title compound as a yellow oil (24 mg, 77%). **^1H NMR** (400 MHz, CDCl_3): δ 4.91 (dd, J = 6.7, 3.3 Hz, 2H), 4.59 (dd, J = 6.8, 2.9 Hz, 2H), 4.48 – 4.40 (m, 2H), 3.37 (s, 6H), 1.79 – 1.65 (m, 4H), 1.59 – 1.22 (m, 16H). **^{13}C NMR** (101 MHz, CDCl_3): δ 94.3, 94.3, 84.8, 84.6, 66.3, 66.2, 55.7, 35.1, 35.0, 26.6, 26.5, 25.9, 25.8, 23.9, 23.8, 22.5, 22.4. **HRMS** (ESI) calc. for $\text{C}_{18}\text{H}_{32}\text{O}_4\text{Na}$ $[\text{M} + \text{Na}]^+$: 335.21928; found: 335.21918. The spectroscopic data was in agreement with the literature.^[73]

Compound 170

Prepared analogously with complex **139•Py** as the catalyst (23 mg, 20 μ mol, 20 mol%) at reflux over 4 h. The catalyst was dissolved in a separate Schlenk

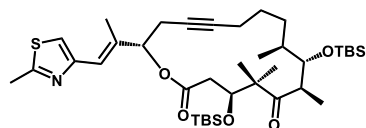
flask in toluene (1 mL) and the solution added dropwise to the solution of the diyne at 110 $^{\circ}\text{C}$. The crude product was washed with an aqueous HCl (3 M, 3×10 mL), the organic phase was dried over magnesium sulfate and filtered, and the solvents were evaporated. Purification of the residue by flash chromatography (toluene/*tert*-butyl methyl ether, 8:2) gave the title compound as a colorless solid (16 mg, 60%). **^1H NMR** (400 MHz, CDCl_3): δ 4.92 (dd, J = 6.8, 5.1 Hz, 1H), 4.60 (dd, J = 6.8, 1.7 Hz, 1H), 4.54 – 4.41 (m, 2H), 3.38 (d, J = 0.7 Hz, 3H), 1.90 – 1.82 (m, 1H), 1.88 (bs, 1H), 1.77 – 1.63 (m, 4H), 1.57 – 1.17 (m, 14H). **^{13}C NMR** (101 MHz, CDCl_3): δ 94.3, 87.2, 87.1, 84.1, 83.8, 66.3, 66.2, 63.00, 62.96, 55.7, 37.2, 37.1, 35.0, 34.9, 26.6, 26.5, 25.9, 25.84, 25.79, 25.76, 23.93, 23.91, 23.8, 22.5, 22.4, 22.35, 22.33. **HRMS** (ESI) calc. for $\text{C}_{16}\text{H}_{28}\text{NaO}_3$ $[\text{M} + \text{Na}]^+$: 291.19307; found: 291.19290. The spectroscopic data was in agreement with the literature.^[73]

Compound 171



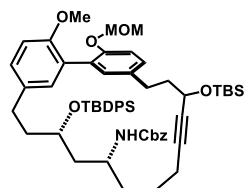
Prepared analogously with complex **139•Py** as the catalyst (23 mg, 20 μ mol, 20 mol%) at reflux temperature. The complex was dissolved in a separate Schlenk flask in toluene (1 mL) and the solution was added dropwise to the solution of the diyne at 110 °C. The crude product was purified by flash chromatography (hexane/ethyl acetate 9:1) to give the title compound as a colorless solid (10 mg, 46%). **^1H NMR** (400 MHz, CDCl_3): δ 4.54 – 4.45 (m, 2H), 1.81 – 1.59 (m, 4H), 1.57 – 1.17 (m, 16H). **^{13}C NMR** (101 MHz, CDCl_3): δ 86.5, 86.3, 63.1, 63.0, 37.2, 37.1, 26.54, 26.51, 25.79, 25.75, 23.9, 22.42, 22.37. **HRMS** (CI) calc. for $\text{C}_{14}\text{H}_{28}\text{NO}_2$ $[\text{M} + \text{NH}_4]^+$: 242.21145; found: 242.21154. The spectroscopic data was in agreement with the literature.^[73]

Compound 174



A 50 mL Schlenk flask was charged with the corresponding diyne (10 mg, 13 μ mol), powdered molecular sieves (250 mg, 5 Å) and toluene (7 mL). Adduct **139•Py** (1 mg, 0.5 μ mol, 5 mol%) was weight out in air and dissolved in toluene (1 mL). The catalyst solution was added dropwise to the solution of the substrate at 60 °C and stirring was continued for 2 h at this temperature. The reaction was quenched with ethanol (5 mL) before the mixture was cooled to ambient temperature and filtered through a short pad of Celite® which was carefully rinsed with ethyl acetate (20 mL) and dichloromethane (10 mL). The solvents were evaporated and the residue was purified by flash chromatography on silica (pentane/diethyl ether, 10:1 to 7:3) to give the title compound as a colorless solid (8 mg, 81%). **^1H NMR** (400 MHz, CDCl_3): δ 6.97 (s, 1H), 6.56 (s, 1H), 5.34 (dd, J = 7.4, 3.4 Hz, 1H), 4.70 (dd, J = 6.4, 4.9 Hz, 1H), 3.93 (dd, J = 6.6, 1.9 Hz, 1H), 3.24 (p, J = 6.9 Hz, 1H), 2.84 – 2.74 (m, 1H), 2.72 (s, 3H), 2.70 – 2.54 (m, 3H), 2.17 (d, J = 1.3 Hz, 3H), 2.15 – 2.06 (m, 4H), 1.17 (s, 3H), 1.15 (s, 3H), 1.11 (s, 3H), 0.94 (s, 3H), 0.91 (s, 9H), 0.87 (s, 9H), 0.10 (s, 6H), 0.09 (s, 3H), 0.07 (s, 6H). **^{13}C NMR** (101 MHz, CDCl_3): δ 216.7, 170.2, 165.1, 152.4, 137.1, 120.5, 116.9, 82.4, 78.1, 77.4, 76.5, 72.8, 54.7, 44.6, 41.8, 39.1, 29.8, 26.4, 26.2, 26.1, 24.3, 21.2, 20.7, 19.4, 18.8, 18.7, 18.5, 17.1, 15.2, 1.2, -3.1, -3.6, -3.90, -3.92. **HRMS** (ESI) calc. for $\text{C}_{38}\text{H}_{65}\text{NO}_5\text{Si}_2\text{SNa}$ $[\text{M} + \text{Na}]^+$: 726.40142; found: 726.40156. The spectroscopic data was in agreement with the literature.^[53]

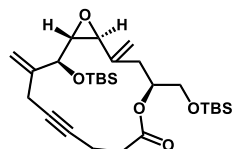
Compound 175



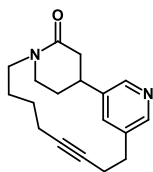
A 50 mL Schlenk flask was charged with the corresponding diyne (10 mg, 10 μ mol), powdered molecular sieves (250 mg, 5 Å) and toluene (5 mL). The mixture was heated to 50 °C. Adduct **139•Py** (0.5 mg, 0.5 μ mol, 5 mol%) was weight out in air and added in one portion. After stirring for 1.5 h at 50 °C, the reaction was quenched with ethanol (5 mL) before the mixture was cooled to ambient temperature and filtered through a short pad of Celite® which was carefully rinsed

with ethyl acetate (20 mL) and dichloromethane (10 mL). The solvents were evaporated and the residue was purified by flash chromatography on silica (hexane/ethyl acetate, 6:1) to give the title compound as a colorless oil (6 mg, 65%). The two diastereomers of compound **175** exists in solution as two rotamers each. **¹H NMR** (600 MHz, [D₈]-toluene): δ 7.85 – 7.62 (m, 4H), 7.31 – 7.15 (m, 9H), 7.14 – 7.04 (m, 2H), 6.98 (d, *J* = 2.3 Hz, 4H), 6.91 – 6.74 (m, 1H), 6.65 – 6.49 (m, 1H), 5.07 – 4.92 (m, 2H), 4.92 – 4.82 (m, 2H), 4.50 – 4.35 (m, 1H), 4.06 – 3.75 (m, 3H), 3.43 – 3.32 (m, 3H), 3.18 – 3.12 (m, 3H), 2.81 – 2.61 (m, 3H), 2.60 – 2.30 (m, 2H), 2.14 – 1.93 (m, 5H), 1.87 – 1.78 (m, 1H), 1.59 – 1.43 (m, 2H), 1.42 – 1.30 (m, 2H), 1.25 – 1.18 (m, 10H), 0.98 – 0.96 (m, 9H), 0.20 – 0.08 (m, 6H). **¹³C NMR** (151 MHz, [D₈]-toluene): δ 169.7, 155.99, 155.95, 155.87, 155.72, 155.7, 155.6, 154.43, 154.41, 154.37, 137.6, 137.5, 137.31, 137.25, 136.5, 136.44, 136.41, 136.38, 136.33, 136.30, 135.5, 135.3, 135.2, 134.9, 134.7, 134.3, 134.2, 133.7, 133.3, 132.5, 132.4, 132.0, 131.9, 130.2, 130.1, 130.0, 129.91, 129.85, 129.2, 128.55, 128.52, 128.44, 128.41, 128.23, 128.22, 128.01, 128.00, 127.9, 127.6, 115.8, 115.70, 115.66, 115.5, 111.4, 111.2, 111.0, 110.9, 95.50, 95.46, 85.4, 85.2, 85.0, 82.7, 82.5, 82.4, 81.8, 71.8, 69.7, 69.5, 66.4, 63.5, 63.1, 62.6, 60.0, 55.29, 55.26, 55.24, 55.19, 55.13, 55.08, 55.0, 49.2, 48.7, 48.4, 43.1, 43.0, 42.6, 42.1, 41.2, 40.8, 40.5, 39.0, 38.6, 33.4, 33.2, 31.5, 30.9, 30.3, 30.1, 27.4, 27.3, 26.11, 26.07, 25.7, 25.3, 24.0, 19.7, 19.6, 18.8, 18.5, 18.4, 18.3, 17.6, 17.5, 14.2, 1.4, -4.1, -4.2, -4.6, -4.7. **HRMS** (ESI) calc. for C₅₈H₇₅O₇NSi₂Na [M + Na]⁺ : 976.49743; found: 976.49749. The spectroscopic data was in agreement with the literature.^[66a]

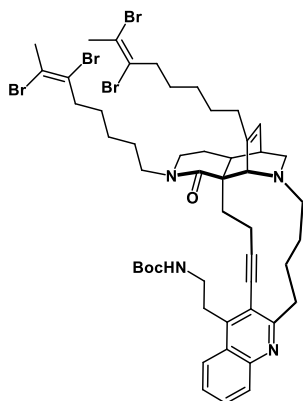
Compound 176



A 50 mL Schlenk flask was charged with the corresponding diyne (10 mg, 17 μmol), powdered molecular sieves (250 mg, 5 Å) and toluene (9 mL). Adduct **139•Py** (2 mg, 2 μmol, 10 mol%) was weight out in air and dissolved in toluene (1 mL). The catalyst solution was added dropwise to the solution of the substrate at 60 °C and stirring was continued for 1.5 h at this temperature. The reaction was quenched with ethanol (5 mL) before the mixture was cooled to ambient temperature and filtered through a short pad of Celite® which was carefully rinsed with ethyl acetate (20 mL) and dichloromethane (10 mL). The solvents were evaporated and the residue was purified by flash chromatography on silica (hexane/ethyl acetate, 22:1) to give the title compound as a colorless solid (9 mg, 94%). **¹H NMR** (400 MHz, CDCl₃): δ 5.31 (s, 1H), 5.18 – 5.15 (m, 1H), 5.14 (s, 1H), 5.08 (d, *J* = 1.1 Hz, 1H), 5.07 – 4.99 (m, 1H), 4.25 (d, *J* = 2.9 Hz, 1H), 3.74 – 3.58 (m, 2H), 3.48 (d, *J* = 2.0 Hz, 1H), 3.26 (dd, *J* = 3.0, 2.1 Hz, 1H), 3.11 – 3.02 (m, 1H), 2.83 – 2.72 (m, 1H), 2.52 – 2.30 (m, 5H), 2.18 (dd, *J* = 15.5, 9.9 Hz, 1H), 0.88 (s, 9H), 0.87 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H), 0.04 (s, 3H), 0.01 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 171.6, 144.8, 141.2, 116.4, 115.6, 79.5, 79.2, 74.4, 73.1, 64.3, 59.9, 56.9, 34.6, 31.7, 26.0, 25.9, 25.8, 21.4, 18.4, 18.3, 15.5, -4.8, -5.0, -5.2, -5.3. **HRMS** (ESI) calc. for C₂₈H₄₈O₅Si₂Na [M + Na]⁺ : 543.29325; found: 543.29340. The spectroscopic data was in agreement with the literature.^[146b]

Compound 177

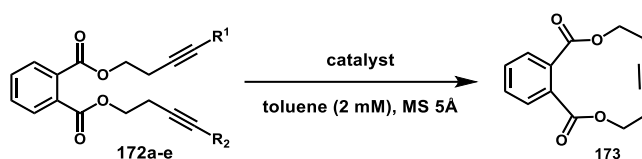
A 50 mL Schlenk flask was charged with the corresponding diyne (20 mg, 59 μmol), powdered molecular sieves (500 mg, 5 $\text{\AA}$) and toluene (30 mL). Adduct **139•Py** (21 mg, 18 μmol , 30 mol%) was weight out in air and dissolved in toluene (1 mL) in a separate Schlenk flask. The catalyst solution was added dropwise to the solution of the substrate stirred at reflux temperature. After 1.5 h, the reaction was quenched by the addition of ethanol (5 mL), the mixture was cooled to ambient temperature and filtered through a short pad of Celite® which was carefully rinsed with ethyl acetate (20 mL) and dichloromethane (10 mL). The solvents were evaporated and the residue was purified by flash chromatography on silica gel (dichloromethane/methanol, 95:5) to give the title compound as a colorless solid (12 mg, 71%). **^1H NMR** (400 MHz, CD_2Cl_2): δ 8.40 (bs, 1H), 8.30 (bs, 1H), 7.40 (t, $J = 2.3$ Hz, 1H), 4.38 (ddd, $J = 13.7, 7.2, 4.0$ Hz, 1H), 3.49 (t, $J = 4.2$ Hz, 1H), 3.21 (td, $J = 12.1, 4.4$ Hz, 1H), 3.09 (ddd, $J = 12.5, 5.6, 2.7$ Hz, 1H), 2.91 (ddd, $J = 13.7, 5.6, 3.2$ Hz, 1H), 2.75 – 2.70 (m, 2H), 2.69 – 2.63 (m, 1H), 2.63 – 2.57 (m, 1H), 2.42 – 2.33 (m, 2H), 2.33 – 2.22 (m, 1H), 2.11 – 2.02 (m, 2H), 1.68 – 1.55 (m, 2H), 1.52 – 1.42 (m, 1H), 1.41 – 1.33 (m, 2H). **^{13}C NMR** (101 MHz, CD_2Cl_2): δ 168.6, 148.4, 148.3, 138.0, 136.7, 134.6, 82.0, 79.5, 47.3, 45.1, 35.7, 34.0, 32.8, 29.9, 28.4, 28.0, 20.9, 18.5. **HRMS** (EI) calc. for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}$ $[\text{M}]^+$: 282.17266; found: 282.17293. The spectroscopic data was in agreement with the literature.^[79c]

Compound 178

A 25 mL Schlenk flask was charged with the corresponding diyne (10 mg, 8.7 μmol), powdered molecular sieves (400 mg, 5 $\text{\AA}$) and toluene (5 mL). Adduct **139•Py** (3 mg, 2.6 μmol , 30 mol%) was weight out in air and dissolved in toluene (1 mL). The catalyst solution was added dropwise to the solution of the substrate stirred at reflux temperature. After stirring for 2 h, the reaction was quenched with ethanol (5 mL) before the mixture was cooled to ambient temperature and filtered through a short pad of Celite® which was carefully rinsed with ethyl acetate (20 mL) and dichloromethane (10 mL). The solvents were evaporated and the residue was purified by flash chromatography on silica (hexane/ethyl acetate, 4:1 with trimethylamine 5%) to give the title compound as a pale brown oil (8 mg, 81%). **^1H NMR** (400 MHz, CDCl_3): δ 8.06 (d, $J = 8.4$ Hz, 1H), 7.99 (dd, $J = 8.4, 1.3$ Hz, 1H), 7.63 (ddd, $J = 8.3, 6.8, 1.3$ Hz, 1H), 7.54 – 7.45 (m, 1H), 5.90 – 5.79 (m, 1H), 4.81 (s, 1H), 3.78 – 3.70 (m, 1H), 3.66 – 3.36 (m, 7H), 3.34 – 3.25 (m, 1H), 3.12 – 2.98 (m, 3H), 2.93 (dd, $J = 9.3, 2.1$ Hz, 1H), 2.86 – 2.77 (m, 1H), 2.75 – 2.58 (m, 6H), 2.46 (d, $J = 34.6$ Hz, 1H), 2.44 (d, $J = 1.0$ Hz, 3H), 2.41 (t, $J = 0.9$ Hz, 3H), 2.34 – 2.19 (m, 4H), 2.17 – 2.06 (m, 1H), 2.03 – 1.91 (m, 1H), 1.90 – 1.81 (m, 1H), 1.73 (dd, $J = 9.3, 2.5$ Hz, 3H),

1.66 – 1.58 (m, 7H), 1.57 – 1.47 (m, 2H), 1.43 (s, 9H), 1.34 (d, $J = 7.2$ Hz, 2H), 1.30 – 1.20 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 172.1, 164.3, 156.0, 146.2, 145.7, 129.3, 126.4, 123.9, 122.4, 122.1, 115.7, 115.3, 102.4, 79.1, 76.3, 61.0, 55.5, 54.5, 52.7, 47.8, 47.1, 45.5, 40.8, 40.5, 40.4, 37.6, 37.2, 35.1, 30.6, 28.9, 28.62, 28.57, 28.0, 27.8, 27.6, 27.3, 26.8, 25.6, 25.3, 13.6. **HRMS** (ESI) calc. for $\text{C}_{50}\text{H}_{67}\text{O}_3\text{N}_4\text{Br}_4$ $[\text{M} + \text{H}]^+$: 1087.19412; found: 1087.19569. The spectroscopic data was in agreement with the literature.^[79b]

RCAM of Diynes Carrying Different End Caps



$\text{R}^1 = \text{R}^2 = n\text{Pr}$

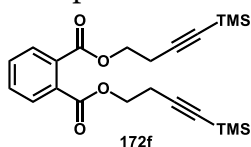
A 100 mL Schlenk flask was charged with substrate **172b** (35 mg, 0.10 mmol), powdered molecular sieves (5Å, 250 mg) and toluene (50 mL). The mixture was heated to 50 °C before adduct **139•Py** (6 mg, 5 μmol , 5 mol%) was weight out in air and added in one portion. After stirring for 4 h at 50 °C, the reaction was quenched with ethanol (5 mL) before the mixture was cooled to ambient temperature and filtered through a short pad of Celite® which was carefully rinsed with ethyl acetate (20 mL). The solvents were evaporated and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate, 4:1) to give the title compound as a colorless solid (22 mg, 90%).

$\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$

A 100 mL Schlenk flask was charged with but-3-yn-1-yl pent-3-yn-1-yl phthalate (**172d**, 28 mg, 0.10 mmol), powdered molecular sieves (1.00 g, 5Å), powdered molecular sieves (1.00 g, 4Å) and toluene (50 mL). Adduct **139•Py** (12 mg, 10 μmol , 10 mol%) was weight out in air and added to the solution in one portion. A stock solution of triphenylborane (0.01 M in toluene, 1.0 mL, 10 μmol , 5 mol%) was added and the resulting mixture stirred for 3 h at ambient temperature. The reaction was quenched by the addition of ethanol (5 mL) and the mixture filtered through a short pad of Celite® which was carefully rinsed with ethyl acetate (20 mL) and dichloromethane (10 mL). The solvents were evaporated and the residue was purified by flash chromatography on silica (hexane/ethyl acetate, 4:1) to give the title compound as a colorless solid (22 mg, 92%). ^1H NMR (400 MHz, CDCl_3): δ 7.69 (dd, $J = 5.7, 3.3$ Hz, 2H), 7.53 (dd, $J = 5.7, 3.3$ Hz, 2H), 4.45 (td, $J = 4.7, 1.5$ Hz, 4H), 2.58 – 2.49 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3): δ 167.9, 133.3, 131.1, 128.5, 79.1, 62.8, 19.9. **HRMS** (EI) calc. for $\text{C}_{14}\text{H}_{12}\text{O}_4$ $[\text{M}]^+$: 244.07301; found: 244.07312. The spectroscopic data was in agreement with the literature.^[127c]

R¹ = TMS, R² = Me

A 100 mL Schlenk flask was charged with substrate **172c** (36 mg, 0.10 mmol) and toluene (50 mL). Adduct **139•Py** (6 mg, 5 μmol, 5 mol%) was weight out in air and added in one portion to the mixture stirred at 100 °C. After 7 h at 100 °C, the reaction was quenched with ethanol (5 mL) before the mixture was cooled to ambient temperature and filtered through a short pad of Celite® which was carefully rinsed with ethyl acetate (20 mL). The solvents were evaporated and the residue was purified by flash chromatography on silica (hexane/ethyl



acetate, 4:1) to give the title compound as a colorless solid (21 mg, 86%). A second fraction was collected as a clear oil that consisted of the bis-silylated diyne **172f** (3 mg, 7%), which analyzed as follows: **¹H NMR** (400 MHz,

CDCl₃): δ 7.78 – 7.73 (m, 2H), 7.58 – 7.52 (m, 2H), 4.40 (t, *J* = 7.2 Hz, 4H), 2.68 (t, *J* = 7.2 Hz, 4H), 0.15 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃): δ 167.2, 132.0, 131.3, 129.2, 102.1, 86.9, 63.4, 20.4, 0.1. **IR** (film): $\tilde{\nu}$ 2961, 2179, 1733, 1273, 1251, 1125, 1081, 1059, 843, 790, 744, 697, 671, 639. **HRMS** (ESI) calc. for C₂₂H₃₀O₄Si₂Na [M + Na]⁺: 437.15749; found: 437.15786.

Alkyne Homo-Metathesis Reaction at Low Temperature

At 0 °C: A 10 mL Schlenk flask was charged with 1-(4-methoxyphenyl)-1-propyne **142** (37 mg, 0.25 mmol), powdered molecular sieves (250 mg, 5Å) and toluene (1.25 mL). The mixture was cooled to 0 °C. Adduct **139•Py** (15 mg, 13 µmol, 5 mol%) was weight out in air and added in one portion to the mixture, followed by triphenylborane (3 mg, 13 µmol, 5 mol%). After stirring for 24 h at 0 °C, the reaction was quenched with ethanol (1 mL) and the mixture allowed to reach ambient temperature. Work-up and purification were conducted as described above. Product **143a** was obtained as a colorless solid (27 mg, 91%), which was identical in all regard to the sample described above.

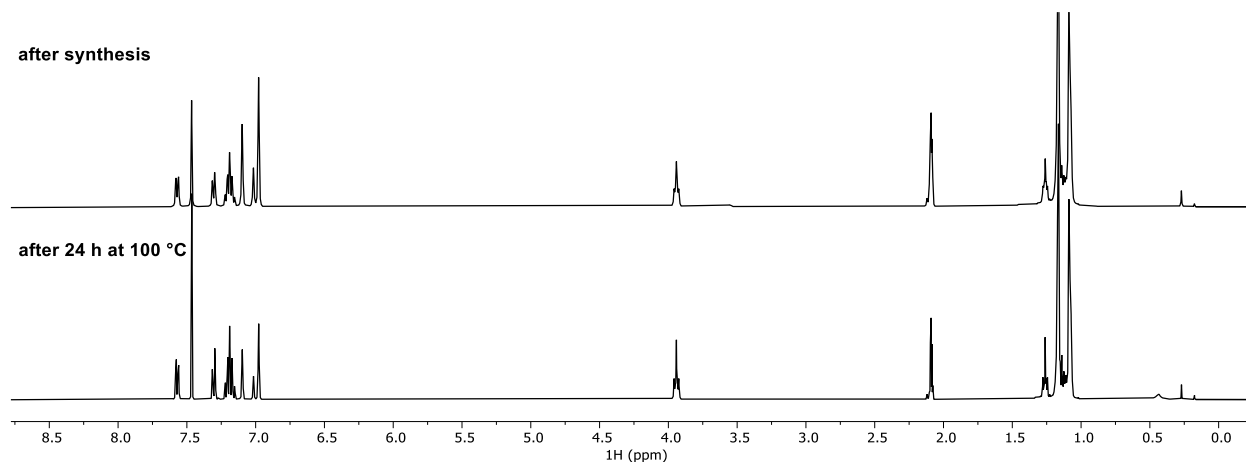
At -20 °C: A 10 mL Schlenk flask was charged with 1-(4-methoxyphenyl)-1-propyne **142** (37 mg, 0.25 mmol), powdered molecular sieves (250 mg, 5Å) and toluene (1.25 mL). The mixture was cooled to -20 °C. Complex **140** (10 mg, 13 µmol, 5 mol%) was weight out in air and added in one portion to the mixture. After stirring for 24 h at -20 °C, the reaction was quenched with ethanol (1 mL) and the mixture allowed to warm to ambient temperature. Work-up and purification were conducted as described to give product **143a** as a colorless solid (25 mg, 84%), which was again identical in all regard to the sample described above.

3.4 Experimental Procedures: Cyclization of Citronellal to Isopulegol

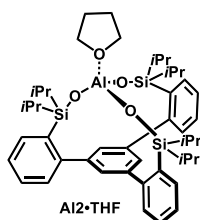
Stability Tests of the Catalysts

Temperature Stability of **Al2•THF** in Solution

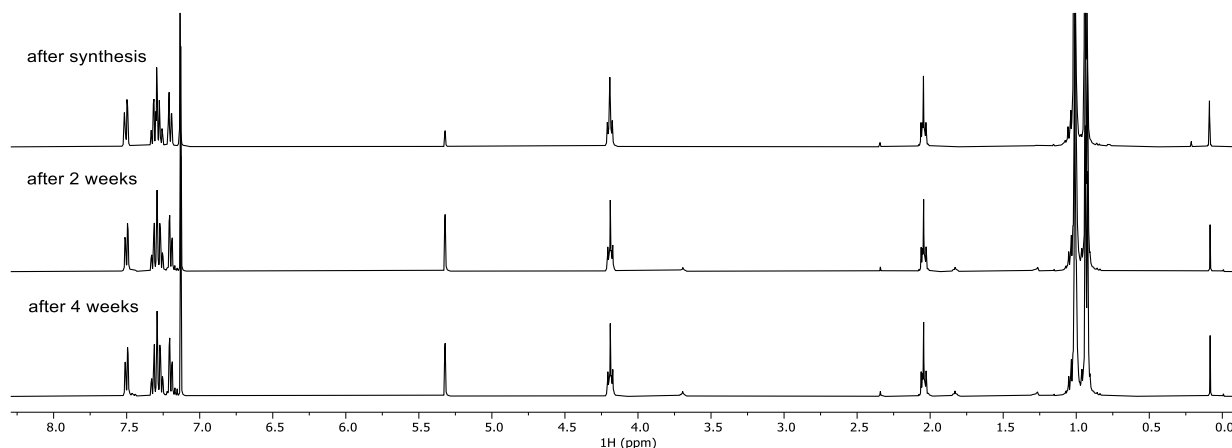
A sample of complex **Al2•THF** (ca. 5 mg) was dissolved in [D₈]-toluene (0.5 mL) in a Schlenk flask and transferred into a flame-dried *J. Young* NMR tube filled with argon. A ¹H NMR spectrum was recorded at 25 °C and the *J. Young* NMR tube was heated to 100 °C for 24 h. Subsequently, another spectrum was recorded to assess the stability of **Al2•THF** in solution.

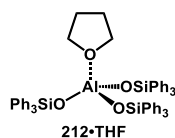


Stability of **Al2•THF** in Air

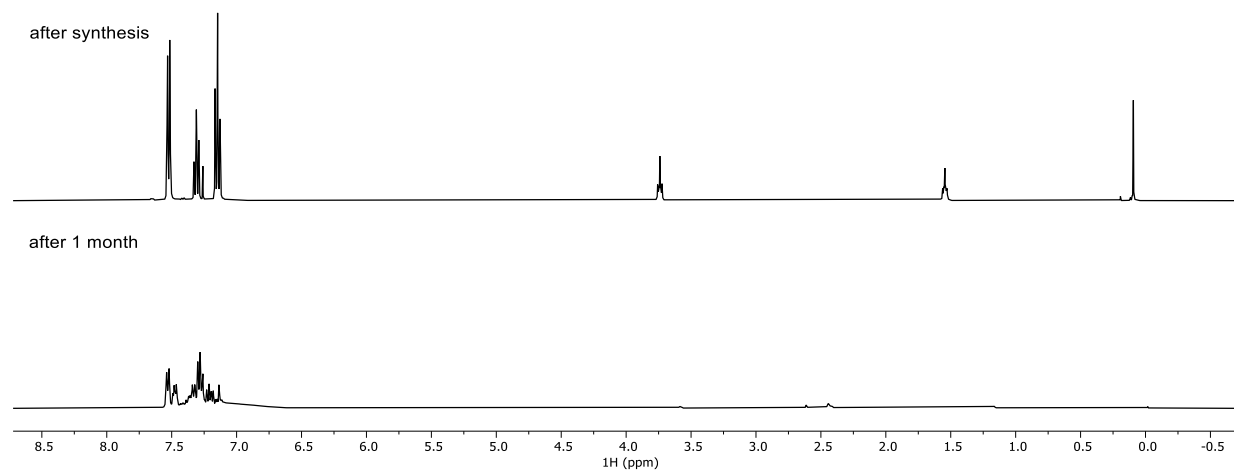


A sample of complex **Al2•THF** was placed in a vial open to air, which was kept on the bench. After two and four weeks, aliquots of this batch (5 mg) were dissolved in [D₈]-toluene (0.5 mL) in a Schlenk flask and transferred into a flame-dried *J. Young* NMR tube filled with argon. The stability was assessed by ¹H NMR spectroscopy at 25 °C.

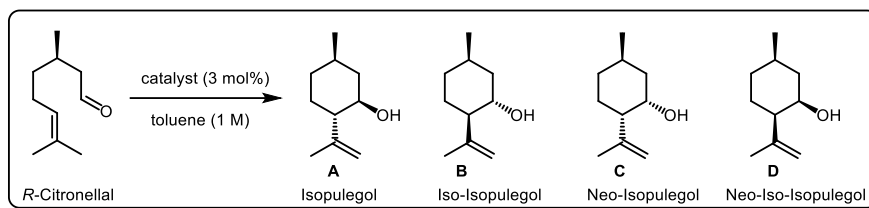


Stability of **212•THF in Air**

A sample of complex **212**•THF was placed in a vial open to air, which was kept on the bench. After one month, an aliquot of this batch (5 mg) was dissolved in [D₈]-toluene (0.5 mL) in a Schlenk flask and transferred into a flame-dried *J. Young* NMR tube filled with argon. The decomposition was assessed by ¹H NMR spectroscopy at 25 °C.



General Procedure for the Cyclization of Citronellal to Isopulegol

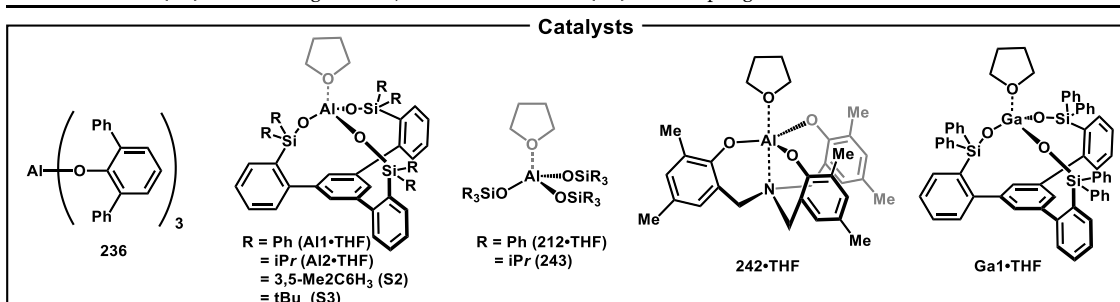


A 25 mL pressure Schlenk flask was charged with the respective complex (41 μ mol, 3 mol%) and toluene (1.38 mL) or a stock solution of the *in situ* generated complex (30 mM in toluene, 1.38 mL, 41 μ mol, 3 mol%). The stock solutions were prepared by addition of trimethylaluminium (2.0 M in hexane, 42 μ L, 83 μ mol) to a solution of the corresponding ligand in toluene (2.76 mL) at 0 °C. The flask with the reaction mixture was cooled to 0 °C (entries 1-6, 8 and 11), kept at ambient temperature (entry 7, 9 and 10) or lowered into an oil bath heated to the respective temperature (entry 11-14) and *R*-citronellal (0.25 mL, 1.38 mmol) was added. The flask was sealed and the solution stirred at the indicate temperature for 2 h – 5 d. The reaction was terminated by the addition of an aqueous solution of sodium hydroxide (2 M, 2 mL) and the organic layer was analyzed by GC.

Table S 1: Conditions and results of the catalyst screening.

Entry	Catalyst	T [°C]	t	Conversion [%] ^a	Product A/B/C/D ^b
1	236 (<i>in situ</i>)	0 to 25	18	>99	99 /0/1/0
2	Al1 •THF	0 to 25	17 h	96	82 /3/15/0
3	212 •THF	0 to 25	18 h	97	77 /2/20/1
4	243 (<i>in situ</i>)	0 to 25	4 d	97	83 /2/15/0
5	242 •THF	0 to 25	18 h	8	77 /3/19/1
6	S2 (<i>in situ</i>)	0 to 25	18 h	96	82 /2/15/1
7	S3 (<i>in situ</i>)	25 to 100	3 h	35	57 /3/39/1
8	Al2 •THF	0 to 25	5 d	80	93 /1/4/2
9	Al2 •THF	25 to 45	24 h	94	93 /1/4/2
10	Al2 •THF	25 to 100	2 h	99	91 /2/4/3
11	Ga1 •THF	0 to 25	18 h	93	78 /3/19/0

^abased on area% (GC) of the starting material; ^bratio based on area% (GC) of the isopulegols.



To determine an absolute yield of isopulegol (**A**) cyclohexanol (73 μ L, 0.69 mmol) was added as an internal standard (*table S2*, entry 12-15).

Table S 2: Comparison of the catalysts at elevated temperatures.

Entry	Catalyst	T [°C]	t	Conversion [%] ^a	Yield A [%] ^c
12	236 (<i>in situ</i>)	60	2 h	68	50
13	243 (<i>in situ</i>)	60	2 h	60	19
14	212•THF	100	2h	99	76
15	Al2•THF	100	2 h	>99	93

^abased on area% (GC) of the starting material; ^cdetermined with cyclohexanol as an internal standard.

Catalyst Recycling Experiment



Figure S 8: Reaction set-up for the catalyst recycling experiment.

A oven-dried, 25 mL, two-necked flask equipped with a distillation apparatus connected to an argon/vacuum manifold was charged with **Al₂•THF** (441 mg, 0.56 mmol, 5 mol%) and Dowtherm™ A (11 mL, mixture of biphenyl and biphenyl ether). The mixture was heated to 100 °C and racemic citronellal (2.00 mL, 11.1 mmol) was added dropwise. After 2 h, the completion of the cyclization was controlled by GC/MS and the mixture was allowed to cool to 80 °C, before vacuum (10⁻³ mbar) was applied to the apparatus. The product was distilled from the reaction mixture (bottom temperature: 100 °C; head temperature: 55 °C) into a receiving flask. Subsequently, the apparatus was filled with argon and the complete removal of the product from the reaction mixture was controlled by GC/MS. Keeping the temperature at 100 °C another batch of racemic citronellal (2.00 mL, 11.1 mmol) was added and the described process was repeated a total of five times.

Table S 3: Results of the catalyst recycling experiment.

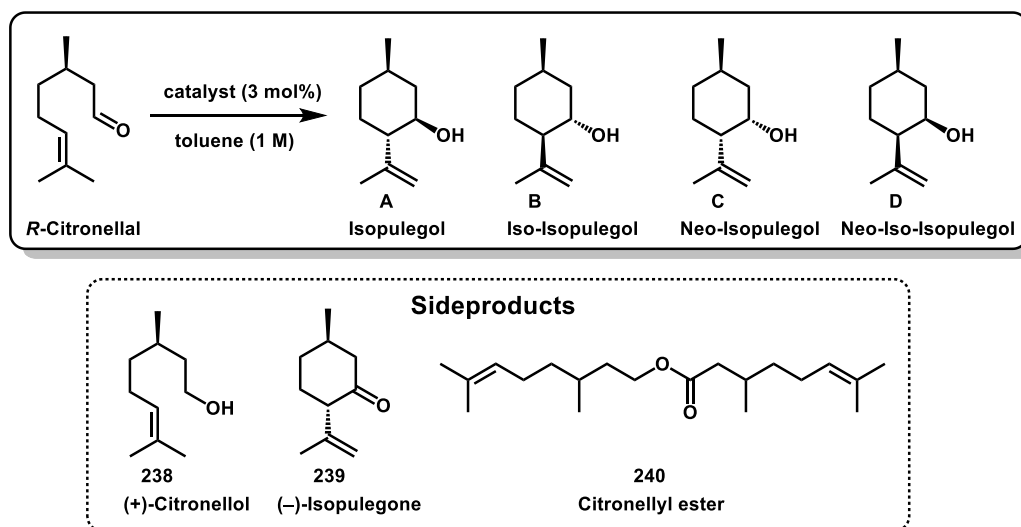
Cycle	Yield Isopulegol [%] ^a
1	94
2	94
3	91
4	94
5	95

^a determined through qNMR with 1,2-dichloroethane.

Yields for the individual batches were determined through qNMR with 1,2-dichloroethane as an internal standard due to varying contamination of the distillate with minor amounts of the high-boiling solvent. The five batches were combined and subjected to flash column chromatography (hexane/ethyl acetate 9:1) to give isopulegol and its stereoisomers (8.11 g, 52.6 mmol, 95%) as a clear liquid. GC-analysis showed the mixture to consist of isopulegol (91%), neo-isopulegol (4%), iso-isopulegol (3%) and neo-iso-isopulegol (2%). No other side products were observed.

Reaction Monitoring by GC

by GC

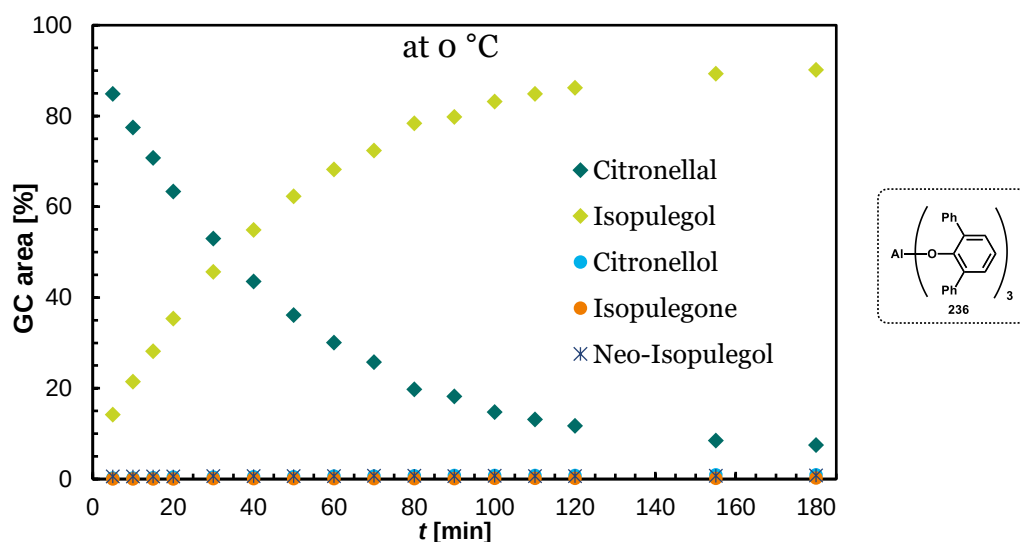
With complex **Al2•THF**:

A 25 mL pressure Schlenk flask was charged with **Al2•THF** (33 mg, 41 μ mol, 3 mol%) and toluene (1.38 mL). The flask was lowered into a preheated oil bath (45 °C or 100 °C) and *R*-citronellal (0.25 mL, 1.38 mmol) was added. The flask was sealed and aliquots were taken from the reaction solution with the tip of a pipette at regular intervals. The aliquots were diluted with toluene (0.5 mL) and treated with an aqueous sodium hydroxide solution (2 M, 0.2 mL). The organic layer was filtered through a HPLC filter and analyzed by GC.

With complex **Al4**:

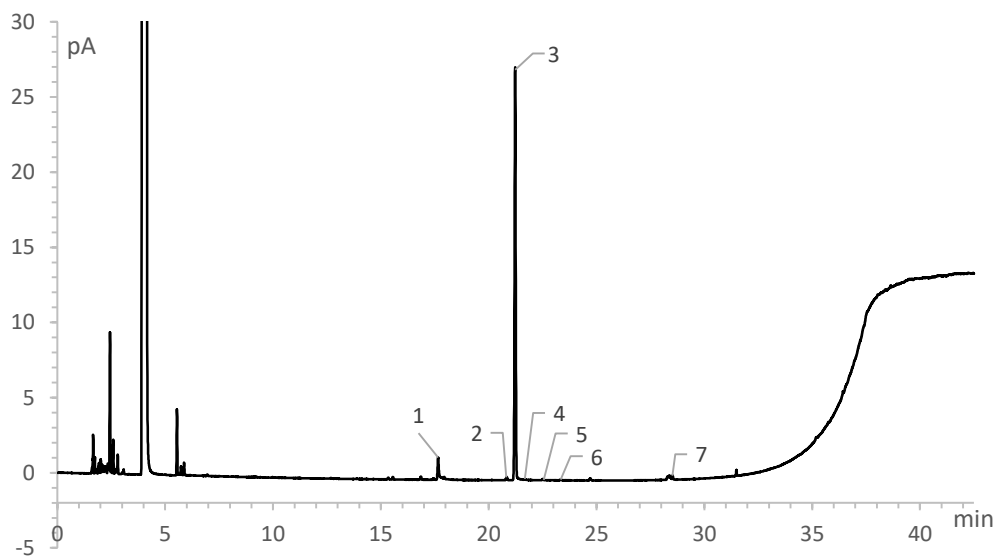
A 25 mL Schlenk flask was charged with 2,6-diphenylphenol (31 mg, 0.13 mmol, 9.3 mol%) and toluene (1.38 mL). The solution was cooled to 0 °C and trimethylaluminum (2.0 M in hexane, 21 μ L, 41 μ mol, 3 mol%) was added dropwise. The catalyst solution was stirred at 0 °C for 1.5 h, before the flask was either allowed to warm to ambient temperature (25 °C), inserted into a preheated oil bath (100 °C) or left at 0 °C. Then *R*-citronellal (0.25 mL, 1.38 mmol) was added and the flask was sealed. Aliquots were taken from the reaction solution with the tip of a pipette at regular intervals. The aliquots were diluted with toluene (0.5 mL) and treated with an aqueous sodium hydroxide solution (2 M, 0.2 mL). The organic layer was filtered through a HPLC filter and analyzed by GC.

Cyclization of Citronellal to Isopulegol with Complex **236** at 0 °C



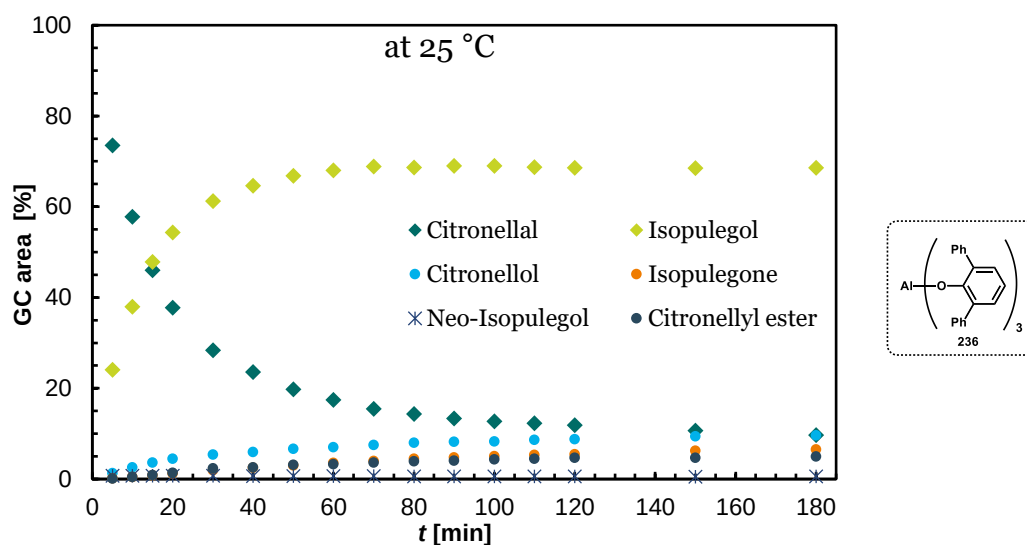
Graph S 1 Consumption of *R*-citronellal and generation of product isopulegol in toluene using complex **236** as the catalyst (3 mol%), as monitored by GC at 0 °C. Citronellol, isopulegone, and neo-isopulegol were only observed in trace amounts.

GC Chromatogram of the Reaction Mixture after 180 min



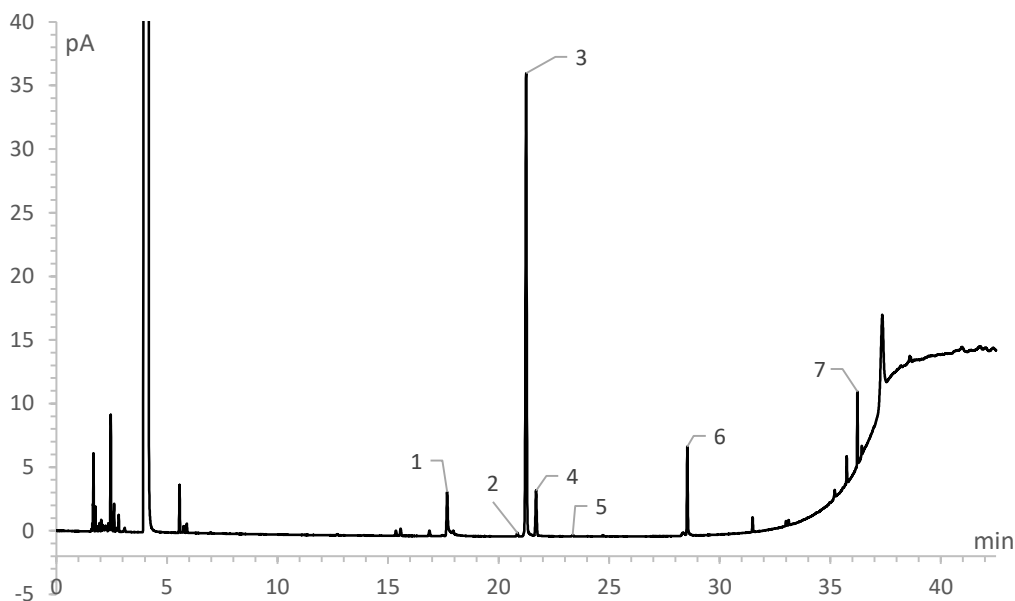
No.	Ret. Time [min]	Rel. Area [%]	Peak Name
1	17.66	7.44	Citronellal
2	20.83	0.74	Neo-Isopulegol
3	21.23	90.11	Isopulegol
4	21.69	0.23	Isopulegone
5	22.52	0.32	Neo-Iso-Isopulegol
6	23.33	0.27	Iso-Isopulegol
7	28.53	0.89	Citronellol

Cyclization of Citronellal to Isopulegol with Complex **236** at 25 °C



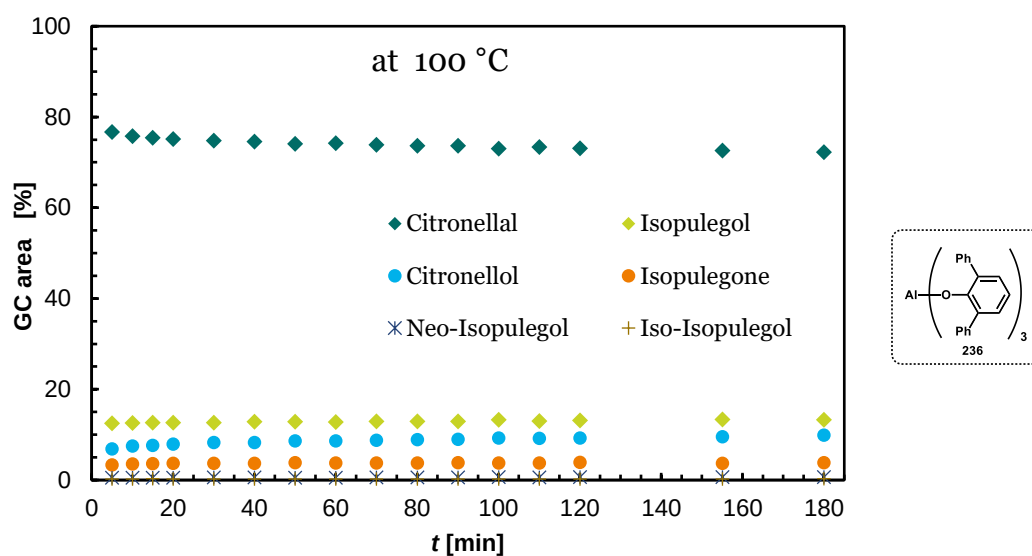
Graph S 2: Consumption of R-citronellal and generation of product isopulegol as well as side products (citronellol, isopulegone, ester **240**, and neo-isopulegol) in toluene using complex **236** as the catalyst (3 mol%), as monitored by GC at 25 °C.

GC Chromatogram of the Reaction Mixture after 180 min



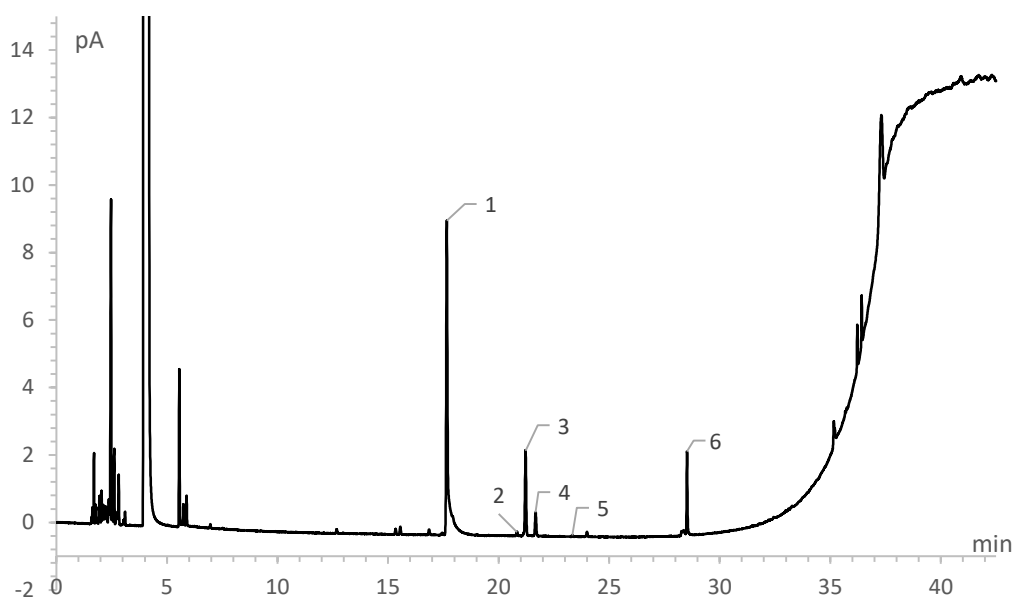
No.	Ret. Time [min]	Rel. Area [%]	Peak Name
1	17.67	9.68	Citronellal
2	20.85	0.58	Neo-Isopulegol
3	21.24	68.56	Isopulegol
4	21.70	6.45	Isopulegone
5	23.36	0.21	Iso-Isopulegol
6	28.53	9.59	Citronellol
7	36.23	4.93	Citronellyl ester

Cyclization of Citronellal to Isopulegol with Complex **Al4** at 100 °C



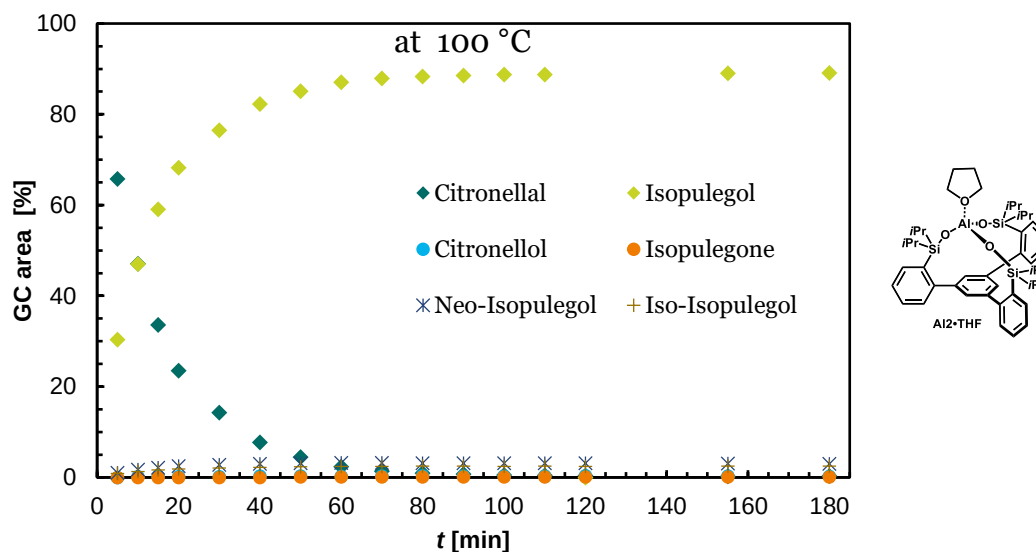
Graph S 3: Consumption of R-citronellal and generation of product isopulegol as well as side products (citronellol, isopulegone, neo-isopulegol, and iso-isopulegol) in toluene using complex **236** as the catalyst (3 mol%), as monitored by GC at 100 °C.

GC Chromatogram of the Reaction Mixture after 180 min



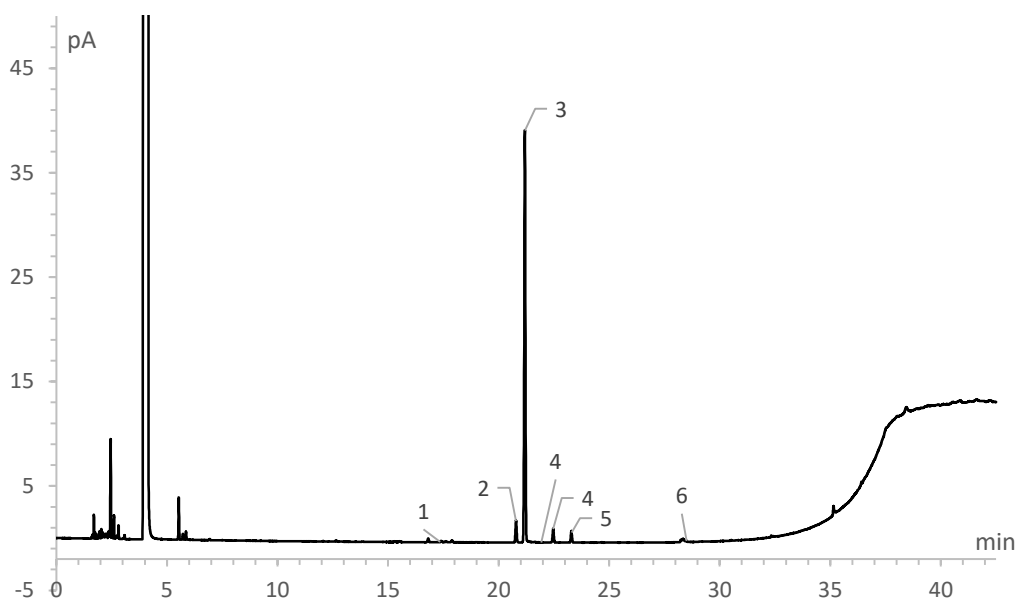
No.	Ret. Time [min]	Rel. Area [%]	Peak Name
1	17.66	72.19	Citronellal
2	20.83	0.62	Neo-Isopulegol
3	21.22	13.24	Isopulegol
4	21.67	3.80	Isopulegone
5	23.34	0.27	Iso-Isopulegol
6	28.52	9.88	Citronellol

Cyclization of Citronellal to Isopulegol with Complex **Al2•THF** at 100 °C



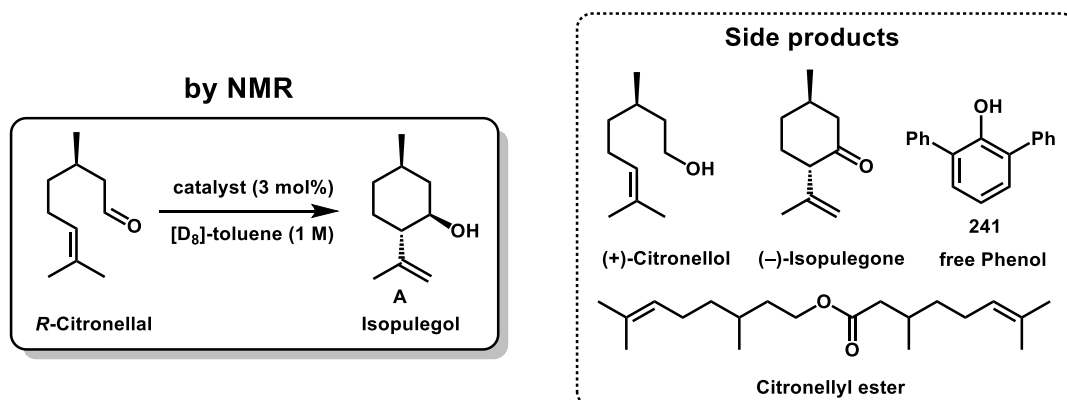
Graph S 4: Consumption of *R*-citronellal and generation of product isopulegol as well as other isomers (neo-isopulegol and iso-isopulegol) in toluene using complex **Al2•THF** as the catalyst (3 mol%), as monitored by GC at 100 °C. Citronellol and isopulegone were only observed in trace amounts.

GC Chromatogram of the Reaction Mixture after 180 min



No.	Ret. Time [min]	Rel. Area [%]	Peak Name
1	17.62	0.32	Citronellal
2	20.79	4.73	Neo-Isopulegol
3	21.19	89.15	Isopulegol
4	21.67	0.10	Isopulegone
5	22.47	2.98	Neo-Iso-Isopulegol
6	28.52	0.24	Citronellol
7	23.29	2.48	Iso-Isopulegol

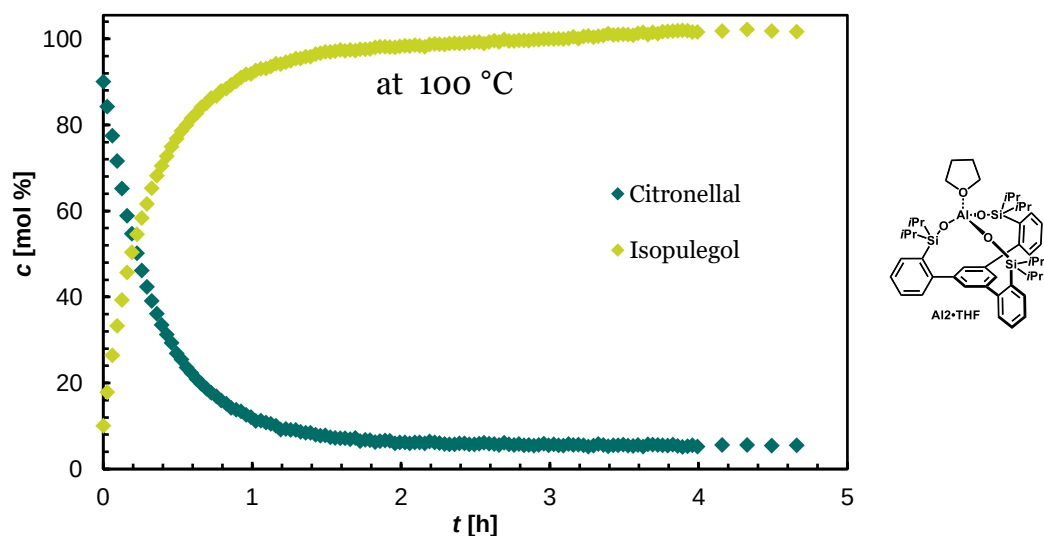
Reaction Monitoring by NMR



A flame-dried *J. Young* NMR tube filled with argon was charged with a stock solution of the respective catalyst (0.03 M in $[D_8]$ -toluene, 0.5 mL, 15 μmol , 3 mol%) and a ^1H NMR spectrum was recorded at the respective temperature (25 $^\circ\text{C}$, 45 $^\circ\text{C}$ or 100 $^\circ\text{C}$). *R*-Citronellal (91 μL , 0.50 mmol) was then added while the catalyst solution was kept at ambient temperature. The *J. Young* NMR tube was inverted three times to ensure mixing, before being inserted into the preheated spectrometer. The conversion of citronellal to isopulegol was monitored by ^1H NMR spectroscopy. The delay between the addition and the first NMR measurement amounts to 2 – 3 min due to the sample loading and shimming.

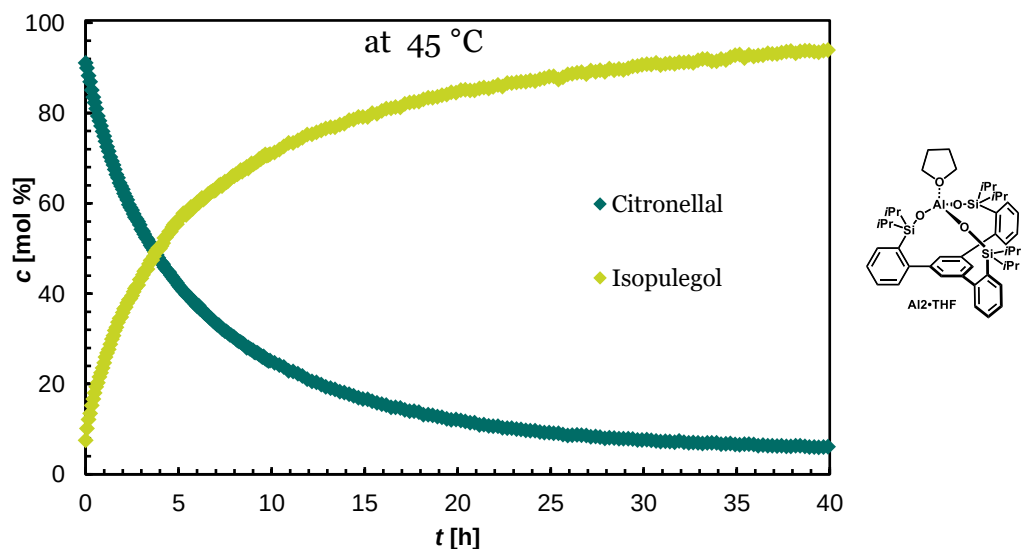
For the **236** system the catalyst was prepared *in situ*: a Schlenk flask was charged with 2,6-diphenylphenol (23 mg, 92 μmol) and $[D_8]$ -toluene (1 mL). The solution was cooled to 0 $^\circ\text{C}$ before trimethyl aluminium (2.0 M in hexane, 15 μL , 30 μmol) was added dropwise. The solution was stirred at 0 $^\circ\text{C}$ for 1.5 h and directly used in the experiment.^[294]

Cyclization of Citronellal to Isopulegol with Complex $\text{Al}_2\cdot\text{THF}$ at 100 °C



Graph S 5: Consumption of R-citronellal and generation of product isopulegol in $[D_8]$ -toluene using complex $\text{Al}_2\cdot\text{THF}$ as the catalyst (3 mol%), as monitored by ^1H NMR spectroscopy at 100 °C. None of the known side products were observed in significant amounts.

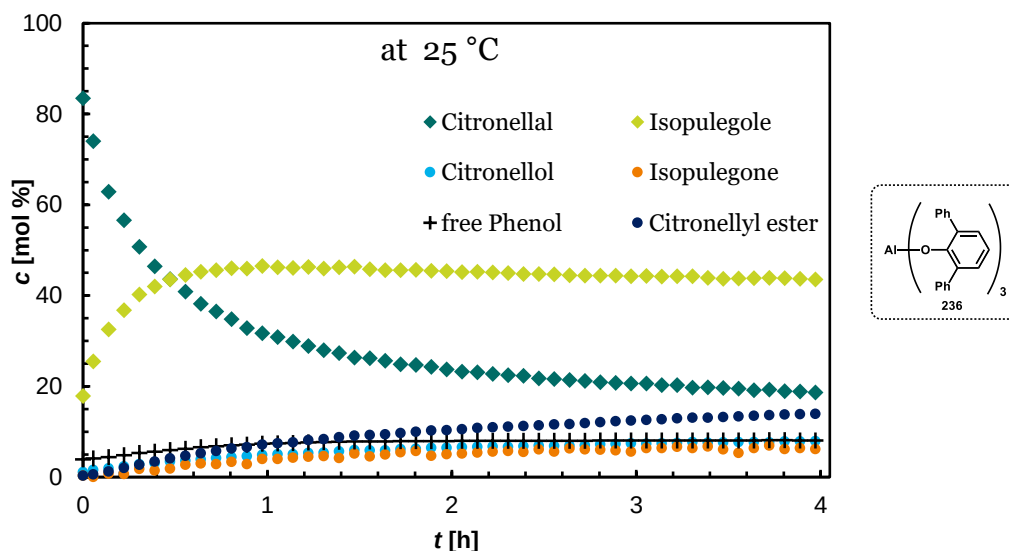
Cyclization of Citronellal to Isopulegol with Complex $\text{Al}_2\cdot\text{THF}$ at 45 °C



Graph S 6: Consumption of R-citronellal and generation of product isopulegol in $[D_8]$ -toluene using complex $\text{Al}_2\cdot\text{THF}$ as the catalyst (3 mol%), as monitored by ^1H NMR spectroscopy at 45 °C. None of the known side products were observed in significant amounts.

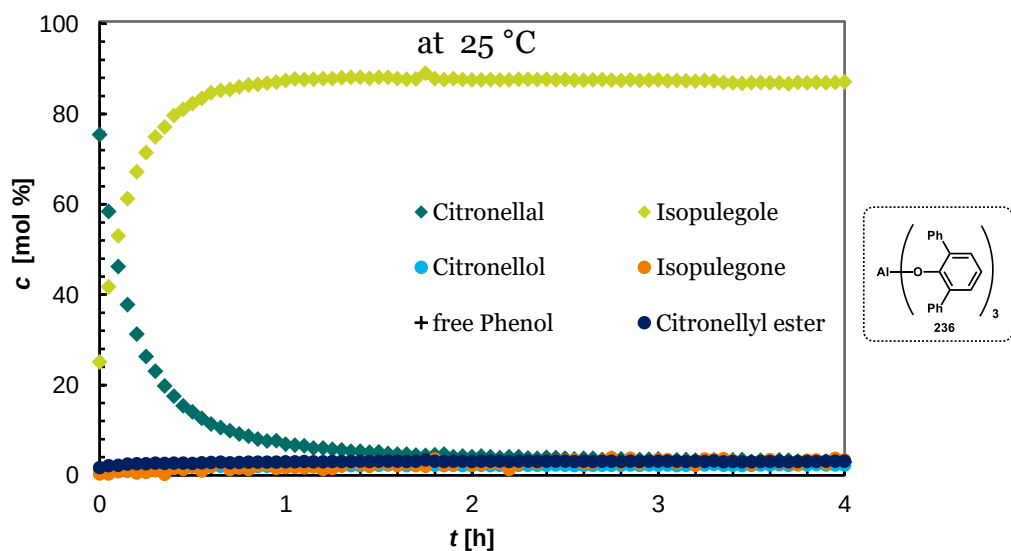
Cyclization of Citronellal to Isopulegol with Complex **236** at 25 °C

First measurement:



Graph S 7: Consumption of R-citronellal and generation of product isopulegol as well as side products (citronellol, isopulegone, citronellyl ester, and free phenol **241**) in $[D_8]$ -toluene using complex **236** as the catalyst (3 mol%), as monitored by 1H NMR spectroscopy at 25 °C.

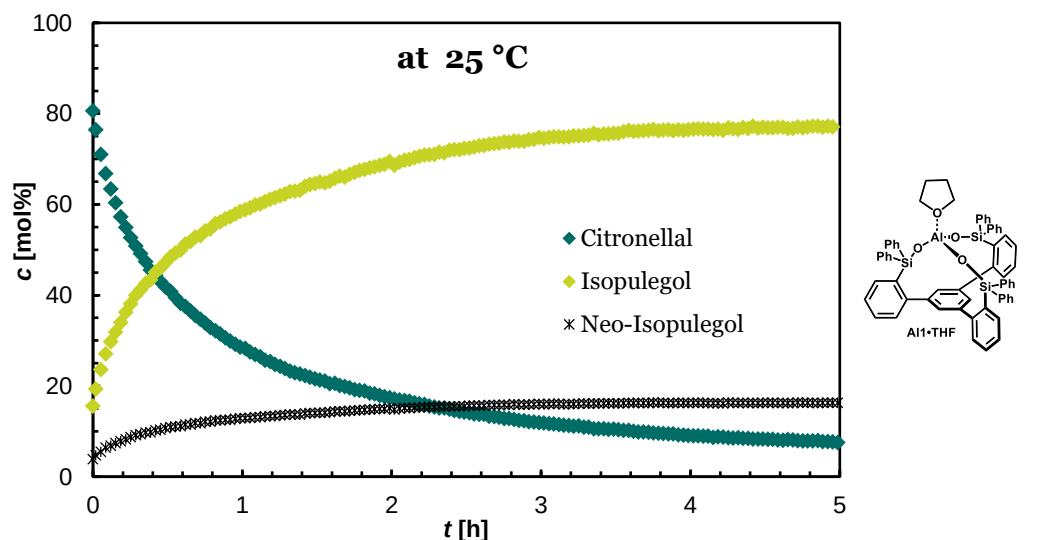
Second measurement:



Graph S 8: Consumption of R-citronellal and generation of product isopulegol as well as side products (citronellol, isopulegone, citronellyl ester, and free phenol **241**) in $[D_8]$ -toluene using complex **236** as the catalyst (3 mol%), as monitored by 1H NMR spectroscopy at 25 °C.

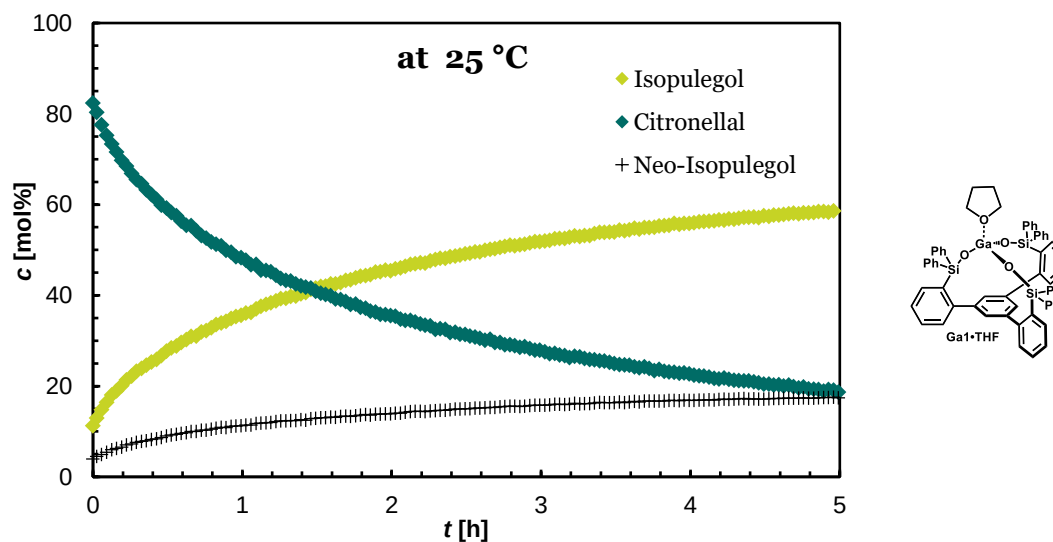
The two shown reaction traces are intended to underline the erratic and irreproducible reaction outcomes observed with catalyst **236** at 25 °C.

Cyclization of Citronellal to Isopulegol with Complex **Al1**•THF at 25 °C



Graph S 9: Consumption of R-citronellal and generation of product isopulegol as well as the other isomer neo-isopulegol in $[D_8]$ -toluene using complex **Al1**•THF as the catalyst (3 mol%), as monitored by 1H NMR spectroscopy at 25 °C.

Cyclization of Citronellal to Isopulegol with Complex **Ga1**•THF at 25 °C

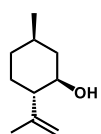


Graph S 10: Consumption of R-citronellal and generation of product isopulegol as well as the other isomer neo-isopulegol in $[D_8]$ -toluene using complex **Ga1**•THF as the catalyst (3 mol%), as monitored by 1H NMR spectroscopy at 25 °C.

Characterization of Isopulegol, Citronellol and Isopulegone

The peaks in the GC chromatogram were assigned by comparison with a racemic sample of the isopulegols (containing isopulegol, iso-isopulegol, neo-isopulegol, and neo-iso-isopulegol) and authentic samples of isopulegol, iso-isopulegol, and neo-isopulegol. Neo-iso-isopulegol was assigned by process of elimination. Authentic samples of citronellol and isopulegone were synthesized as described in the following and the peaks in the GC chromatogram assigned by comparison. The citronellyl ester **240** was assigned based on descriptions in the literature and GC/MS.^[294, 321]

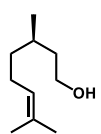
Isopulegol



¹H NMR (400 MHz, CDCl₃): 4.90 (s, 1H), 4.85 (s, 1H), 3.46 (td, $J = 10.1, 4.2$ Hz, 1H), 2.08 – 2.00 (m, 1H), 1.92 – 1.83 (m, 2H), 1.71 (s, 3H), 1.70 – 1.64 (m, 1H), 1.60 (bs, 1H), 1.56 – 1.23 (m, 2H), 1.04 – 0.85 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): 146.8, 113.0, 70.5, 54.3, 42.8, 34.5, 31.6, 29.8, 22.4, 19.3.

The spectroscopic data was found to be in agreement with the data reported in the literature.^[322]

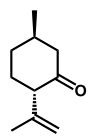
Citronellol (238)



A 50 mL Schlenk flask was charged with sodium borohydride (496 mg, 13.1 mmol) and dry methanol (8.5 mL). The suspension was cooled to 0 °C and *R*-citronellal (2.35 mL, 13.0 mmol) was added dropwise over 5 min. After 1.5 h, the reaction was quenched by the addition of water (20 mL). Layers were separated and the aqueous layer was extracted with *tert*-butyl methyl ether (3 × 20 mL). The combined organic layers were dried over magnesium sulfate, filtered and solvents were removed under reduced pressure (rotary evaporation). The residue was purified by flash chromatography on silica (hexane/ethyl acetate 2% to 20%) to give the title compound as a colorless oil (1.10 g, 54%).

¹H NMR (400 MHz, [D₈]-toluene): 130.8, 60.8, 40.3, 37.7, 29.5, 25.9, 25.8, 19.7, 17.6. ¹³C NMR (100 MHz, [D₈]-toluene): 5.19 – 5.08 (m, 1H), 3.44 – 3.30 (m, 2H), 2.06 – 1.89 (m, 2H), 1.67 (s, 3H), 1.56 (s, 3H), 1.53 – 1.36 (m, 2H), 1.36 – 1.25 (m, 1H), 1.23 – 1.06 (m, 2H), 0.82 (d, $J = 6.6$ Hz, 3H), 0.51 (bs, 1H).

Isopulegone (239)

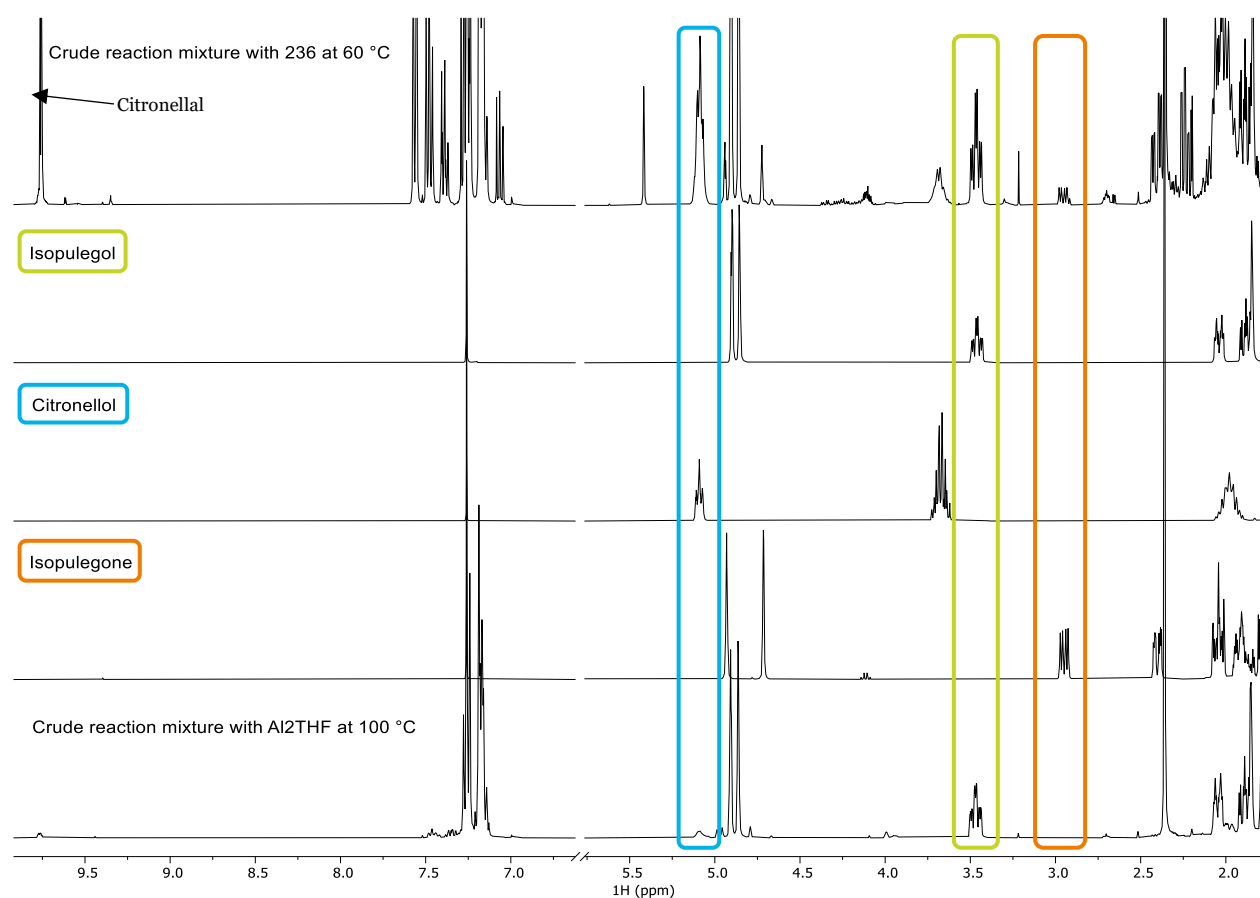


A 250 mL, two-necked round bottomed flask equipped with an argon manifold was charged with pyridinium chlorochromate (5.66 g, 26.3 mmol) and dichloromethane (83 mL). Neo-isopulegol (3.00 mL, 17.5 mmol) was added at ambient temperature. After 4 h, diethyl ether (83 mL) was added and the mixture was filtered through a three layer column (celite®, silica, and activated charcoal). The filtrate was washed with a saturated aqueous solution of thiosulfate (50 mL) and a saturated aqueous solution of sodium

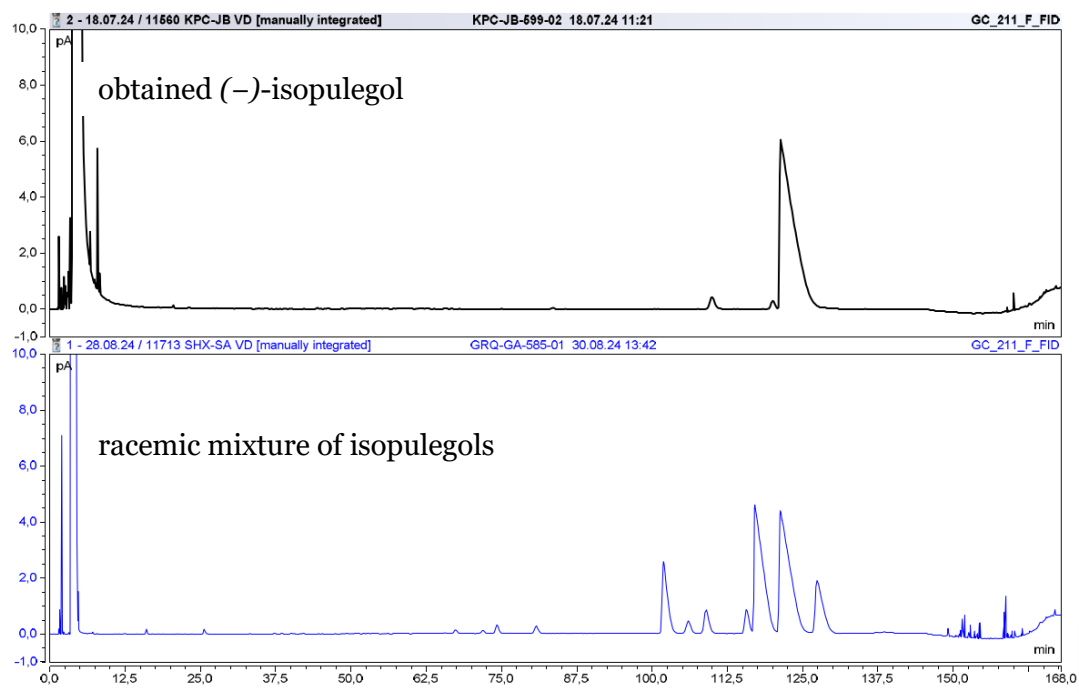
bicarbonate (50 mL). The organic layer was dried over magnesium sulfate, filtered, and the solvents were removed at reduced pressure (rotary evaporation). The title compound was obtained as a clear liquid (1.60 g, 60%).

^1H NMR (400 MHz, $[\text{D}_8]$ -toluene): 4.91 (p, $J = 1.5$ Hz, 1H), 4.68 (dt, $J = 1.8, 0.9$ Hz, 1H), 2.55 (ddt, $J = 13.0, 5.6, 1.0$ Hz, 1H), 2.16 (ddd, $J = 13.0, 3.7, 2.1$ Hz, 1H), 1.79 (dd, $J = 1.5, 0.8$ Hz, 3H), 1.71 – 1.62 (m, 1H), 1.56 – 1.30 (m, 4H), 0.90 (ddd, $J = 13.0, 4.0, 2.1$ Hz, 1H), 0.69 (d, $J = 6.3$ Hz, 3H). **^{13}C NMR** (100 MHz, $[\text{D}_8]$ -toluene): 206.9, 144.3, 112.4, 57.6, 50.4, 35.0, 33.9, 31.3, 22.2.

^1H NMR spectra of crude reaction mixtures, product and side products, 400 MHz, CDCl_3



Chiral GC traces of the obtained (–)-isopulegol and a racemic mixture of the isopulegol diastereomers.

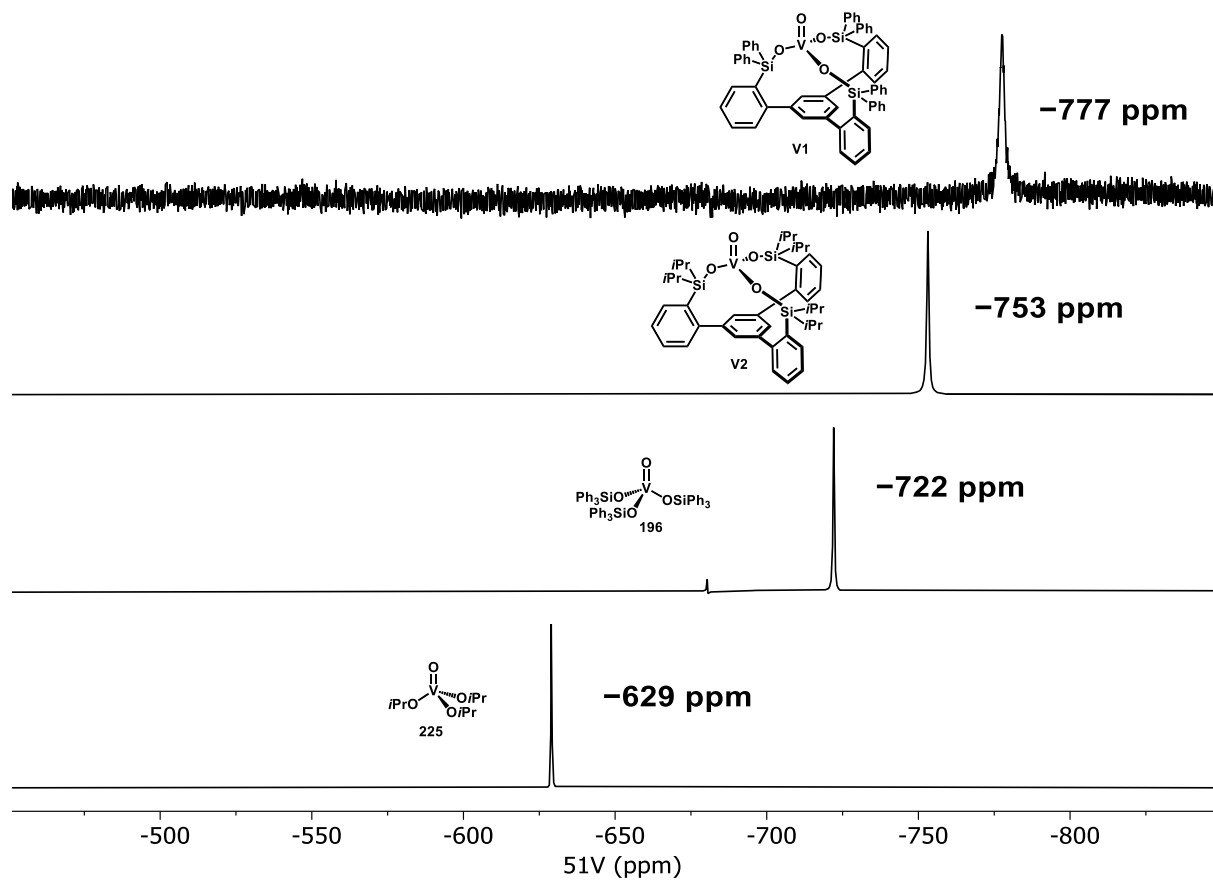


Conditions: injector: 220 °C; detector: 350 °C; temperature program: 60 °C isotherm at 145 min 8 °C/min to 220 °C, 3 min isotherm; gas: 0.6 bar (H₂).

3.5 Additional Characterization and ssNMR

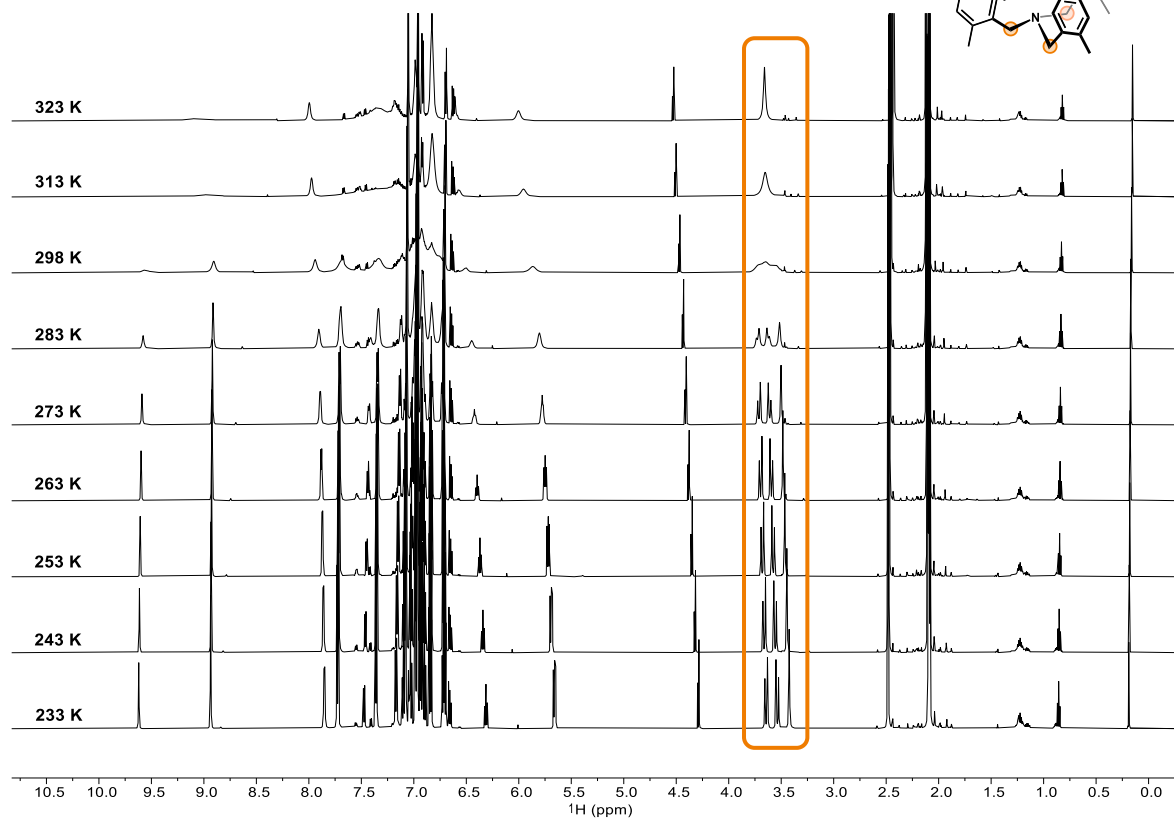
^{51}V NMR

^{51}V NMR spectra of **V1**, **V2**, **196**, and **225**, 158 MHz, $[\text{D}_8]$ -toluene, 298 K

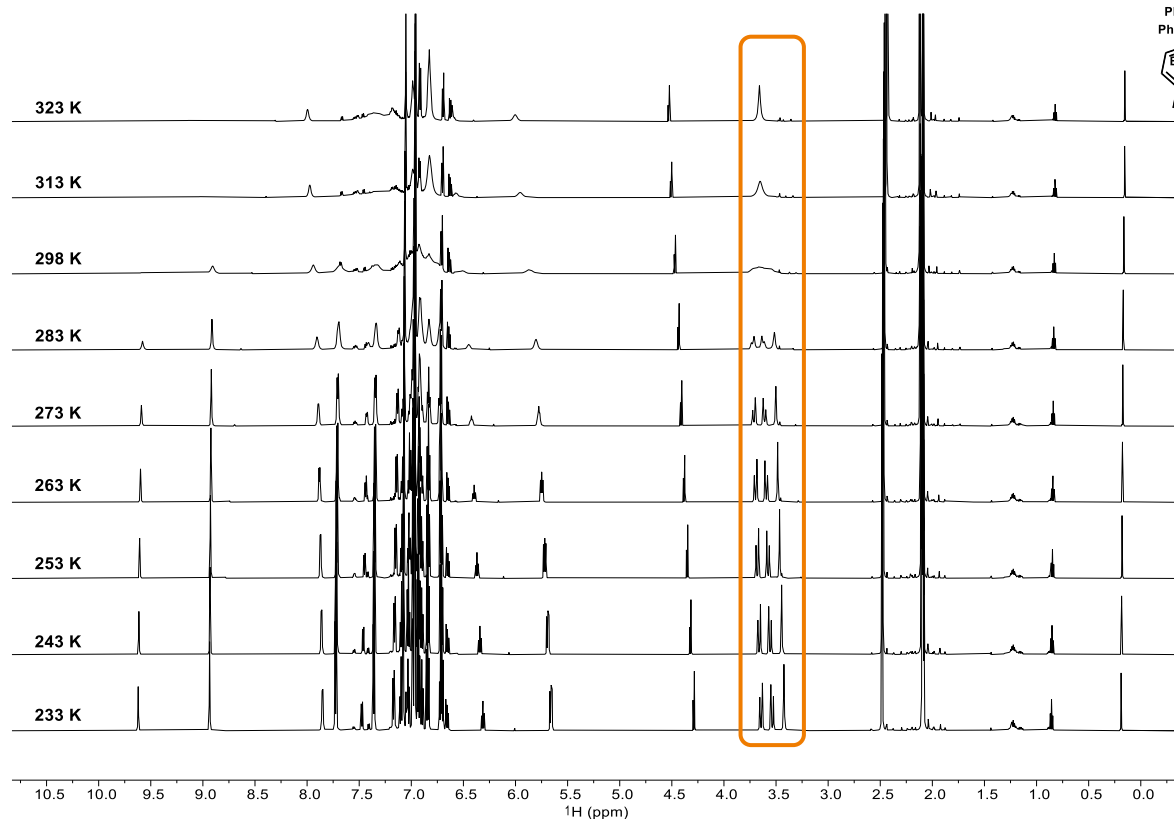


VT-NMR Studies of Pyridine Adducts

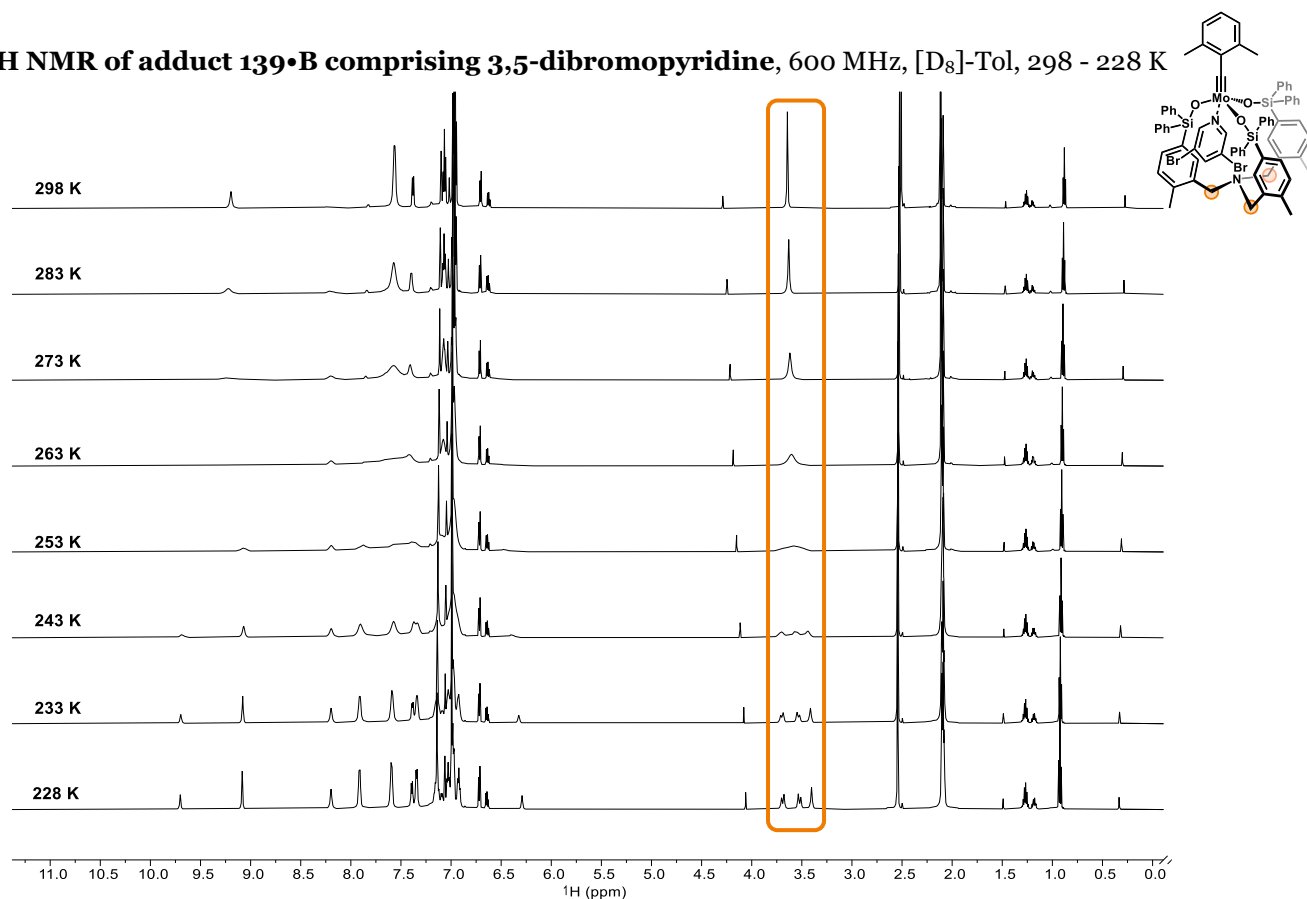
^1H NMR of Adduct **139**•Py, 600 MHz, $[\text{D}_8]$ -toluene/ CD_2Cl_2 , 323 - 233 K



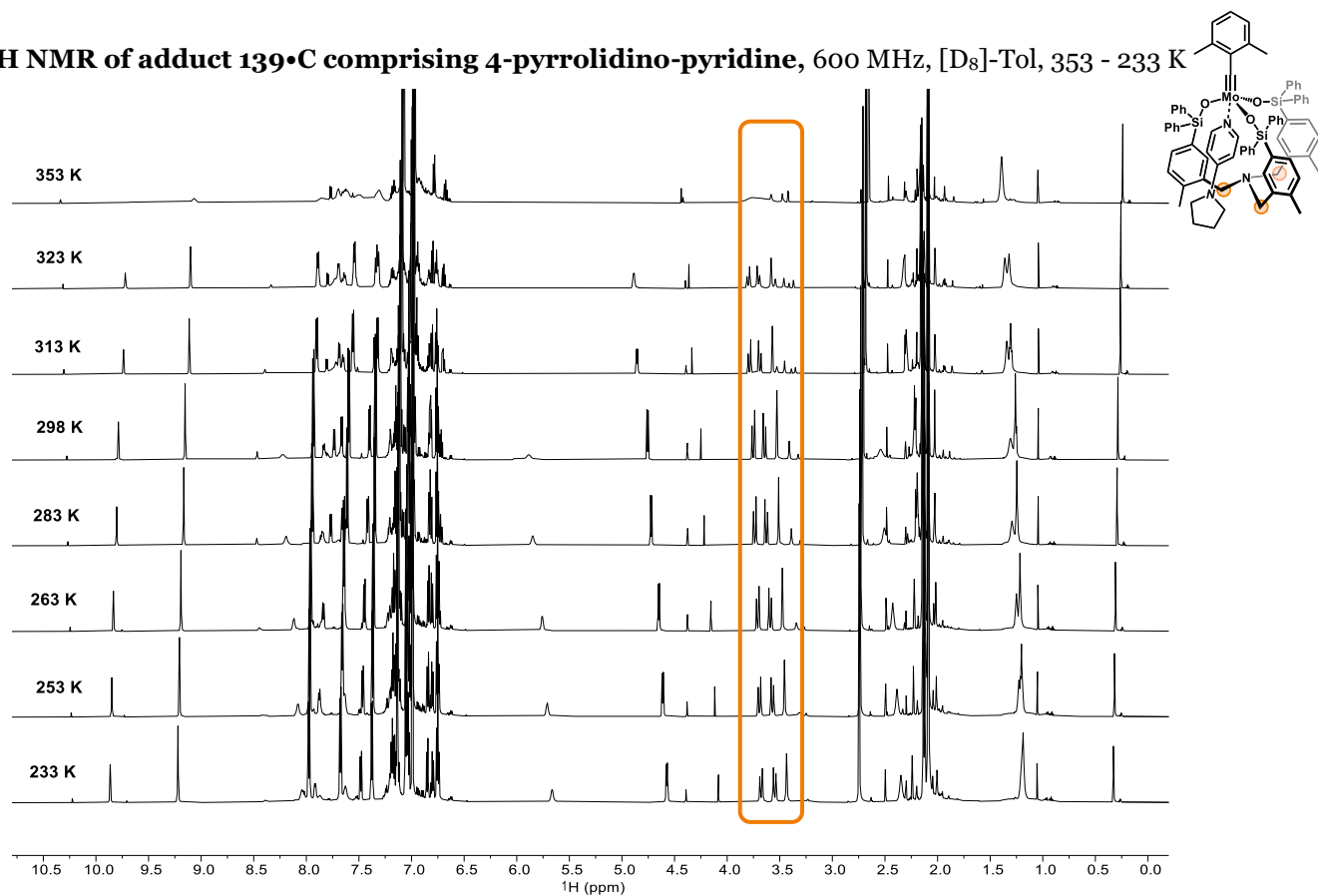
^1H NMR of adduct **139**•A comprising 3-bromopyridine, 600 MHz, $[\text{D}_8]$ -toluene, 323 - 233 K



¹H NMR of adduct 139•B comprising 3,5-dibromopyridine, 600 MHz, [D₈]-Tol, 298 - 228 K



¹H NMR of adduct 139•C comprising 4-pyrrolidino-pyridine, 600 MHz, [D₈]-Tol, 353 - 233 K



Gutmann–Beckett Method

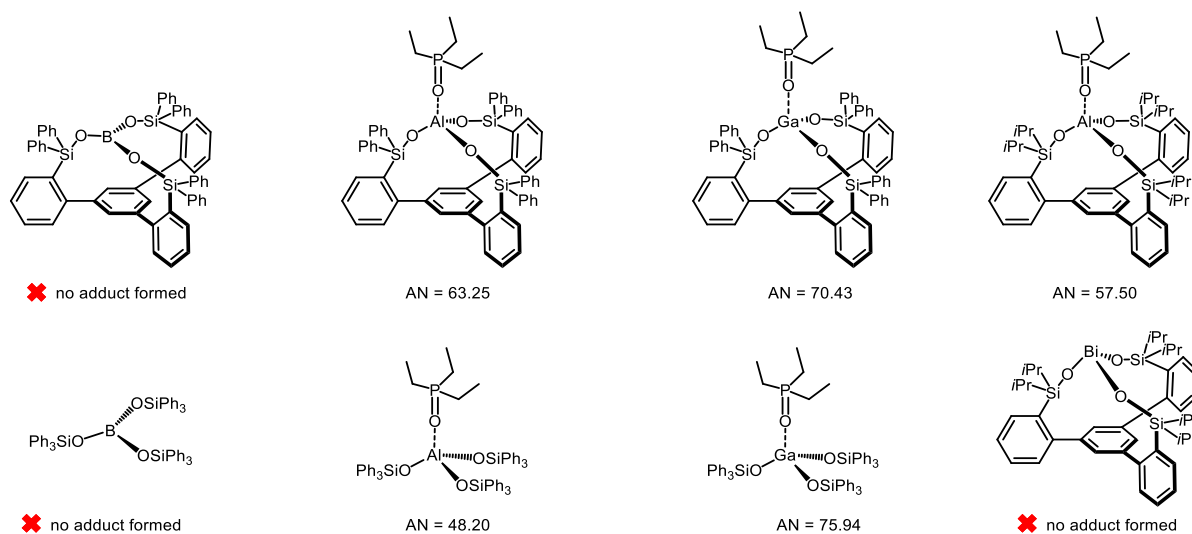


Figure S 9: Results from the measurement of the Lewis acid acceptor number (AN) using the Gutmann-Beckett method (Et_3PO , CD_2Cl_2).

A flame-dried NMR tube filled with argon was charged with a stock solution of the respective complex (0.5 mL, 0.02 M in CD_2Cl_2 , 0.01 mmol) and a ^1H -NMR spectrum was recorded at ambient temperature. A stock solution of triethylphosphine oxide (100 μL , 0.1 M in CD_2Cl_2 , 0.01 mmol) was added and a ^{31}P NMR spectrum recorded at ambient temperature. The ^{31}P chemical shift of the formed adduct was converted into the acceptor number (AN) with the following formula:^[221, 229]

$$\text{AN} = 2.21 \times (\delta_{\text{adduct}} - 41.0)$$

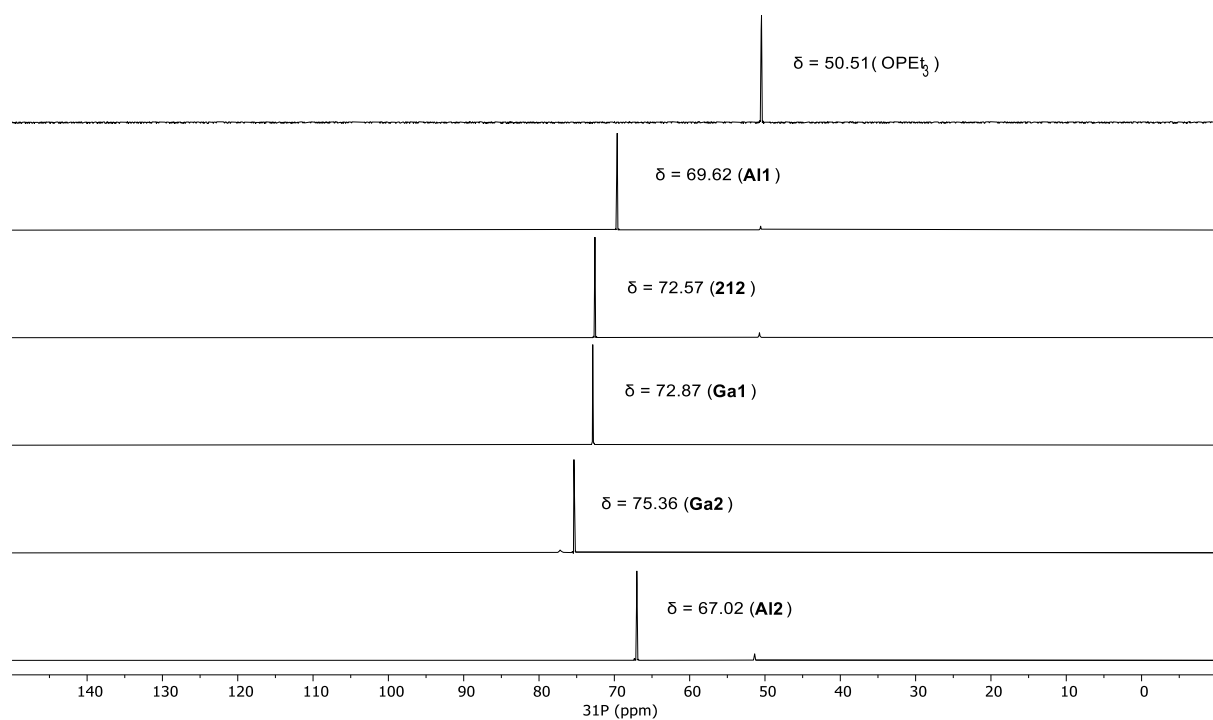
Table S 4: ^{31}P chemical shifts and calculated AN for the respective complexes using the Gutmann-Beckett method.

Complex	^{31}P chemical shift	AN
B1	—	—
B2	—	—
Al1	69.62 ppm	63.25
212	72.57 ppm	69.77
Ga1	72.87 ppm	70.43
214	75.36 ppm	75.94
Al2	67.02 ppm	57.50
242	62.81 ppm	48.20 ⁹ ; [232]
Bi1	—	—

The boron and bismuth containing complexes did not form adducts with triethylphosphine oxide.

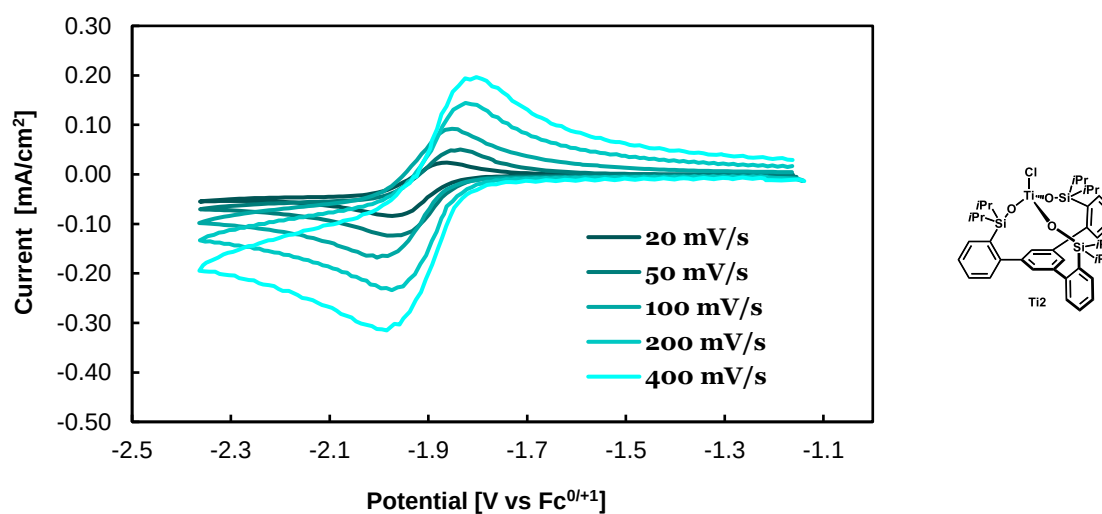
⁹ A previously determined AN for **242** by Whiteoak *et al.* is given as 62.02. Presumably the number is mislabeled and actually refers to the ^{31}P -shift as this is in good agreement with our experimental results.

^{31}P NMR spectra of triethylphosphine oxide and its adducts with complexes **Al1**, **212**, **Ga1**, **214**, and **Al2**, 400 MHz, CD_2Cl_2 , 298 K



Cyclic Voltammetry

The cyclic voltammograms of the respective titanium complexes **Ti2**, **216**, and **224** were recorded using a 3-electrode cell in an argon-filled glovebox. The set up was equilibrated with a solution of tetrabutylammonium hexafluorophosphate in tetrahydrofuran (1.0 M), prior to introducing tetrahydrofuran solutions of the analytes (**Ti2**: 1.0 mM, **216** and **224** 0.5 mM). Cyclic voltammograms were collected using different scan rates at ambient temperature covering an initial potential window of -3.0 to 1.0 V. Ferrocene was added as the internal standard to the experiment showing a defined electrochemical response. The potential is given in V vs $F^{0/+}$.



Graph 19: Cyclo voltammogram of **Ti2** recorded in THF (1.0 mM analyte, 1.0 M $[nBu_4N][PF_6]$ supporting electrolyte, $T = 298$ K, stationary glassy carbon working electrode, with variable scan rates).

Solid State NMR

All solid-state NMR spectra were recorded on a Bruker Avance III HD 500WB spectrometer using double-bearing MAS probes (DVT BL4) at resonance frequencies of, 160.481 MHz, 130.334 MHz, and 152.542 MHz for ^{11}B , ^{27}Al , and ^{71}Ga , respectively. The chemical shifts were referenced indirectly relative to the ^1H shift of TMS in an external neat sample. All spectra were processed in Topspin 3.6. Samples were packed into a 4-mm ZrO_2 rotor from Bruker and closed with a KelF or Vespel rotor turbine cap. For air sensitive samples, the powder was transferred and packed into a rotor inside an argon-filled glove box.

To measure a ^{11}B spectrum (spin-3/2) of the **B1** complex (C_Q : a few MHz), a high power excitation pulse with ^1H -decoupling (hpdec) under MAS condition at 10 kHz was chosen to measure the central transition (CT) as well as full breadth of the signal (CT+ST).

To measure the ^{27}Al spectrum (spin-5/2) of the **Al1•THF** complex (C_Q : a few tens of MHz), a high power excitation pulse (onepulse) under MAS condition at 8-11 kHz was chosen to measure the central transition (CT). In order to access the full breadth of the spectrum (several MHz), a Wideband Uniform Smooth Truncation-Carr-Purcell Meiboom-Gill (WURST-QCPMG) spectrum was recorded on a non-spinning sample with a sweep width of 1.7MHz and a carrier frequency of 0 ppm.

In order to measure the very broad ^{71}Ga central transition (spin-3/2) of the **Ga1•THF** complex (C_Q : a several tens of MHz), nine WURST-QCPMG spectra were recorded on a non-spinning sample, each with a sweep width of 5 MHz while varying the carrier frequency in steps of approx. 1400 ppm (431 kHz). Non-overlapping individual sections of 1400 ppm from the middle of each subspectra were then co-added to result in a ^{71}Ga spectrum of 12700 ppm.

For the NMR simulation of the quadrupolar interaction of ^{11}B , and ^{71}Ga , the “sola” module within Topspin 3.6 of Bruker was used. Quadrupolar parameters were estimated from spectral similarity optimized by hand and/or by the fitting function within sola. The most important parameters that were adjusted and extracted were C_Q , η_Q , δ_{iso} , and line broadening.

DFT-GIPAW Calculations

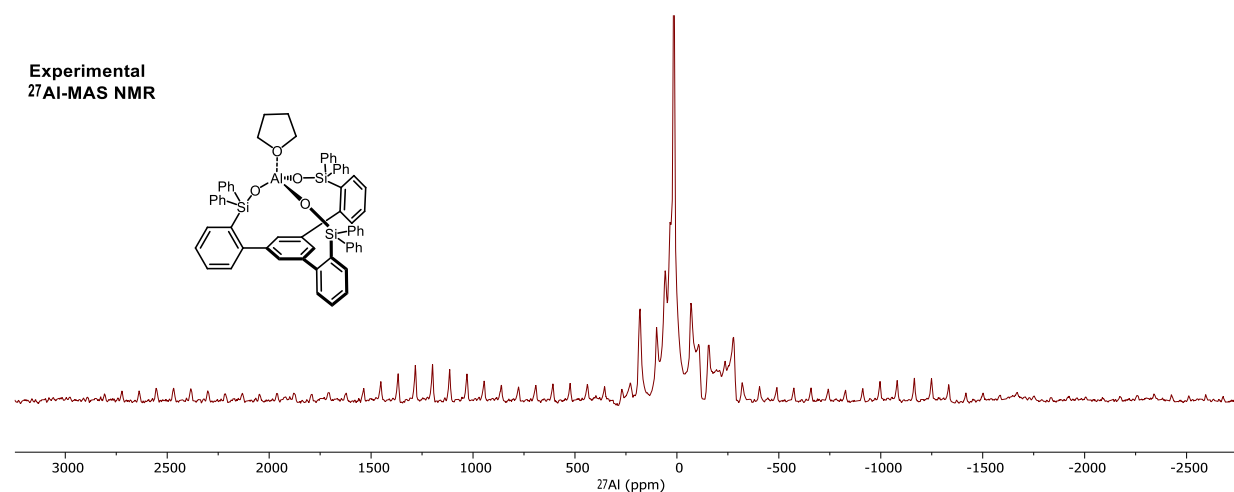
For comparison of the **B1** complex spectra, a DFT calculations was carried out using the CASTEP code starting with a X-ray structure of $\text{B}(\text{OSiPh}_3)_3$ (**211**).^[222a] The calculations employed the PBE exchange-correlation functional, using ultrasoft pseudopotentials generated on the fly and a plane wave cutoff energy of 800 eV. The crystal structure was optimized, relaxing all atomic positions while fixing the unit cell parameters to experimental values. The optimization, which employed a BFGS optimizer, was considered converged when

the maximal residual force on an atom fell below 0.001 eV/Å and when the maximal atomic displacement with respect to the previous step was smaller than 0.0005 Å.

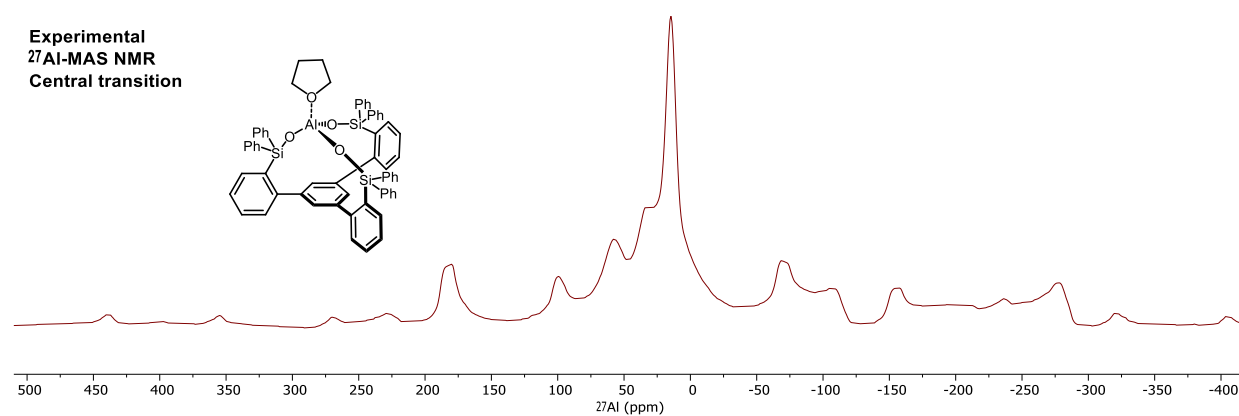
DFT calculations of the isotropic shielding parameter σ_{iso} , the quadrupole coupling constant C_Q , and the asymmetry parameter η employed the gauge-including projector augmented wave (GIPAW) method as implemented in the CASTEP package. Calculations were performed on the DFT-optimized structure. In terms of exchange-correlation functional, pseudopotentials, cutoff energy, and k-meshes, the same settings as for the optimizations were used for the DFT-GIPAW calculations.

²⁷Al ssNMR

²⁷Al-MAS NMR spectrum of Al1•THF, 8001 Hz (onepulse), 298 K.

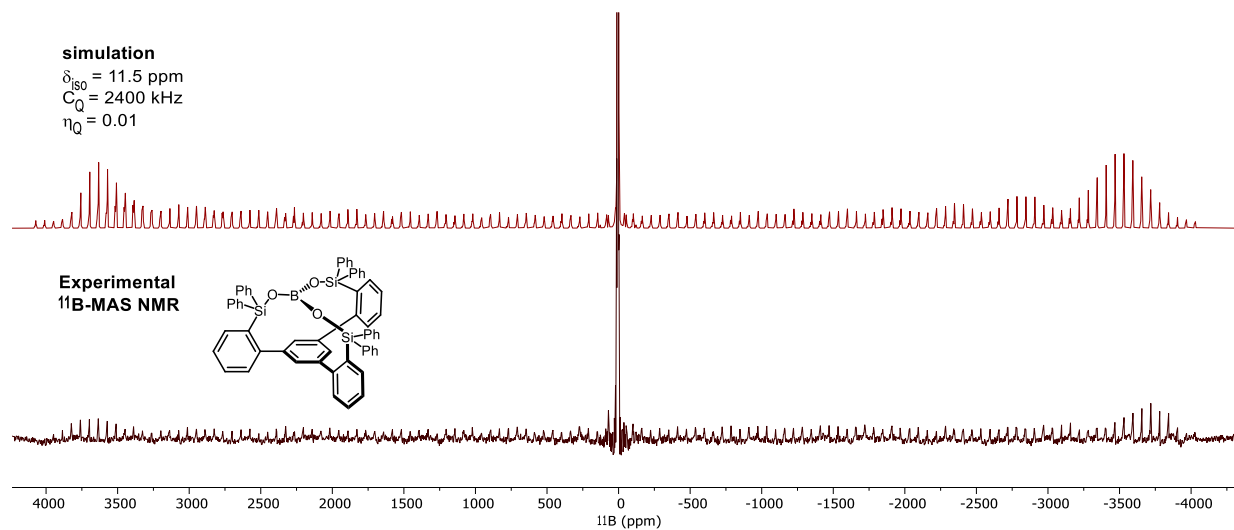


²⁷Al-MAS NMR spectrum of Al1•THF showing the CT, 8001 Hz (onepulse), 298 K.

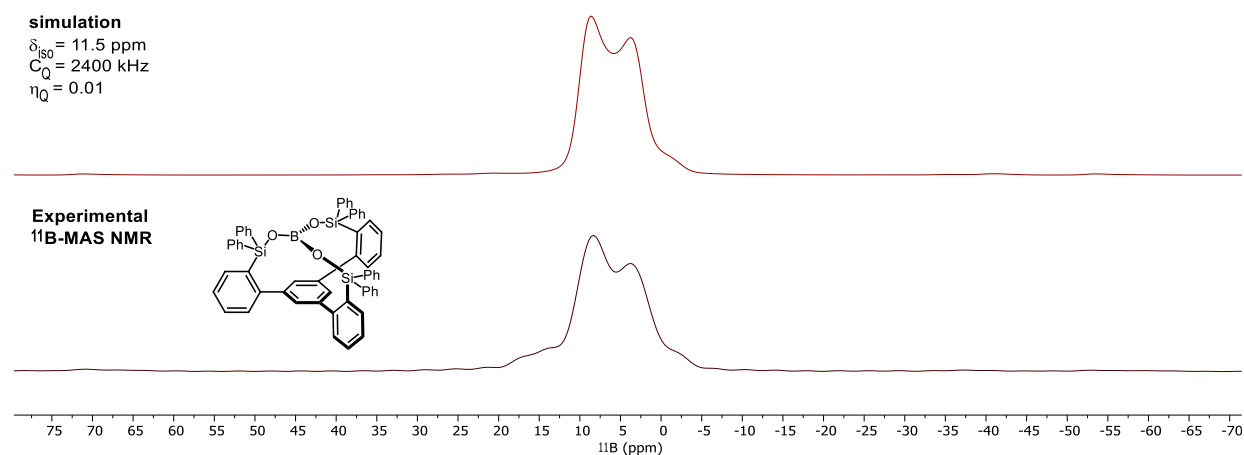


^{11}B ssNMR

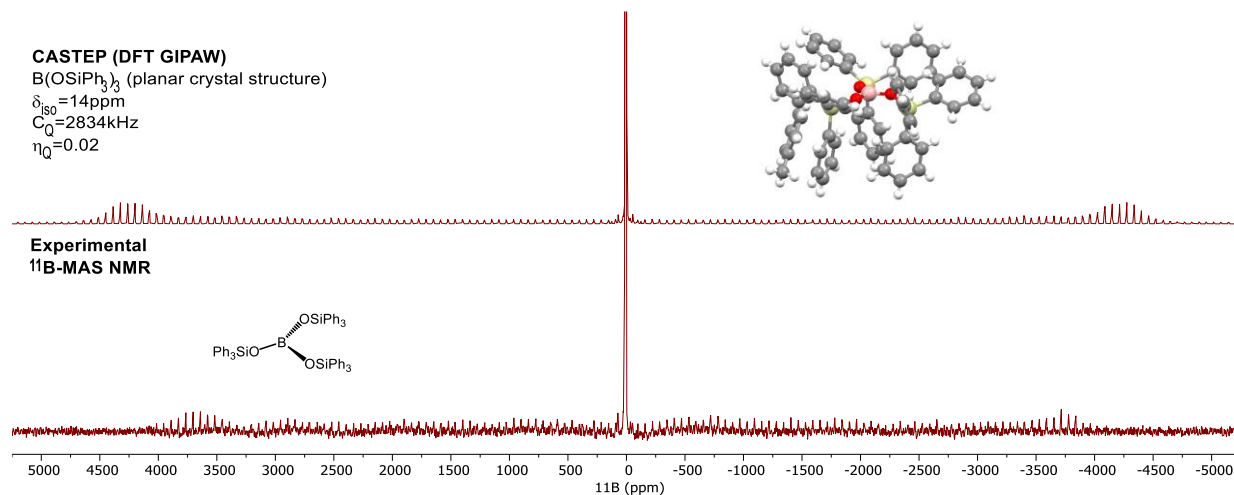
^{11}B -MAS NMR spectrum and simulation of B1, 5000 Hz, 298 K.



^{11}B -MAS NMR spectrum and simulation of B1 showing the CT, 5000 Hz, 298 K.

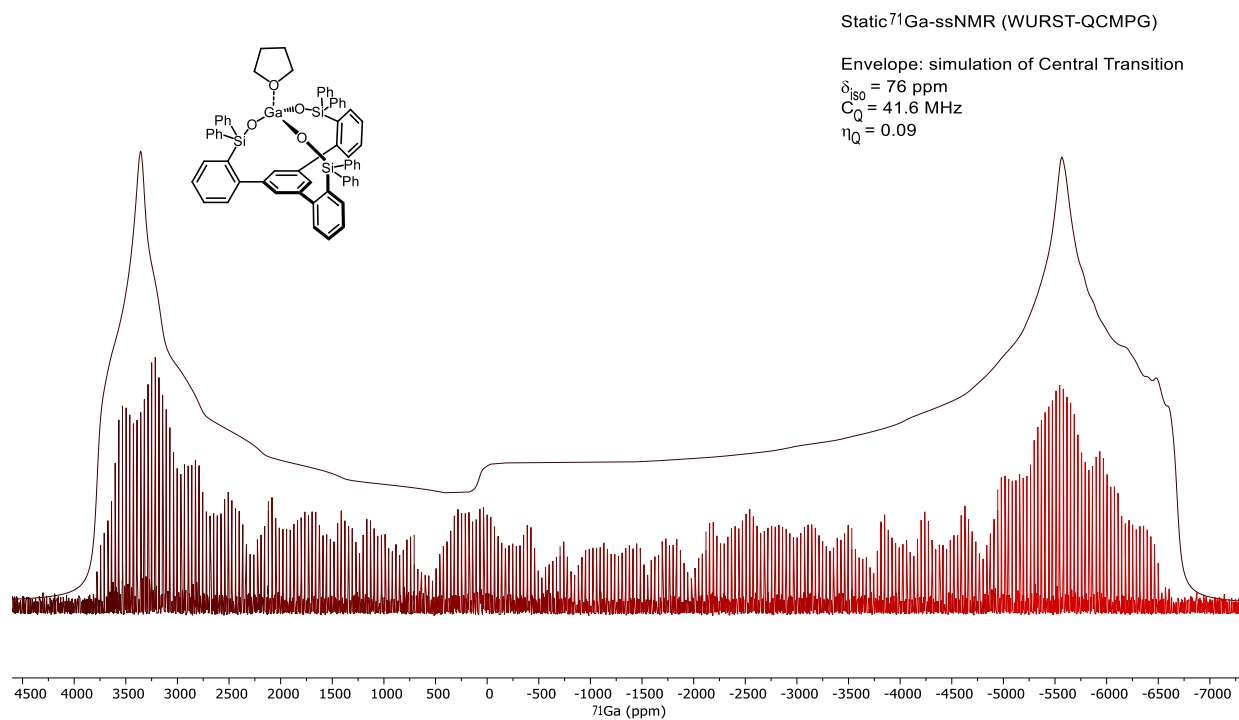


^{11}B -MAS NMR spectrum of 211 (calculated and experimental), 5000 Hz, 298 K.

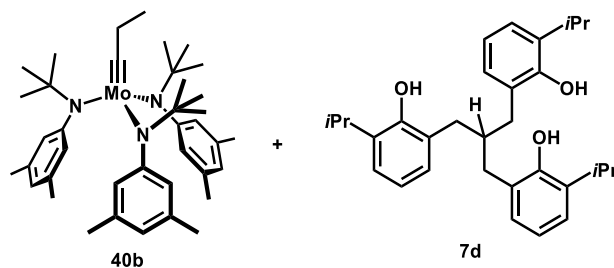


^{71}Ga ssNMR

^{71}Ga NMR (WURST-QCPMG) spectrum and simulation of $\text{Ga1}\cdot\text{THF}$ showing the CT, 298 K.

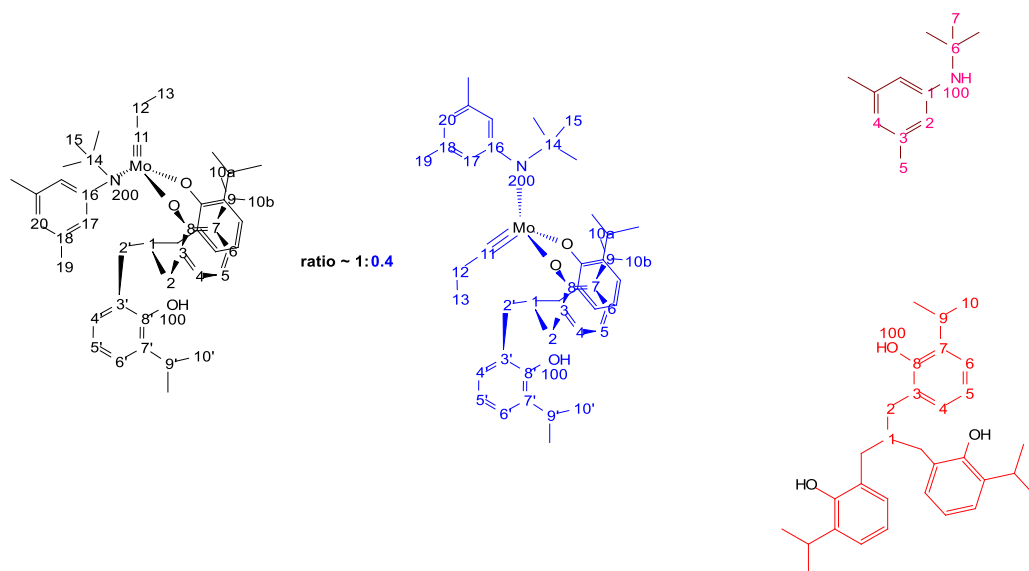


NMR Studies of the Catalytic System with a Triphenol Ligand



A 5 mL Schlenk flask was charged with molybdenum alkylidyne complex **40b** (10 mg, 15 μmol) and deuterated chloroform (1.0 mL). Ligand **7d** (6.9 mg, 15 μmol) was added and the resulting solution was stirred at ambient temperature. After 1 h, the solution was transferred into a flame-dried *J. Young* NMR tube filled with argon and analyzed by NMR spectroscopy.

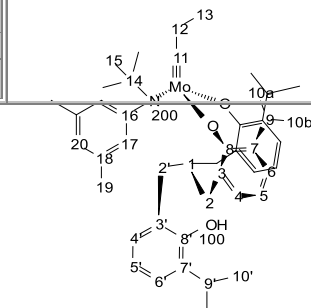
Molecules detected in the mixture



Assignments of the NMR signals to the two major organometallic species

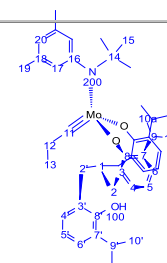
Atom	δ (ppm)	HSQC	COSY	HMBC	NOESY
1 C	42.413	1		2', 2a, 2b	
H	2.392	1	2', 2b	2, 2', 3, 3'	2a, 4', 100
2 C	41.787	2a, 2b		1, 2', 2a, 2b, 4	
Ha	3.267	2	2b	1, 2, 2', 3, 4, 8	1, 2b
Hb	2.476	2	1, 2a	1, 2, 2', 3, 4, 8	2', 2a, 4
2' C	36.750	2'		1, 2a, 2b, 4'	
H2	2.812	2'	1	1, 2, 3', 4', 8'	2b, 4, 4'
3 C	129.330			1, 2a, 2b, 5	
3' C	125.990			1, 2', 5', 100	
4 C	127.758	4		2a, 2b, 6	
H	6.656	4	5	2, 6, 8	2', 2b
4' C	128.779	4'		2', 6'	
H	6.742	4'	5'	2', 6', 8'	1, 2'
5 C	120.227	5			
H	6.605	5	4, 6	3, 7, 8	
5' C	119.927	5'			
H	6.538	5'	4', 6'	3', 7'	
6 C	123.601	6		4, 9	
H	7.021	6	5	4, 8, 9	10a, 10b
6' C	123.950	6'		4', 9'	
H	6.825	6'	5'	4', 8', 9'	10'
7 C	136.054			5, 9, 10a, 10b	
7' C	134.177			5', 9', 100	
8 C	164.361			2a, 2b, 4, 5, 6, 9	
8' C	151.145			2', 4', 6', 9', 100	
9 C	26.171	9		6, 10a, 10b	
H	3.635	9	10a, 10b	6, 7, 8, 10a, 10b	10a, 10b, 13, 15, 17

Atom	δ (ppm)	HSQC	COSY	HMBC	NOESY
9' C	26.825	9'		6'	
H	2.839	9'	10'	6', 7', 8', 10'	10', 100
10' C	22.771	10'		9', 10'	
H3	1.001	10'	9'	10'	6', 9'
10a C	21.910	10a		9, 10b	
H3	1.333	10a	9	7, 9, 10b	6, 9, 13, 17, 100
10b C	24.902	10b		9, 10a	
H3	1.233	10b	9	7, 9, 10a	6, 9
11 C	314.017			12, 13	
12 C	41.835	12		13	
H2	1.670	12	13	11, 13	13
13 C	12.029	13		12	
H3	-0.035	13	12	11, 12	9, 10a, 12
14 C	62.142			15	
15 C	29.341	15		15	
H3	1.521	15		14, 15, 200	9, 17
16 C	159.475			17	
17 C	125.022	17		17, 19, 20	
H	6.881	17	19	16, 17, 19, 20	9, 10a, 15, 19
18 C	136.694			19	
19 C	21.555	19		17, 20	
H3	2.362	19	17, 20	17, 18, 20	17
20 C	126.380	20		17, 19	
H	6.808	20	19	17, 19	
100 O					
H	4.091			3', 7', 8'	1, 9', 10a
200 N	-96.762			15	

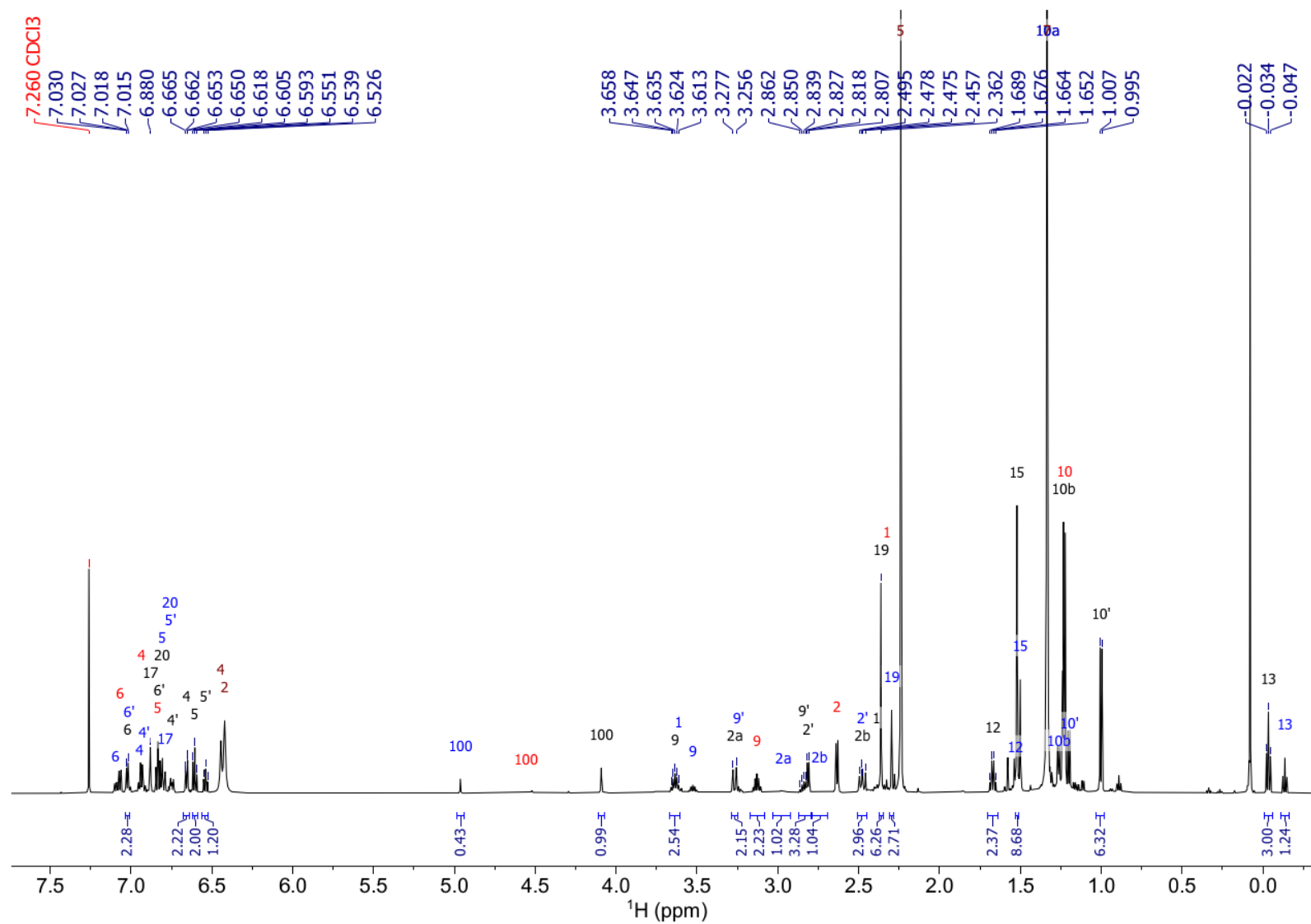


Atom	δ (ppm)	HSQC	COSY	HMBC	NOESY
1 C	34.462	1			
H	3.615	1		2	100
2 C	40.570	2a, 2b		1, 4	
Ha	2.967	2			4
Hb	2.742	2			4
2' C	37.315	2'		4'	
H2	2.476	2'			100
3' C	127.882				
3' C	126.156			5', 100	
4 C	129.526	4		5, 6	
H	6.947	4		2, 6, 8	2a, 2b
4' C	128.690	4'		6'	
H	6.919	4'	5'	2', 6', 8'	
5 C	120.864	5			
H	6.805	5	6	3, 4, 7	
5' C	119.828	5'			
H	6.754	5'	4', 6'	3', 7'	
6 C	123.923	6		4, 9	
H	7.096	6	5	4, 8, 9	10a
6' C	124.388	6'		4', 9'	
H	7.012	6'	5'	4', 8', 9'	
7 C	136.547			5, 9, 10a, 10b	
7' C	135.145			5', 9', 100	
8 C	165.285			4, 6, 9	
8' C	151.304			4', 6', 9', 100	
9 C	26.917	9		6, 10a, 10b	
H	3.526	9	10a, 10b	6, 7, 8, 10a, 10b	10a, 10b, 15, 17

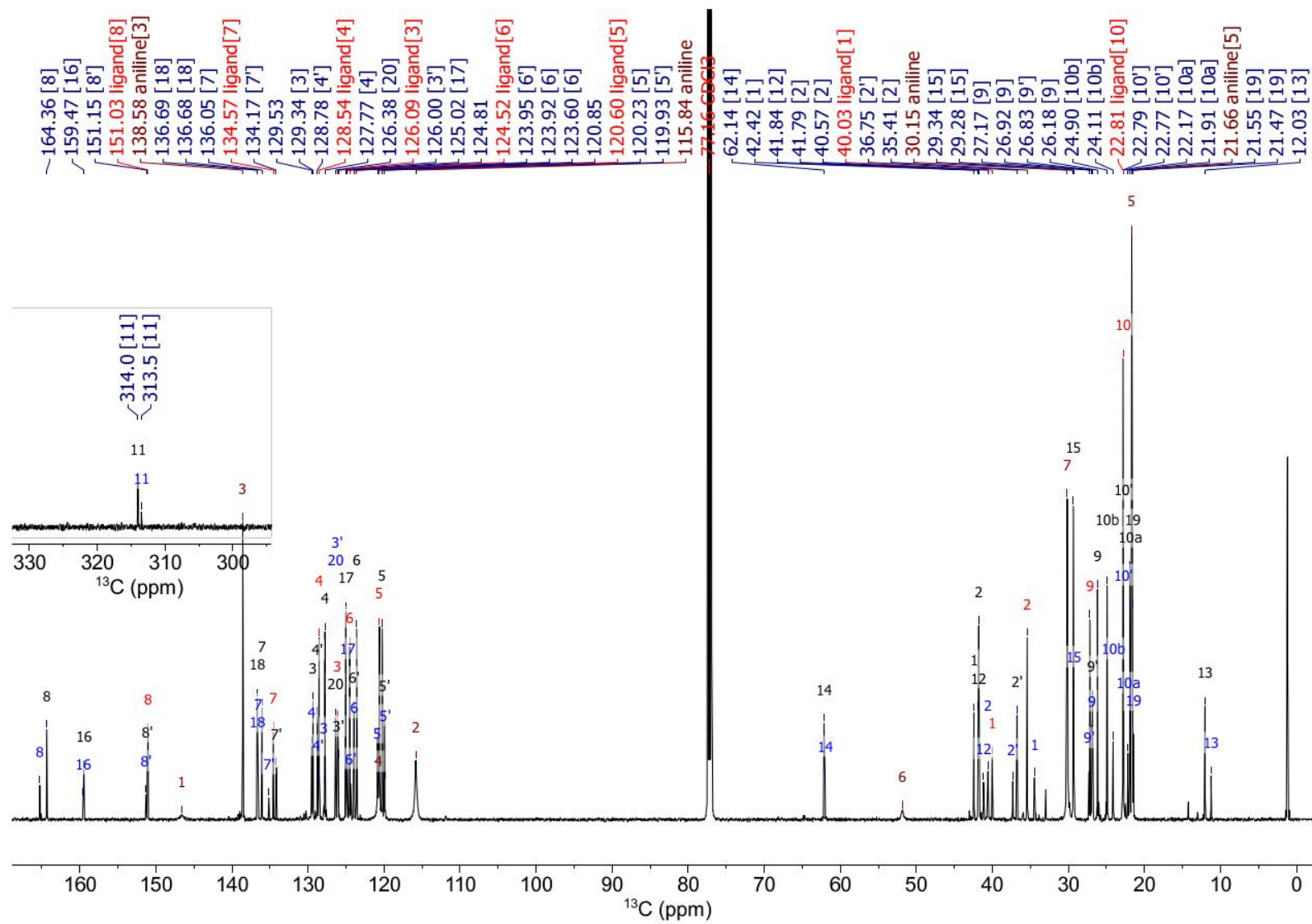
Atom	δ (ppm)	HSQC	COSY	HMBC	NOESY
9' C	27.287	9'		6'	
H	3.243	9'	10'	6', 7', 8', 10'	10'
10' C	22.788	10'		9'	
H3	1.198	10'	9'		9'
10a C	22.159	10a		9, 10b	
H3	1.333	10a	9	7, 9, 10b	6, 9, 17
10b C	24.100	10b		9, 10a	
H3	1.263	10b	9	7, 9, 10a	9
11 C	313.495			12, 13	
12 C	41.167	12		13	
H2	1.532	12	13	11, 13	
13 C	11.233			12	
H3	-0.136		12	11, 12	
14 C	61.992			15	
15 C	29.282	15		15	
H3	1.500	15		14, 15, 200	9, 17
16 C	159.568			17	
17 C	124.812	17		17, 19, 20	
H	6.789	17	19	16, 17, 19, 20	9, 10a, 15
18 C	136.676			19	
19 C	21.466	19		17, 20	
H3	2.296	19	17, 20	17, 18, 20	
20 C	126.350	20		17, 19	
H	6.758	20	19	17, 19	
100 O					
H	4.963			3', 7', 8'	1, 2'
200 N	-95.800			15	



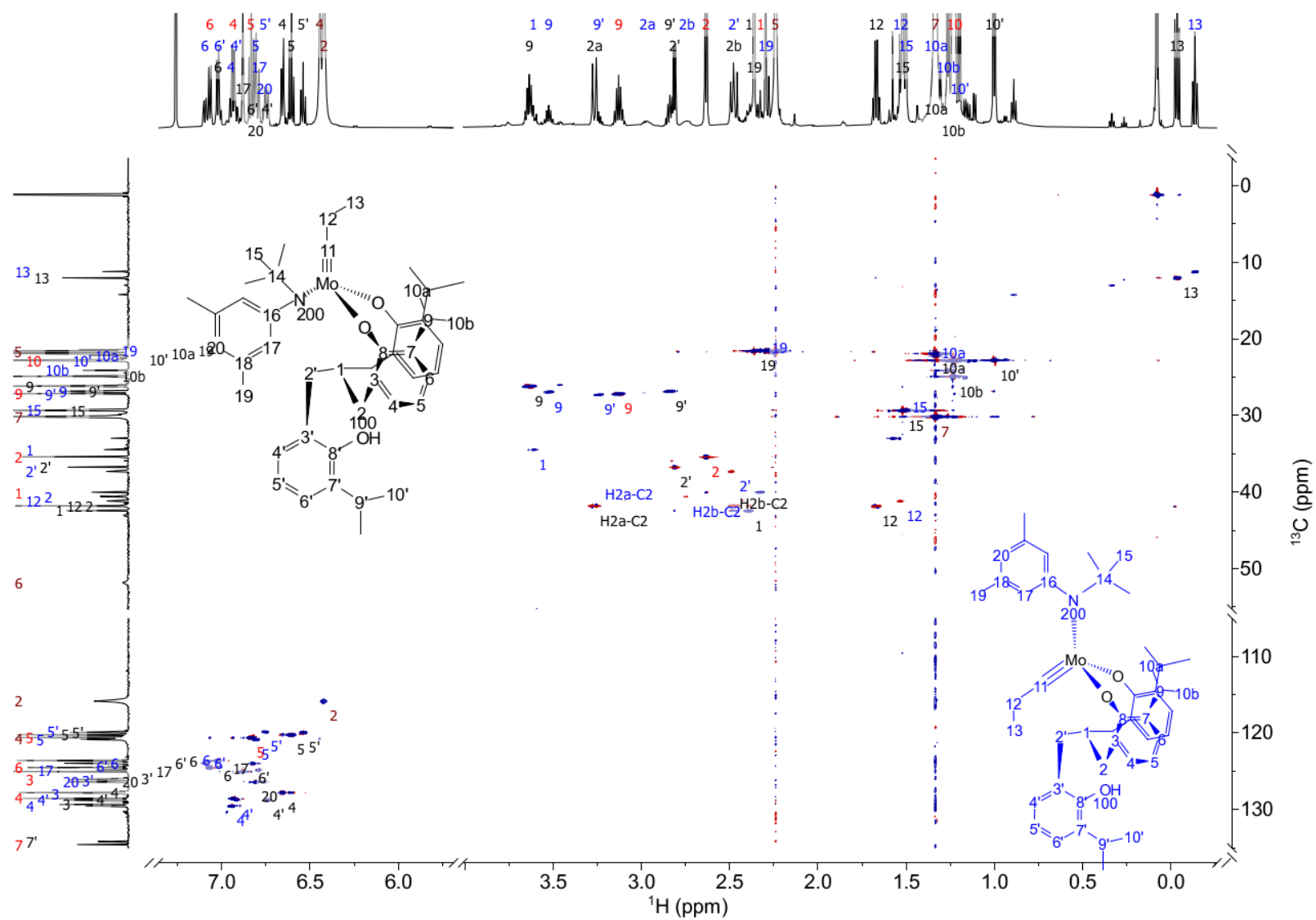
^1H NMR of the mixture, 600 MHz, CDCl_3 , 298 K

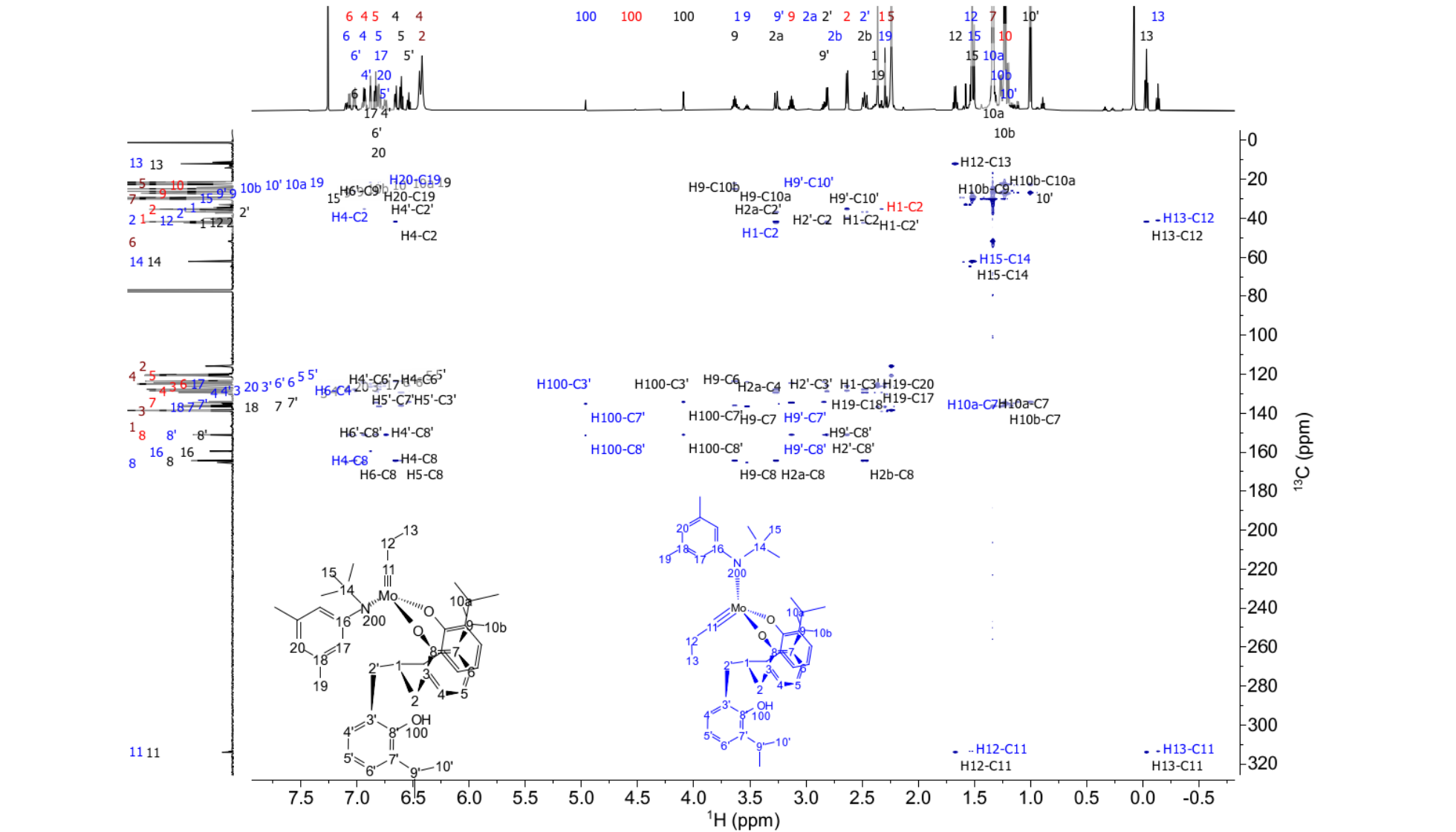


^{13}C NMR of the mixture, 151 MHz, CDCl_3 , 298 K

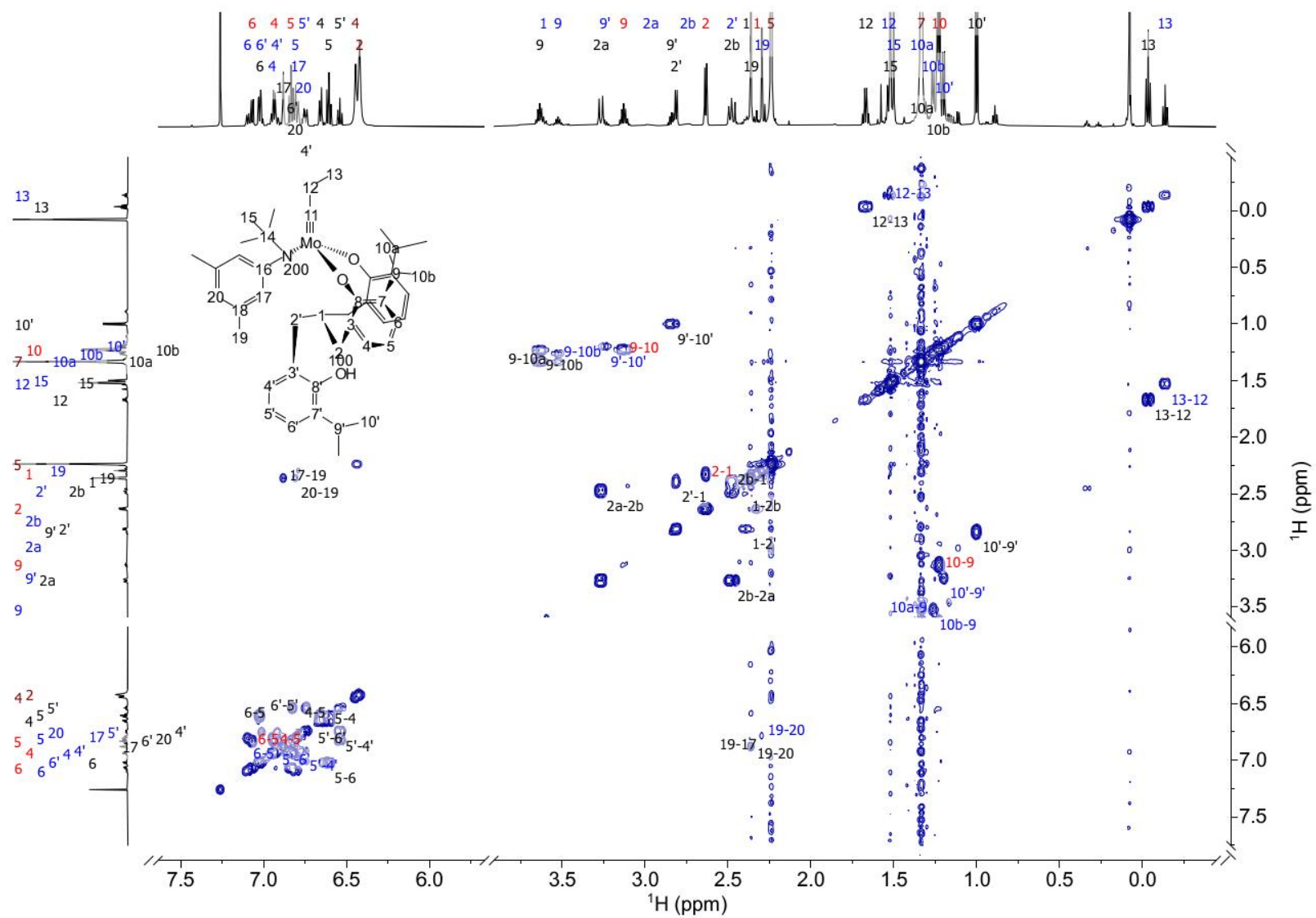


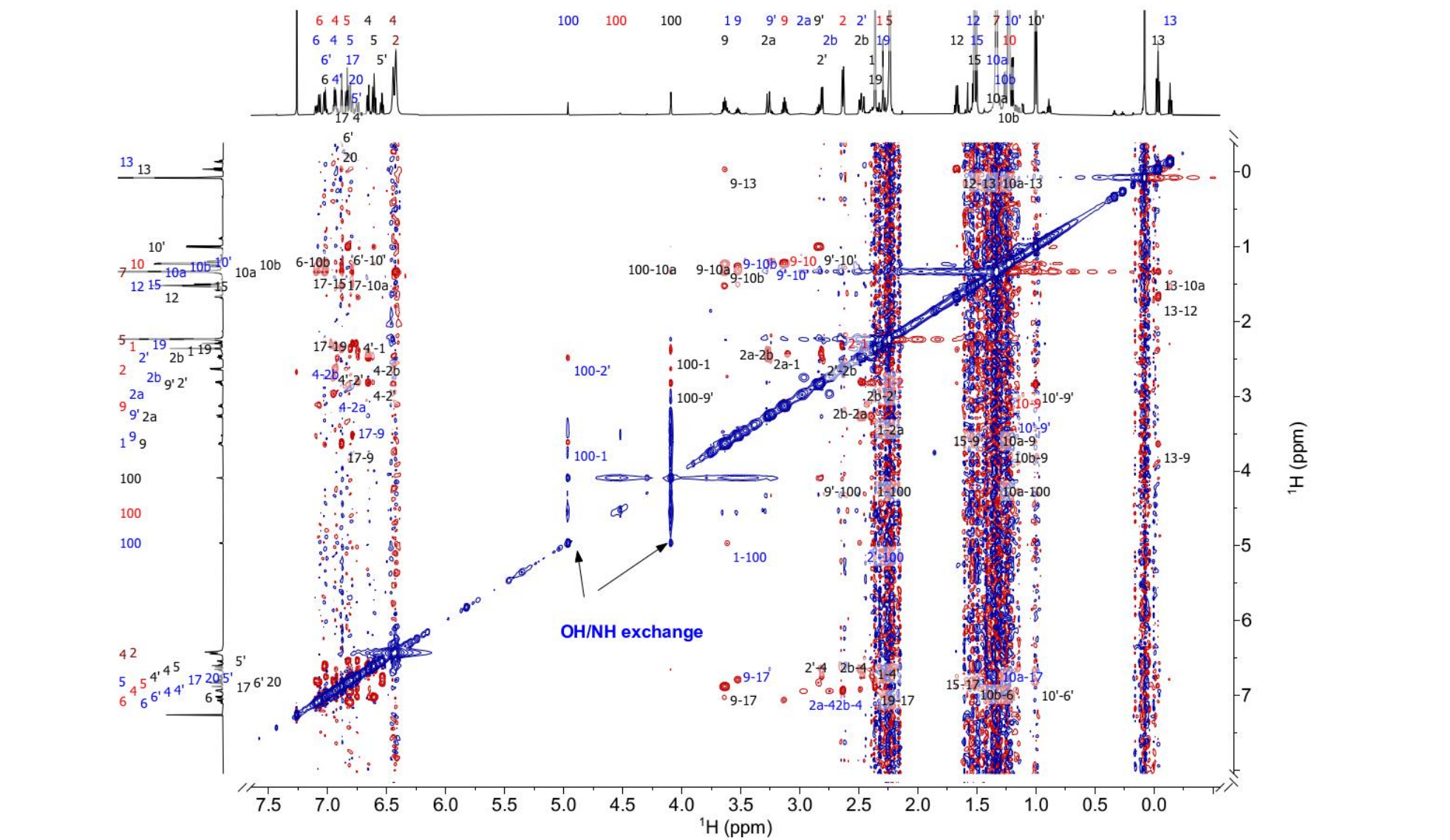
2D ^1H - ^{13}C HSQC of the mixture, 600 MHz, CDCl_3 , 298 K



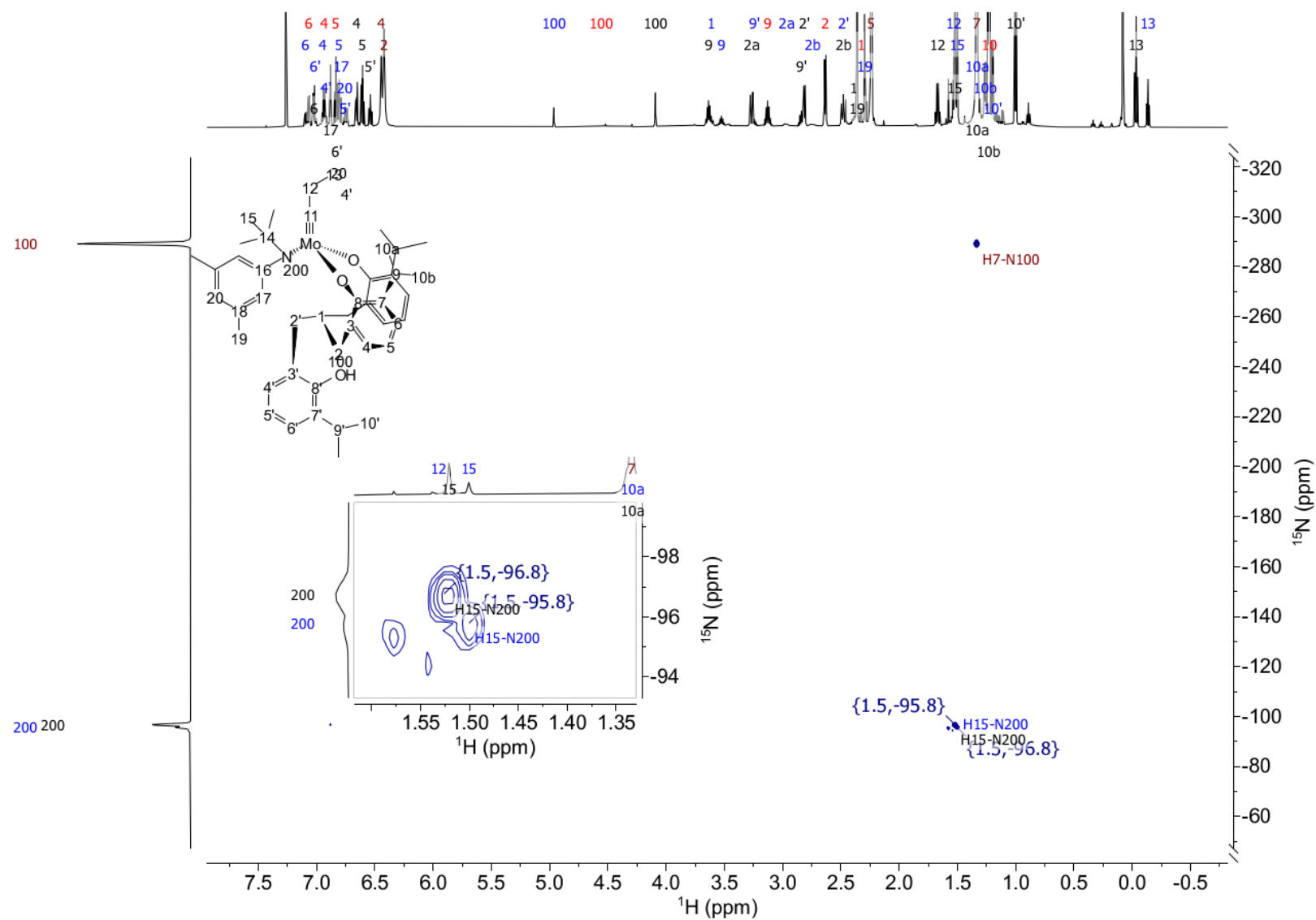


2D ^1H - ^1H COSY of the mixture, 600 MHz, CDCl_3 , 298 K





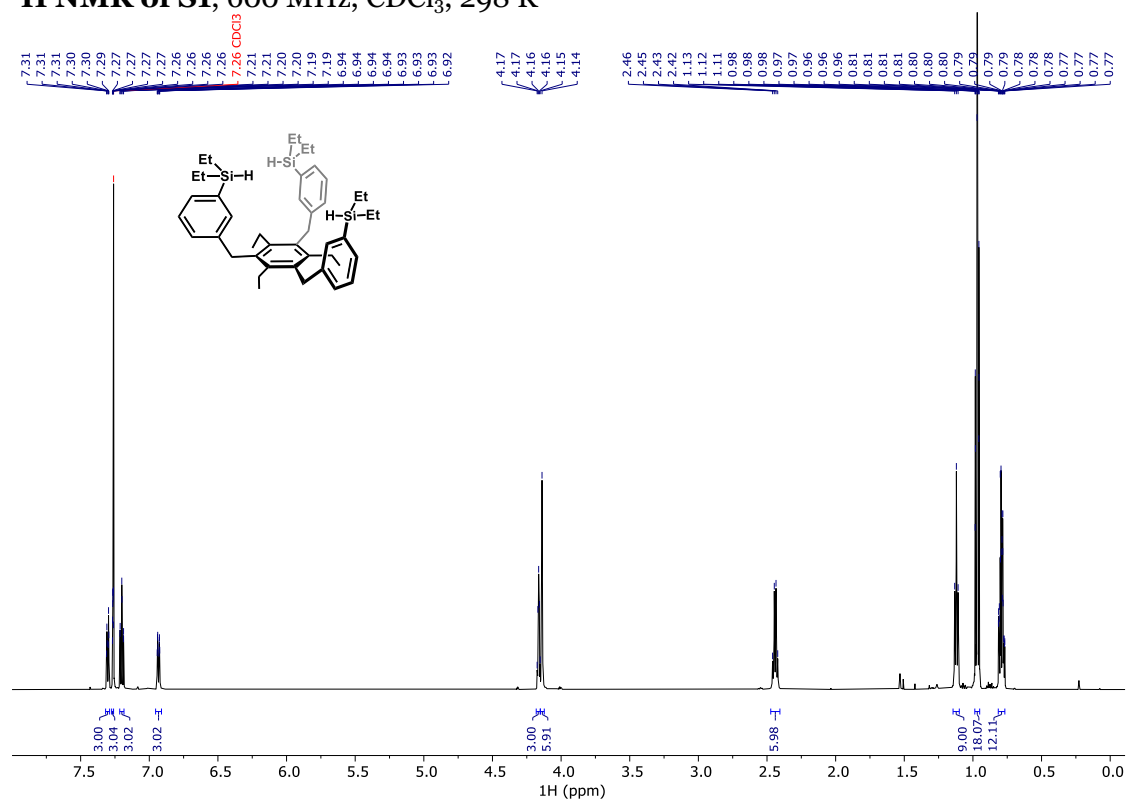
2D ^1H - ^{15}N HMBC of the mixture, 600 MHz, CDCl_3 , 298 K



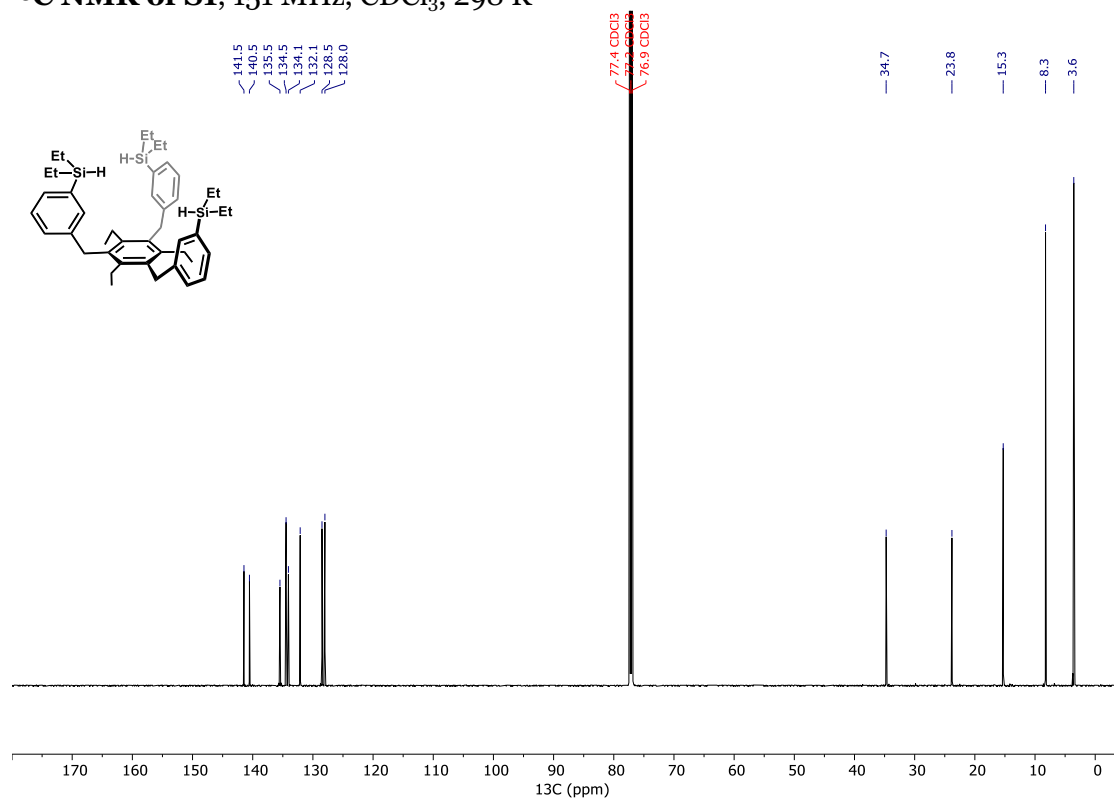
4 Appendix

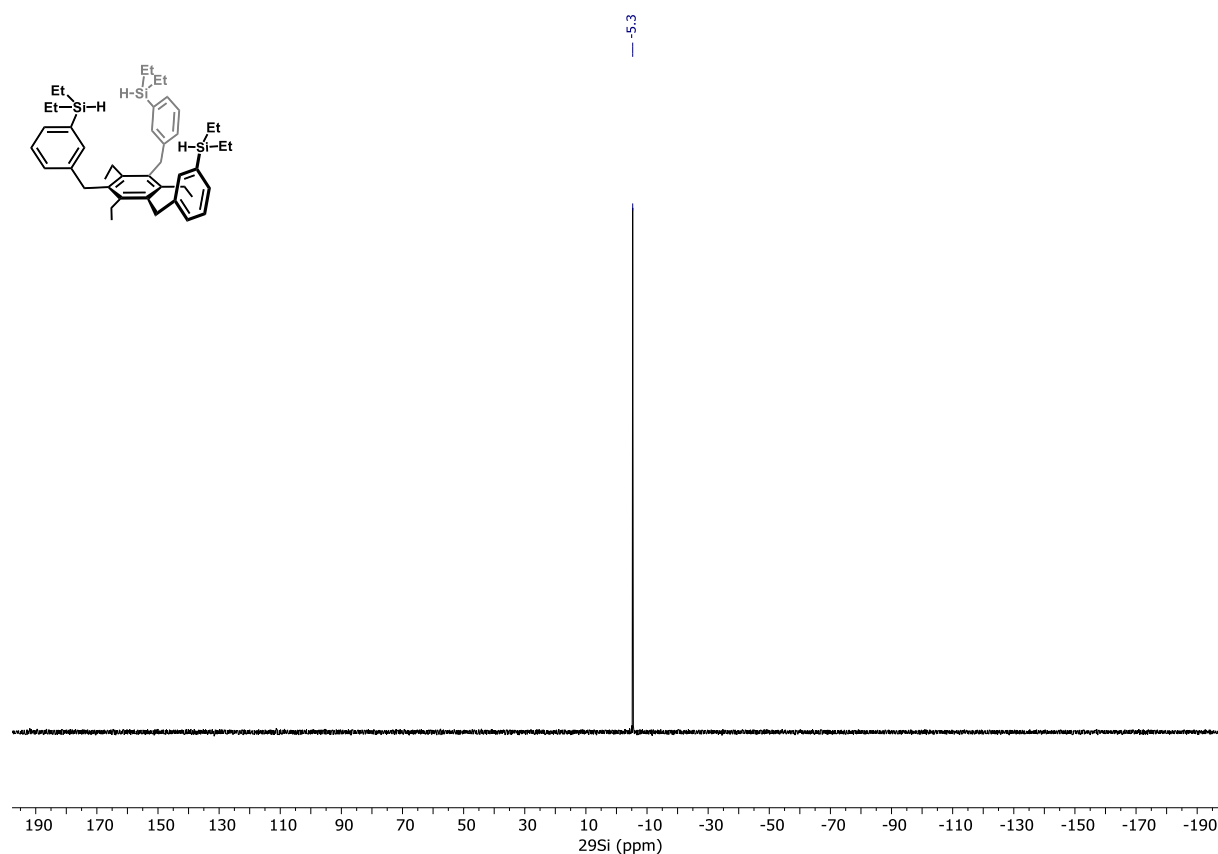
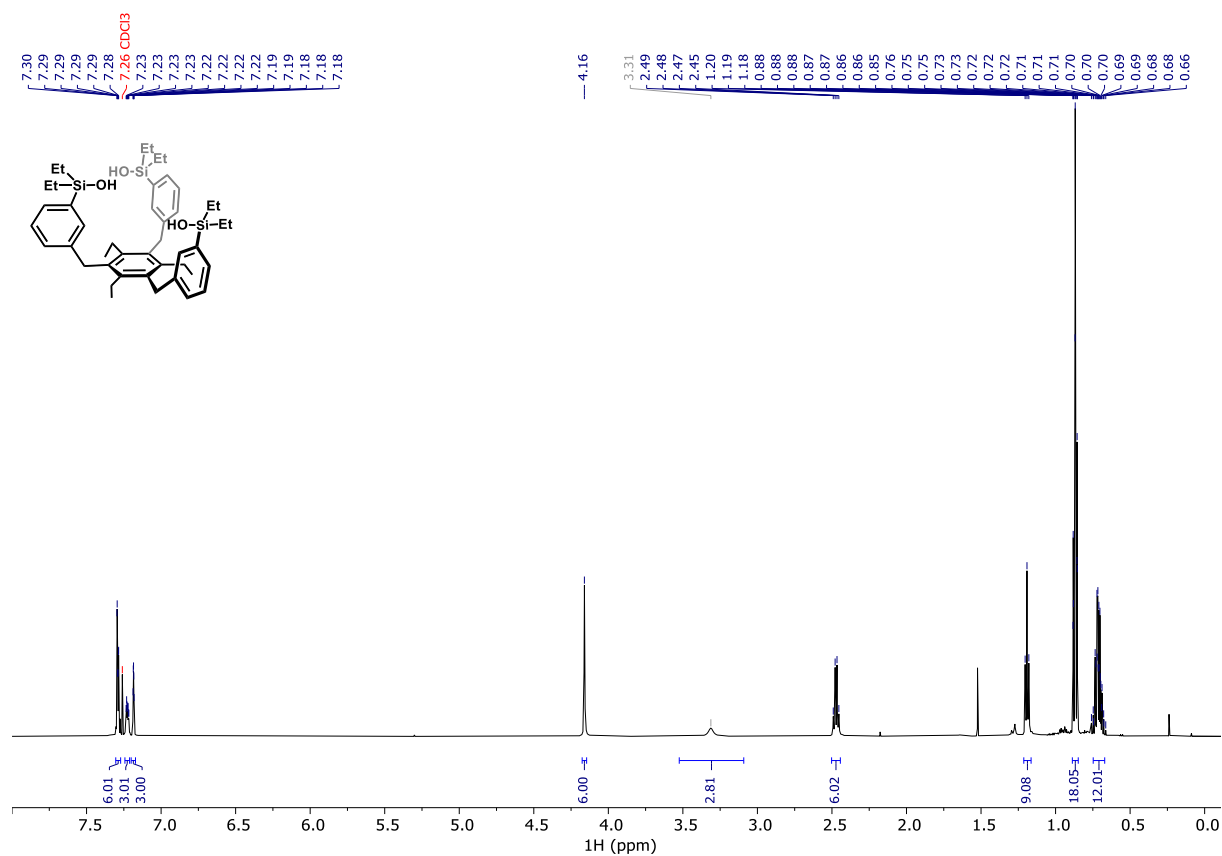
4.1 Relevant NMR Spectra

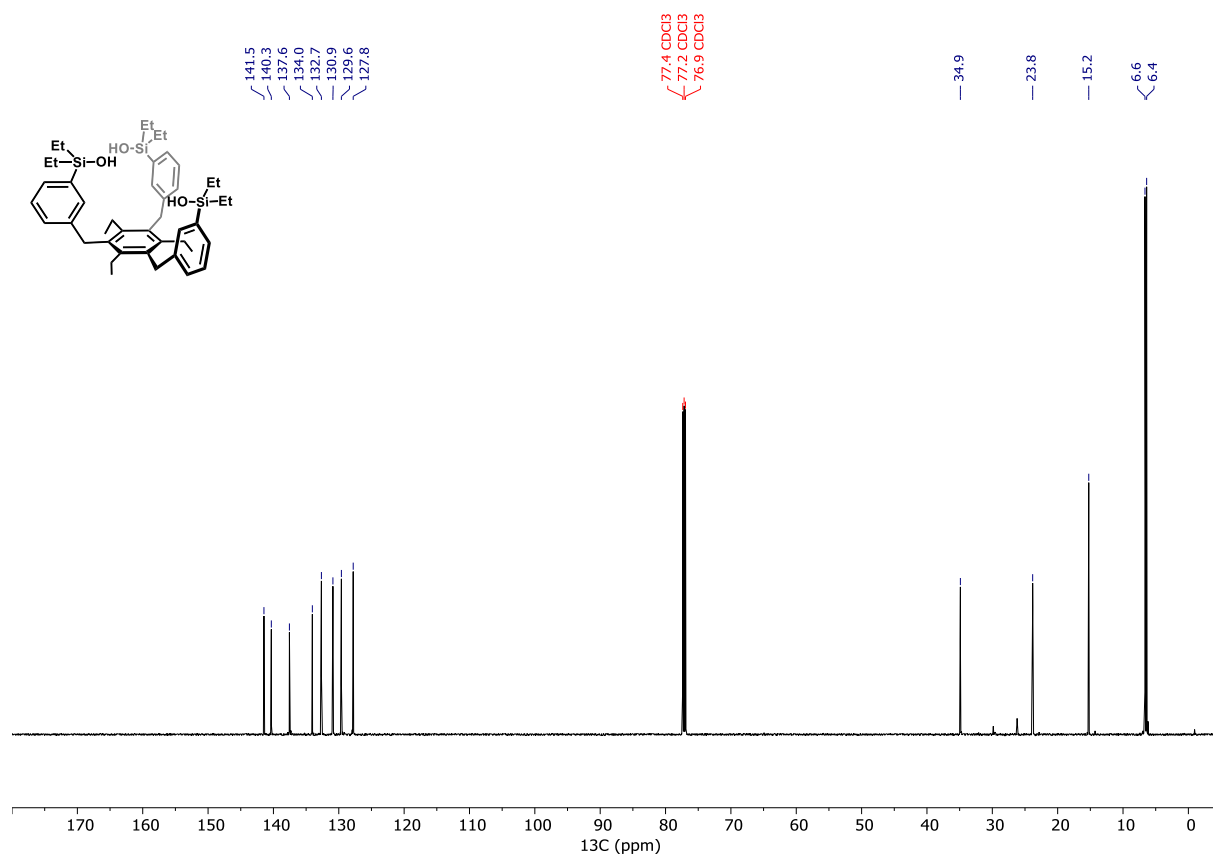
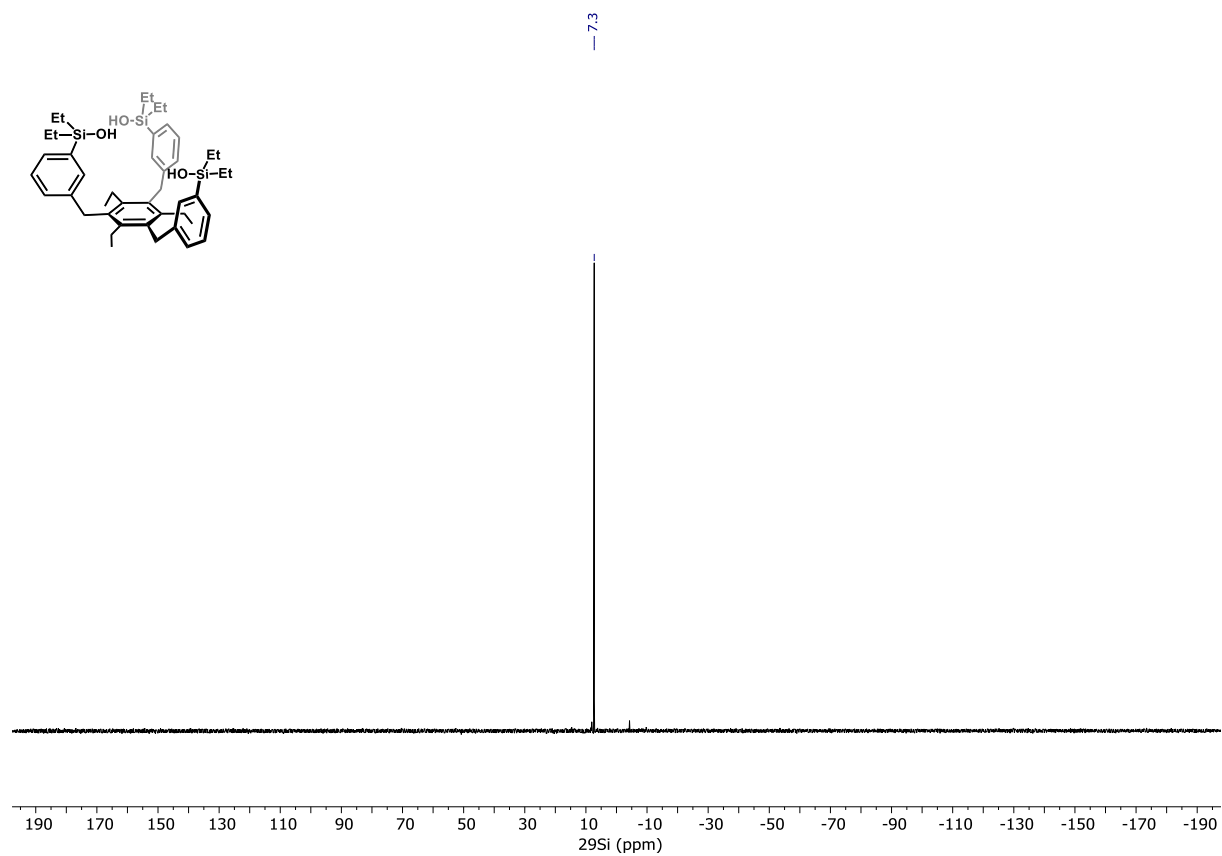
^1H NMR of **S1**, 600 MHz, CDCl_3 , 298 K

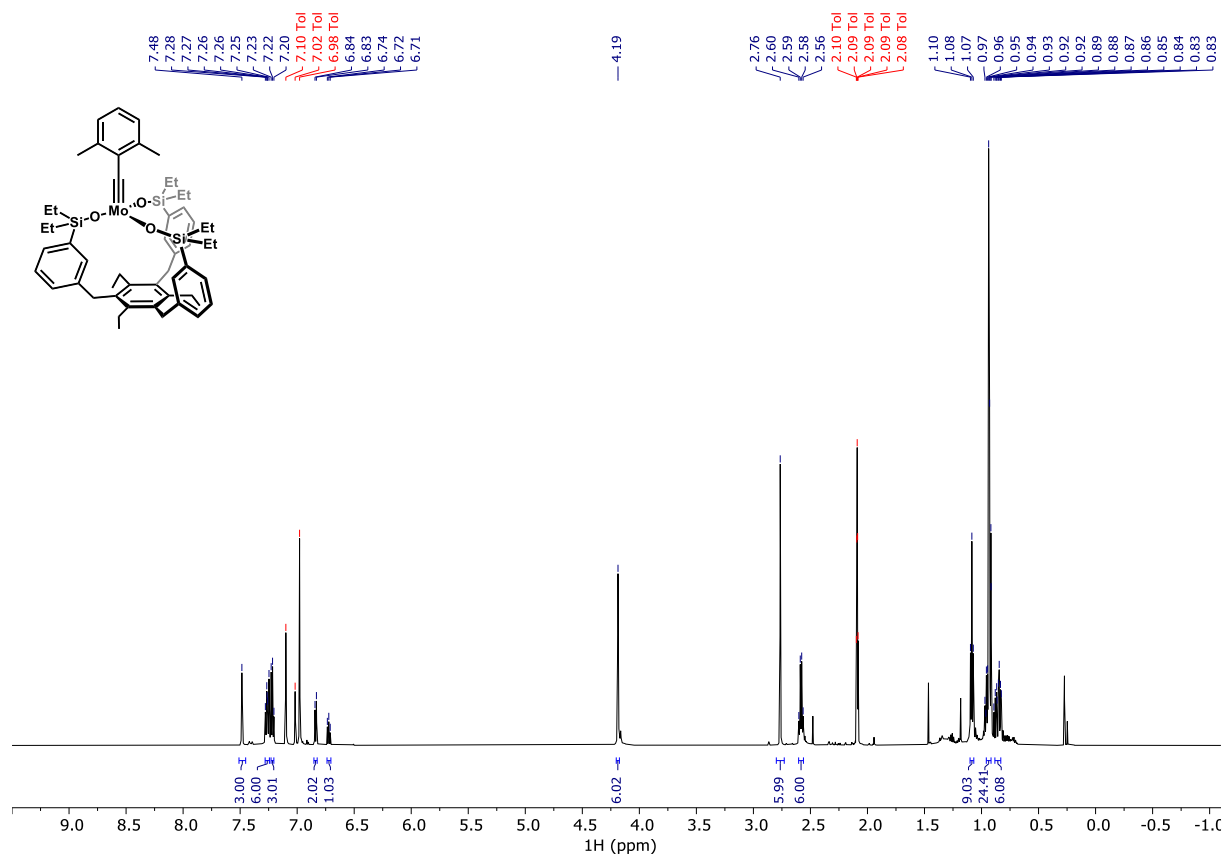
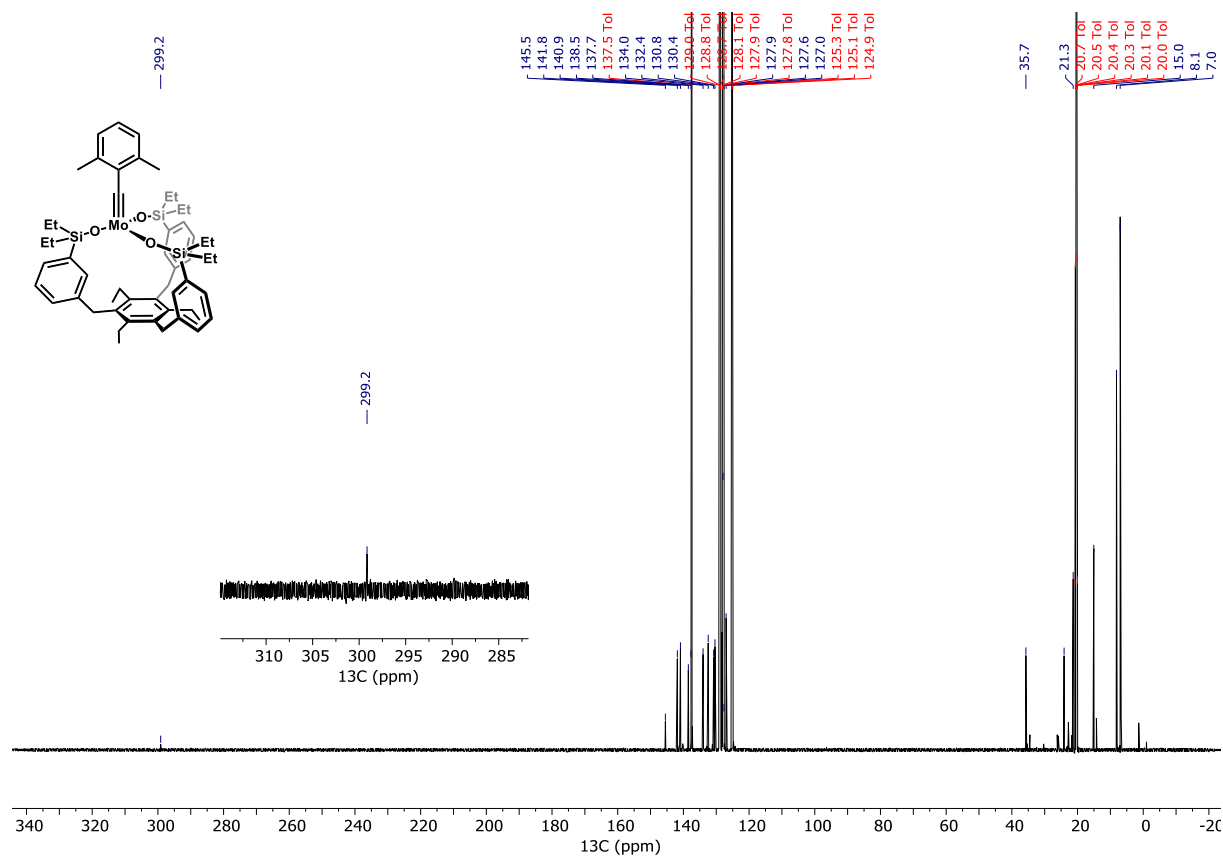


^{13}C NMR of **S1**, 151 MHz, CDCl_3 , 298 K

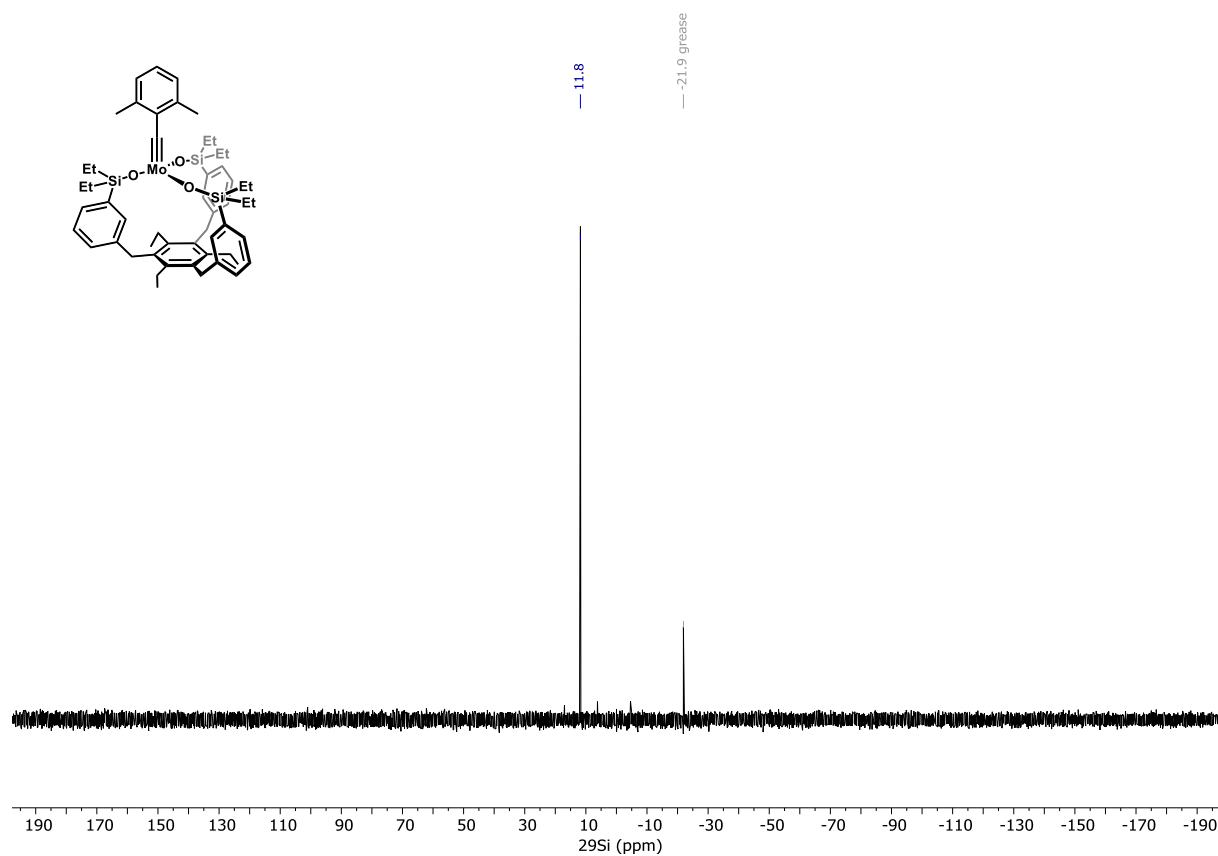


^{29}Si NMR of **S1, 119 MHz, CDCl_3 , 298 K** **^1H NMR of **115b**, 600 MHz, CDCl_3 , 298 K**

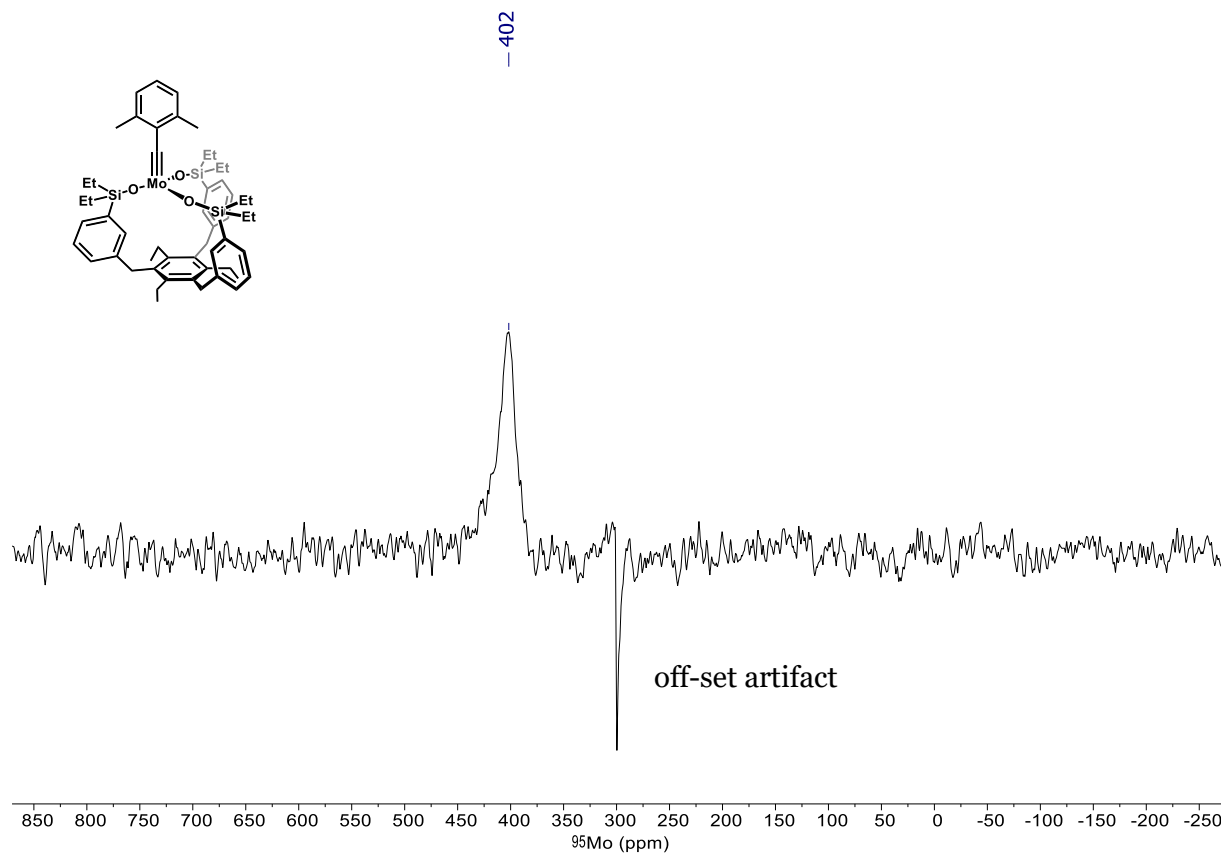
^{13}C NMR of **115b, 151 MHz, CDCl_3 , 298 K** **^{29}Si NMR of **115b**, 119 MHz, CDCl_3 , 298 K**

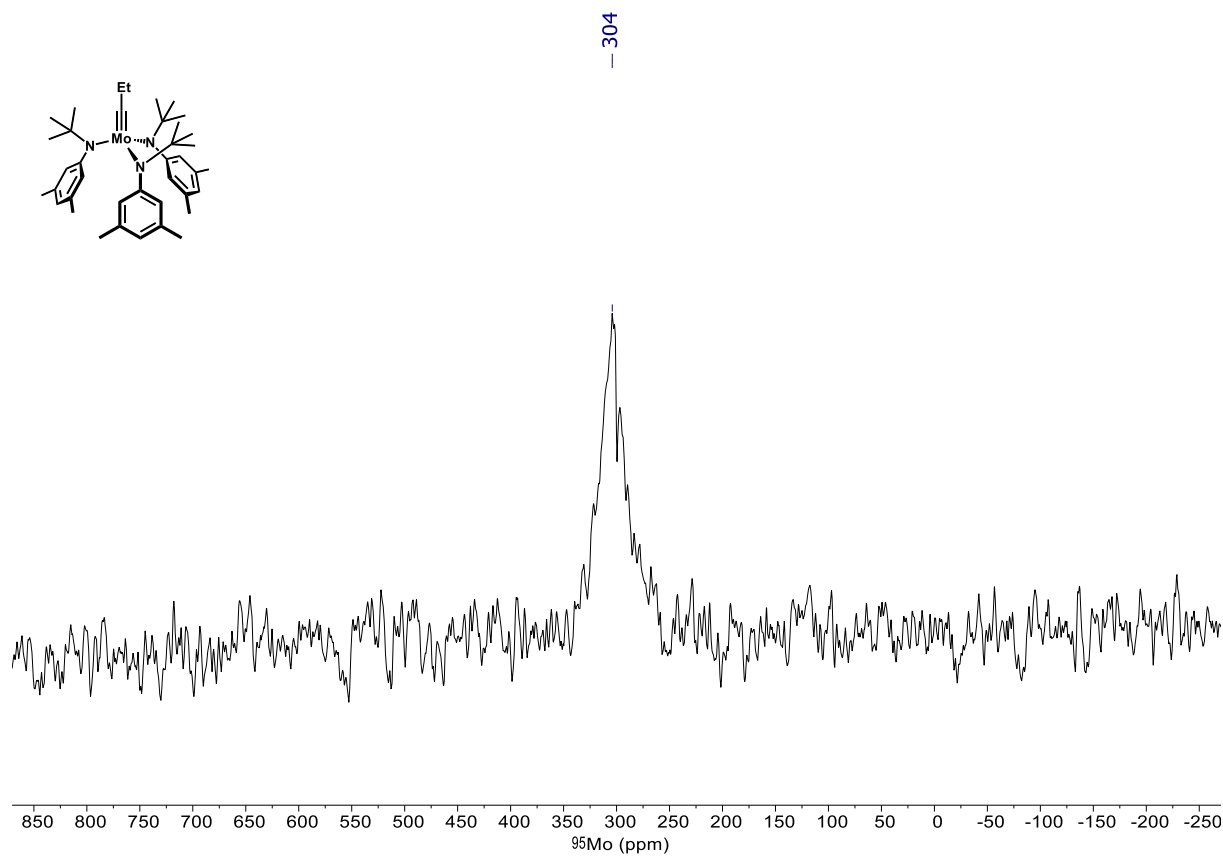
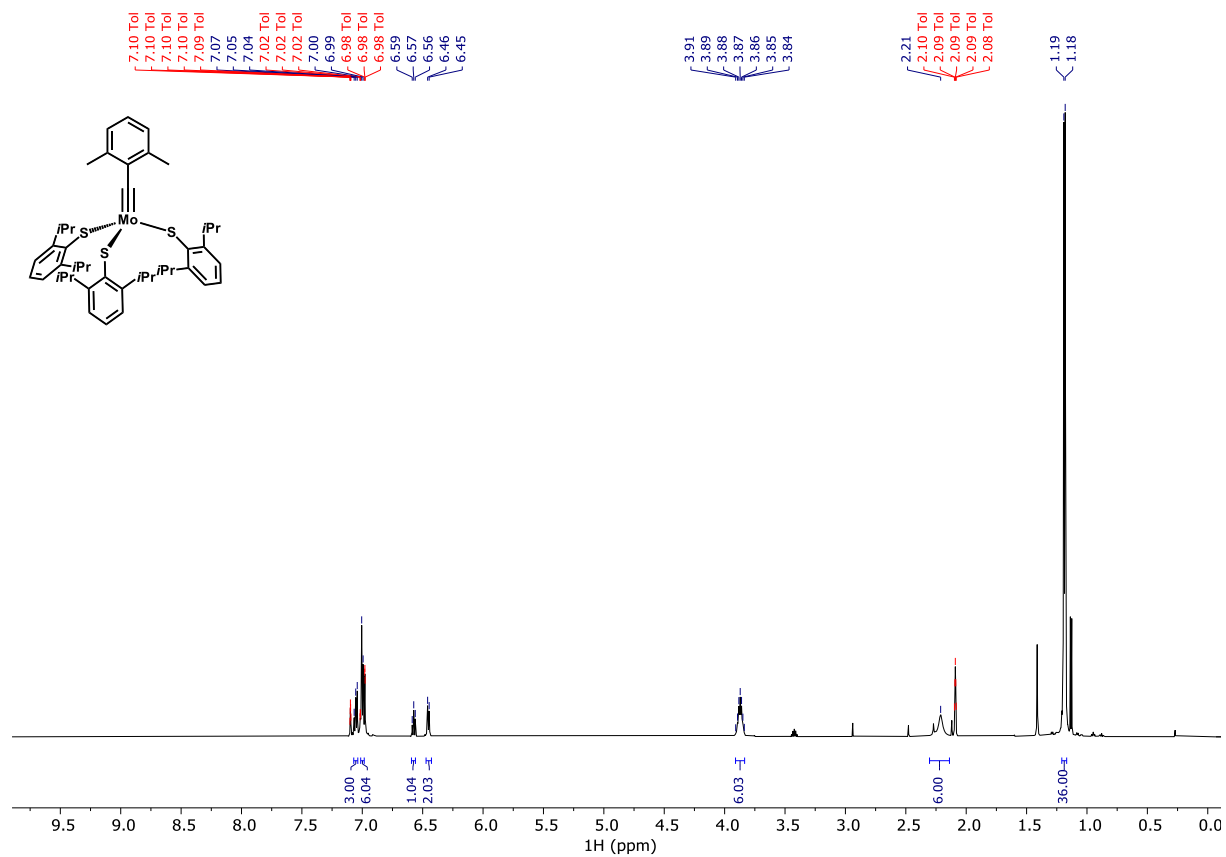
¹H NMR of 138, 600 MHz, [D₈]-toluene, 298 K**¹³C NMR of 138**, 151 MHz, [D₈]-toluene, 298 K

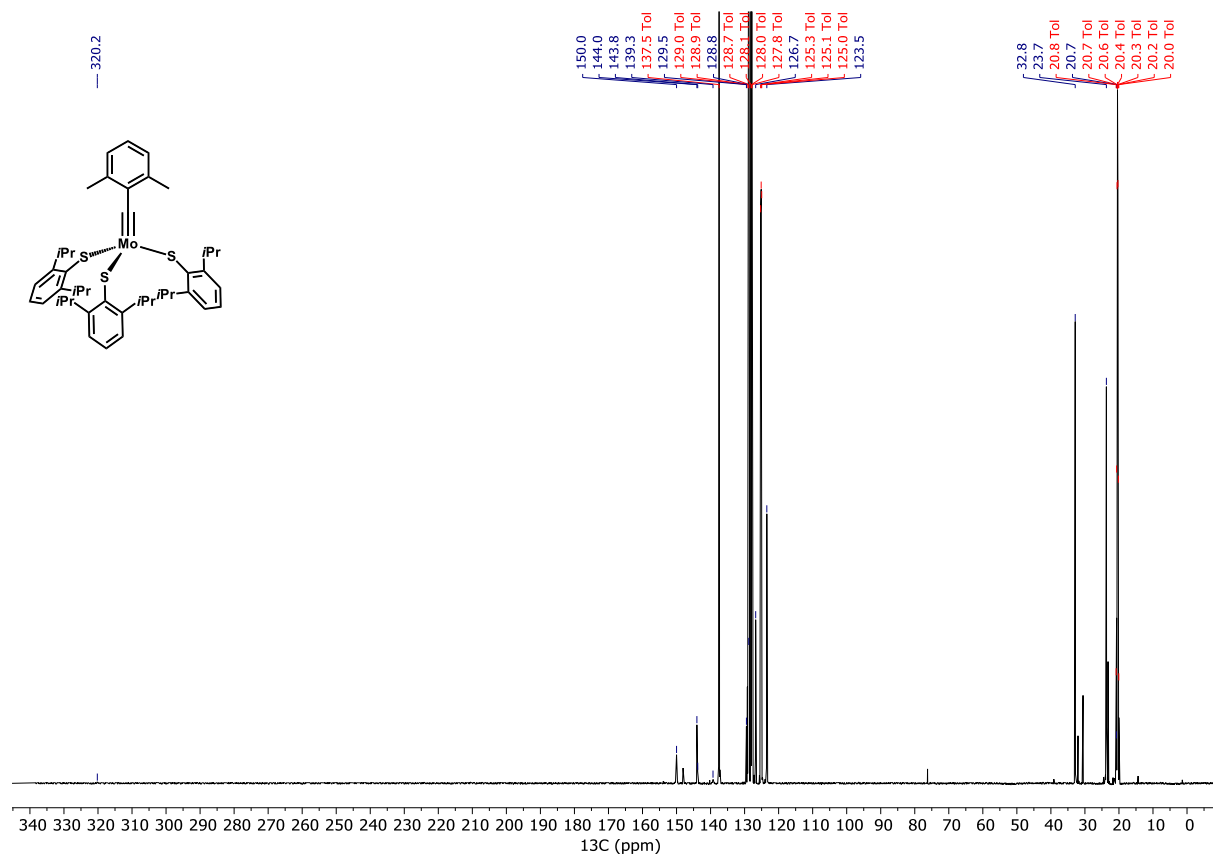
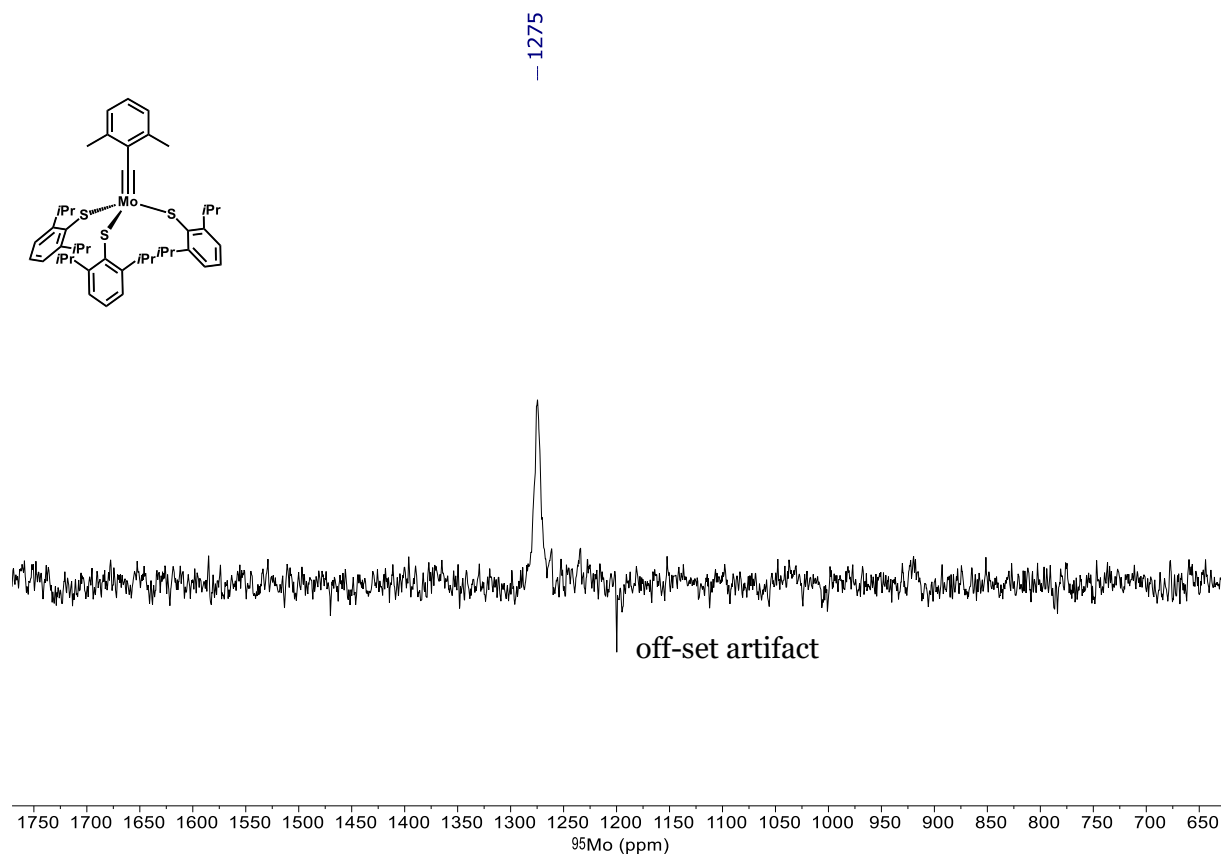
^{29}Si NMR of **138, 60 MHz, $[\text{D}_8]$ -toluene, 298 K**

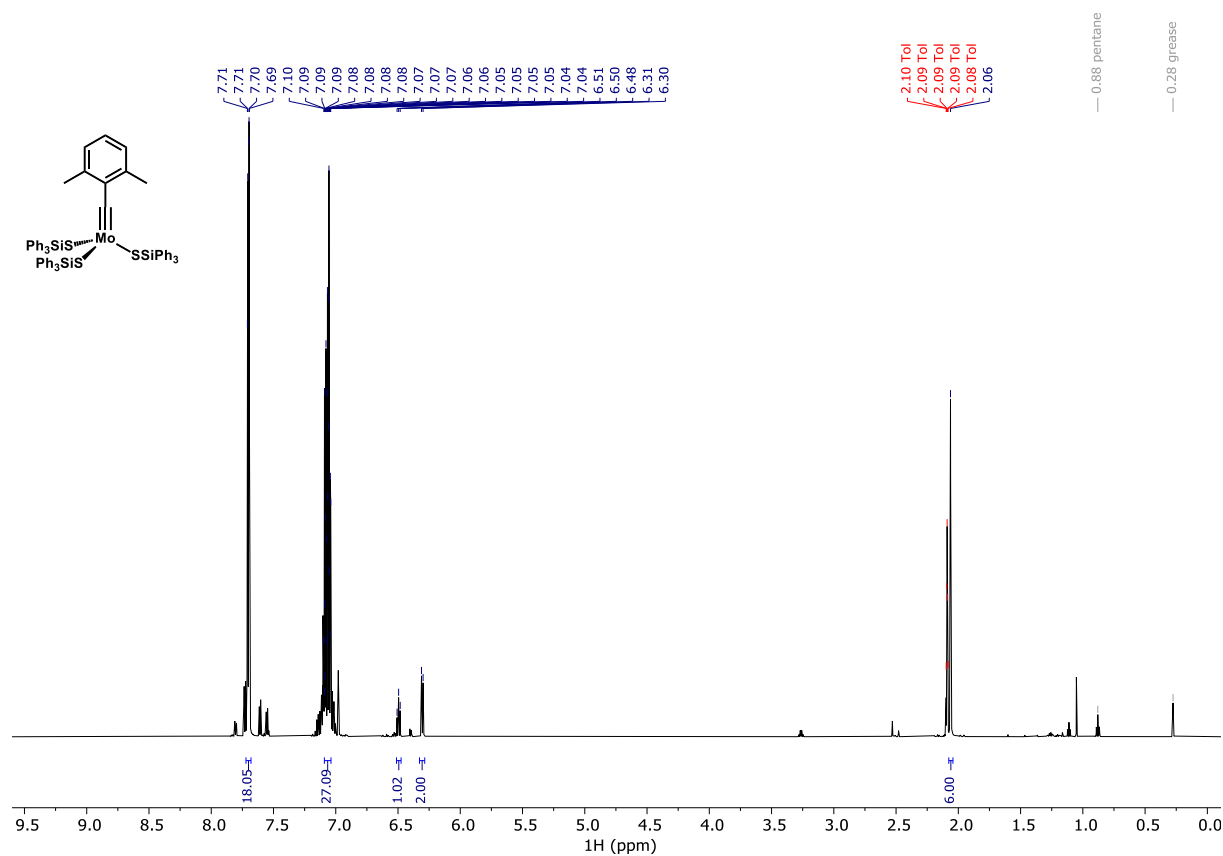
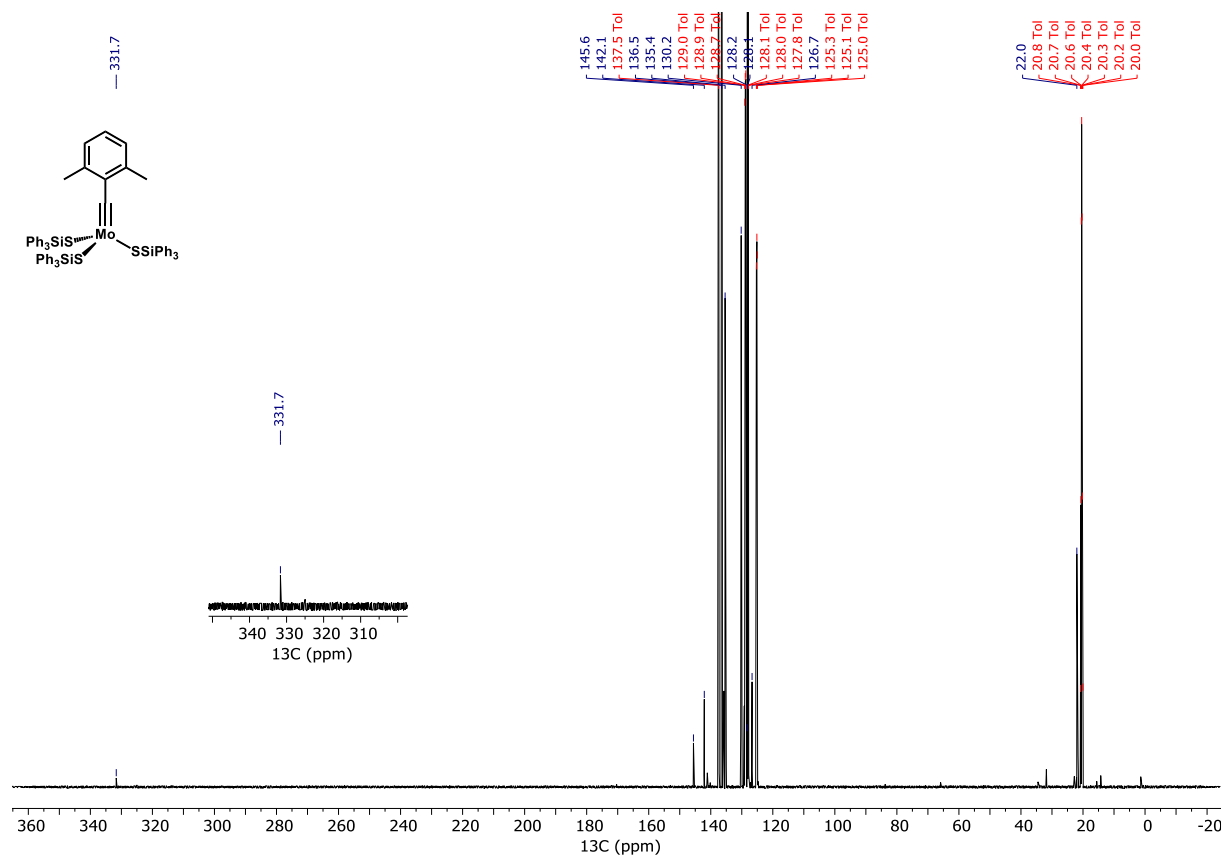


^{95}Mo NMR of **138, 26 MHz, $[\text{D}_8]$ -toluene, 298 K**

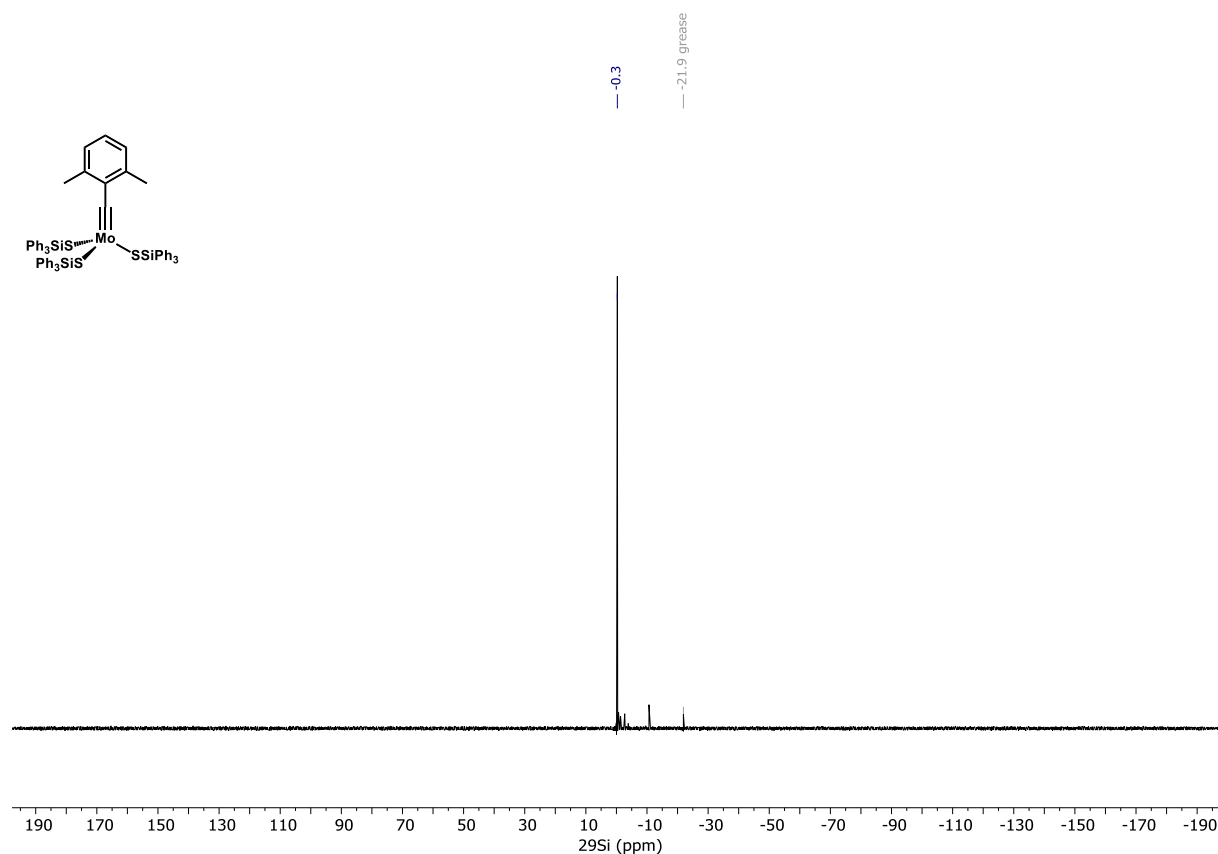


^{95}Mo NMR of **4ob, 26 MHz, $[\text{D}_8]$ -toluene, 333 K** **^1H NMR of **183**, 600 MHz, $[\text{D}_8]$ -toluene, 298 K**

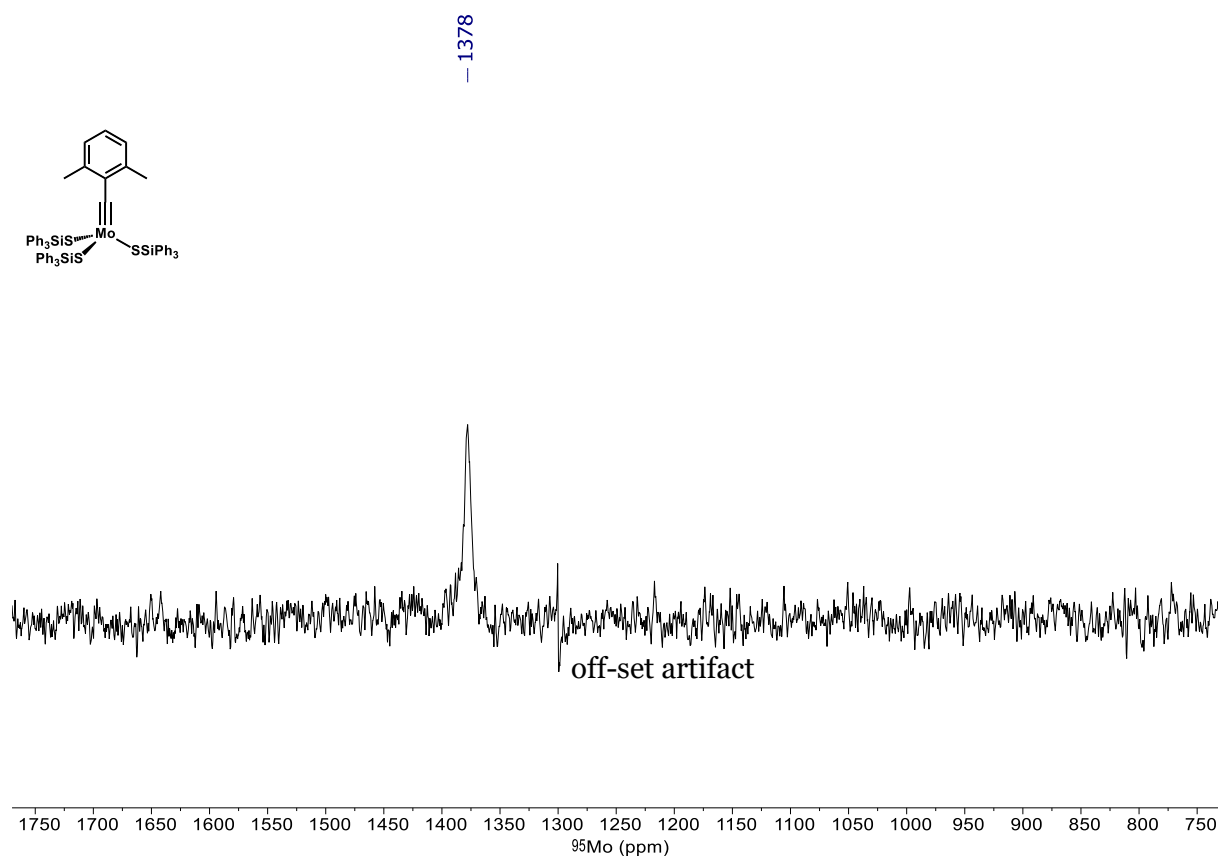
^{13}C NMR of **183**, 151 MHz, $[\text{D}_8]$ -toluene, 298 K **^{95}Mo NMR of **183****, 26 MHz, $[\text{D}_8]$ -toluene, 333 K

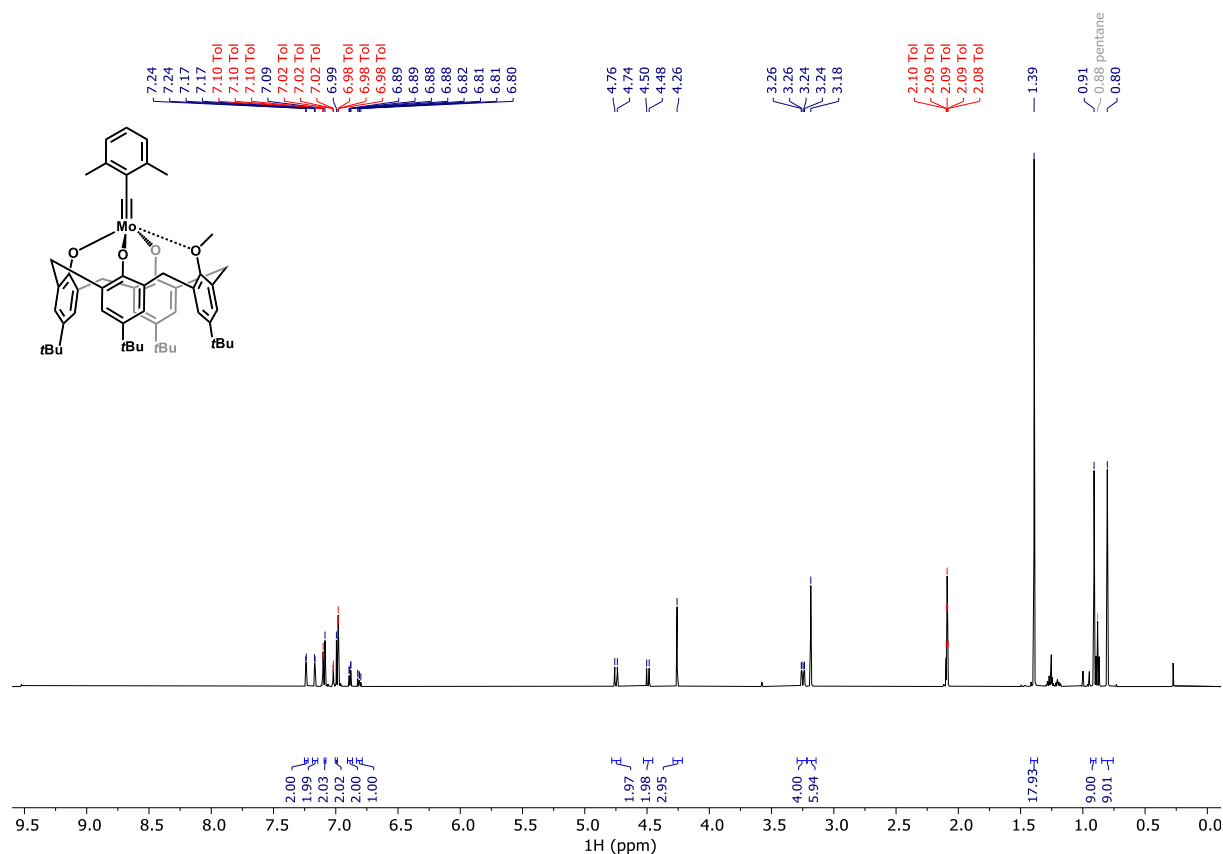
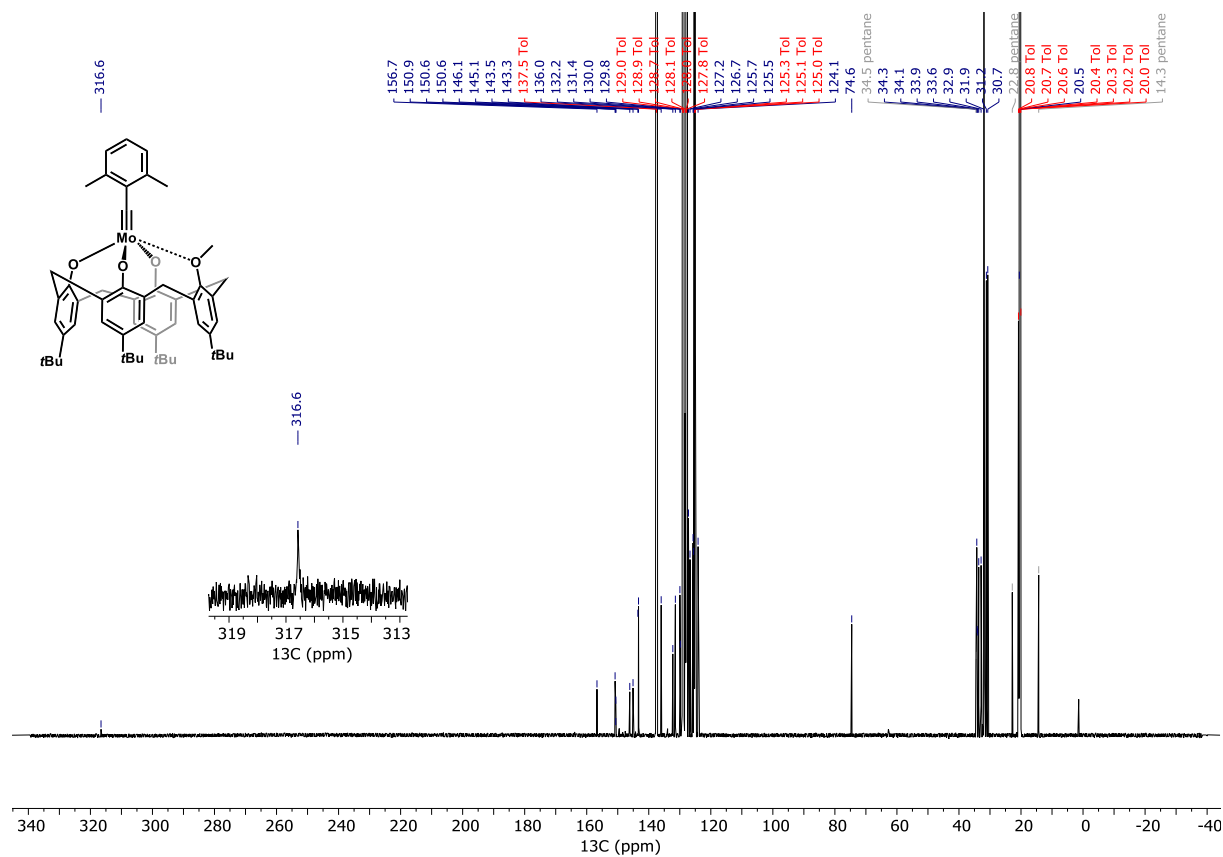
^1H NMR of **184, 600 MHz, $[\text{D}_8]$ -toluene, 298 K** **^{13}C NMR of **184**, 151 MHz, $[\text{D}_8]$ -toluene, 298 K**

^{29}Si NMR of **184, 60 MHz, $[\text{D}_8]$ -toluene, 298 K**



^{95}Mo NMR of **184, 26 MHz, $[\text{D}_8]$ -toluene, 333 K**



¹H NMR of 186, 600 MHz, [D₈]-toluene, 298 K**¹³C NMR of 186**, 151 MHz, [D₈]-toluene, 298 K

4.2 Crystallographic Data

Single Crystal Structure Analysis of **114**

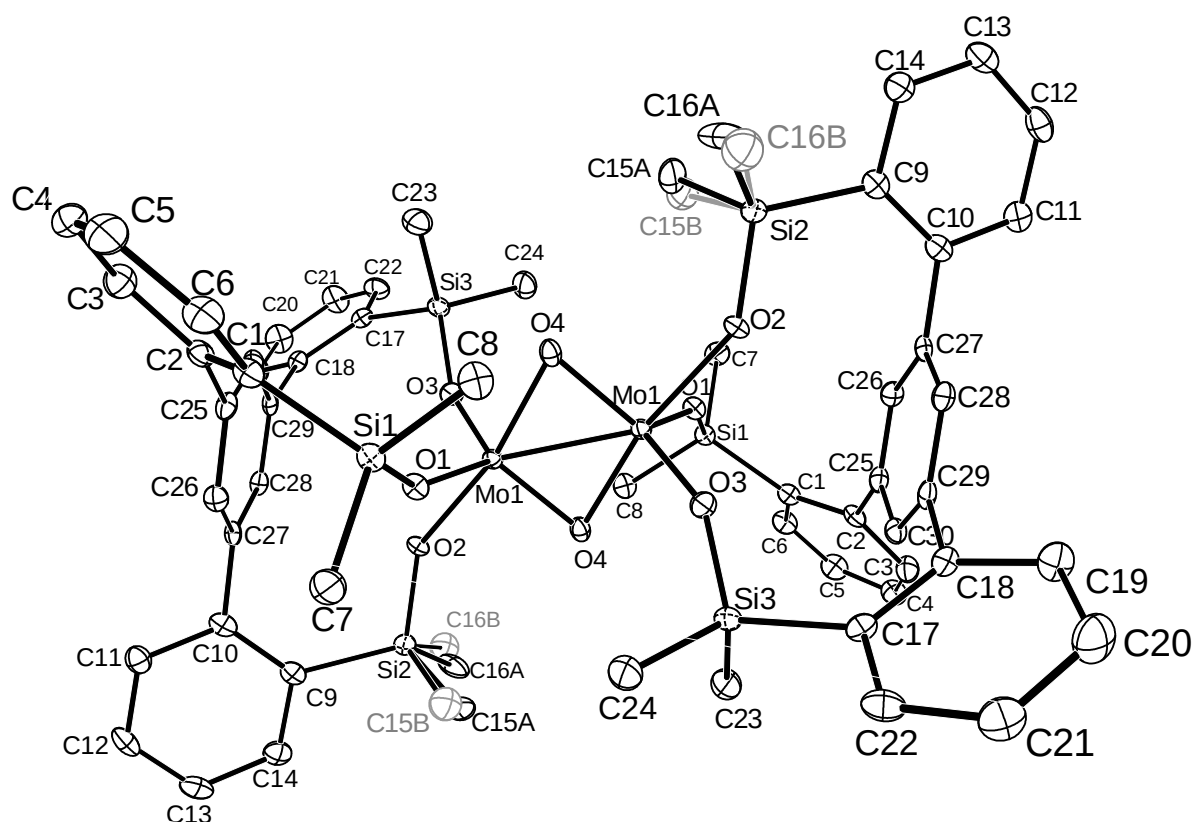


Figure S 10: The solid state structure of **114**. H atoms and additional solvent molecules have been removed for clarity. Main structure shown in black and disordered parts shown in grey.

Table S 5: Crystal data and structure refinement of **114**.

Identification code	14517	
Empirical formula	$C_{72}H_{78}Mo_2O_8Si_6$	
Color	yellow	
Formula weight	$1431.76 \text{ g} \cdot \text{mol}^{-1}$	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	P $\bar{1}$, (no. 2)	
Unit cell dimensions	$a = 10.5363(4) \text{ Å}$	$\alpha = 88.836(3)^\circ$.
	$b = 11.4371(5) \text{ Å}$	$\beta = 74.743(2)^\circ$.
	$c = 15.4420(7) \text{ Å}$	$\gamma = 79.496(2)^\circ$.
Volume	$1764.41(13) \text{ Å}^3$	

Z	1	
Density (calculated)	1.347 Mg · m ⁻³	
Absorption coefficient	0.510 mm ⁻¹	
F(000)	742 e	
Crystal size	0.089 x 0.085 x 0.02 mm ³	
θ range for data collection	1.367 to 28.770°.	
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20	
Reflections collected	38789	
Independent reflections	8946 [R _{int} = 0.0732]	
Reflections with I > 2 σ (I)	6495	
Completeness to θ = 25.242°	99.7 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.97	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8946 / 0 / 413	
Goodness-of-fit on F ²	1.010	
Final R indices [I > 2 σ (I)]	R ₁ = 0.0453	wR ² = 0.0769
R indices (all data)	R ₁ = 0.0806	wR ² = 0.0873
Largest diff. peak and hole	0.8 and -1.0 e · Å ⁻³	

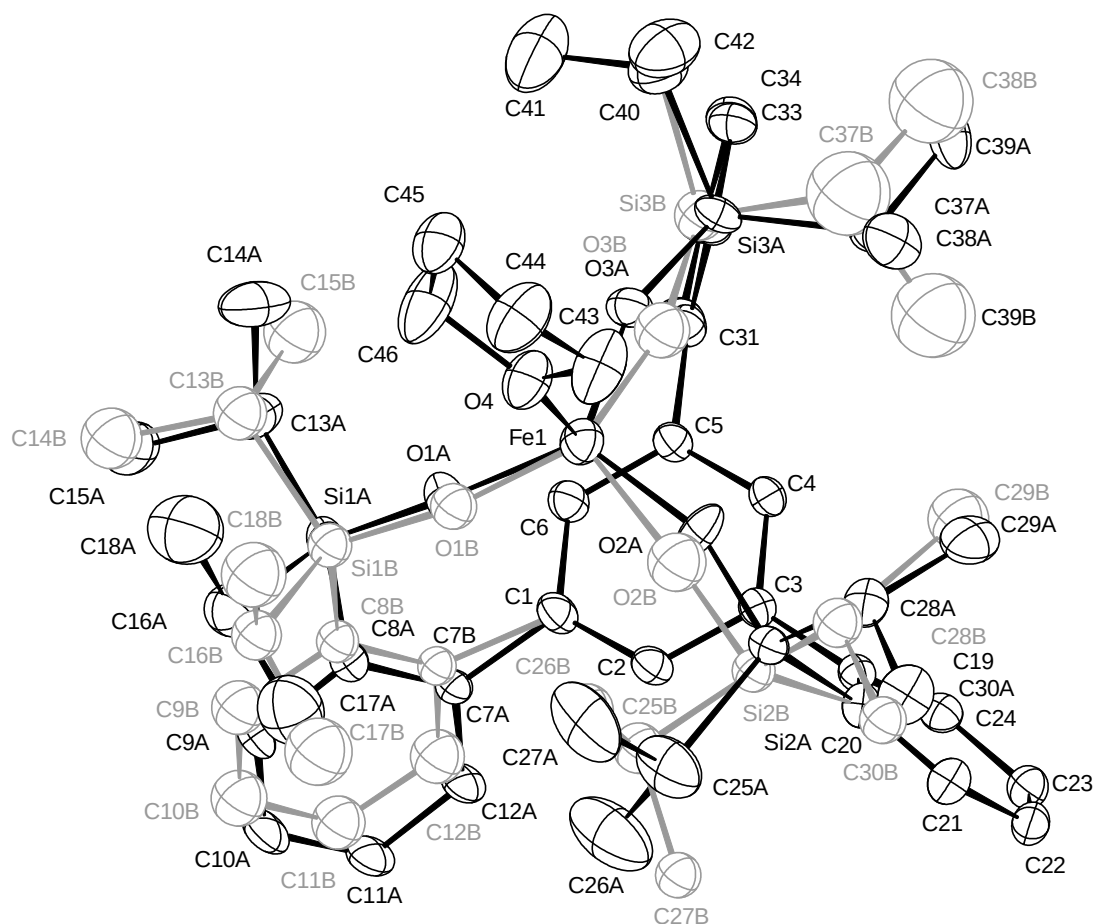
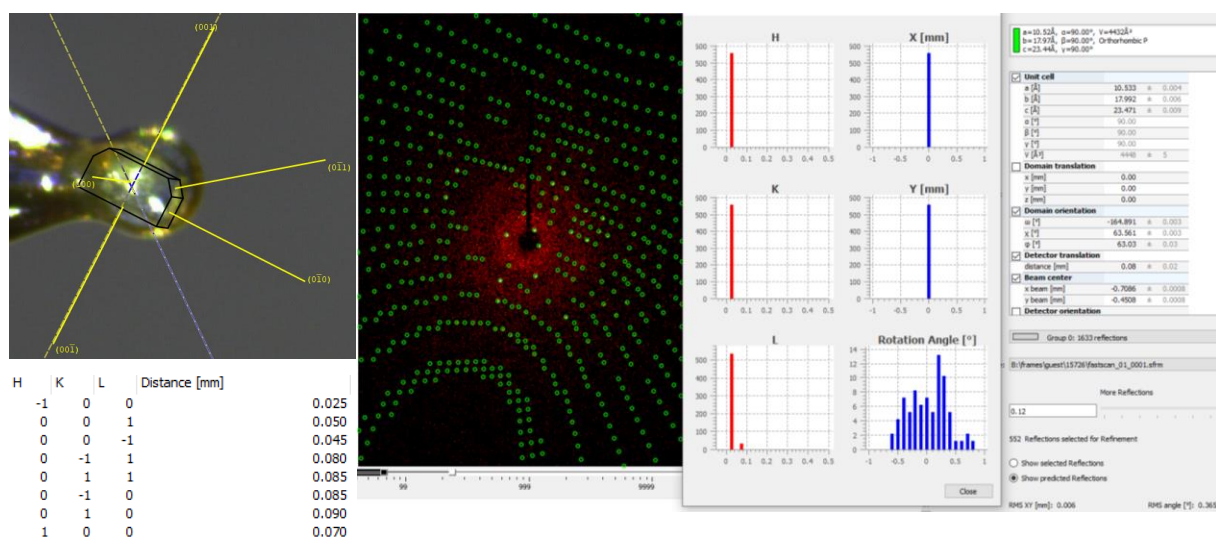
Single Crystal Structure Analysis of **Fe1•THF**

Figure S 11: The solid state structure of **Fe1•THF**. H atoms have been removed for clarity and disordered regions shown in grey.

$C_{46}H_{65}FeO_4Si_3$, $M_r = 822.10 \text{ g mol}^{-1}$, light yellow prism, crystal size $0.180 \times 0.140 \times 0.100 \text{ mm}^3$, orthorhombic, space group $P2_12_12_1$ [19], $a = 10.5157(5) \text{ \AA}$, $b = 17.9750(7) \text{ \AA}$, $c = 23.4408(10) \text{ \AA}$, $V = 4430.8(3) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $D_{calc} = 1.232 \text{ g}\cdot\text{cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.462 \text{ mm}^{-1}$, Gaussian correction ($T_{min} = 0.9071$, $T_{max} = 0.9447$), Bruker-AXS D8 Venture with Photon III detector and I μ S Diamond microfocus Mo-anode X-ray source, $2.123 < \theta < 30.563^\circ$, 900235 measured reflections, 13564 independent reflections, 12658 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0933$. The structure was solved by *SHELXS* and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0502$ [$I > 2\sigma(I)$], $wR_2 = 0.1493$ [all data], 605 parameters, 45 restraints and an absolute structure parameter Flack $x = 0.004(17)$.

Figure S 12: Crystal faces and unit cell determination/refinement of **Fe1•THF**.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 3.11	113	118	95.8	72.23	69.95	102.84	0.0521	0.0254
3.11 - 1.99	265	265	100.0	148.47	23.14	149.37	0.0479	0.0068
1.99 - 1.56	374	374	100.0	156.43	13.88	135.15	0.0543	0.0062
1.56 - 1.35	379	379	100.0	162.34	11.27	120.62	0.0621	0.0067
1.35 - 1.22	378	378	100.0	163.95	8.05	105.34	0.0782	0.0077
1.22 - 1.13	369	369	100.0	164.38	4.84	83.52	0.1038	0.0096
1.13 - 1.06	371	371	100.0	160.21	4.38	77.74	0.1105	0.0104
1.06 - 1.00	424	424	100.0	156.54	3.64	67.66	0.1264	0.0120
1.00 - 0.95	403	403	100.0	132.83	2.50	50.42	0.1569	0.0162
0.95 - 0.92	308	308	100.0	120.81	2.24	45.43	0.1684	0.0185
0.92 - 0.88	464	464	100.0	116.11	1.91	39.51	0.1852	0.0210
0.88 - 0.85	408	408	100.0	108.92	1.71	34.58	0.2017	0.0242
0.85 - 0.83	299	299	100.0	107.28	1.73	33.70	0.2084	0.0247
0.83 - 0.81	327	327	100.0	105.50	1.45	30.55	0.2356	0.0281
0.81 - 0.79	373	373	100.0	99.68	1.26	26.36	0.2544	0.0328
0.79 - 0.77	406	406	100.0	98.64	1.03	21.99	0.2977	0.0387
0.77 - 0.75	434	434	100.0	97.25	0.87	19.62	0.3399	0.0450
0.75 - 0.73	522	522	100.0	88.36	0.73	15.35	0.3848	0.0567
0.73 - 0.72	259	259	100.0	77.59	0.73	13.53	0.4083	0.0635
0.72 - 0.71	289	289	100.0	75.46	0.74	13.15	0.4119	0.0650
0.71 - 0.70	328	328	100.0	69.74	0.62	10.69	0.4435	0.0933
0.80 - 0.70	2430	2430	100.0	87.42	0.84	17.04	0.3481	0.0530
Inf - 0.70	7493	7498	99.9	120.34	5.07	54.52	0.0951	0.0154

Table S 6: Crystal data and structure refinement of **Fe1•THF**.

Identification code	15726	
Empirical formula	C ₄₆ H ₆₅ Fe O ₄ Si ₃	
Color	light yellow	
Formula weight	822.10 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁ , (no. 19)	
Unit cell dimensions	a = 10.5157(5) Å	α = 90°.
	b = 17.9750(7) Å	β = 90°.
	c = 23.4408(10) Å	γ = 90°.
Volume	4430.8(3) Å ³	
Z	4	
Density (calculated)	1.232 Mg·m ⁻³	
Absorption coefficient	0.462 mm ⁻¹	
F(000)	1764 e	
Crystal size	0.180 x 0.140 x 0.100 mm ³	
θ range for data collection	2.123 to 30.563°.	
Index ranges	-15 ≤ h ≤ 15, -25 ≤ k ≤ 25, -33 ≤ l ≤ 33	
Reflections collected	900235	
Independent reflections	13564 [R _{int} = 0.0933]	
Reflections with I > 2σ(I)	12658	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9447 and 0.9071	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13564 / 45 / 605	
Goodness-of-fit on F ²	1.088	
Final R indices [I > 2σ(I)]	R ₁ = 0.0502	wR ² = 0.1421
R indices (all data)	R ₁ = 0.0553	wR ² = 0.1493
Absolute structure parameter	0.004(17)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.674 and -0.833 e·Å ⁻³	

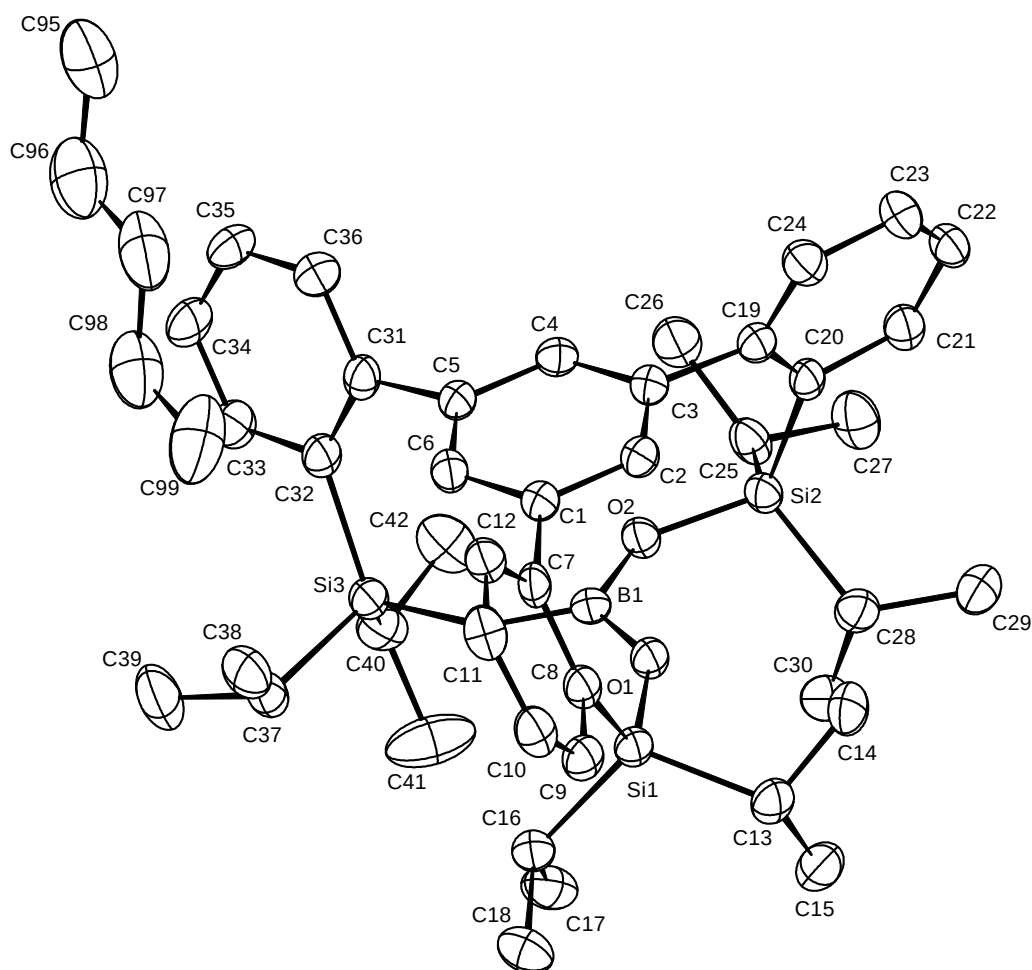
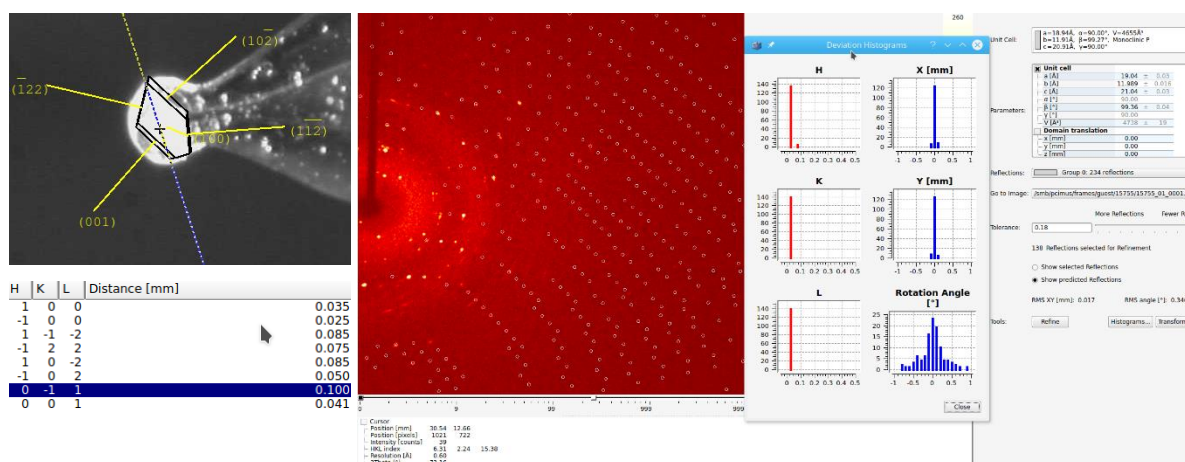
Single Crystal Structure Analysis of **B1**

Figure S 13: The solid state structure of **B1**. H atoms have been removed for clarity.

$C_{47}H_{69}BO_3Si_3$, $M_r = 777.10 \text{ g mol}^{-1}$, colourless prism, crystal size $0.281 \times 0.203 \times 0.07 \text{ mm}^3$, monoclinic, space group $P2_1/c$ [14], $a = 18.7887(14) \text{ \AA}$, $b = 11.8062(9) \text{ \AA}$, $c = 20.7180(15) \text{ \AA}$, $\beta = 99.165(4)^\circ$, $V = 4537.1(6) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $D_{\text{calc}} = 1.138 \text{ g}\cdot\text{cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.462 \text{ mm}^{-1}$, Gaussian correction ($T_{\text{min}} = 0.97267$, $T_{\text{max}} = 0.99221$), Bruker-AXS Kappa Mach3 with APEX-II detector and $I\mu S$ microfocus Mo-anode X-ray source, $1.098 < \theta < 28.282^\circ$, 111629 measured reflections, 11267 independent reflections, 6038 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.1603$. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0575$ [$I > 2\sigma(I)$], $wR_2 = 0.1535$ [all data], 501 parameters and 0 restraints.

Figure S 14: Crystal faces and unit cell determination/refinement of **B1**.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 3.18	178	178	100.0	13.04	79.82	27.22	0.0410	0.0275
3.18 - 2.09	420	420	100.0	14.47	31.42	23.66	0.0506	0.0288
2.09 - 1.64	600	600	100.0	14.85	16.18	19.35	0.0809	0.0354
1.64 - 1.43	575	575	100.0	15.02	12.13	17.59	0.0972	0.0398
1.43 - 1.29	621	621	100.0	14.97	10.95	14.93	0.1145	0.0446
1.29 - 1.20	573	573	100.0	14.62	8.69	13.08	0.1450	0.0540
1.20 - 1.12	659	659	100.0	14.37	6.89	10.88	0.1746	0.0655
1.12 - 1.07	519	519	100.0	12.26	4.60	7.76	0.2369	0.1013
1.07 - 1.02	643	643	100.0	10.24	3.72	5.77	0.2957	0.1392
1.02 - 0.98	577	577	100.0	9.24	3.63	5.16	0.3141	0.1560
0.98 - 0.94	699	699	100.0	8.40	2.74	4.06	0.3879	0.2136
0.94 - 0.91	598	598	100.0	7.74	2.50	3.40	0.4230	0.2544
0.91 - 0.89	453	453	100.0	7.04	2.54	3.31	0.4176	0.2638
0.89 - 0.86	764	764	100.0	6.88	1.81	2.35	0.5325	0.3826
0.86 - 0.84	577	577	100.0	6.68	1.69	2.06	0.5745	0.4300
0.84 - 0.82	612	612	100.0	6.55	1.33	1.61	0.6265	0.5559
0.82 - 0.80	689	689	100.0	6.35	1.23	1.49	0.6718	0.6307
0.80 - 0.79	350	350	100.0	6.23	1.24	1.41	0.7000	0.6583
0.79 - 0.77	807	807	100.0	6.14	1.06	1.19	0.7439	0.7788
0.77 - 0.76	455	455	100.0	5.93	0.85	0.93	0.8240	1.0309
0.76 - 0.75	446	446	100.0	5.84	0.65	0.74	0.9250	1.3439
0.85 - 0.75	3672	3672	100.0	6.24	1.13	1.33	0.7086	0.7115
Inf - 0.75	11815	11815	100.0	9.73	6.59	7.17	0.1397	0.1019

Table S 7: Crystal data and structure refinement of **B1**.

Identification code	15755	
Empirical formula	C ₄₇ H ₆₉ B O ₃ Si ₃	
Color	colourless	
Formula weight	777.10 g · mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c, (no. 14	
Unit cell dimensions	a = 18.7887(14) Å	α = 90°.
	b = 11.8062(9) Å	β = 99.165(4)°.
	c = 20.7180(15) Å	γ = 90°.
Volume	4537.1(6) Å ³	
Z	4	
Density (calculated)	1.138 Mg · m ⁻³	
Absorption coefficient	0.143 mm ⁻¹	
F(000)	1688 e	
Crystal size	0.281 x 0.203 x 0.07 mm ³	
θ range for data collection	1.098 to 28.282°.	
Index ranges	-25 ≤ h ≤ 25, -15 ≤ k ≤ 15, -27 ≤ l ≤ 27	
Reflections collected	111629	
Independent reflections	11267 [R _{int} = 0.1603]	
Reflections with I > 2σ(I)	6038	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.97	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11267 / 0 / 501	
Goodness-of-fit on F ²	1.009	
Final R indices [I > 2σ(I)]	R ₁ = 0.0575	wR ² = 0.1167
R indices (all data)	R ₁ = 0.1426	wR ² = 0.1535
Largest diff. peak and hole	0.4 and -0.4 e · Å ⁻³	

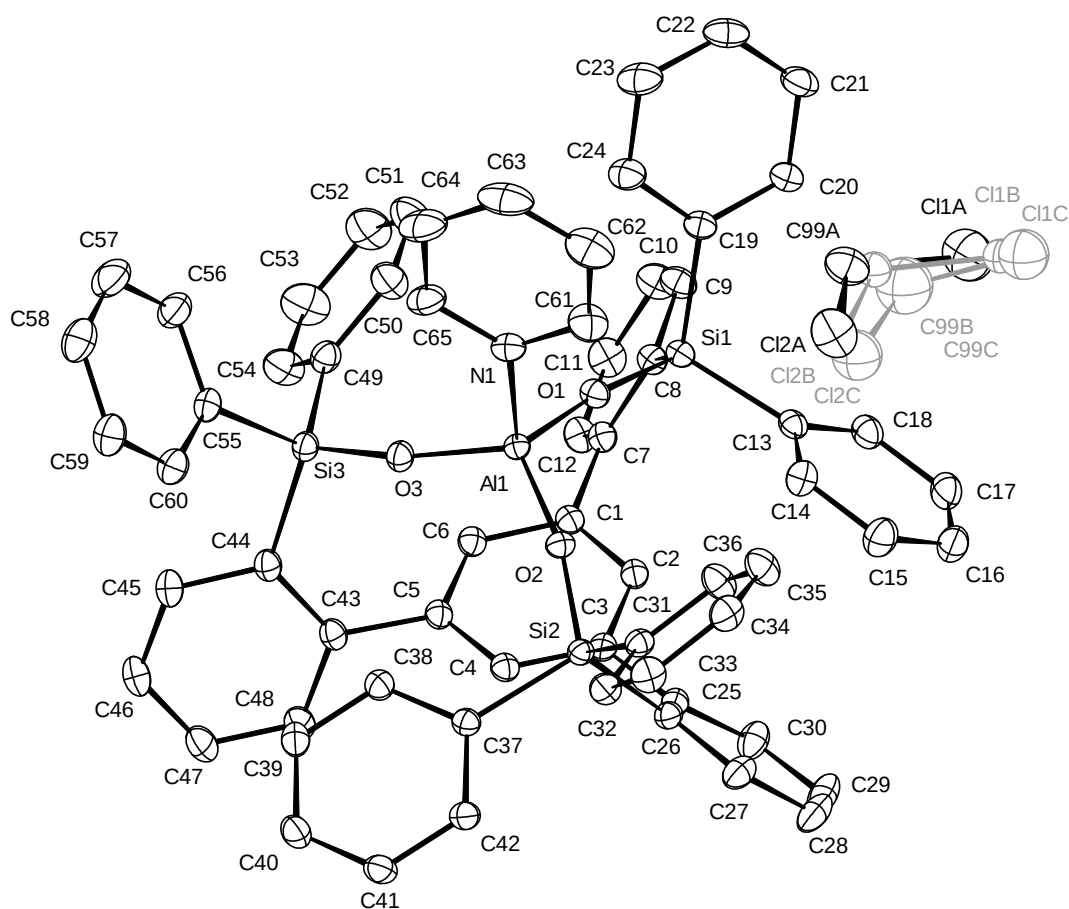
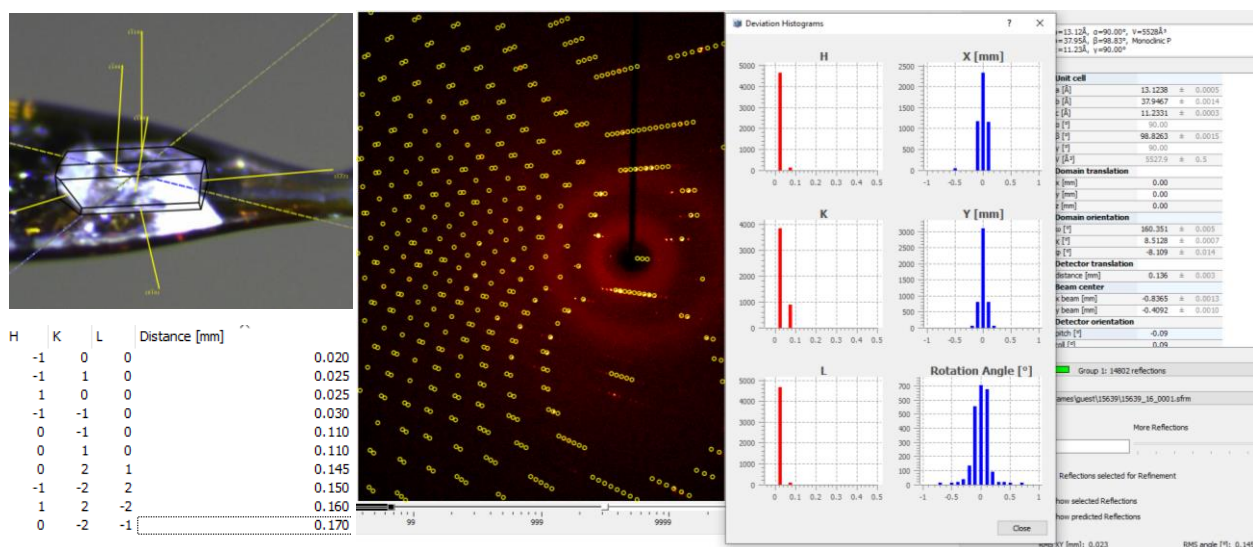
Single Crystal Structure Analysis of **Al1•Py**

Figure S 15: The solid state structure of **Al1•Py**. H atoms have been removed for clarity and disordered regions shown in grey.

$\text{C}_{66} \text{H}_{52} \text{Al} \text{Cl}_2 \text{N} \text{O}_3 \text{Si}_3$, $M_r = 1089.23 \text{ g mol}^{-1}$, colourless block, crystal size $0.368 \times 0.220 \times 0.050 \text{ mm}^3$, monoclinic, space group $P2_1/c$ [14], $a = 13.1238(5) \text{ \AA}$, $b = 37.9467(14) \text{ \AA}$, $c = 11.2331(3) \text{ \AA}$, $\beta = 98.826(2)^\circ$, $V = 5527.9(3) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $D_{\text{calc}} = 1.309 \text{ g}\cdot\text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.248 \text{ mm}^{-1}$, Gaussian correction ($T_{\text{min}} = 0.9105$, $T_{\text{max}} = 1.0000$), Bruker-AXS D8 Venture with Photon III detector and I μ S Diamond microfocus Mo-anode X-ray source, $1.902 < \theta < 31.538^\circ$, 371590 measured reflections, 18412 independent reflections, 16274 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.0483$. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0390$ [$I > 2\sigma(I)$], $wR_2 = 0.1074$ [all data], 711 parameters and 5 restraints.

Figure S 16: Crystal faces and unit cell determination/refinement of $Al_1 \bullet Py$

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.77	285	292	97.6	25.16	76.40	94.00	0.0391	0.0259
2.77 - 1.85	651	651	100.0	32.69	29.15	109.90	0.0295	0.0124
1.85 - 1.46	965	965	100.0	27.67	16.32	91.97	0.0276	0.0082
1.46 - 1.28	925	925	100.0	24.87	14.53	81.18	0.0305	0.0088
1.28 - 1.16	952	952	100.0	23.91	11.60	71.36	0.0360	0.0096
1.16 - 1.08	895	895	100.0	23.40	6.95	57.86	0.0436	0.0118
1.08 - 1.01	1017	1017	100.0	23.04	7.08	54.67	0.0441	0.0122
1.01 - 0.96	951	951	100.0	21.73	5.32	46.02	0.0529	0.0148
0.96 - 0.92	892	892	100.0	20.99	4.62	40.57	0.0560	0.0167
0.92 - 0.88	1052	1052	100.0	19.56	3.80	34.35	0.0655	0.0199
0.88 - 0.85	954	954	100.0	19.27	3.51	31.15	0.0699	0.0216
0.85 - 0.82	1080	1080	100.0	19.04	3.06	28.47	0.0781	0.0243
0.82 - 0.80	790	790	100.0	18.69	3.02	27.31	0.0807	0.0257
0.80 - 0.78	923	923	100.0	18.21	2.52	23.18	0.0959	0.0300
0.78 - 0.76	984	984	100.0	17.67	2.31	21.51	0.1056	0.0333
0.76 - 0.74	1113	1113	100.0	17.12	2.13	19.62	0.1179	0.0371
0.74 - 0.73	582	582	100.0	16.58	1.88	17.68	0.1352	0.0421
0.73 - 0.71	1296	1296	100.0	14.84	1.69	14.72	0.1549	0.0507
0.71 - 0.70	700	700	100.0	14.88	1.69	14.37	0.1580	0.0516
0.70 - 0.68	1685	1696	99.4	13.55	1.57	12.60	0.1780	0.0611
0.78 - 0.68	6360	6371	99.8	15.50	1.85	16.30	0.1389	0.0462
Inf - 0.68	18692	18710	99.9	20.03	6.99	40.70	0.0473	0.0181

Table S 8: Crystal data and structure refinement of **Al₁•Py**.

Identification code	15639	
Empirical formula	C ₆₆ H ₅₂ Al Cl ₂ N O ₃ Si ₃	
Color	colourless	
Formula weight	1089.23 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c, (no. 14)	
Unit cell dimensions	a = 13.1238(5) Å	α = 90°.
	b = 37.9467(14) Å	β = 98.826(2)°.
	c = 11.2331(3) Å	γ = 90°.
Volume	5527.9(3) Å ³	
Z	4	
Density (calculated)	1.309 Mg·m ⁻³	
Absorption coefficient	0.248 mm ⁻¹	
F(000)	2272 e	
Crystal size	0.368 x 0.220 x 0.050 mm ³	
θ range for data collection	1.902 to 31.538°.	
Index ranges	-19 ≤ h ≤ 19, -55 ≤ k ≤ 55, -16 ≤ l ≤ 16	
Reflections collected	371590	
Independent reflections	18412 [R _{int} = 0.0483]	
Reflections with I > 2σ(I)	16274	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Numerical	
Max. and min. transmission	1.0000 and 0.9105	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	18412 / 5 / 711	
Goodness-of-fit on F ²	1.072	
Final R indices [I > 2σ(I)]	R ₁ = 0.0390	wR ² = 0.1024
R indices (all data)	R ₁ = 0.0452	wR ² = 0.1074
Extinction coefficient	n/a	
Largest diff. peak and hole	0.583 and -0.450 e·Å ⁻³	

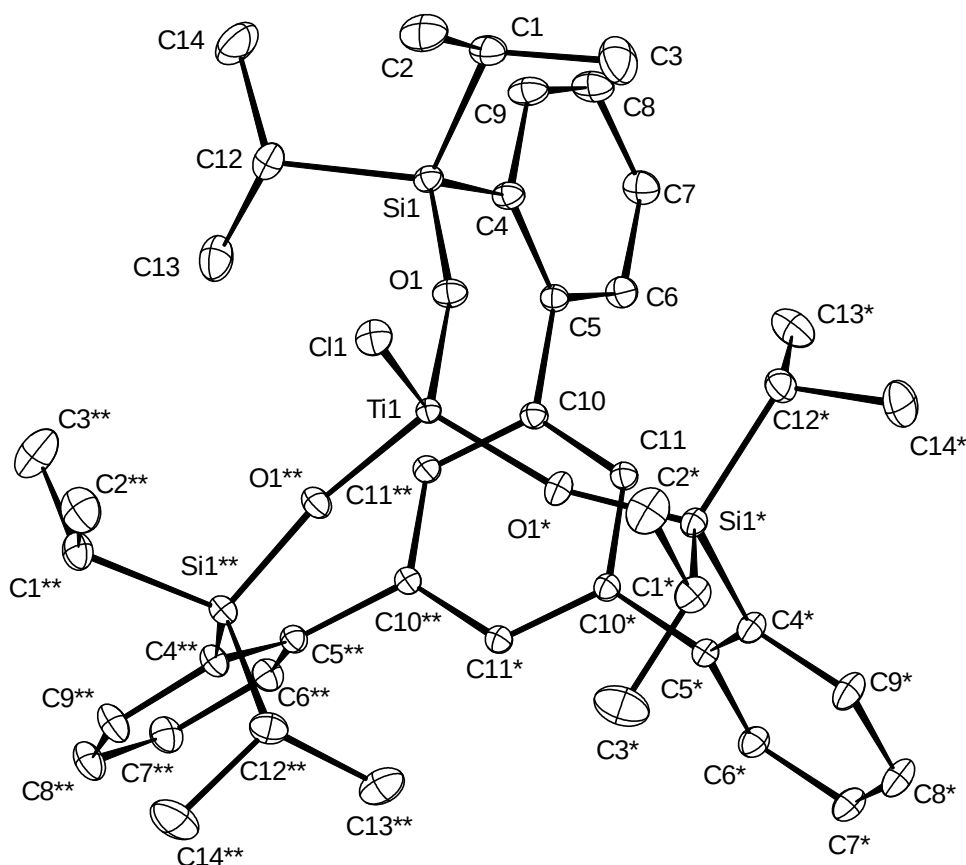
Single Crystal Structure Analysis of **Ti2**

Figure S 17: The solid state structure of **Ti2**. H atoms have been removed for clarity.

$\text{C}_{46}\text{H}_{66}\text{ClO}_3\text{Si}_3\text{Ti}$, $M_r = 831.608 \text{ g mol}^{-1}$, colourless prism, crystal size $0.254 \times 0.183 \times 0.10 \text{ mm}^3$, trigonal, space group $P\bar{3}$ [147], $a = 15.6513(12) \text{ \AA}$, $c = 10.6282(12) \text{ \AA}$, $V = 2254.7(4) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $D_{\text{calc}} = 1.225 \text{ g cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.366 \text{ mm}^{-1}$, Gaussian correction ($T_{\text{min}} = 0.95673$, $T_{\text{max}} = 0.96866$), Bruker-AXS Kappa Mach3 with APEX-II detector and I μ S microfocus Mo-anode X-ray source, $1.920 < \theta < 37.040^\circ$, 96811 measured reflections, 7623 independent reflections, 6568 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.0284$. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*). The final structure refinement was performed by *olex2.refine* 1.5 (L-M) together with NoSpherA2 (atomic form factors) against F^2 to $R_1 = 0.0140$ [$I > 2\sigma(I)$], $wR_2 = 0.0243$ [all data] with 322 parameters and 0 restraints.

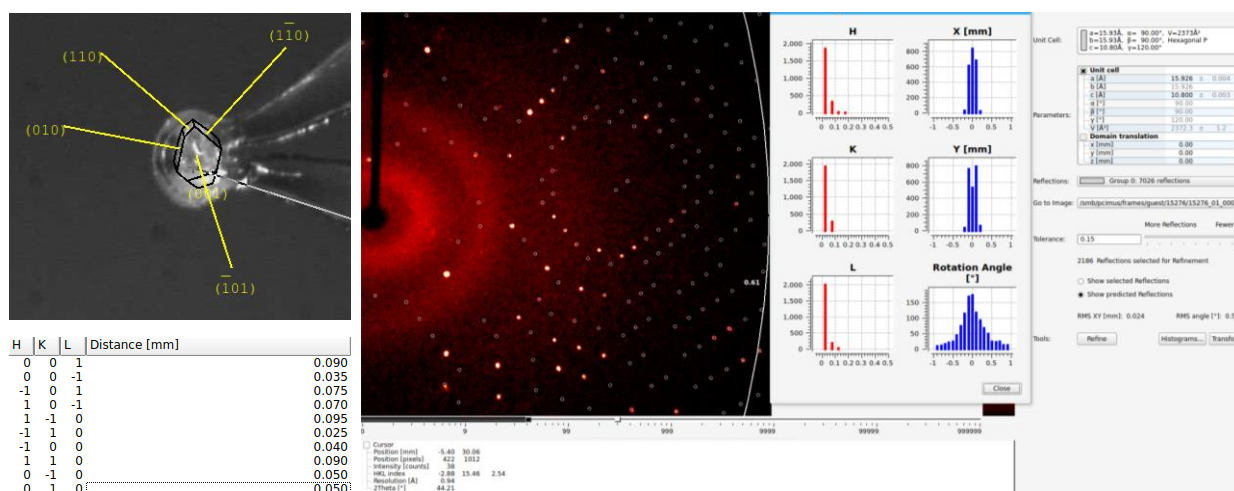


Figure S 18: Crystal faces and unit cell determination/refinement of **Ti₂**.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.41	116	116	100.0	26.99	95.08	182.01	0.0198	0.0050
2.41 - 1.61	266	266	100.0	28.17	39.87	147.47	0.0183	0.0051
1.61 - 1.27	392	392	100.0	27.82	28.77	133.42	0.0191	0.0055
1.27 - 1.11	376	376	100.0	26.52	18.22	103.53	0.0242	0.0065
1.11 - 1.01	388	388	100.0	19.47	14.99	79.13	0.0266	0.0085
1.01 - 0.94	367	367	100.0	15.27	11.40	63.64	0.0324	0.0113
0.94 - 0.88	422	422	100.0	12.83	9.72	50.12	0.0370	0.0135
0.88 - 0.84	344	344	100.0	11.83	8.37	43.30	0.0398	0.0157
0.84 - 0.80	409	409	100.0	11.18	8.00	38.97	0.0422	0.0170
0.80 - 0.77	384	384	100.0	10.68	7.13	35.92	0.0464	0.0191
0.77 - 0.74	434	434	100.0	10.15	5.95	30.78	0.0550	0.0227
0.74 - 0.72	334	334	100.0	9.77	5.81	29.34	0.0573	0.0241
0.72 - 0.70	363	363	100.0	9.36	4.79	24.52	0.0673	0.0285
0.70 - 0.68	418	418	100.0	8.99	4.41	22.49	0.0711	0.0314
0.68 - 0.66	458	458	100.0	8.74	4.04	20.73	0.0782	0.0345
0.66 - 0.65	261	261	100.0	8.35	3.93	18.55	0.0813	0.0365
0.65 - 0.63	555	555	100.0	8.09	3.53	17.69	0.0877	0.0411
0.63 - 0.62	339	339	100.0	7.79	3.03	15.48	0.1046	0.0480
0.62 - 0.61	321	321	100.0	7.39	2.76	13.50	0.1142	0.0537
0.61 - 0.60	347	347	100.0	7.08	2.73	12.98	0.1202	0.0581
0.60 - 0.59	332	391	84.9	2.62	1.96	6.11	0.1417	0.1441
0.69 - 0.59	2813	2872	97.9	7.29	3.30	15.96	0.0913	0.0492
Inf - 0.59	7626	7685	99.2	12.60	10.39	46.31	0.0281	0.0147

The final structure refinement was carried out with using aspherical scattering factors with NoSpherA2.^[323] DFT-calculated with ORCA using a B3LYP functional and def2-TZVPP basis set, whereby the H atom positions were refined using anisotropic atomic displacement parameters.

NoSpherA2 implementation of HAR makes use of tailor-made aspherical atomic form factors calculated on-the-fly from a Hirshfeld-partitioned electron density (ED) - not from spherical-atom form factors. The ED is calculated from a gaussian basis set single determinant SCF wave function - either Hartree-Fock or DFT using selected functional - for a fragment of the crystal. This fragment can be embedded in an electrostatic crystal field by employing cluster charges or modelled using implicit solvation models, depending on the software used. The following options were used:

SOFTWARE:	ORCA 5.0
PARTITIONING:	NoSpherA2
INT ACCURACY:	Normal
METHOD:	B3LYP
BASIS SET:	def2-TZVPP
CHARGE:	0
MULTIPLICITY:	1
DATE:	2024-09-25_11-32-48

Table S 9: Crystal data and structure refinement of **Ti2**.

Identification code	15276	
Empirical formula	C _{45.75} H ₆₆ Cl O ₃ Si ₃ Ti [+ solvent]	
Color	colourless	
Formula weight	831.608 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	P-3, (no. 147)	
Unit cell dimensions	a = 15.6513(12) Å	α = 90°.
	b = 15.6513(12) Å	β = 90°.
	c = 10.6282(12) Å	γ = 120°.
Volume	2254.7(4) Å ³	
Z	2	
Density (calculated)	1.225 Mg·m ⁻³	
Absorption coefficient	0.366 mm ⁻¹	
F(000)	892.767 e	
Crystal size	0.254 x 0.183 x 0.10 mm ³	
θ range for data collection	1.92 to 37.04°.	
Index ranges	-26 ≤ h ≤ 26, -25 ≤ k ≤ 26, -17 ≤ l ≤ 17	
Reflections collected	96811	
Independent reflections	7623 [R _{int} = 0.0284]	
Reflections with I > 2σ(I)	6568	
Completeness to θ = 25.2417°	99.89 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.96866 and 0.95673	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7623 / 0 / 322	
Goodness-of-fit on F ²	1.0560	
Final R indices [I > 2σ(I)]	R ₁ = 0.0140	wR ² = 0.0226
R indices (all data)	R ₁ = 0.0211	wR ² = 0.0243
Largest diff. peak and hole	0.2198 and -0.2290 e·Å ⁻³	

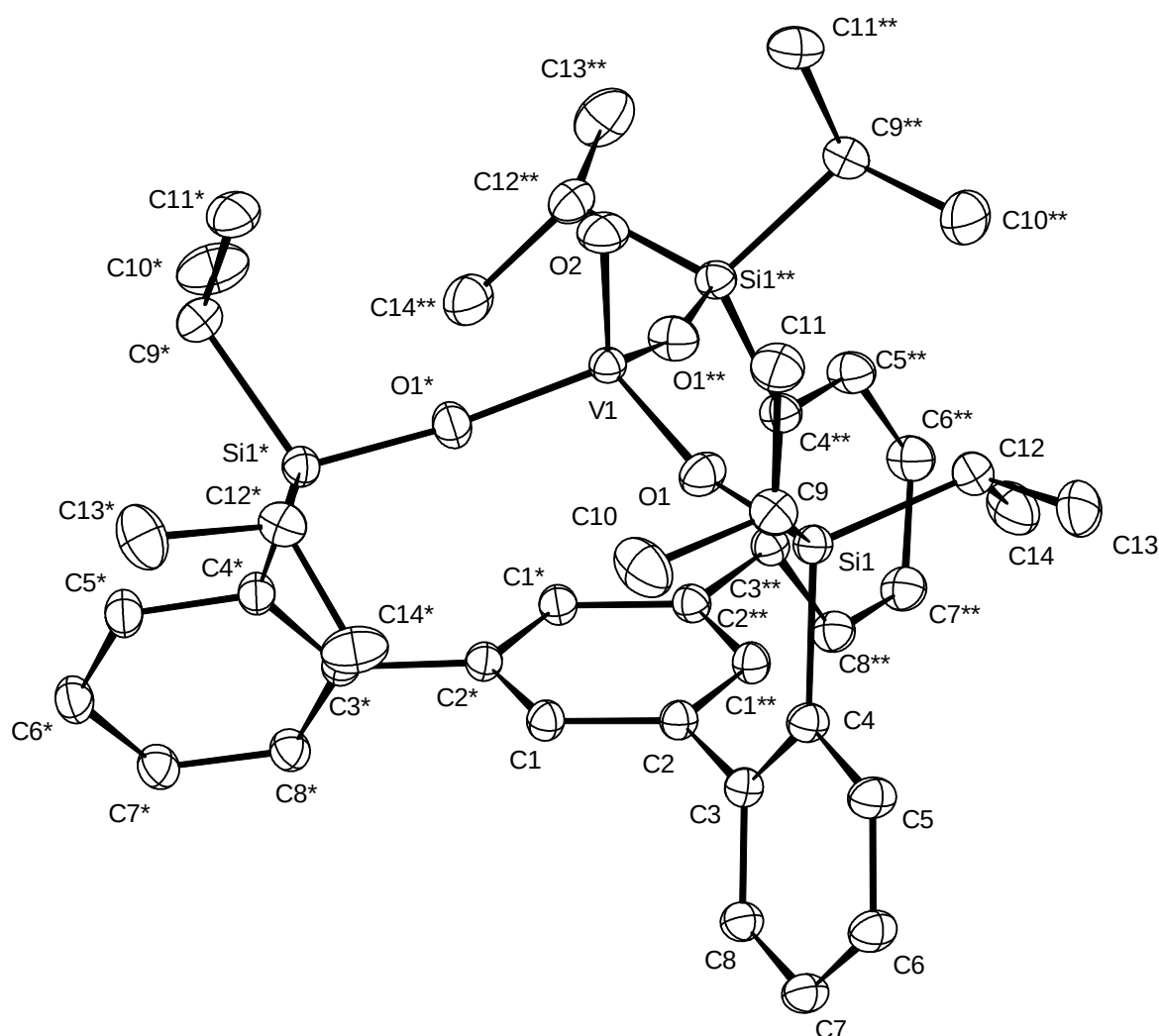
Single Crystal Structure Analysis of **V2**

Figure S 19: The solid state structure of **V2**. H atoms have been removed for clarity.

$\text{C}_{46} \text{H}_{65} \text{O}_5 \text{Si}_3 \text{V}$, $M_r = 833.224 \text{ g mol}^{-1}$, translucent colourless prism, crystal size $0.091 \times 0.084 \times 0.063 \text{ mm}^3$, trigonal, space group $P\bar{3}$ [147], $a = 15.6513(12) \text{ \AA}$, $c = 10.7026(4) \text{ \AA}$, $V = 2264.76(10) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $D_{\text{calc}} = 1.222 \text{ g cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.341 \text{ mm}^{-1}$, Gaussian correction ($T_{\text{min}} = 0.9587$, $T_{\text{max}} = 0.9929$), Bruker-AXS D8 Venture with Photon III detector and I μ S Diamond microfocus Mo-anode X-ray source, $2.610 < \theta < 33.14^\circ$, 104925 measured reflections, 5712 independent reflections, 4651 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.0484$. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*). The final structure refinement was performed by *olex2.refine 1.5* (L-M) together with NoSpherA2 (atomic form factors) against F^2 to $R_1 = 0.0249$ [$I > 2\sigma(I)$], $wR_2 = 0.0659$ [all data] with 322 parameters and 0 restraints.

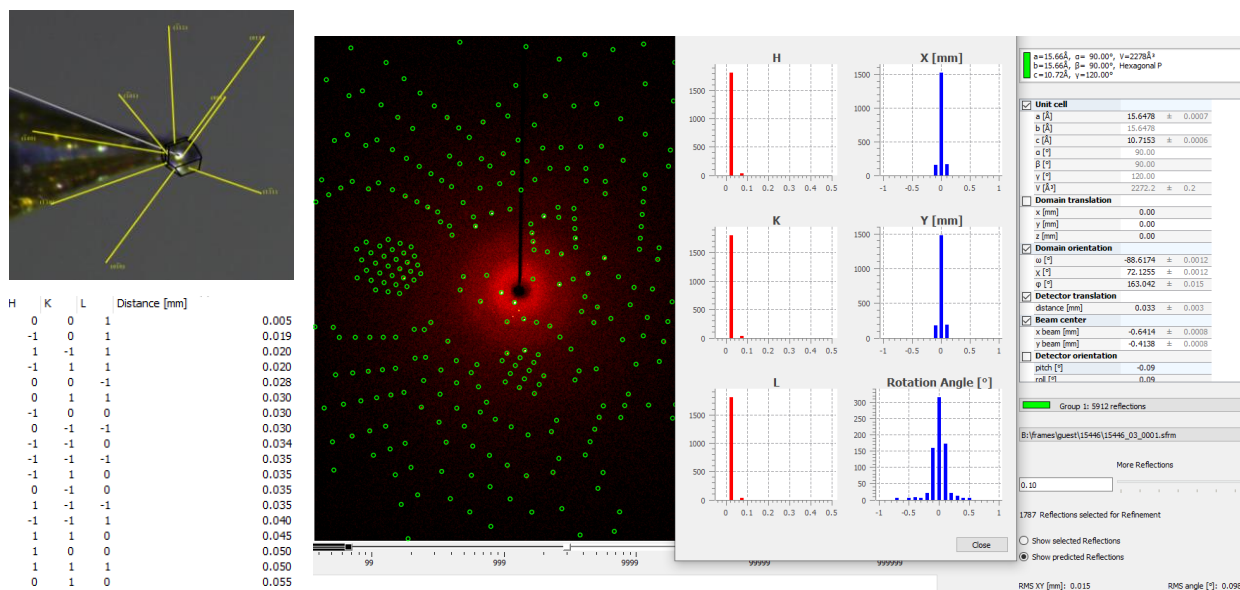


Figure S 20: Crystal faces and unit cell determination/refinement of V2.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.62	88	89	98.9	25.47	92.37	125.95	0.0212	0.0114
2.62 - 1.77	198	198	100.0	28.65	32.83	105.27	0.0266	0.0065
1.77 - 1.40	300	300	100.0	28.57	25.07	94.02	0.0291	0.0072
1.40 - 1.22	286	286	100.0	28.44	19.94	82.43	0.0330	0.0083
1.22 - 1.11	289	289	100.0	27.88	12.54	63.29	0.0438	0.0105
1.11 - 1.03	298	298	100.0	27.62	10.44	56.95	0.0532	0.0122
1.03 - 0.97	272	272	100.0	26.92	7.16	43.02	0.0667	0.0157
0.97 - 0.92	305	305	100.0	27.03	6.98	42.83	0.0701	0.0165
0.92 - 0.88	300	300	100.0	24.39	5.61	34.19	0.0832	0.0205
0.88 - 0.85	267	267	100.0	21.50	4.72	28.29	0.0917	0.0247
0.85 - 0.81	380	380	100.0	19.88	5.34	29.56	0.0869	0.0246
0.81 - 0.79	239	239	100.0	18.42	3.88	21.84	0.1099	0.0326
0.79 - 0.77	255	255	100.0	17.40	4.14	22.79	0.1107	0.0333
0.77 - 0.75	278	278	100.0	17.01	3.26	18.92	0.1267	0.0409
0.75 - 0.73	320	320	100.0	15.90	2.61	14.59	0.1532	0.0509
0.73 - 0.71	357	357	100.0	10.76	2.92	13.13	0.1496	0.0607
0.71 - 0.70	182	182	100.0	7.26	2.14	8.18	0.1687	0.0939
0.70 - 0.68	412	412	100.0	4.99	2.16	6.48	0.1658	0.1224
0.68 - 0.67	240	241	99.6	3.63	1.94	5.12	0.1708	0.1665
0.67 - 0.66	225	231	97.4	2.55	1.81	3.81	0.1843	0.2319
0.66 - 0.65	237	269	88.1	1.75	1.68	2.84	0.2110	0.2980
0.75 - 0.65	1973	2012	98.1	7.08	2.25	8.25	0.1578	0.1224
Inf - 0.65	5728	5768	99.3	18.19	8.90	35.85	0.0475	0.0223

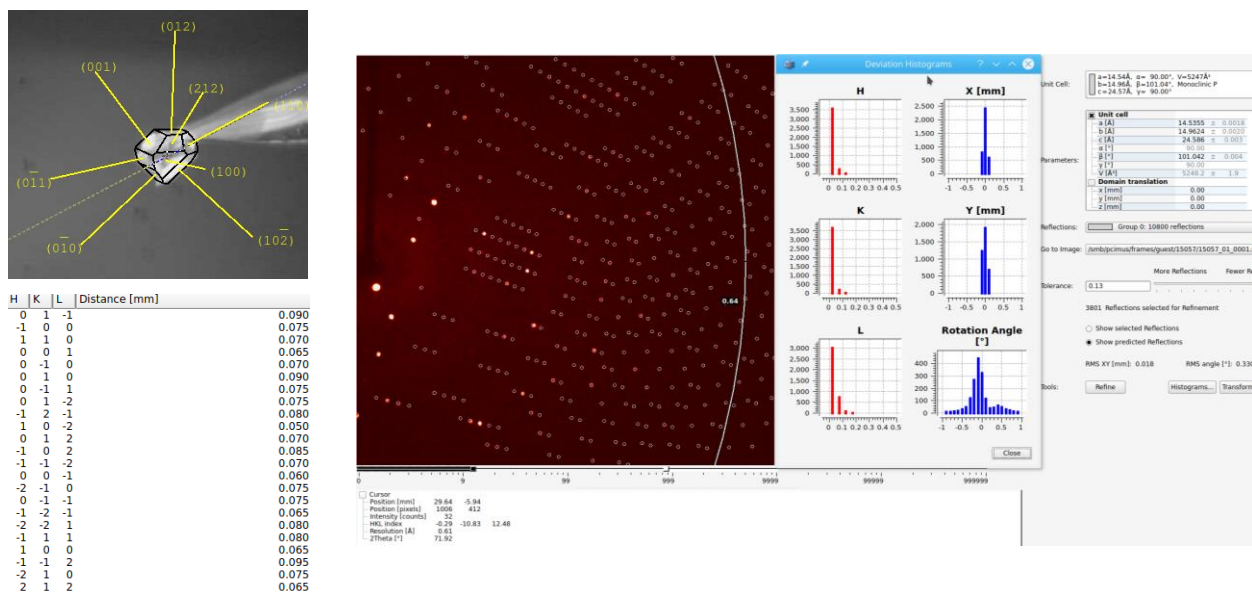
The final structure refinement was carried out with using aspherical scattering factors with NoSpherA2.^[323] DFT-calculated with ORCA using a B3LYP functional and def2-TZVPP basis set, whereby the H atom positions were refined using anisotropic atomic displacement parameters.

NoSpherA2 implementation of HAR makes use of tailor-made aspherical atomic form factors calculated on-the-fly from a Hirshfeld-partitioned electron density (ED) - not from spherical-atom form factors. The ED is calculated from a gaussian basis set single determinant SCF wave function - either Hartree-Fock or DFT using selected functional - for a fragment of the crystal. This fragment can be embedded in an electrostatic crystal field by employing cluster charges or modelled using implicit solvation models, depending on the software used. The following options were used:

SOFTWARE:	ORCA 5.0
PARTITIONING:	NoSpherA2
INT ACCURACY:	Normal
METHOD:	B3LYP
BASIS SET:	def2-TZVPP
CHARGE:	0
MULTIPLICITY:	1
DATE:	2024-10-15_16-41-56

Table S 10: Crystal data and structure refinement of **V2**.

Identification code	15446	
Empirical formula	C ₄₆ H ₆₅ O ₅ Si ₃ V	
Color	translucent colourless	
Formula weight	833.224 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	<i>P</i> -3, (no. 147)	
Unit cell dimensions	a = 15.6315(3) Å	α = 90°.
	b = 15.6315(3) Å	β = 90°.
	c = 10.7026(4) Å	γ = 120°.
Volume	2264.76(10) Å ³	
Z	2	
Density (calculated)	1.222 Mg·m ⁻³	
Absorption coefficient	0.341 mm ⁻¹	
F(000)	893.574 e	
Crystal size	0.091 x 0.084 x 0.063 mm ³	
θ range for data collection	2.61 to 33.14°.	
Index ranges	-23 ≤ h ≤ 22, -24 ≤ k ≤ 24, -15 ≤ l ≤ 16	
Reflections collected	104925	
Independent reflections	5712 [R _{int} = 0.0484]	
Reflections with I > 2σ(I)	4651	
Completeness to θ = 25.2417°	99.38 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9929 and 0.9587	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5712 / 0 / 322	
Goodness-of-fit on F ²	1.0418	
Final R indices [I > 2σ(I)]	R ₁ = 0.0249	wR ² = 0.0612
R indices (all data)	R ₁ = 0.0370	wR ² = 0.0659
Largest diff. peak and hole	0.2645 and -0.2857 e·Å ⁻³	

Figure S 22: Crystal faces and unit cell determination/refinement of **V1**.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.60	343	344	99.7	16.68	37.87	111.27	0.0177	0.0065
2.60 - 1.71	811	811	100.0	18.07	13.00	100.62	0.0213	0.0072
1.71 - 1.35	1131	1131	100.0	18.12	8.35	80.88	0.0244	0.0083
1.35 - 1.18	1129	1129	100.0	17.77	7.28	70.49	0.0287	0.0093
1.18 - 1.07	1141	1141	100.0	15.76	4.42	52.85	0.0368	0.0128
1.07 - 0.99	1153	1153	100.0	11.66	3.74	39.65	0.0418	0.0170
0.99 - 0.93	1169	1169	100.0	9.65	2.67	29.31	0.0527	0.0233
0.93 - 0.88	1227	1227	100.0	8.24	2.30	24.37	0.0574	0.0287
0.88 - 0.84	1186	1186	100.0	7.70	2.11	21.17	0.0650	0.0328
0.84 - 0.81	1057	1057	100.0	7.35	2.02	19.87	0.0698	0.0361
0.81 - 0.78	1207	1207	100.0	7.05	1.73	17.05	0.0775	0.0423
0.78 - 0.75	1431	1431	100.0	6.75	1.51	14.62	0.0872	0.0493
0.75 - 0.73	1088	1088	100.0	6.53	1.28	12.46	0.0995	0.0588
0.73 - 0.71	1194	1194	100.0	6.27	1.16	11.00	0.1092	0.0665
0.71 - 0.70	675	675	100.0	6.13	1.14	10.67	0.1164	0.0695
0.70 - 0.68	1425	1425	100.0	5.93	1.06	9.79	0.1216	0.0766
0.68 - 0.66	1585	1585	100.0	5.67	0.95	8.52	0.1388	0.0885
0.66 - 0.65	885	885	100.0	5.53	0.74	6.94	0.1637	0.1118
0.65 - 0.64	934	934	100.0	5.29	0.73	6.57	0.1791	0.1197
0.64 - 0.63	1009	1009	100.0	5.27	0.73	6.52	0.1800	0.1198
0.63 - 0.62	944	1116	84.6	3.18	0.59	4.43	0.1988	0.1972
0.72 - 0.62	8061	8233	97.9	5.34	0.88	7.94	0.1426	0.0993
Inf - 0.62	22724	22897	99.2	8.90	3.28	27.86	0.0351	0.0240

Table S 11: Crystal data and structure refinement of **V1**.

Identification code	15057	
Empirical formula	C ₁₂₁ H ₉₂ Cl ₂ O ₈ Si ₆ V ₂	
Color	yellow	
Formula weight	2015.26 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n, (no. 14)	
Unit cell dimensions	a = 14.3394(10) Å	α = 90°.
	b = 14.7593(10) Å	β = 101.003(2)°.
	c = 24.2381(16) Å	γ = 90°.
Volume	5035.4(6) Å ³	
Z	2	
Density (calculated)	1.329 Mg·m ⁻³	
Absorption coefficient	0.370 mm ⁻¹	
F(000)	2092 e	
Crystal size	0.163 x 0.158 x 0.154 mm ³	
θ range for data collection	1.534 to 33.727°.	
Index ranges	-22 ≤ h ≤ 21, -23 ≤ k ≤ 23, -37 ≤ l ≤ 37	
Reflections collected	190757	
Independent reflections	20105 [R _{int} = 0.0347]	
Reflections with I > 2σ(I)	16581	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.96825 and 0.96034	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	20105 / 0 / 685	
Goodness-of-fit on F ²	1.027	
Final R indices [I > 2σ(I)]	R ₁ = 0.0399	wR ² = 0.1101
R indices (all data)	R ₁ = 0.0522	wR ² = 0.1193
Extinction coefficient	n/a	
Largest diff. peak and hole	1.198 and -1.420 e·Å ⁻³	

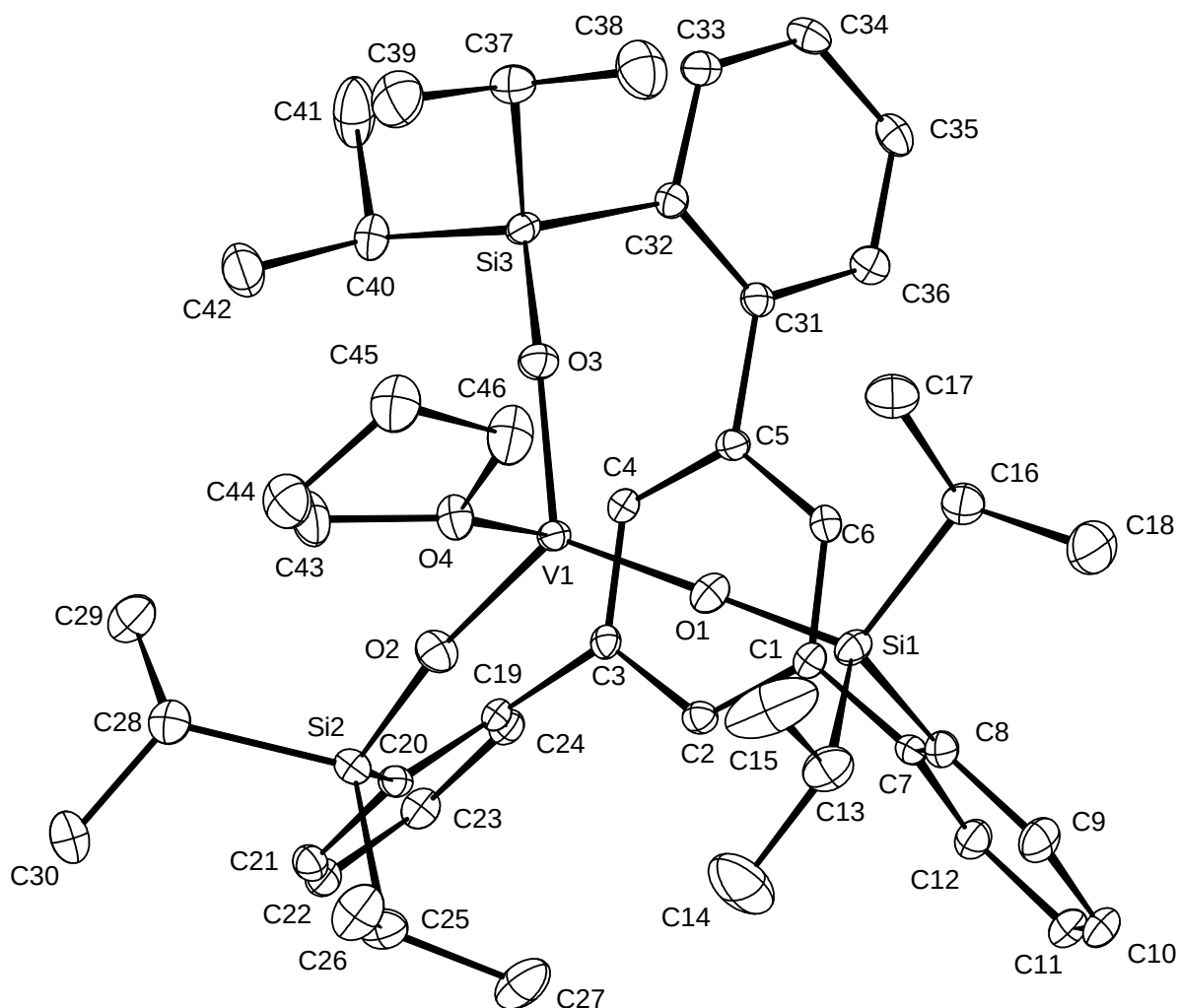
Single Crystal Structure analysis of **V3**

Figure S 23: The solid state structure of **V3**. H atoms have been removed for clarity.

$C_{46} H_{65} O_4 Si_3 V$, $M_r = 817.19 \text{ g mol}^{-1}$, blue plate, crystal size $0.141 \times 0.092 \times 0.072 \text{ mm}^3$, orthorhombic, space group $P2_12_12_1$ [19], $a = 10.5985(10) \text{ \AA}$, $b = 17.9432(17) \text{ \AA}$, $c = 23.306(2) \text{ \AA}$, $V = 4432.1(7) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $D_{calc} = 1.225 \text{ g cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.346 \text{ mm}^{-1}$, Gaussian correction ($T_{min} = 0.96749$, $T_{max} = 0.98507$), Bruker-AXS Kappa Mach3 with APEX-II detector and I μ S microfocus Mo-anode X-ray source, $1.432 < \theta < 30.638^\circ$, 147049 measured reflections, 13620 independent reflections, 11070 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0910$. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0395$ [$I > 2\sigma(I)$], $wR_2 = 0.0833$ [all data] with 743 parameters, 0 restraint and an absolute structure parameter Flack $x = 0.014(7)$.

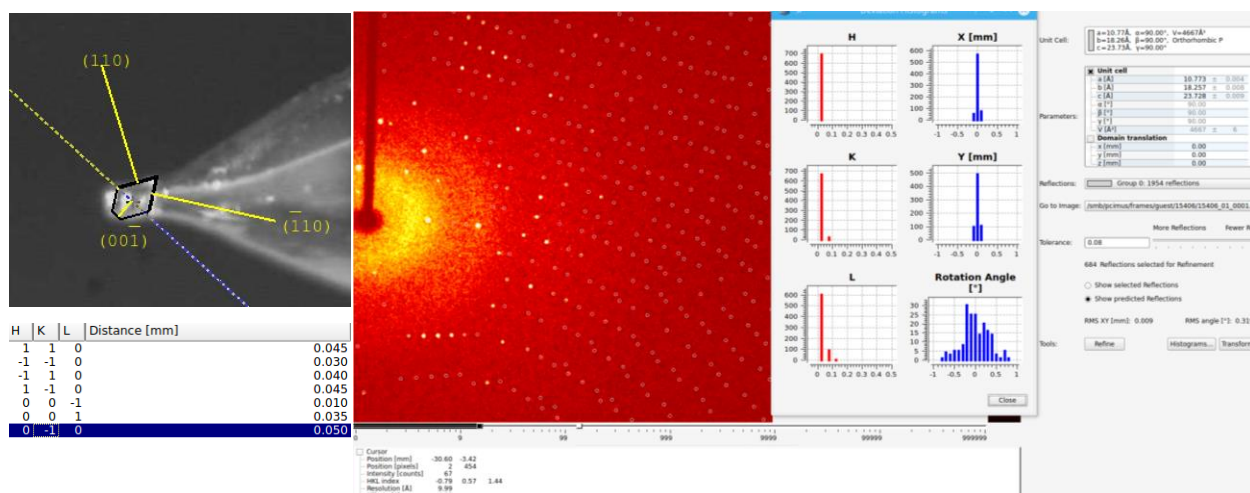


Figure S 24: Crystal faces and unit cell determination/refinement of **V3**.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.86	205	206	99.5	18.33	65.32	96.62	0.0200	0.0084
2.86 - 1.91	479	479	100.0	19.18	25.38	68.68	0.0353	0.0115
1.91 - 1.50	702	702	100.0	19.10	16.94	51.93	0.0505	0.0152
1.50 - 1.31	692	692	100.0	18.97	16.33	46.10	0.0582	0.0170
1.31 - 1.19	698	698	100.0	18.43	11.06	34.46	0.0809	0.0234
1.19 - 1.10	739	739	100.0	17.21	8.52	26.85	0.1021	0.0312
1.10 - 1.04	629	629	100.0	13.53	8.27	21.55	0.1127	0.0396
1.04 - 0.99	668	668	100.0	11.59	6.75	16.74	0.1349	0.0526
0.99 - 0.94	803	803	100.0	10.02	5.08	12.00	0.1658	0.0735
0.94 - 0.91	581	581	100.0	8.96	4.62	10.26	0.1822	0.0862
0.91 - 0.88	636	636	100.0	8.42	4.65	9.50	0.1884	0.0911
0.88 - 0.85	759	759	100.0	7.86	4.40	8.75	0.1965	0.1015
0.85 - 0.82	842	842	100.0	7.64	4.36	8.14	0.2072	0.1072
0.82 - 0.80	665	665	100.0	7.35	3.74	7.00	0.2378	0.1281
0.80 - 0.78	733	733	100.0	7.16	3.31	6.14	0.2657	0.1467
0.78 - 0.76	761	761	100.0	7.03	2.95	5.43	0.2953	0.1687
0.76 - 0.75	433	433	100.0	6.67	2.43	4.48	0.3484	0.2086
0.75 - 0.73	951	951	100.0	6.68	2.29	4.09	0.3624	0.2247
0.73 - 0.72	491	491	100.0	6.33	2.28	3.78	0.3611	0.2378
0.72 - 0.71	527	527	100.0	6.50	2.23	3.81	0.3854	0.2437
0.71 - 0.70	663	722	91.8	5.18	2.16	3.31	0.3999	0.2945
0.80 - 0.70	4559	4618	98.7	6.52	2.55	4.50	0.3329	0.2079
Inf - 0.70	13657	13717	99.6	10.74	7.57	18.31	0.0873	0.0553

Table S 12: Crystal data and structure refinement of **V3**.

Identification code	15406	
Empirical formula	C ₄₆ H ₆₅ O ₄ Si ₃ V	
Color	blue	
Formula weight	817.19 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁ , (no. 19)	
Unit cell dimensions	a = 10.5985(10) Å	α = 90°.
	b = 17.9432(17) Å	β = 90°.
	c = 23.306(2) Å	γ = 90°.
Volume	4432.1(7) Å ³	
Z	4	
Density (calculated)	1.225 Mg·m ⁻³	
Absorption coefficient	0.346 mm ⁻¹	
F(000)	1752 e	
Crystal size	0.141 x 0.092 x 0.072 mm ³	
θ range for data collection	1.432 to 30.638°.	
Index ranges	-15 ≤ h ≤ 15, -25 ≤ k ≤ 25, -33 ≤ l ≤ 33	
Reflections collected	147049	
Independent reflections	13620 [R _{int} = 0.0910]	
Reflections with I > 2σ(I)	11070	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98507 and 0.96749	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13620 / 0 / 743	
Goodness-of-fit on F ²	1.041	
Final R indices [I > 2σ(I)]	R ₁ = 0.0395	wR ² = 0.0749
R indices (all data)	R ₁ = 0.0623	wR ² = 0.0833
Absolute structure parameter	0.014(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.357 and -0.308 e·Å ⁻³	

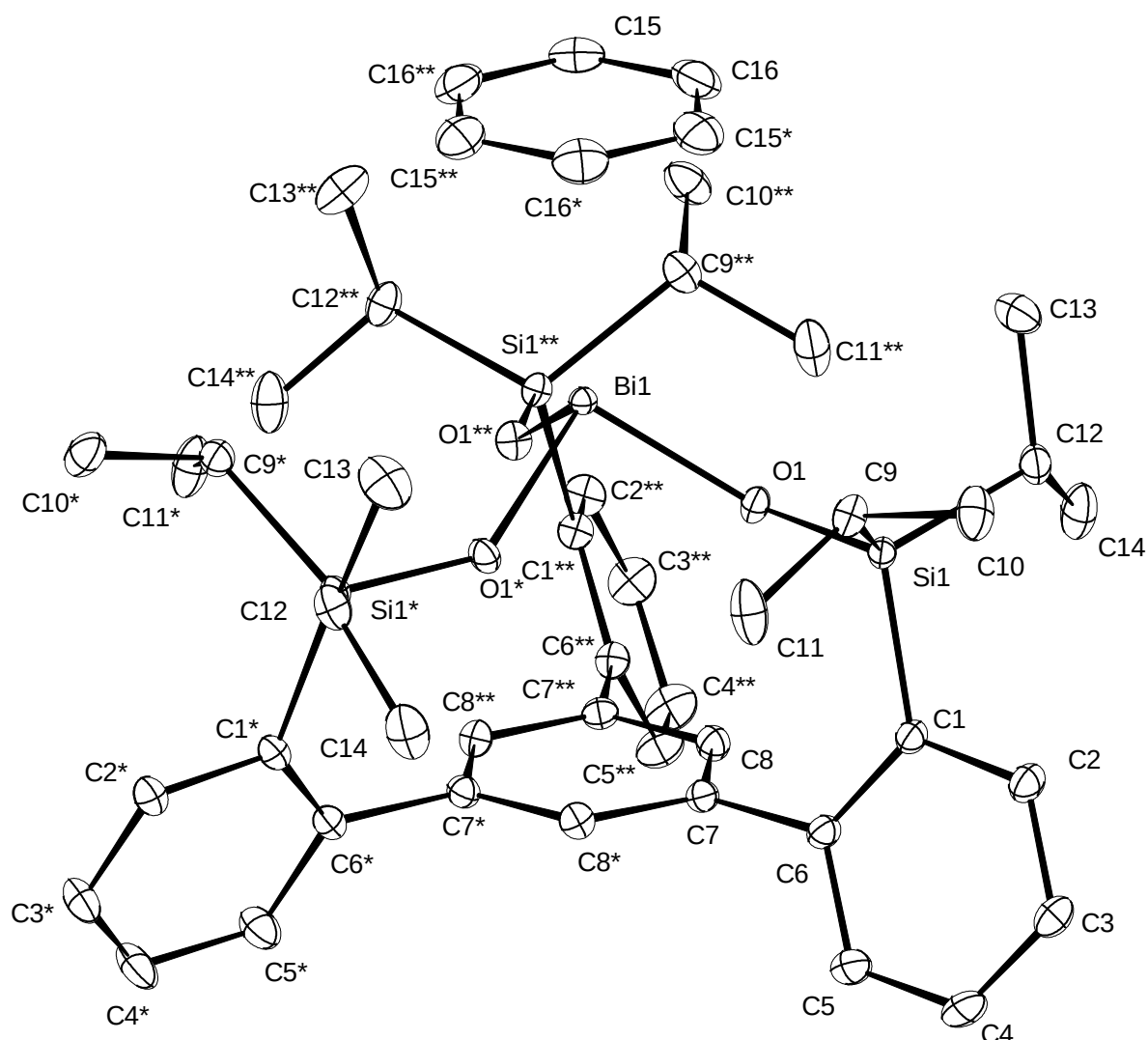
Single Crystal Structure analysis of **Bi1•C₆H₆**

Figure S 25: The solid state structure of **Bi1•C₆H₆**. H atoms have been removed for clarity.

$\text{C}_{48} \text{H}_{63} \text{Bi} \text{O}_3 \text{Si}_3$, $M_r = 981.270 \text{ g mol}^{-1}$, colorless prism, crystal size $0.194 \times 0.149 \times 0.14 \text{ mm}^3$, hexagonal, space group $P6_3$ [173], $a = 12.4716(4) \text{ \AA}$, $c = 17.0405(9) \text{ \AA}$, $V = 2295.39(16) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $D_{\text{calc}} = 1.420 \text{ g cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 3.957 \text{ mm}^{-1}$, Gaussian correction ($T_{\text{min}} = 0.64087$, $T_{\text{max}} = 0.74753$), Bruker-AXS Kappa Mach3 with APEX-II detector and I μ S microfocus Mo-anode X-ray source, $1.89 < \theta < 33.78^\circ$, 152734 measured reflections, 6074 independent reflections, 5921 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.0286$. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0146$ [$I > 2\sigma(I)$], $wR_2 = 0.0391$ [all data] with 171 parameters, 1 restraint and an absolute structure parameter Flack $x = 0.0051(14)$.

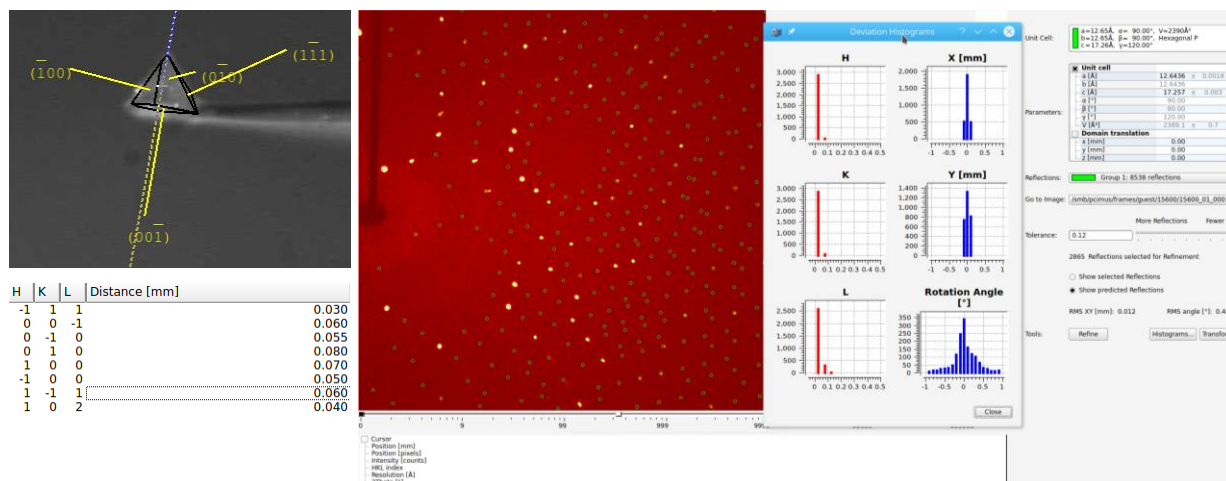


Figure S 26: Crystal faces and unit cell determination/refinement of $\text{Bi1}\cdot\text{C}_6\text{H}_6$.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.74	48	49	98.0	52.84	104.60	103.49	0.0502	0.0114
2.74 - 1.77	110	111	99.1	72.62	57.70	122.22	0.0490	0.0075
1.77 - 1.40	160	160	100.0	78.76	50.67	122.79	0.0466	0.0080
1.40 - 1.21	172	172	100.0	78.21	36.75	120.35	0.0488	0.0078
1.21 - 1.10	149	149	100.0	75.20	30.48	107.64	0.0528	0.0082
1.10 - 1.02	165	165	100.0	62.87	27.56	95.54	0.0550	0.0095
1.02 - 0.96	147	147	100.0	55.49	25.09	84.85	0.0589	0.0099
0.96 - 0.91	167	167	100.0	50.01	19.97	77.20	0.0607	0.0112
0.91 - 0.87	163	163	100.0	46.37	19.73	73.11	0.0610	0.0118
0.87 - 0.83	178	178	100.0	44.96	17.99	68.61	0.0590	0.0124
0.83 - 0.80	186	186	100.0	42.92	15.79	62.98	0.0633	0.0134
0.80 - 0.78	115	115	100.0	42.06	15.54	61.72	0.0723	0.0139
0.78 - 0.76	144	144	100.0	39.51	14.29	55.39	0.0659	0.0153
0.76 - 0.74	151	151	100.0	40.23	12.08	52.97	0.0724	0.0158
0.74 - 0.72	177	177	100.0	38.00	11.74	50.92	0.0756	0.0170
0.72 - 0.70	192	192	100.0	37.35	10.52	45.73	0.0825	0.0181
0.70 - 0.69	111	111	100.0	36.92	12.08	50.63	0.0768	0.0174
0.69 - 0.67	234	234	100.0	34.74	10.22	43.73	0.0795	0.0196
0.67 - 0.66	108	108	100.0	35.50	8.41	39.06	0.0900	0.0214
0.66 - 0.65	143	143	100.0	33.10	9.35	38.31	0.0842	0.0221
0.65 - 0.64	145	157	92.4	20.69	9.56	31.76	0.0814	0.0345
0.74 - 0.64	1110	1122	98.9	33.82	10.33	43.20	0.0805	0.0208
Inf - 0.64	3165	3179	99.6	48.09	21.61	70.39	0.0561	0.0119

Table S 13: Crystal data and structure refinement of **Bi•C₆H₆**.

Identification code	15600	
Empirical formula	C ₄₈ H ₆₃ Bi O ₃ Si ₃	
Color	colourless	
Formula weight	981.270 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	P6 ₃ , (no. 173)	
Unit cell dimensions	a = 12.4716(4) Å	α = 90°.
	b = 12.4716(4) Å	β = 90°.
	c = 17.0405(9) Å	γ = 120°.
Volume	2295.39(16) Å ³	
Z	2	
Density (calculated)	1.420 Mg·m ⁻³	
Absorption coefficient	3.957 mm ⁻¹	
F(000)	994.337 e	
Crystal size	0.194 x 0.149 x 0.14 mm ³	
θ range for data collection	1.89 to 33.78°.	
Index ranges	-19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -26 ≤ l ≤ 26	
Reflections collected	152734	
Independent reflections	6074 [R _{int} = 0.0286]	
Reflections with I > 2σ(I)	5921	
Completeness to θ = 25.2417°	99.86 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.74753 and 0.64087	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6074 / 1 / 171	
Goodness-of-fit on F ²	1.0065	
Final R indices [I > 2σ(I)]	R ₁ = 0.0146	wR ² = 0.0389
R indices (all data)	R ₁ = 0.0151	wR ² = 0.0391
Absolute structure parameter	0.0051(14)	
Largest diff. peak and hole	0.4507 and -0.2217 e·Å ⁻³	

Single Crystal Structure analysis of Ga1•Py

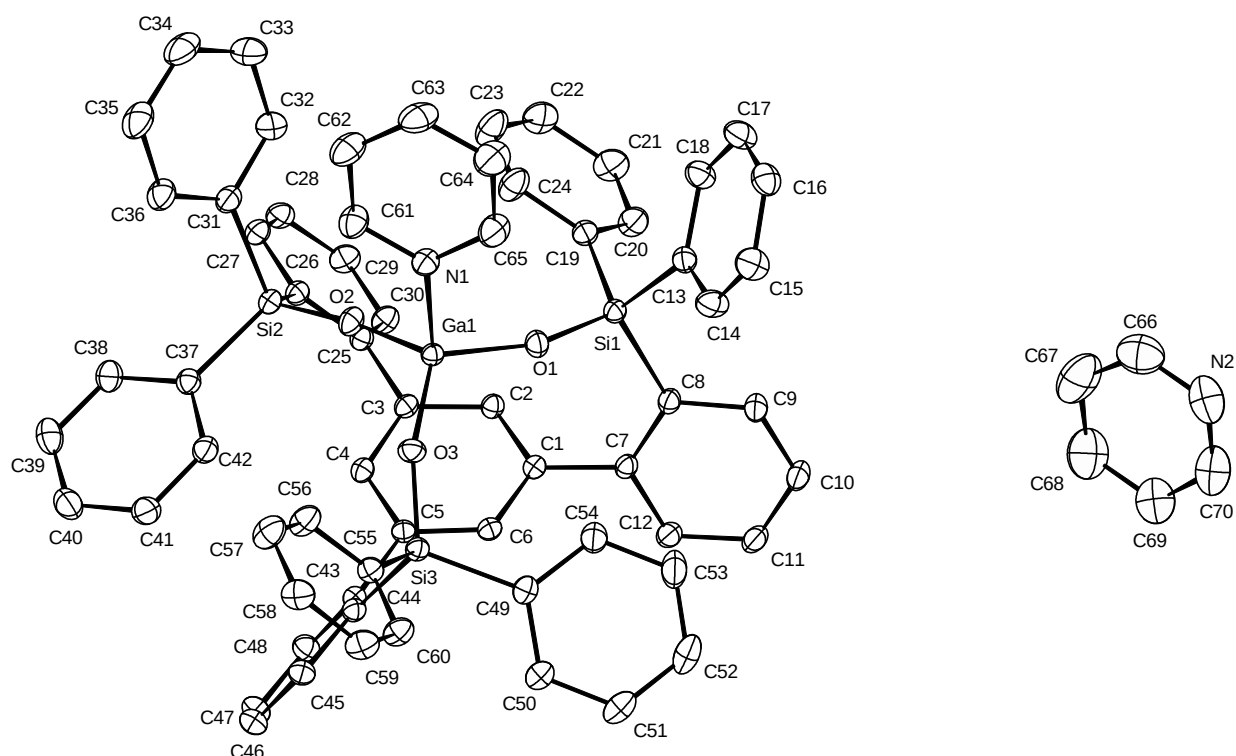
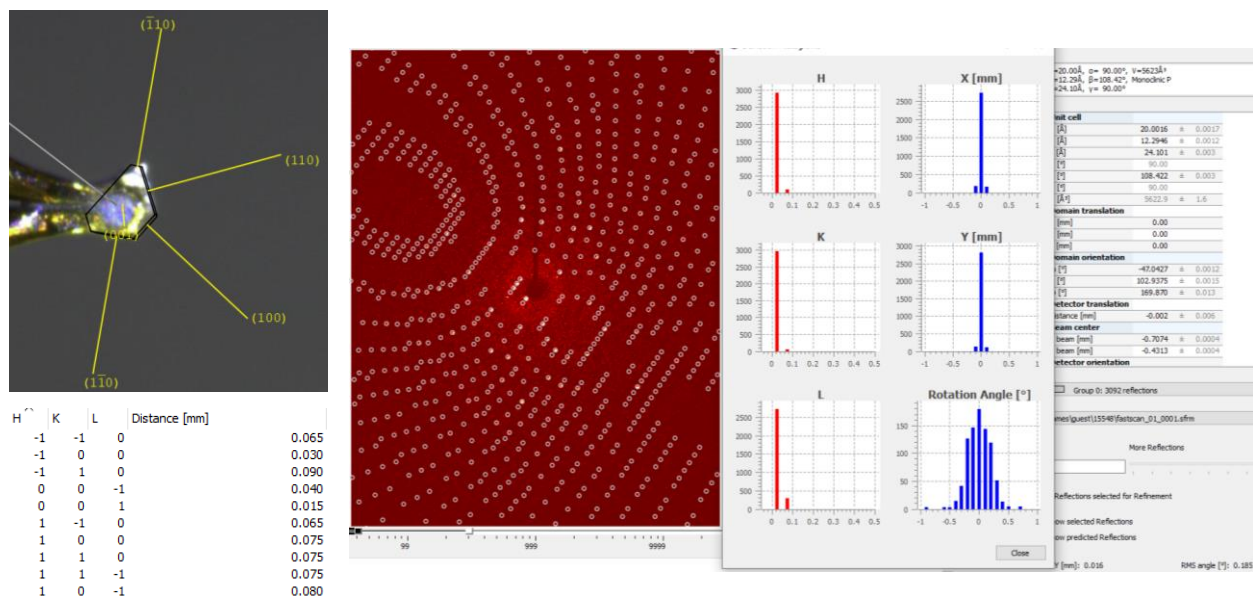


Figure S 27: The solid state structure of **Ga1•Py**. H atoms have been removed for clarity.

$C_{70}H_{55}GaN_2O_3Si_3$, $M_r = 1126.15 \text{ g mol}^{-1}$, clear colorless prism, crystal size $0.168 \times 0.162 \times 0.081 \text{ mm}^3$, monoclinic, space group $P2_1/c$ [14], $a = 24.0972(10) \text{ \AA}$, $b = 12.2933(5) \text{ \AA}$, $c = 19.9969(8) \text{ \AA}$, $\beta = 108.406(2)^\circ$, $V = 5620.7(4) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $D_{\text{calc}} = 1.331 \text{ g}\cdot\text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.605 \text{ mm}^{-1}$, Gaussian correction ($T_{\text{min}} = 0.9139$, $T_{\text{max}} = 0.9919$), Bruker-AXS D8 Venture with Photon III detector and I μ S Diamond microfocus Mo-anode X-ray source, $1.881 < \theta < 34.373^\circ$, 595164 measured reflections, 23530 independent reflections, 19469 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.0616$. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0359$ [$I > 2\sigma(I)$], $wR_2 = 0.0987$ [all data] with 712 parameters and 0 restraints.

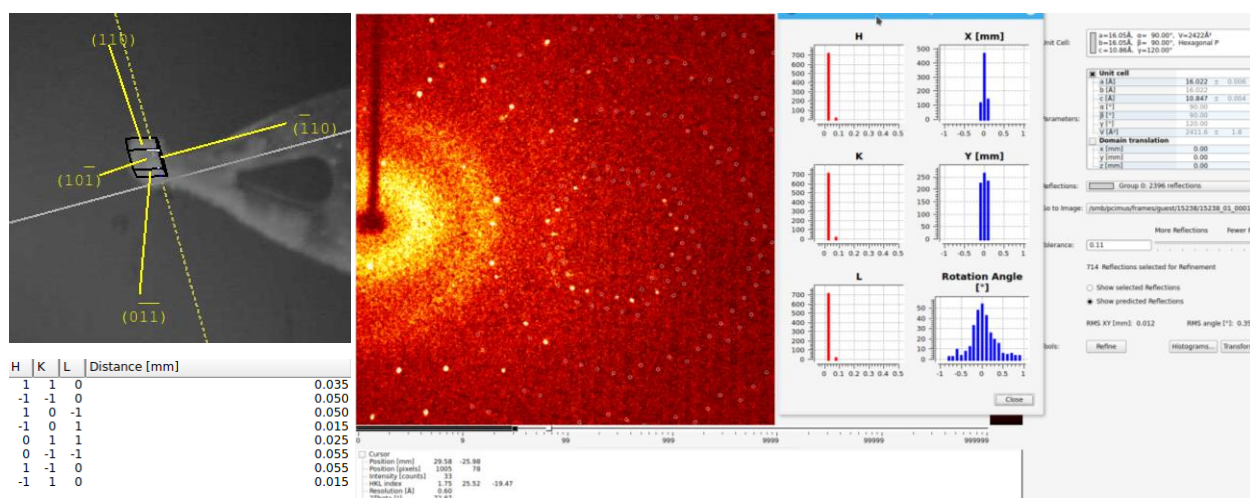
Figure S 28: Crystal faces and unit cell determination/refinement of *Ga1•Py*.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.63	368	375	98.1	32.89	92.73	97.89	0.0293	0.0205
2.63 - 1.74	861	861	100.0	40.66	37.22	98.62	0.0291	0.0070
1.74 - 1.37	1241	1241	100.0	40.86	25.34	85.63	0.0360	0.0080
1.37 - 1.19	1272	1272	100.0	41.41	20.06	74.74	0.0429	0.0089
1.19 - 1.08	1243	1243	100.0	40.44	13.41	59.24	0.0561	0.0112
1.08 - 1.00	1248	1248	100.0	37.75	11.39	51.68	0.0637	0.0130
1.00 - 0.94	1256	1256	100.0	31.55	8.91	41.53	0.0743	0.0167
0.94 - 0.89	1326	1326	100.0	28.11	7.38	33.92	0.0877	0.0205
0.89 - 0.85	1281	1281	100.0	26.91	6.39	29.74	0.0971	0.0235
0.85 - 0.82	1095	1095	100.0	25.72	5.80	26.62	0.1055	0.0265
0.82 - 0.79	1334	1334	100.0	24.88	5.16	24.21	0.1196	0.0300
0.79 - 0.77	974	974	100.0	24.17	4.38	21.02	0.1343	0.0348
0.77 - 0.74	1683	1683	100.0	23.19	4.03	18.80	0.1443	0.0389
0.74 - 0.72	1275	1275	100.0	19.56	3.24	14.06	0.1726	0.0529
0.72 - 0.71	695	695	100.0	17.88	3.55	13.83	0.1806	0.0545
0.71 - 0.69	1507	1507	100.0	17.94	2.74	11.46	0.2031	0.0664
0.69 - 0.67	1713	1713	100.0	16.67	2.53	10.18	0.2184	0.0751
0.67 - 0.66	928	928	100.0	11.84	2.32	7.81	0.2399	0.1023
0.66 - 0.65	980	980	100.0	9.16	2.11	6.43	0.2536	0.1305
0.65 - 0.64	1046	1048	99.8	6.94	1.91	5.02	0.2621	0.1751
0.64 - 0.63	1122	1181	95.0	4.86	1.80	4.05	0.2672	0.2216
0.73 - 0.63	8650	8711	99.3	13.02	2.46	8.85	0.2113	0.1004
Inf - 0.63	24448	24516	99.7	24.85	9.44	32.51	0.0602	0.0233

Table S 14: Crystal data and structure refinement of **Ga1•Py**.

Identification code	15548	
Empirical formula	C ₇₀ H ₅₅ Ga N ₂ O ₃ Si ₃	
Color	clear colourless	
Formula weight	1126.15 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c, (no. 14)	
Unit cell dimensions	a = 24.0972(10) Å	α = 90°.
	b = 12.2933(5) Å	β = 108.406(2)°.
	c = 19.9969(8) Å	γ = 90°.
Volume	5620.7(4) Å ³	
Z	4	
Density (calculated)	1.331 Mg·m ⁻³	
Absorption coefficient	0.605 mm ⁻¹	
F(000)	2344 e	
Crystal size	0.168 x 0.162 x 0.081 mm ³	
θ range for data collection	1.881 to 34.373°.	
Index ranges	-38 ≤ h ≤ 38, -19 ≤ k ≤ 19, -31 ≤ l ≤ 31	
Reflections collected	595164	
Independent reflections	23530 [R _{int} = 0.0616]	
Reflections with I > 2σ(I)	19469	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9919 and 0.9139	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	23530 / 0 / 712	
Goodness-of-fit on F ²	1.069	
Final R indices [I > 2σ(I)]	R ₁ = 0.0359	wR ² = 0.0911
R indices (all data)	R ₁ = 0.0492	wR ² = 0.0987
Extinction coefficient	n/a	
Largest diff. peak and hole	0.523 and -0.405 e·Å ⁻³	

Figure S 30: Crystal faces and unit cell determination/refinement of Ti_3 .

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.69	82	82	100.0	27.33	109.65	113.39	0.0233	0.0078
2.69 - 1.80	196	196	100.0	28.56	38.27	84.19	0.0295	0.0084
1.80 - 1.43	277	277	100.0	28.71	25.47	73.56	0.0364	0.0097
1.43 - 1.25	275	275	100.0	27.99	22.33	63.21	0.0410	0.0108
1.25 - 1.13	282	282	100.0	27.09	12.97	46.82	0.0595	0.0144
1.13 - 1.05	263	263	100.0	22.18	11.09	37.95	0.0722	0.0184
1.05 - 0.99	281	281	100.0	17.56	8.71	28.00	0.0888	0.0244
0.99 - 0.94	275	275	100.0	14.98	6.47	21.90	0.1081	0.0334
0.94 - 0.90	267	267	100.0	13.58	6.51	19.93	0.1175	0.0362
0.90 - 0.86	317	317	100.0	12.15	5.75	17.03	0.1229	0.0432
0.86 - 0.83	268	268	100.0	11.68	5.14	14.67	0.1382	0.0493
0.83 - 0.81	235	235	100.0	11.23	5.00	13.68	0.1384	0.0533
0.81 - 0.78	353	353	100.0	10.86	4.23	11.88	0.1622	0.0630
0.78 - 0.76	278	278	100.0	10.59	3.59	10.05	0.1837	0.0751
0.76 - 0.74	311	311	100.0	10.14	3.04	8.57	0.2062	0.0898
0.74 - 0.73	152	152	100.0	9.95	2.59	7.13	0.2633	0.1068
0.73 - 0.71	358	358	100.0	9.62	2.86	7.65	0.2514	0.1027
0.71 - 0.70	198	198	100.0	9.32	2.14	5.88	0.2945	0.1366
0.70 - 0.68	400	400	100.0	9.16	2.20	5.80	0.3213	0.1381
0.68 - 0.67	260	260	100.0	8.56	1.98	5.06	0.3566	0.1607
0.67 - 0.66	134	182	73.6	2.85	1.14	2.10	0.4730	0.5166
0.76 - 0.66	1813	1861	97.4	8.79	2.39	6.38	0.2749	0.1322
Inf - 0.66	5462	5510	99.1	14.96	9.78	25.09	0.0575	0.0282

Table S 15: Crystal data and structure refinement of **Ti3**.

Identification code	15238	
Empirical formula	C ₄₆ H ₆₉ O ₃ Si ₃ Ti	
Color	colourless	
Formula weight	811.19 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	<i>P</i> -3, (no. 147)	
Unit cell dimensions	a = 15.7366(7) Å	α = 90°.
	b = 15.7366(7) Å	β = 90°.
	c = 10.6748(5) Å	γ = 120°.
Volume	2289.3(2) Å ³	
Z	2	
Density (calculated)	1.177 Mg·m ⁻³	
Absorption coefficient	0.303 mm ⁻¹	
F(000)	875 e	
Crystal size	0.214 x 0.097 x 0.084 mm ³	
θ range for data collection	1.494 to 32.029°.	
Index ranges	-23 ≤ h ≤ 23, -23 ≤ k ≤ 23, -15 ≤ l ≤ 15	
Reflections collected	81901	
Independent reflections	5330 [R _{int} = 0.0594]	
Reflections with I > 2σ(I)	4216	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98452 and 0.96869	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5330 / 0 / 156	
Goodness-of-fit on F ²	1.029	
Final R indices [I > 2σ(I)]	R ₁ = 0.0409	wR ² = 0.1063
R indices (all data)	R ₁ = 0.0562	wR ² = 0.1151
Extinction coefficient	n/a	
Largest diff. peak and hole	0.772 and -0.461 e·Å ⁻³	

Single Crystal Structure analysis of V4

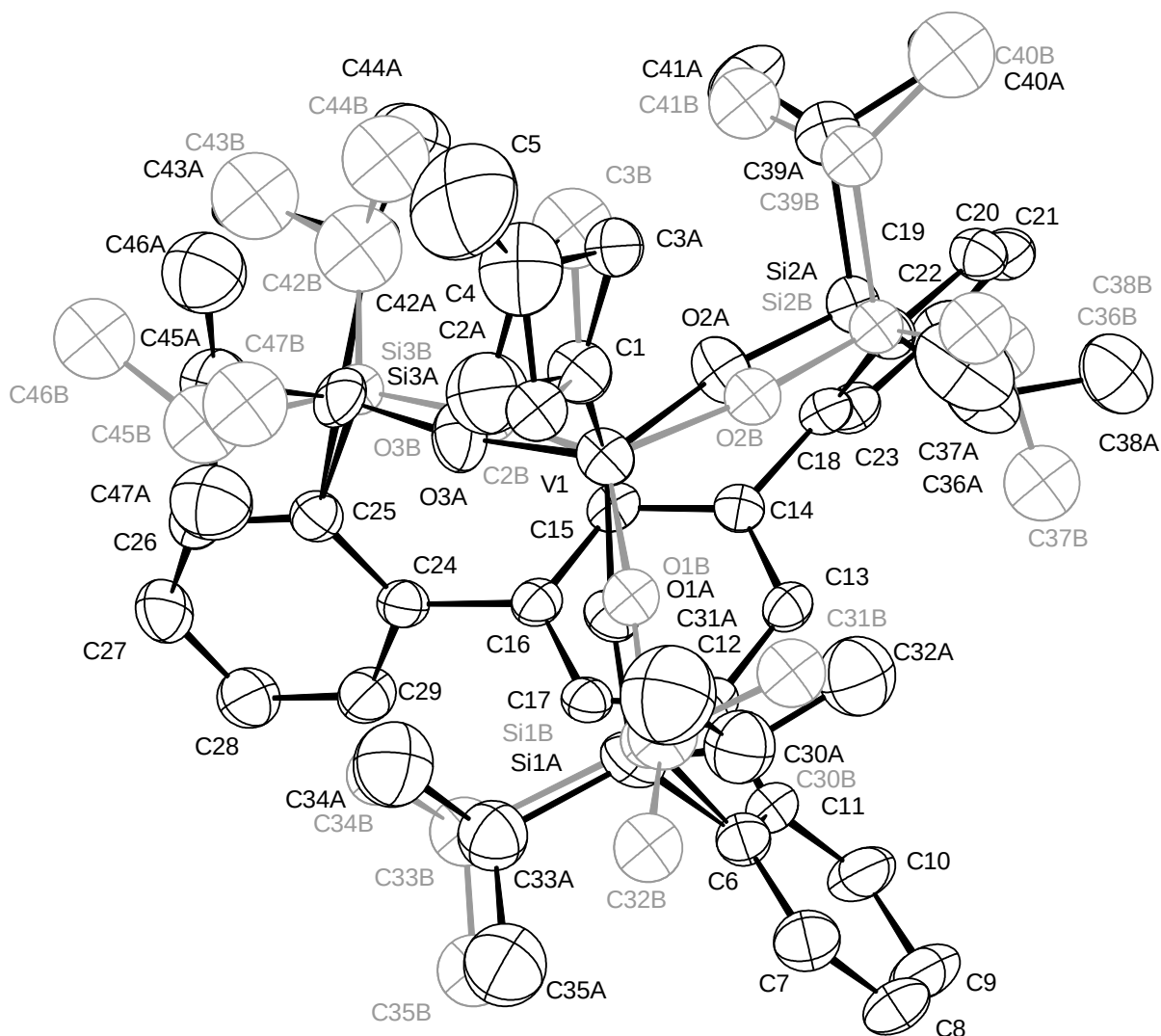


Figure S 31: The solid state structure of **V4**. H atoms have been removed for clarity and disordered regions shown in grey.

$\text{C}_{47} \text{H}_{63} \text{O}_3 \text{Si}_3 \text{V}$, $M_r = 811.18 \text{ g mol}^{-1}$, blue prism, crystal size $0.155 \times 0.145 \times 0.041 \text{ mm}^3$, orthorhombic, space group $P2_12_12_1$ [19], $a = 10.4705(5) \text{ \AA}$, $b = 18.1070(7) \text{ \AA}$, $c = 23.5337(11) \text{ \AA}$, $V = 4461.7(3) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $D_{\text{calc}} = 1.208 \text{ g}\cdot\text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.341 \text{ mm}^{-1}$, Gaussian correction ($T_{\text{min}} = 0.96171$, $T_{\text{max}} = 0.98832$), Bruker-AXS Kappa Mach3 with APEX-II detector and I μ S microfocus Mo-anode X-ray source, $1.419 < \theta < 28.698^\circ$, 133701 measured reflections, 11527 independent reflections, 7793 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.1024$. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0633$ [$I > 2\sigma(I)$], $wR_2 = 0.1772$ [all data] with 616 parameters and 272 restraints and an absolute structure parameter Flack $x = 0.42(4)$.

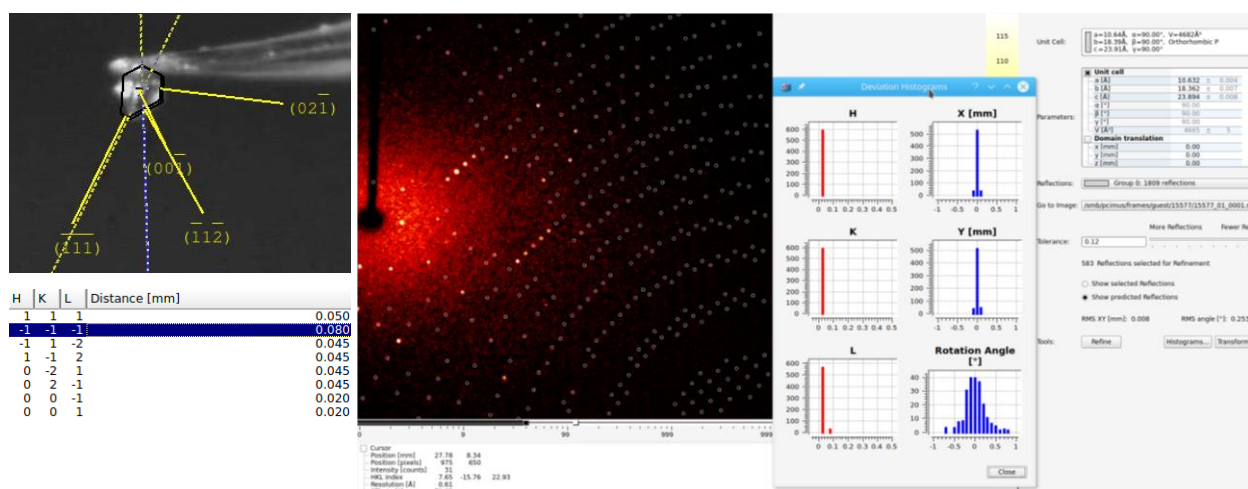


Figure S 32: Crystal faces and unit cell determination/refinement of V4.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.99	183	183	100.0	18.13	76.92	89.87	0.0228	0.0095
2.99 - 1.98	423	423	100.0	19.03	24.04	66.11	0.0382	0.0122
1.98 - 1.57	615	615	100.0	19.11	14.44	48.51	0.0571	0.0166
1.57 - 1.37	614	614	100.0	18.87	11.64	38.58	0.0708	0.0203
1.37 - 1.25	582	582	100.0	18.66	8.63	30.46	0.0933	0.0265
1.25 - 1.15	680	680	100.0	17.99	5.41	21.13	0.1353	0.0390
1.15 - 1.09	544	544	100.0	16.50	4.42	17.12	0.1656	0.0512
1.09 - 1.03	664	664	100.0	12.94	3.79	12.53	0.1952	0.0693
1.03 - 0.99	530	530	100.0	11.36	2.68	8.75	0.2461	0.1021
0.99 - 0.95	627	627	100.0	10.05	1.99	6.16	0.3121	0.1448
0.95 - 0.92	570	570	100.0	9.25	1.74	5.14	0.3597	0.1760
0.92 - 0.89	634	634	100.0	8.43	1.51	4.21	0.3925	0.2141
0.89 - 0.86	704	704	100.0	7.96	1.35	3.55	0.4417	0.2539
0.86 - 0.84	558	558	100.0	7.70	1.18	3.06	0.4980	0.3008
0.84 - 0.82	588	588	100.0	7.57	1.07	2.69	0.5210	0.3419
0.82 - 0.80	629	629	100.0	7.34	0.82	2.06	0.6128	0.4557
0.80 - 0.78	741	741	100.0	7.10	0.75	1.81	0.6591	0.5245
0.78 - 0.77	373	373	100.0	7.03	0.63	1.51	0.7167	0.6375
0.77 - 0.75	837	837	100.0	6.87	0.47	1.10	0.8075	0.8739
0.75 - 0.74	466	466	100.0	6.54	0.44	1.01	0.8374	0.9920
0.74 - 0.73	489	489	100.0	6.53	0.33	0.71	0.9186	1.3234
0.83 - 0.73	3851	3851	100.0	6.98	0.62	1.49	0.7080	0.6478
Inf - 0.73	12051	12051	100.0	11.38	5.21	14.31	0.0968	0.0624

Refined as an inversion twin.

Table S 16: Crystal data and structure refinement of **V4**.

Identification code	15577	
Empirical formula	C ₄₇ H ₆₃ O ₃ Si ₃ V	
Color	blue	
Formula weight	811.18 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁ , (no. 19)	
Unit cell dimensions	a = 10.4705(5) Å	α = 90°.
	b = 18.1070(7) Å	β = 90°.
	c = 23.5337(11) Å	γ = 90°.
Volume	4461.7(3) Å ³	
Z	4	
Density (calculated)	1.208 Mg·m ⁻³	
Absorption coefficient	0.341 mm ⁻¹	
F(000)	1736 e	
Crystal size	0.155 x 0.145 x 0.041 mm ³	
θ range for data collection	1.419 to 28.698°.	
Index ranges	-14 ≤ h ≤ 14, -24 ≤ k ≤ 24, -31 ≤ l ≤ 31	
Reflections collected	133701	
Independent reflections	11527 [R _{int} = 0.1024]	
Reflections with I > 2σ(I)	7793	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98832 and 0.96171	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11527 / 272 / 616	
Goodness-of-fit on F ²	1.034	
Final R indices [I > 2σ(I)]	R ₁ = 0.0633	wR ² = 0.1522
R indices (all data)	R ₁ = 0.1080	wR ² = 0.1772
Absolute structure parameter	0.42(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.586 and -0.571 e·Å ⁻³	

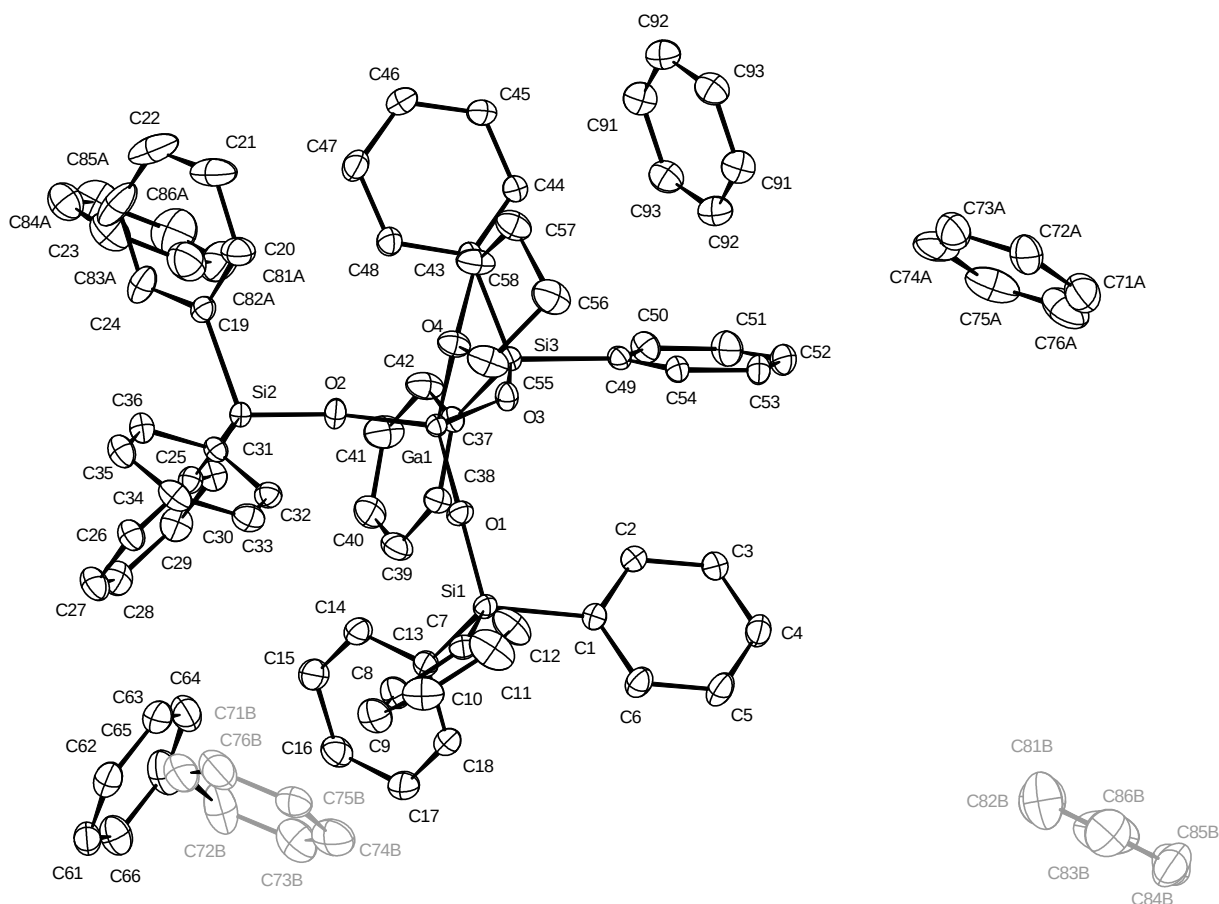
Single Crystal Structure analysis of **214**•THF

Figure S 33: The solid state structure of **214**•THF. H atoms have been removed for clarity and disordered regions shown in grey.

$C_{79}H_{74}GaO_4Si_3$, $M_r = 1241.37 \text{ g mol}^{-1}$, colourless prism, crystal size $0.222 \times 0.165 \times 0.158 \text{ mm}^3$, triclinic, space group $P-1$ [19], $a = 10.8776(13) \text{ \AA}$, $b = 14.9065(17) \text{ \AA}$, $c = 21.135(2) \text{ \AA}$, $\alpha = 79.153(3)^\circ$, $\beta = 83.005(3)^\circ$, $\gamma = 84.279(3)^\circ$, $V = 3330.4(7) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $D_{\text{calc}} = 1.238 \text{ g}\cdot\text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.517 \text{ mm}^{-1}$, Gaussian correction ($T_{\text{min}} = 0.9052$, $T_{\text{max}} = 0.9977$), Bruker-AXS D8 Venture with Photon III detector and I μ S Diamond microfocus Mo-anode X-ray source, $2.261 < \theta < 32.076^\circ$, 850242 measured reflections, 23232 independent reflections, 20142 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.0764$. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0342$ [$I > 2\sigma(I)$], $wR_2 = 0.0920$ [all data] with 845 parameters and 0 restraints.

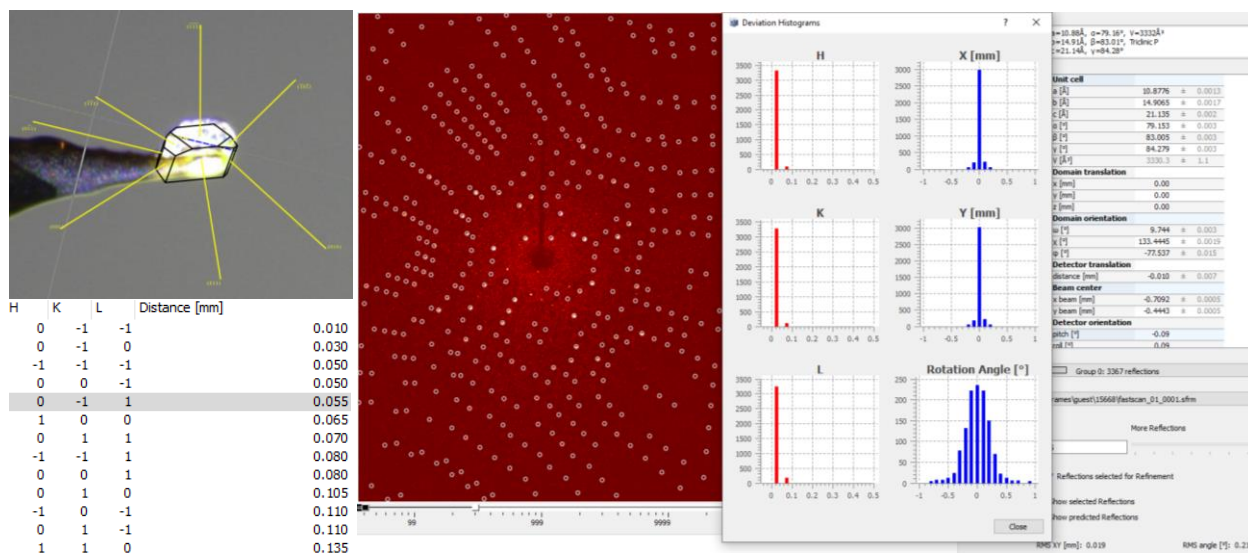


Figure S 34: Crystal faces and unit cell determination/refinement of **214•THF**.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.69	350	356	98.3	46.63	49.14	123.29	0.0285	0.0248
2.69 - 1.81	814	814	100.0	55.40	19.46	117.90	0.0316	0.0067
1.81 - 1.44	1179	1179	100.0	54.99	13.18	98.15	0.0388	0.0072
1.44 - 1.25	1209	1209	100.0	54.70	10.85	86.33	0.0493	0.0083
1.25 - 1.14	1138	1138	100.0	53.36	7.76	66.80	0.0614	0.0100
1.14 - 1.06	1141	1141	100.0	50.54	5.37	54.82	0.0795	0.0130
1.06 - 0.99	1320	1320	100.0	42.54	4.85	46.22	0.0860	0.0154
0.99 - 0.95	994	994	100.0	38.95	4.52	39.64	0.0928	0.0172
0.95 - 0.90	1407	1407	100.0	37.11	3.57	33.91	0.1110	0.0209
0.90 - 0.87	1027	1027	100.0	34.14	3.17	30.02	0.1247	0.0245
0.87 - 0.84	1146	1146	100.0	33.41	2.79	26.86	0.1384	0.0272
0.84 - 0.81	1389	1389	100.0	32.40	2.42	22.99	0.1563	0.0314
0.81 - 0.79	1012	1012	100.0	31.68	2.21	21.24	0.1707	0.0347
0.79 - 0.77	1131	1131	100.0	30.86	2.10	20.29	0.1805	0.0373
0.77 - 0.75	1268	1268	100.0	30.17	1.90	18.05	0.1974	0.0414
0.75 - 0.73	1356	1356	100.0	27.55	1.80	16.25	0.2096	0.0463
0.73 - 0.72	788	788	100.0	26.35	1.39	12.99	0.2405	0.0586
0.72 - 0.70	1654	1654	100.0	26.04	1.33	12.33	0.2586	0.0629
0.70 - 0.69	886	886	100.0	23.57	1.13	10.09	0.2941	0.0772
0.69 - 0.68	918	918	100.0	23.74	1.16	10.41	0.2933	0.0759
0.68 - 0.67	1110	1147	96.8	21.54	1.02	8.83	0.3213	0.0956
0.77 - 0.67	7980	8017	99.5	25.80	1.42	13.01	0.2425	0.0601
Inf - 0.67	23237	23280	99.8	36.52	5.09	38.20	0.0740	0.0196

Table S 17: Crystal data and structure refinement of **214•THF**.

Identification code	15668	
Empirical formula	C ₇₉ H ₇₄ Ga O ₄ Si ₃	
Color	colourless	
Formula weight	1241.37 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1, (no. 2)	
Unit cell dimensions	a = 10.8776(13) Å	α = 79.153(3)°.
	b = 14.9065(17) Å	β = 83.005(3)°.
	c = 21.135(2) Å	γ = 84.279(3)°.
Volume	3330.4(7) Å ³	
Z	2	
Density (calculated)	1.238 Mg·m ⁻³	
Absorption coefficient	0.517 mm ⁻¹	
F(000)	1306 e	
Crystal size	0.222 x 0.165 x 0.158 mm ³	
θ range for data collection	2.261 to 32.076°.	
Index ranges	-16 ≤ h ≤ 16, -22 ≤ k ≤ 22, -31 ≤ l ≤ 31	
Reflections collected	850242	
Independent reflections	23232 [R _{int} = 0.0764]	
Reflections with I > 2σ(I)	20142	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9977 and 0.9052	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	23232 / 0 / 845	
Goodness-of-fit on F ²	1.069	
Final R indices [I > 2σ(I)]	R ₁ = 0.0342	wR ² = 0.0858
R indices (all data)	R ₁ = 0.0430	wR ² = 0.0920
Extinction coefficient	n/a	
Largest diff. peak and hole	0.762 and -0.424 e·Å ⁻³	

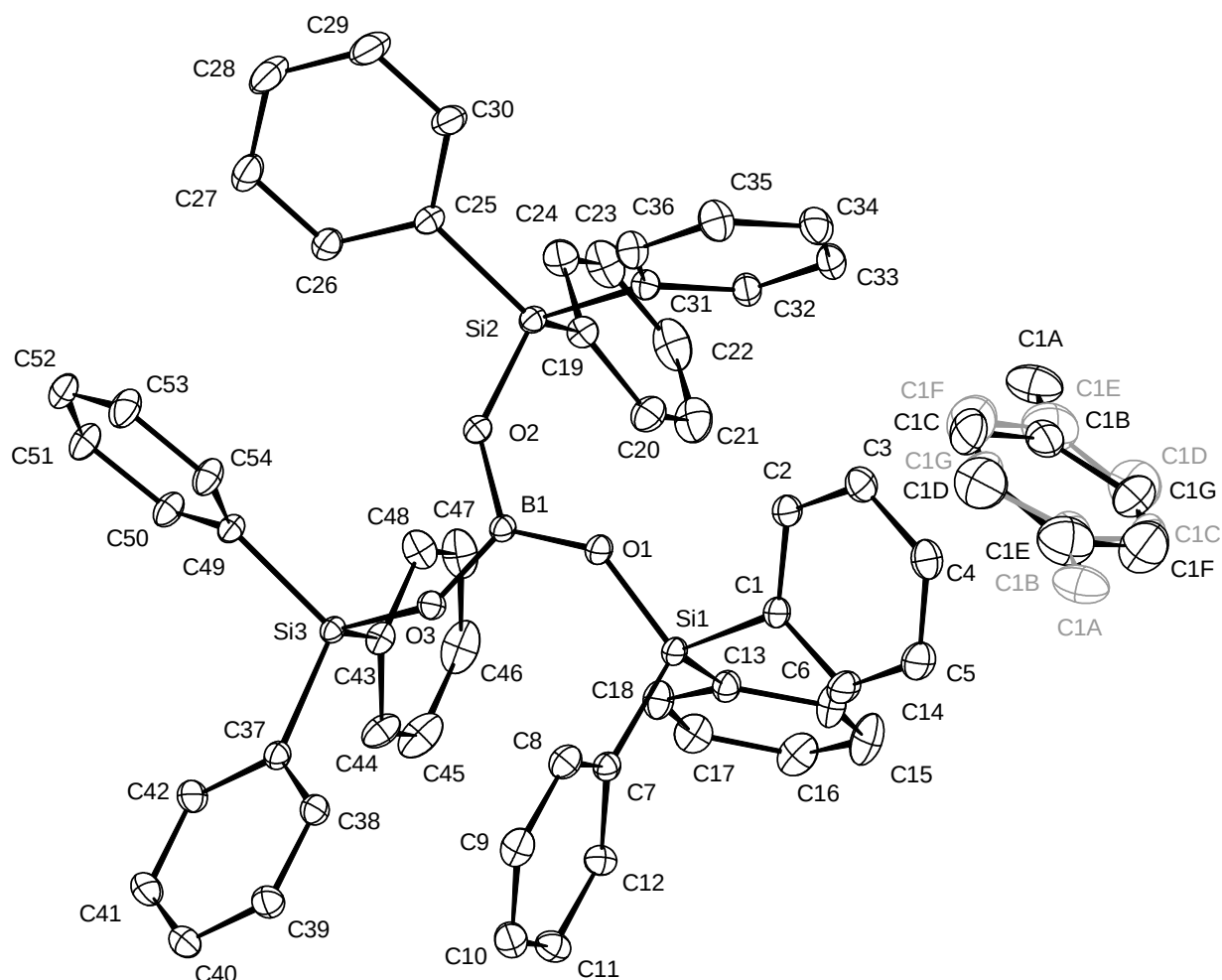
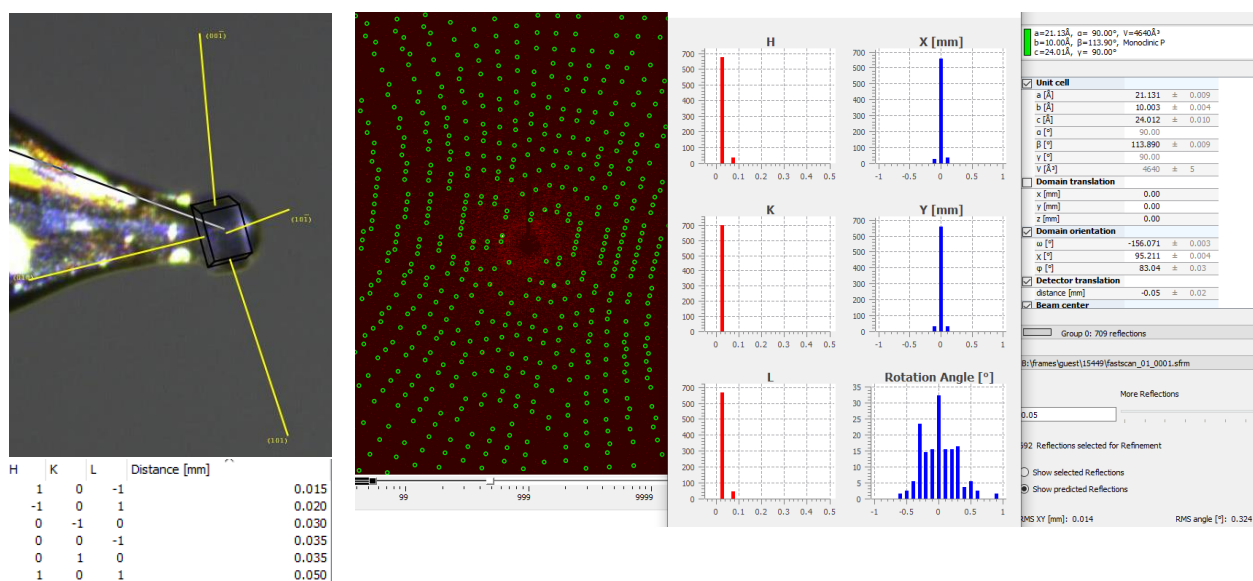
Single Crystal Structure analysis of **211**

Figure S 35: The solid state structure of **211**. H atoms have been removed for clarity and disordered regions shown in grey.

C₁₁₅ H₉₈ B₂ O₆ Si₆, $M_r = 1766.217 \text{ g mol}^{-1}$, colourless plate, crystal size 0.107 x 0.071 x 0.040 mm³, monoclinic, space group $P2_1/n$ [14], $a = 21.131(9) \text{ \AA}$, $b = 10.003(4) \text{ \AA}$, $c = 24.012(10) \text{ \AA}$, $\beta = 113.890(9)^\circ$, $V = 4640(3) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $D_{\text{calc}} = 1.264 \text{ g cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.149 \text{ mm}^{-1}$, Gaussian correction ($T_{\text{min}} = 0.9481$, $T_{\text{max}} = 0.9922$), Bruker-AXS D8 Venture with Photon III detector and I μ S Diamond microfocus Mo-anode X-ray source, $2.24 < \theta < 32.07^\circ$, 588053 measured reflections, 16168 independent reflections, 12750 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.1023$. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*). The final structure refinement was performed by olex2.refine 1.5 (L-M) together with NoSpherA2 (atomic form factors) against F^2 to $R_1 = 0.0238$ [$I > 2\sigma(I)$], $wR_2 = 0.0472$ [all data] with 1042 parameters and 119 restraints.

Figure S 36: Crystal faces and unit cell determination/refinement of **211**.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.83	259	266	97.4	43.34	74.42	51.26	0.0283	0.0285
2.83 - 1.86	601	601	100.0	51.40	31.51	53.34	0.0393	0.0133
1.86 - 1.47	839	839	100.0	52.07	18.65	45.31	0.0560	0.0148
1.47 - 1.27	895	895	100.0	52.73	14.33	41.00	0.0717	0.0160
1.27 - 1.15	884	884	100.0	51.88	14.29	38.01	0.0784	0.0171
1.15 - 1.07	809	809	100.0	51.88	9.08	31.26	0.1055	0.0204
1.07 - 1.00	929	929	100.0	44.10	6.80	25.68	0.1273	0.0259
1.00 - 0.95	867	867	100.0	39.14	6.01	22.27	0.1406	0.0299
0.95 - 0.91	807	807	100.0	36.24	6.13	21.12	0.1440	0.0318
0.91 - 0.87	999	999	100.0	33.83	5.12	17.77	0.1606	0.0368
0.87 - 0.84	829	829	100.0	32.89	4.16	15.56	0.1886	0.0435
0.84 - 0.82	656	656	100.0	32.16	3.59	14.58	0.2119	0.0496
0.82 - 0.79	1087	1087	100.0	31.19	3.37	13.11	0.2206	0.0536
0.79 - 0.77	809	809	100.0	30.52	2.98	11.52	0.2475	0.0614
0.77 - 0.75	916	916	100.0	29.62	3.04	11.44	0.2461	0.0624
0.75 - 0.73	1008	1008	100.0	26.55	2.37	8.75	0.2997	0.0833
0.73 - 0.72	556	556	100.0	24.56	2.21	7.85	0.3226	0.0954
0.72 - 0.70	1189	1189	100.0	23.14	1.90	6.72	0.3532	0.1144
0.70 - 0.69	641	641	100.0	22.40	1.90	6.46	0.3693	0.1212
0.69 - 0.68	691	691	100.0	22.15	1.91	6.17	0.3709	0.1245
0.68 - 0.67	715	715	100.0	21.93	1.91	5.96	0.3738	0.1278
0.77 - 0.67	5716	5716	100.0	24.56	2.20	7.75	0.3176	0.0983
Inf - 0.67	16986	16993	100.0	35.69	7.81	20.44	0.0974	0.0310

NoSpherA2.^[324] DFT-calculated with ORCA using a B3LYP functional and def2-TZVPP basis set, whereby the H atom positions were refined using anisotropic atomic displacement parameters.

NoSpherA2 implementation of HAR makes use of tailor-made aspherical atomic form factors calculated on-the-fly from a Hirshfeld-partitioned electron density (ED) - not from spherical-atom form factors. The ED is calculated from a gaussian basis set single determinant SCF wave function - either Hartree-Fock or DFT using selected functional - for a fragment of the crystal. This fragment can be embedded in an electrostatic crystal field by employing cluster charges or modelled using implicit solvation models, depending on the software used. The following options were used:

SOFTWARE:	ORCA 5.0
PARTITIONING:	NoSpherA2
INT ACCURACY:	Normal
METHOD:	B3LYP
BASIS SET:	def2-TZVPP
CHARGE:	0
MULTIPLICITY:	1
DATE:	2024-10-10_14-17-54

Table S 18: Crystal data and structure refinement of **211**.

Identification code	15449	
Empirical formula	C ₁₁₅ H ₉₈ B ₂ O ₆ Si ₆	
Color	colourless	
Formula weight	1766.217 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n, (no. 14)	
Unit cell dimensions	a = 21.131(9) Å	α = 90°.
	b = 10.003(4) Å	β = 113.890(9)°.
	c = 24.012(10) Å	γ = 90°.
Volume	4640(3) Å ³	
Z	2	
Density (calculated)	1.264 Mg·m ⁻³	
Absorption coefficient	0.149 mm ⁻¹	
F(000)	1861.922 e	
Crystal size	0.107 x 0.071 x 0.040 mm ³	
θ range for data collection	2.24 to 32.07°.	
Index ranges	-31 ≤ h ≤ 31, -14 ≤ k ≤ 14, -35 ≤ l ≤ 35	
Reflections collected	588053	
Independent reflections	16168 [R _{int} = 0.1023]	
Reflections with I > 2σ(I)	12750	
Completeness to θ = 25.2417°	99.88 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9922 and 0.9481	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	16168 / 119 / 1042	
Goodness-of-fit on F ²	1.0978	
Final R indices [I > 2σ(I)]	R ₁ = 0.0238	wR ² = 0.0404
R indices (all data)	R ₁ = 0.0412	wR ² = 0.0472
Largest diff. peak and hole	0.3022 and -0.2539 e·Å ⁻³	

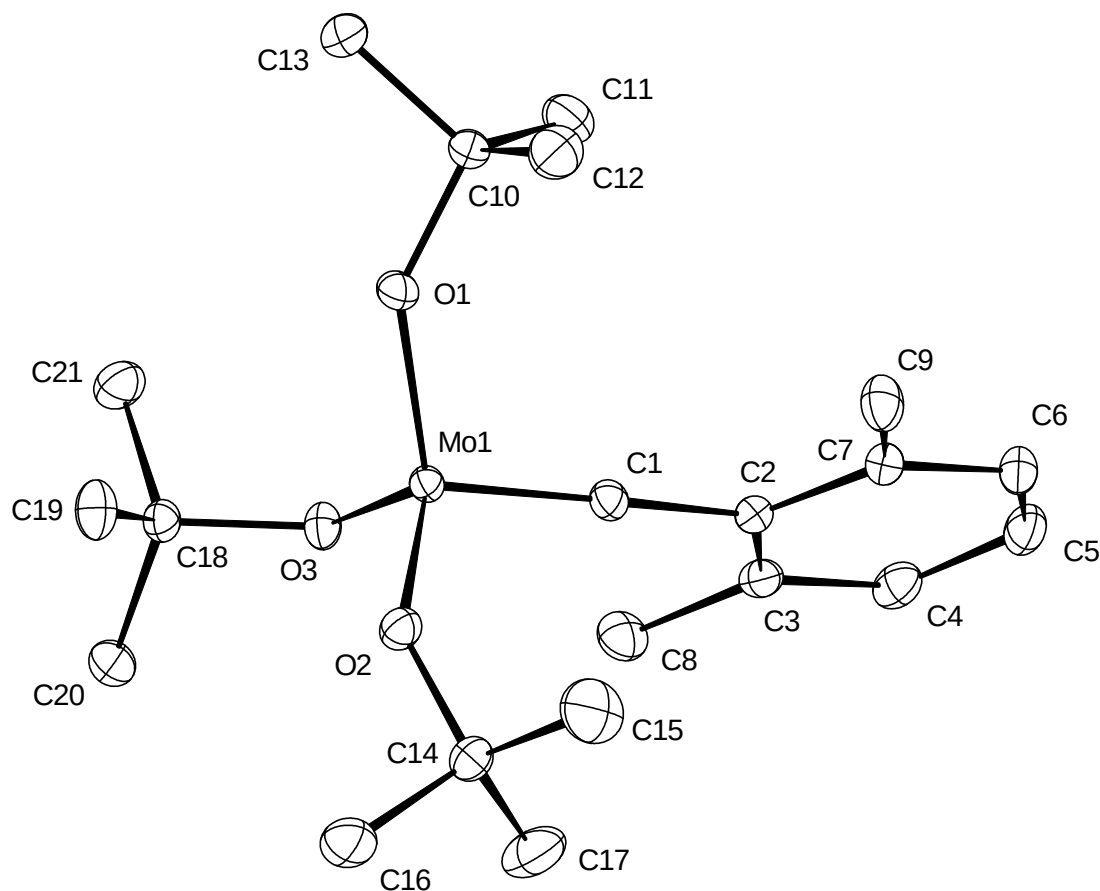
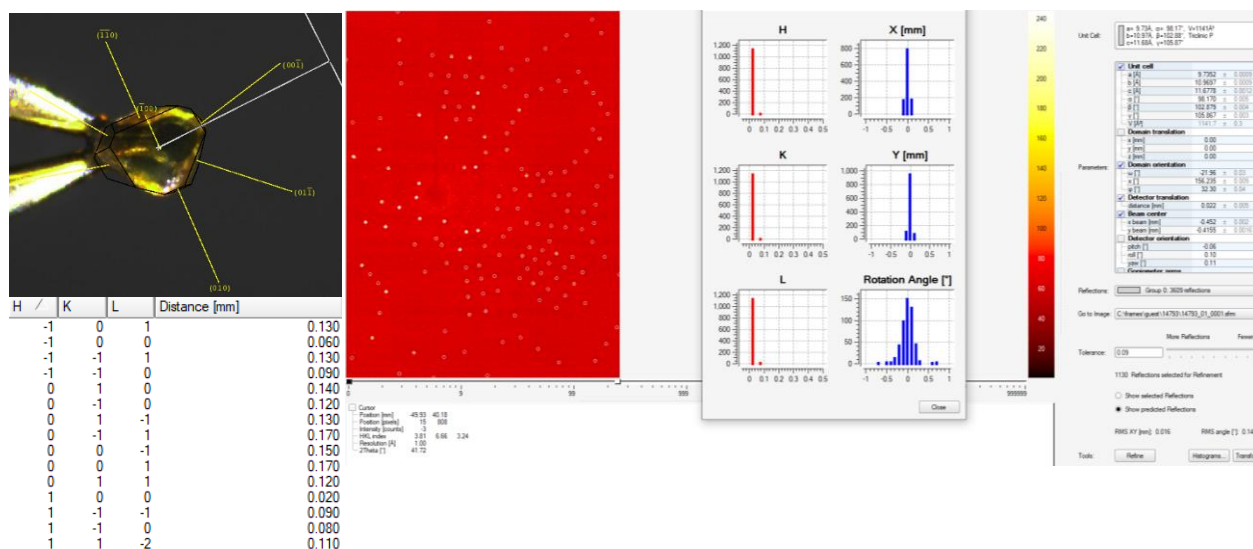
Single Crystal Structure analysis of **18b**

Figure S 37: The molecular structure of **18b**. H atoms have been removed for clarity.

X-ray Crystal Structure Analysis of **18b**:

$C_{21}H_{36}MoO_3$, $M_r = 432.44 \text{ g mol}^{-1}$, yellow prism, crystal size $0.335 \times 0.324 \times 0.12 \text{ mm}^3$, triclinic, space group $P-1$ [2], $a = 9.695(2) \text{ \AA}$, $b = 10.945(3) \text{ \AA}$, $c = 11.647(3) \text{ \AA}$, $\alpha = 98.330(10)^\circ$, $\beta = 102.841(9)^\circ$, $\gamma = 105.806(10)^\circ$, $V = 1131.3(4) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $D_{calc} = 1.270 \text{ g}\cdot\text{cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.594 \text{ mm}^{-1}$, numerical absorption correction ($T_{min} = 0.8630$, $T_{max} = 0.9569$), Bruker AXS D8-Venture diffractometer with I μ S Diamond Mo-anode X-ray source and PHOTON III detector, $1.982 < \theta < 33.345^\circ$, 198517 measured reflections, 8706 independent reflections, 8284 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0421$. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0163$ [$I > 2\sigma(I)$], $wR_2 = 0.0428$ [all data], 237 parameters and 0 restraints.

Full .cif data for the compound are available under the CCDC number CCDC 2293662.

Figure S38. Crystal faces and unit cell determination/refinement of compound **18b**.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.56	131	142	92.3	32.64	200.75	145.61	0.0277	0.0088
2.56 - 1.74	311	311	100.0	40.10	137.28	136.75	0.0268	0.0058
1.74 - 1.38	445	445	100.0	38.74	104.38	128.57	0.0287	0.0064
1.38 - 1.21	431	431	100.0	31.47	81.89	103.65	0.0319	0.0076
1.21 - 1.10	448	448	100.0	27.66	57.79	86.84	0.0376	0.0091
1.10 - 1.02	460	460	100.0	26.25	47.69	76.43	0.0428	0.0101
1.02 - 0.96	440	440	100.0	25.25	44.57	72.25	0.0463	0.0110
0.96 - 0.91	463	463	100.0	24.37	38.97	65.38	0.0483	0.0120
0.91 - 0.87	472	472	100.0	23.42	34.18	60.30	0.0536	0.0132
0.87 - 0.84	383	383	100.0	22.96	31.71	55.67	0.0561	0.0141
0.84 - 0.81	464	464	100.0	21.47	28.03	49.62	0.0619	0.0161
0.81 - 0.79	352	352	100.0	21.03	26.27	46.99	0.0672	0.0170
0.79 - 0.76	600	600	100.0	19.67	23.90	41.98	0.0669	0.0190
0.76 - 0.74	435	435	100.0	17.71	23.22	37.77	0.0717	0.0213
0.74 - 0.72	509	509	100.0	17.61	19.61	33.83	0.0805	0.0238
0.72 - 0.71	275	275	100.0	17.57	18.43	31.69	0.0820	0.0252
0.71 - 0.69	565	565	100.0	17.21	17.07	29.06	0.0881	0.0274
0.69 - 0.68	343	343	100.0	16.88	15.34	26.36	0.0983	0.0308
0.68 - 0.67	334	334	100.0	16.75	14.56	24.80	0.1017	0.0325
0.67 - 0.65	846	888	95.3	13.67	13.43	20.69	0.1111	0.0487
0.75 - 0.65	3113	3155	98.7	16.25	16.44	27.47	0.0913	0.0316
Inf - 0.65	8707	8760	99.4	22.66	41.04	58.32	0.0420	0.0131

One reflection was shadowed by the beamstop and omitted (OMIT 0 0 1) from data set before the final refinement cycles due to high $I/\sigma I$ (> 10).

Table S 19: Crystal data and structure refinement of compound **18b**.

Identification code	14793	
Empirical formula	C ₂₁ H ₃₆ Mo O ₃	
Color	yellow	
Formula weight	432.44 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1, (no. 2)	
Unit cell dimensions	a = 9.695(2) Å	α = 98.330(10)°.
	b = 10.945(3) Å	β = 102.841(9)°.
	c = 11.647(3) Å	γ = 105.806(10)°.
Volume	1131.3(4) Å ³	
Z	2	
Density (calculated)	1.270 Mg·m ⁻³	
Absorption coefficient	0.594 mm ⁻¹	
F(000)	456 e	
Crystal size	0.335 x 0.324 x 0.12 mm ³	
θ range for data collection	1.982 to 33.345°.	
Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17	
Reflections collected	198517	
Independent reflections	8706 [R _{int} = 0.0421]	
Reflections with I > 2σ(I)	8284	
Completeness to θ = 25.242°	99.7 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9569 and 0.8630	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8706 / 0 / 237	
Goodness-of-fit on F ²	1.078	
Final R indices [I > 2σ(I)]	R ₁ = 0.0163	wR ² = 0.0423
R indices (all data)	R ₁ = 0.0179	wR ² = 0.0428
Extinction coefficient	n/a	
Largest diff. peak and hole	0.474 and -0.419 e·Å ⁻³	

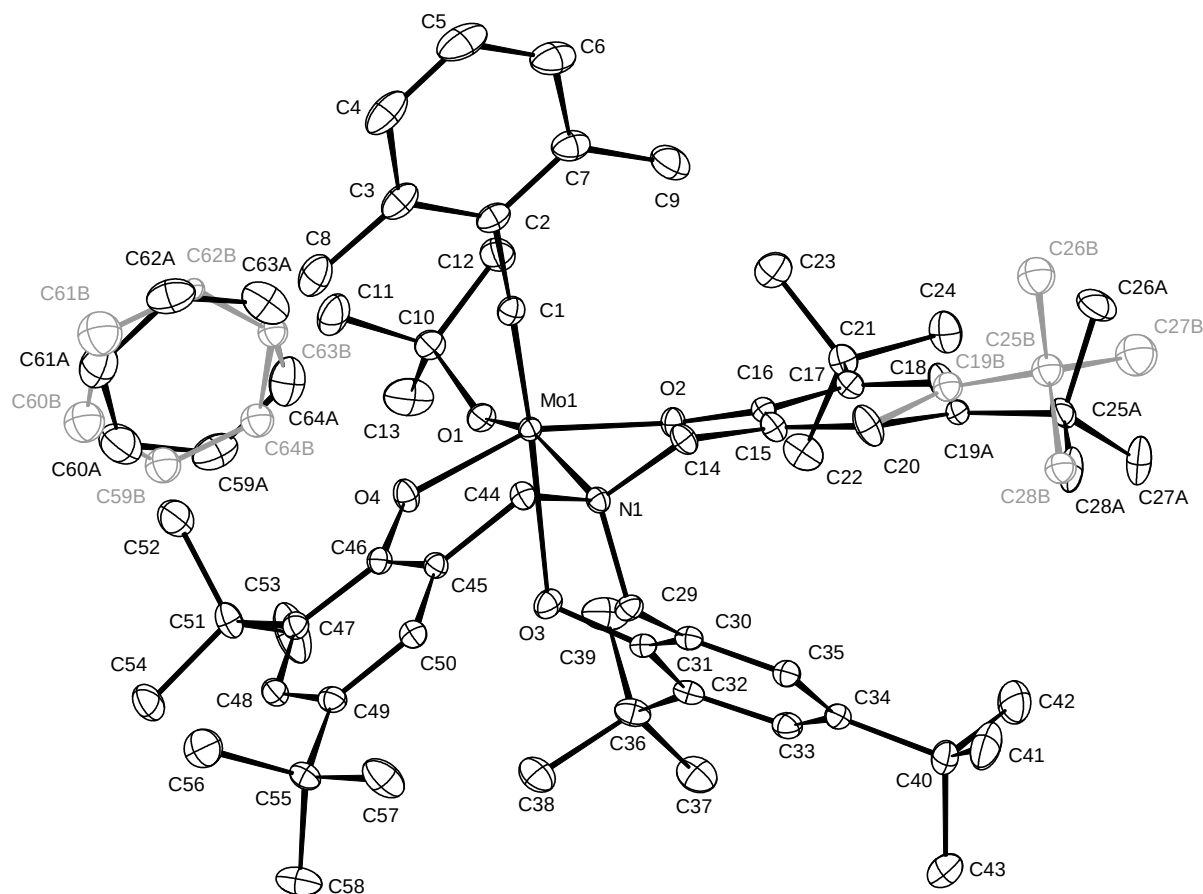
Single Crystal Structure analysis of **118**

Figure S 39: The molecular structure of **118** benzene solvate. H atoms have been removed for clarity. Main structure shown in black and disordered parts shown in grey.

X-ray Crystal Structure Analysis of **118** benzene solvate:

$C_{64}H_{91}MoNO_4$, $M_r = 1034.31 \text{ g mol}^{-1}$, orange block, crystal size $0.14 \times 0.081 \times 0.081 \text{ mm}^3$, monoclinic, space group $P2_1/n$ [14], $a = 14.2159(8) \text{ \AA}$, $b = 18.0559(10) \text{ \AA}$, $c = 22.4512(13) \text{ \AA}$, $\beta = 90.396(2)^\circ$, $V = 5762.7(6) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $D_{calc} = 1.192 \text{ g cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.274 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.8992$, $T_{max} = 1.0000$), Bruker-AXS Kappa Mach3 with APEX-II detector and I μ S microfocus Mo-anode X-ray source, $1.447 < \theta < 30.998^\circ$, 192900 measured reflections, 18380 independent reflections, 14663 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0696$. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0327$ [$I > 2\sigma(I)$], $wR_2 = 0.0798$ [all data], 693 parameters and 0 restraints.

Full .cif data for the compound are available under the CCDC number CCDC 2293663.

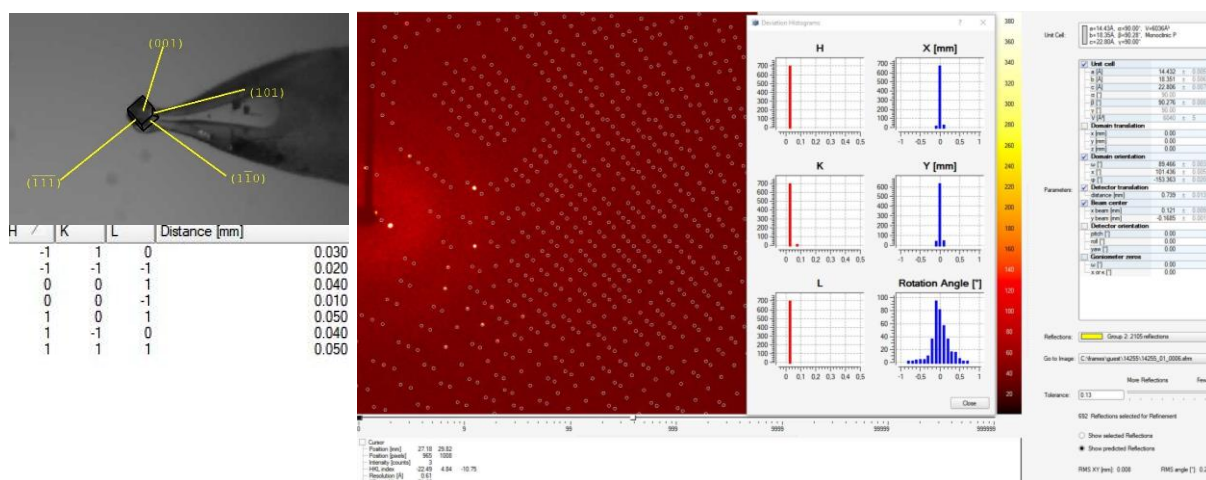


Figure S 40: Crystal faces and unit cell determination/refinement of compound **118** benzene solvate.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.78	316	316	100.0	16.75	99.90	76.14	0.0244	0.0092
2.78 - 1.84	738	738	100.0	18.09	50.35	64.50	0.0315	0.0106
1.84 - 1.45	1049	1049	100.0	18.29	31.44	54.83	0.0414	0.0127
1.45 - 1.26	1081	1081	100.0	18.16	23.95	46.28	0.0519	0.0152
1.26 - 1.14	1095	1095	100.0	17.54	20.16	40.05	0.0632	0.0176
1.14 - 1.06	1020	1020	100.0	14.89	16.52	30.72	0.0756	0.0230
1.06 - 1.00	993	993	100.0	11.74	14.10	24.88	0.0869	0.0299
1.00 - 0.95	1017	1017	100.0	10.15	12.65	20.98	0.0980	0.0354
0.95 - 0.91	1025	1025	100.0	8.91	10.84	17.74	0.1120	0.0427
0.91 - 0.87	1184	1184	100.0	7.99	9.81	15.40	0.1244	0.0497
0.87 - 0.84	1029	1029	100.0	7.69	8.74	13.56	0.1357	0.0573
0.84 - 0.81	1223	1223	100.0	7.34	7.74	11.67	0.1561	0.0660
0.81 - 0.79	870	870	100.0	7.17	8.08	11.65	0.1575	0.0676
0.79 - 0.77	1031	1031	100.0	6.88	7.27	10.42	0.1765	0.0759
0.77 - 0.75	1079	1079	100.0	6.76	6.44	9.03	0.1983	0.0873
0.75 - 0.73	1260	1260	100.0	6.47	6.68	9.10	0.2000	0.0893
0.73 - 0.72	643	643	100.0	6.39	5.71	7.89	0.2261	0.1059
0.72 - 0.70	1453	1453	100.0	6.16	5.15	6.98	0.2562	0.1202
0.70 - 0.69	815	816	99.9	5.97	5.01	6.67	0.2697	0.1284
0.69 - 0.67	1652	1700	97.2	4.98	4.48	5.35	0.3024	0.1779
0.67 - 0.66	250	562	44.5	0.81	3.07	1.77	0.4402	0.6185
0.76 - 0.66	6625	6986	94.8	5.54	5.31	6.97	0.2440	0.1326
Inf - 0.66	20823	21184	98.3	9.67	13.83	20.99	0.0692	0.0394

A resolution cut off (SHEL 999 0.69) was applied to exclude poorly determined intensities at high diffraction angles. A 'Bu substituted aromatic subgroup shows a slight twofold positional disorder. This has been described with fixed occupancies of 65:35% respectively. Another twofold positional disorder can be found in the solute benzene molecule. This was described with a fixed occupancy of 90:10% and AFIX was used to fit the minor part into a hexagonal shape. Isotropic atomic displacement parameters were used to describe the minor moieties. In addition, the H position in the vicinity of the O3 atom could be located in the residual electron density map and its position was freely refined. An additional indication of the position of a H atom bonded to O3 is given by the difference in bond length of Mo(1)-O(3): 2.4717(10) Å compared to the Mo(1)-O(2): 1.9628(9) Å and Mo(1)-O(4): 2.0000(9) Å bonds.

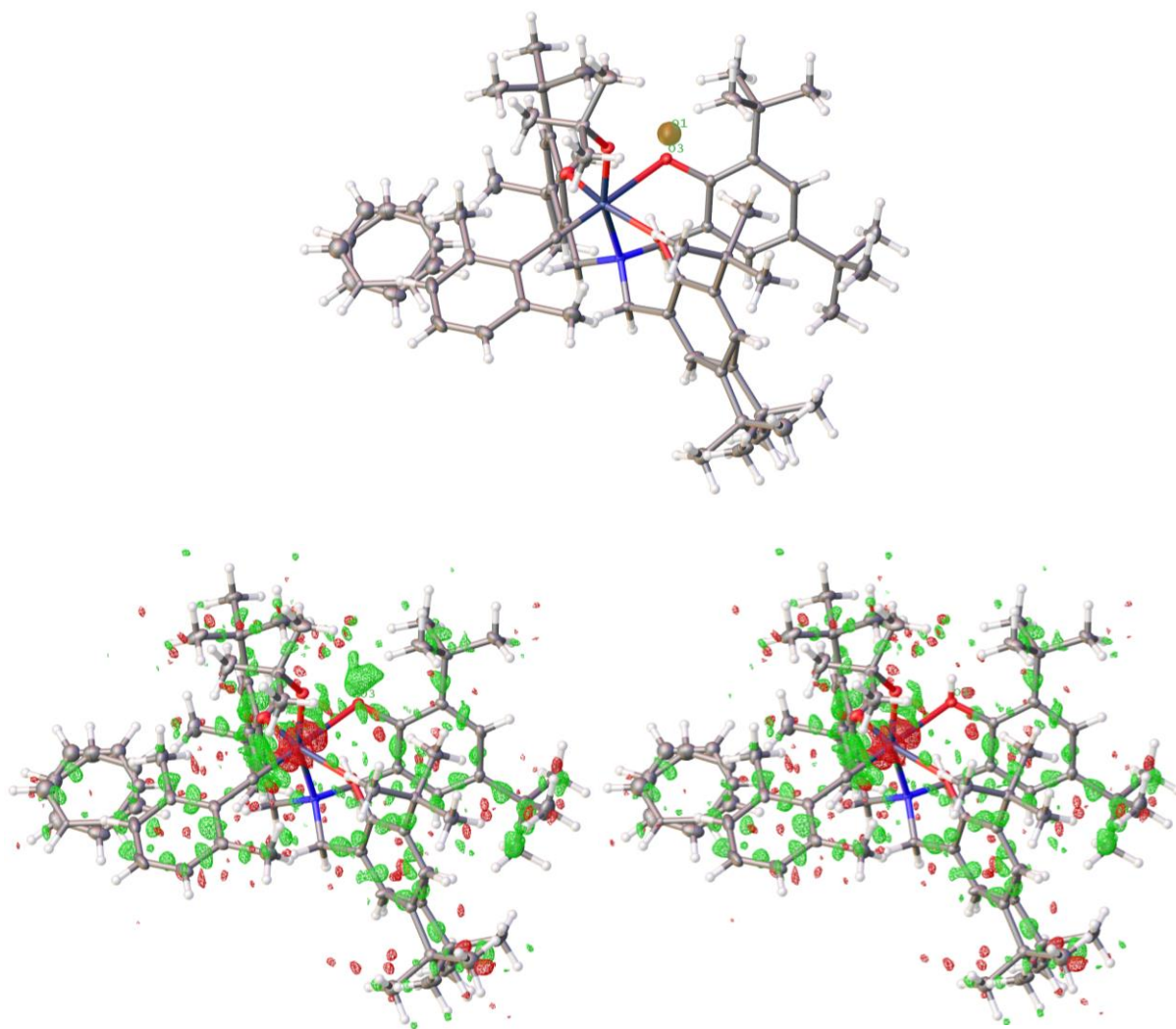


Figure S 41: Structure (top) and residual electron density peak (brown sphere) of $0.78 \text{ e}/\text{\AA}^{-3}$ in the vicinity of O3. Difference density distribution (bottom) of compound **118** before (left) and after (right) adding a H atom to O3 (source: Olex2, diff-map, level $0.3 \text{ e}/\text{\AA}^3$, $0.1 \text{ \AA}$ resolution).

Table S 20: Crystal data and structure refinement of compound **118** benzene solvate.

Identification code	14255	
Empirical formula	C ₆₄ H ₉₁ Mo N O ₄	
Color	orange	
Formula weight	1034.31 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n, (no. 14)	
Unit cell dimensions	a = 14.2159(8) Å	α = 90°.
	b = 18.0559(10) Å	β = 90.396(2)°.
	c = 22.4512(13) Å	γ = 90°.
Volume	5762.7(6) Å ³	
Z	4	
Density (calculated)	1.192 Mg·m ⁻³	
Absorption coefficient	0.274 mm ⁻¹	
F(000)	2224 e	
Crystal size	0.14 x 0.081 x 0.081 mm ³	
θ range for data collection	1.447 to 30.998°.	
Index ranges	-20 ≤ h ≤ 20, -26 ≤ k ≤ 26, -32 ≤ l ≤ 32	
Reflections collected	192900	
Independent reflections	18380 [R _{int} = 0.0696]	
Reflections with I > 2σ(I)	14663	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.0000 and 0.8992	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	18380 / 0 / 693	
Goodness-of-fit on F ²	1.028	
Final R indices [I > 2σ(I)]	R ₁ = 0.0327	wR ² = 0.0728
R indices (all data)	R ₁ = 0.0502	wR ² = 0.0798
Extinction coefficient	n/a	
Largest diff. peak and hole	0.467 and -0.536 e·Å ⁻³	

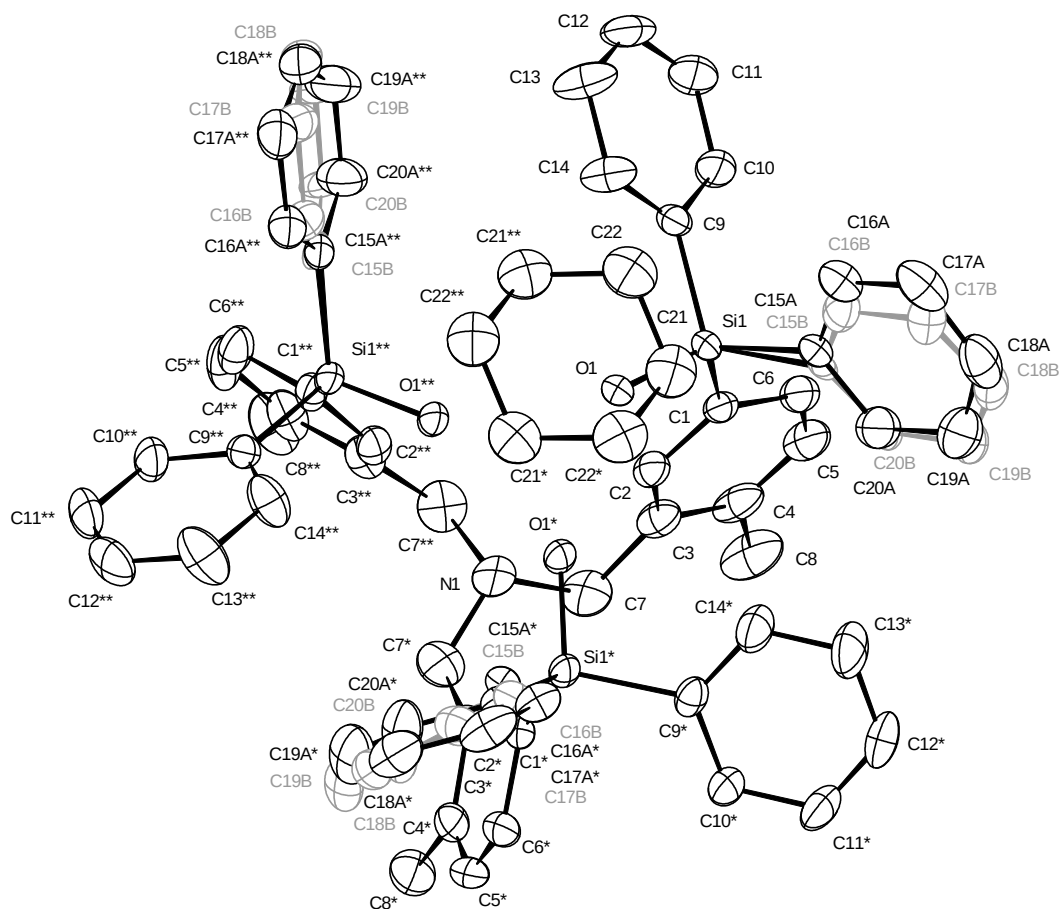
Single Crystal Structure analysis of **116b**

Figure S 42: The molecular structure of **116b** cyclohexane solvate. H atoms have been removed for clarity. Main structure shown in black and disordered parts shown in grey.

X-ray Crystal Structure Analysis of **116b** cyclohexane solvate:

$C_{66}H_{69}NO_3Si_3$, $M_r = 1008.49 \text{ g mol}^{-1}$, colourless plate, crystal size $0.17 \times 0.12 \times 0.05 \text{ mm}^3$, trigonal, space group $R\bar{3}$ [148], $a = 14.2662(11) \text{ \AA}$, $c = 49.894(2) \text{ \AA}$, $V = 8794.1(14) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 6$, $D_{\text{calc}} = 1.143 \text{ g cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.436 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{\text{min}} = 0.95533$, $T_{\text{max}} = 0.99219$), Bruker AXS Enraf-Nonius KappaCCD diffractometer with a FR591 rotating Mo-anode X-ray source, $3.300 < \theta < 30.503^\circ$, 67174 measured reflections, 5982 independent reflections, 4120 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.0744$. The structure was solved by *SHELXS* and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0587$ [$I > 2\sigma(I)$], $wR_2 = 0.1356$ [all data], 277 parameters and 72 restraints.

Full .cif data for the compound are available under the CCDC number CCDC 2293659.

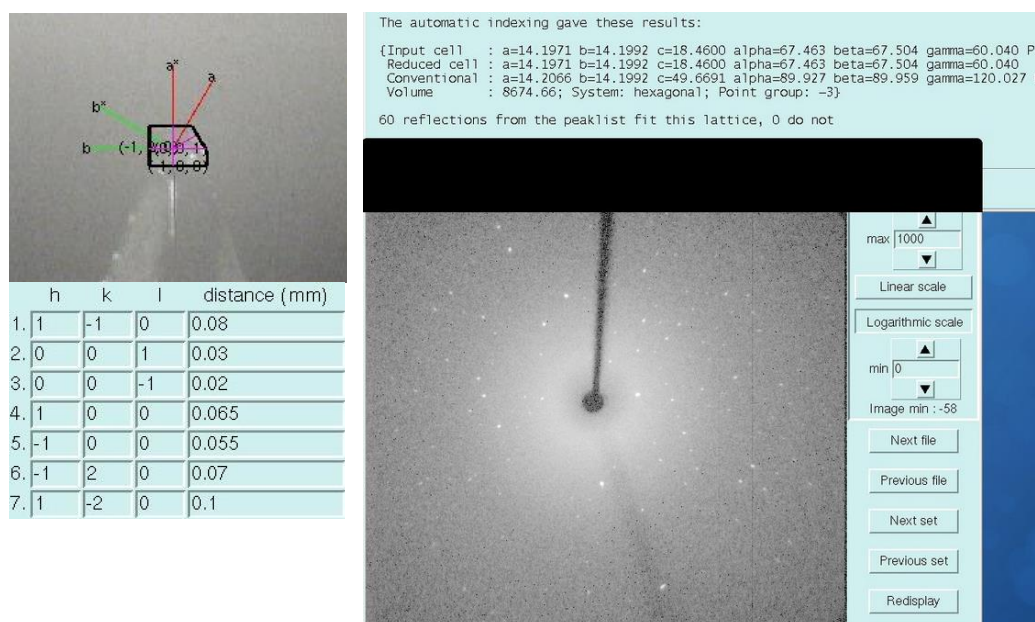


Figure S43. Crystal faces and unit cell determination/refinement of compound **116b** cyclohexane solvate.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.69	102	110	92.7	17.08	103.14	100.46	0.0299	0.0079
2.69 - 1.80	241	241	100.0	19.36	32.34	72.92	0.0324	0.0090
1.80 - 1.44	338	338	100.0	18.68	12.95	48.12	0.0457	0.0140
1.44 - 1.26	344	344	100.0	16.72	11.97	38.68	0.0487	0.0174
1.26 - 1.14	360	360	100.0	15.32	9.83	30.96	0.0606	0.0223
1.14 - 1.06	333	333	100.0	14.14	5.65	20.41	0.0906	0.0353
1.06 - 1.00	342	342	100.0	13.16	3.82	14.37	0.1285	0.0516
1.00 - 0.95	326	326	100.0	12.33	4.04	13.84	0.1312	0.0547
0.95 - 0.91	340	340	100.0	11.80	3.02	10.76	0.1663	0.0731
0.91 - 0.87	392	392	100.0	11.13	2.82	9.74	0.1923	0.0847
0.87 - 0.84	328	328	100.0	10.74	2.17	7.47	0.2449	0.1121
0.84 - 0.82	283	283	100.0	9.51	1.78	5.84	0.3133	0.1489
0.82 - 0.79	428	428	100.0	7.97	1.78	4.97	0.3046	0.1685
0.79 - 0.77	341	341	100.0	6.90	1.63	4.13	0.3257	0.2031
0.77 - 0.75	363	363	100.0	6.75	1.18	3.01	0.4489	0.2897
0.75 - 0.73	407	407	100.0	6.39	1.10	2.65	0.4601	0.3342
0.73 - 0.72	223	223	100.0	6.44	0.85	2.04	0.5499	0.4384
0.72 - 0.70	494	494	100.0	6.12	0.82	1.90	0.5931	0.4861
0.70 - 0.69	260	260	100.0	6.01	0.78	1.70	0.6305	0.5442
0.69 - 0.68	265	265	100.0	5.88	0.82	1.75	0.6201	0.5357
0.68 - 0.67	275	276	99.6	5.50	0.73	1.43	0.6814	0.6534
0.77 - 0.67	2287	2288	100.0	6.18	0.91	2.13	0.5459	0.4358
Inf - 0.67	6785	6794	99.9	10.57	6.13	15.44	0.0726	0.0492

A resolution cut off (SHEL 999 0.7) was applied to exclude poorly determined reflections at high diffraction angles. Three reflections (OMIT 0 1 5; OMIT -2 2 2; OMIT 0 1 8) with high $I/\sigma(I)$ were excluded before the final refinement cycles. One terminal phenyl ring shows a disorder over two positions. It was refined using a free variable (FVAR) and occupancies of 65.747:34.253% were determined. The ISOR (0.01 0.02) instruction was used equalise the thermal ellipsoids of the disordered parts. In addition, the structure contains a second cyclohexane molecule that is located on a crystallographic special position. Due to the disorder over several positions, a proper refinement was

not suitable. Therefore, a solvent mask (SQUEEZE routine in Olex2) was applied to exclude the remaining electron density. This procedure resulted in a structure model with a void volume of 447.58 Å³, corresponding to 5.1% of the unit cell volume (calculated with Mercury 2021.2.0 program, probe radius of 1.2 Å and an approximate grid spacing of 0.7 Å).

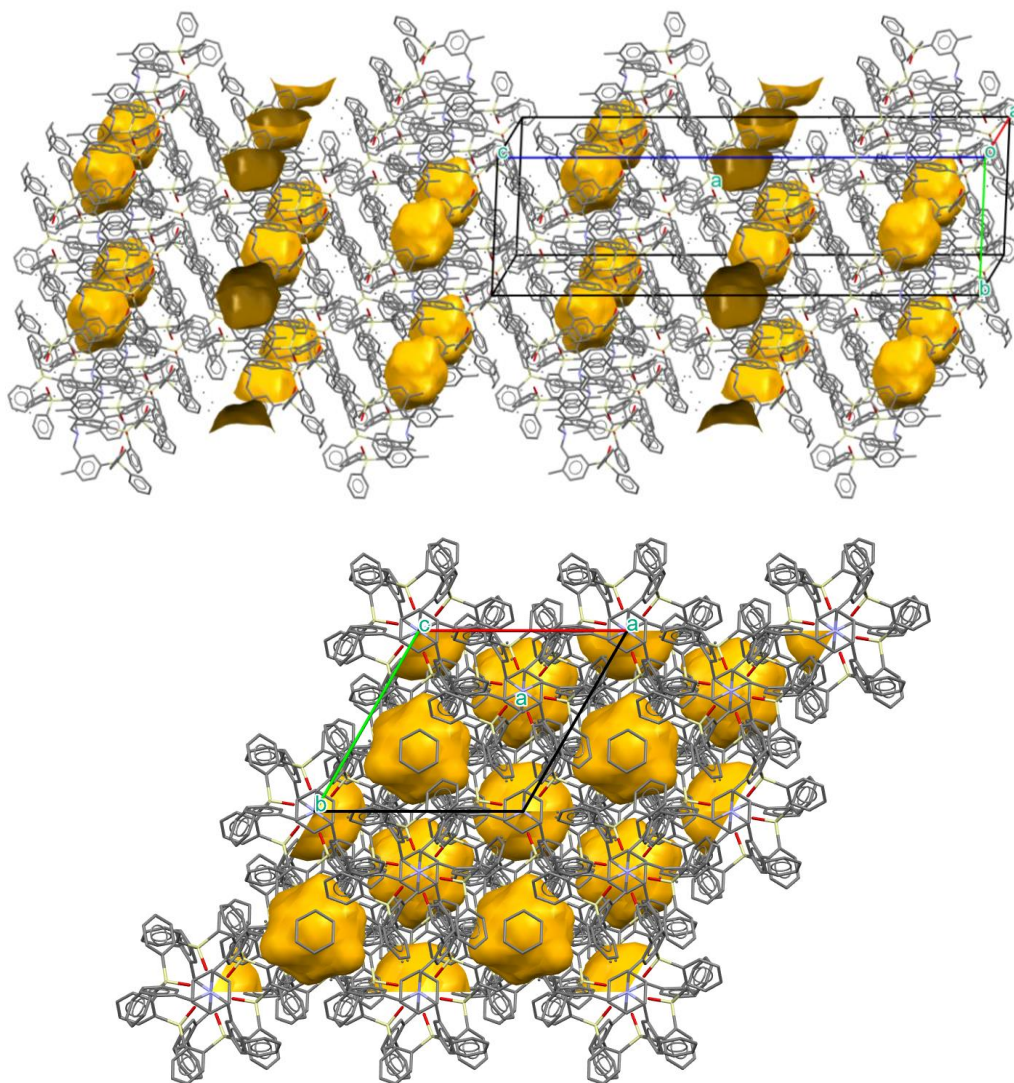


Figure S44. Solvent accessible voids (orange brown surface) in the structure of **116b** cyclohexane solvate in a random orientation (top) and along the crystallographic c axis (bottom).

Table S 21: Crystal data and structure refinement of compound **116b** cyclohexane solvate.

Identification code	10535	
Empirical formula	C ₆₆ H ₆₉ N O ₃ Si ₃	
Color	colorless	
Formula weight	1008.49 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R-3, (no. 148)	
Unit cell dimensions	a = 14.2662(11) Å	α = 90°.
	b = 14.2662(11) Å	β = 90°.
	c = 49.894(2) Å	γ = 120°.
Volume	8794.1(14) Å ³	
Z	6	
Density (calculated)	1.143 Mg·m ⁻³	
Absorption coefficient	0.126 mm ⁻¹	
F(000)	3228 e	
Crystal size	0.17 x 0.12 x 0.05 mm ³	
θ range for data collection	3.300 to 30.503°.	
Index ranges	-19 ≤ h ≤ 20, -20 ≤ k ≤ 20, -71 ≤ l ≤ 71	
Reflections collected	67174	
Independent reflections	5982 [R _{int} = 0.0744]	
Reflections with I > 2σ(I)	4120	
Completeness to θ = 25.242°	99.7 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99412 and 0.98250	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5982 / 72 / 277	
Goodness-of-fit on F ²	1.035	
Final R indices [I > 2σ(I)]	R ₁ = 0.0587	wR ² = 0.1200
R indices (all data)	R ₁ = 0.0954	wR ² = 0.1356
Extinction coefficient	n/a	
Largest diff. peak and hole	0.352 and -0.378 e·Å ⁻³	

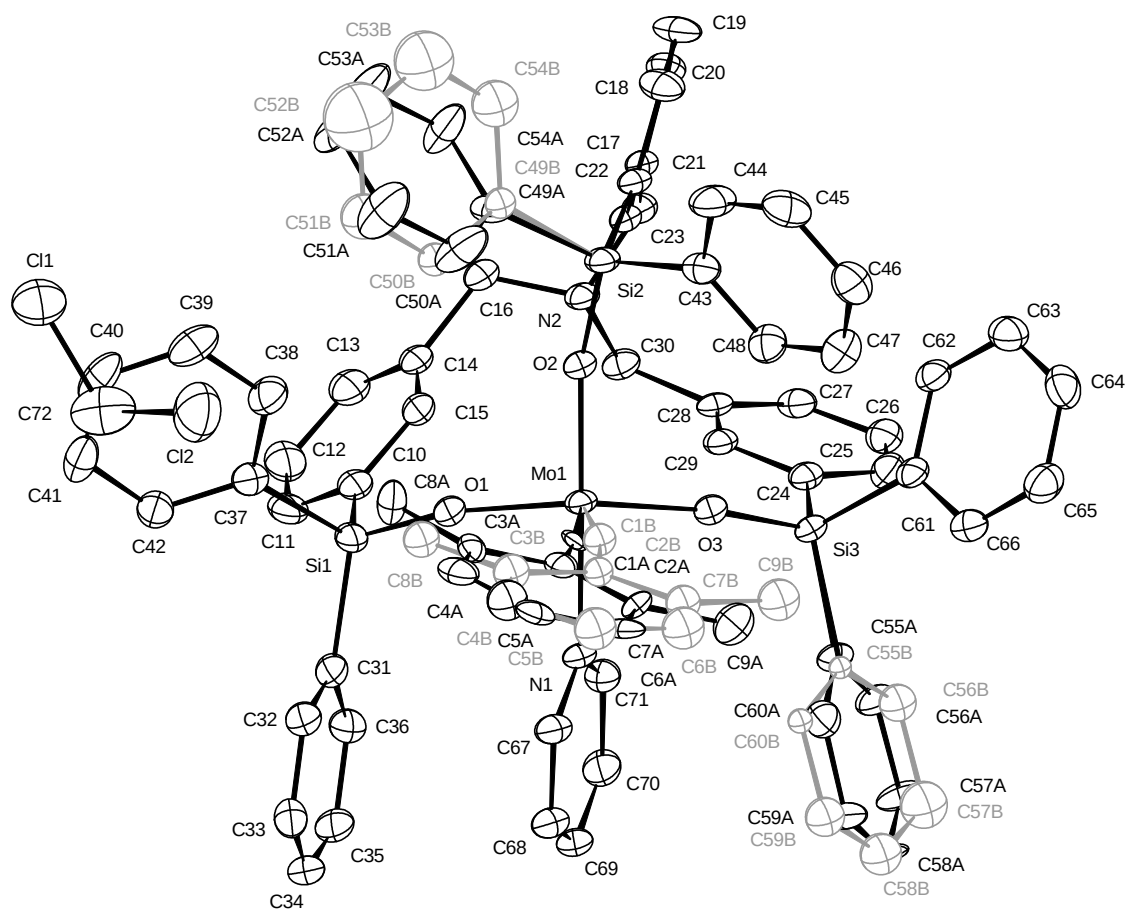
Single Crystal Structure analysis of **139a•Py**

Figure S45. The molecular structure of **139a•Py** dichloromethane solvate. H atoms have been removed for clarity. Main structure shown in black and disordered parts shown in grey.

X-ray Crystal Structure Analysis of **139a•Py** dichloromethane solvate:

$C_{72}H_{64}Cl_2MoN_2O_3Si_3$, $M_r = 1256.36 \text{ g mol}^{-1}$, violet plate, crystal size $0.153 \times 0.05 \times 0.007 \text{ mm}^3$, monoclinic, space group $P2_1/c$ [14], $a = 20.887(3) \text{ \AA}$, $b = 12.7056(18) \text{ \AA}$, $c = 26.768(4) \text{ \AA}$, $\beta = 107.864(3)^\circ$, $V = 6761.2(16) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $D_{calc} = 1.234 \text{ g}\cdot\text{cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.372 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.97410$, $T_{max} = 0.99858$), Bruker-AXS Kappa Mach3 with APEX-II detector and I μ S microfocus Mo-anode X-ray source, $1.599 < \theta < 26.732^\circ$, 143560 measured reflections, 14302 independent reflections, 9833 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0972$. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0493$ [$I > 2\sigma(I)$], $wR_2 = 0.1216$ [all data], 812 parameters and 36 restraints.

Full .cif data for the compound are available under the CCDC number CCDC 2293661.

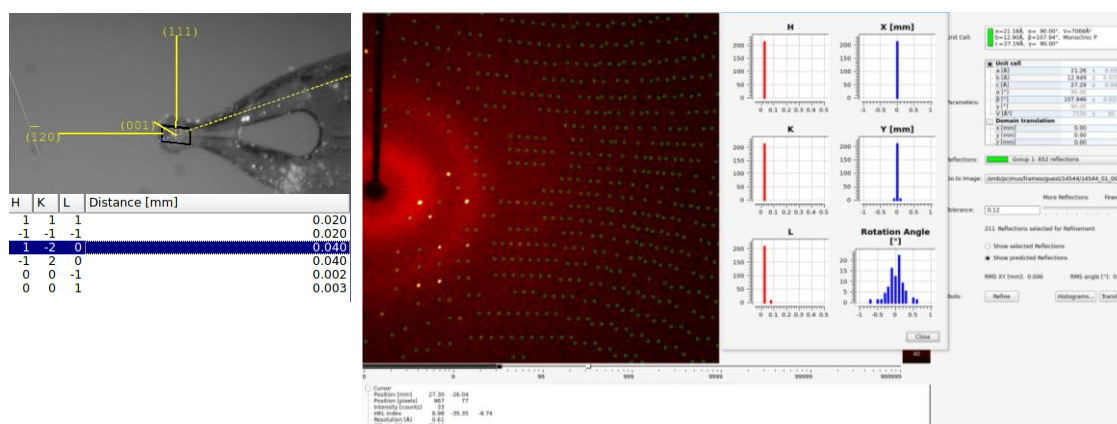


Figure S46. Crystal faces and unit cell determination/refinement of compound **139a•Py** dichloromethane solvate.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 3.31	232	233	99.6	13.52	74.18	47.72	0.0252	0.0142
3.31 - 2.17	554	554	100.0	14.98	33.88	40.71	0.0348	0.0164
2.17 - 1.72	754	754	100.0	15.30	24.54	36.42	0.0484	0.0193
1.72 - 1.49	787	787	100.0	15.37	17.90	31.19	0.0600	0.0225
1.49 - 1.35	786	786	100.0	15.39	13.70	26.79	0.0762	0.0273
1.35 - 1.25	780	780	100.0	15.20	13.08	24.25	0.0861	0.0299
1.25 - 1.18	728	728	100.0	14.88	10.22	19.49	0.1069	0.0373
1.18 - 1.11	908	908	100.0	14.23	8.40	16.68	0.1256	0.0458
1.11 - 1.06	766	766	100.0	11.32	8.14	13.58	0.1390	0.0595
1.06 - 1.02	784	784	100.0	9.50	6.24	9.70	0.1777	0.0891
1.02 - 0.99	641	641	100.0	8.46	5.56	8.08	0.2062	0.1082
0.99 - 0.96	750	750	100.0	7.71	5.34	7.28	0.2136	0.1218
0.96 - 0.93	831	831	100.0	6.96	4.55	6.04	0.2446	0.1522
0.93 - 0.90	920	920	100.0	6.28	4.36	5.19	0.2713	0.1728
0.90 - 0.88	719	719	100.0	5.82	3.64	4.19	0.3111	0.2164
0.88 - 0.86	770	770	100.0	5.62	3.51	3.97	0.3286	0.2318
0.86 - 0.84	823	823	100.0	5.54	3.26	3.62	0.3582	0.2561
0.84 - 0.82	926	926	100.0	5.33	3.08	3.28	0.3756	0.2843
0.82 - 0.81	506	506	100.0	5.37	2.81	2.93	0.4152	0.3108
0.81 - 0.79	1017	1060	95.9	4.64	2.11	2.13	0.4837	0.4491
0.79 - 0.78	422	677	62.3	1.45	2.28	1.48	0.4529	0.6476
0.88 - 0.78	4464	4762	93.7	4.71	2.86	2.99	0.3867	0.3253
Inf - 0.78	15404	15703	98.1	9.44	9.51	13.62	0.0916	0.0691

The crystal investigated showed only moderate scattering intensities even with higher exposure times per frame. A resolution cut off (SHEL 999 0.79) was applied to exclude poorly determined intensities at higher diffraction angles. Eight reflections (OMIT 1 0 0; 22 7 2; 1 0 4; -1 0 4; -1 0 6; 3 1 3; -4 2 3; -4 2 10) with high $I/\sigma(I)$ were excluded before the final refinement cycles. The structure shows some disordered parts. Two of the phenyl rings connected to Si2 and Si3 are disordered over two positions. Both aryl rings were described with fixed occupancies of 70:30%. An AFIX instruction was applied to force one of the aryl rings into a hexagonal shape. Furthermore, the alkyne ligand attached to the Mo central atom shows a twofold positional disorder. This was described with fixed atomic occupancies of 60:40%. Isotropic displacement parameters were applied for minor parts of the disordered subunits. The

ISOR (0.008 0.02) instruction was used equalise the thermal ellipsoids of six carbon atoms in the disordered parts.

In addition, the structure contains a second solute molecule (mixture of DCM and pentane) which is located on a crystallographic special position. Due to the disorder over several positions, a proper refinement was not suitable. Therefore, a solvent mask (SQUEEZE routine in Olex2) was applied to exclude the remaining electron density. This procedure resulted in a structure model with a void volume of 719.01 Å³, corresponding to 10.6% of the unit cell volume (calculated with Mercury 2021.2.0 program, probe radius of 1.2 Å and an approximate grid spacing of 0.7 Å).

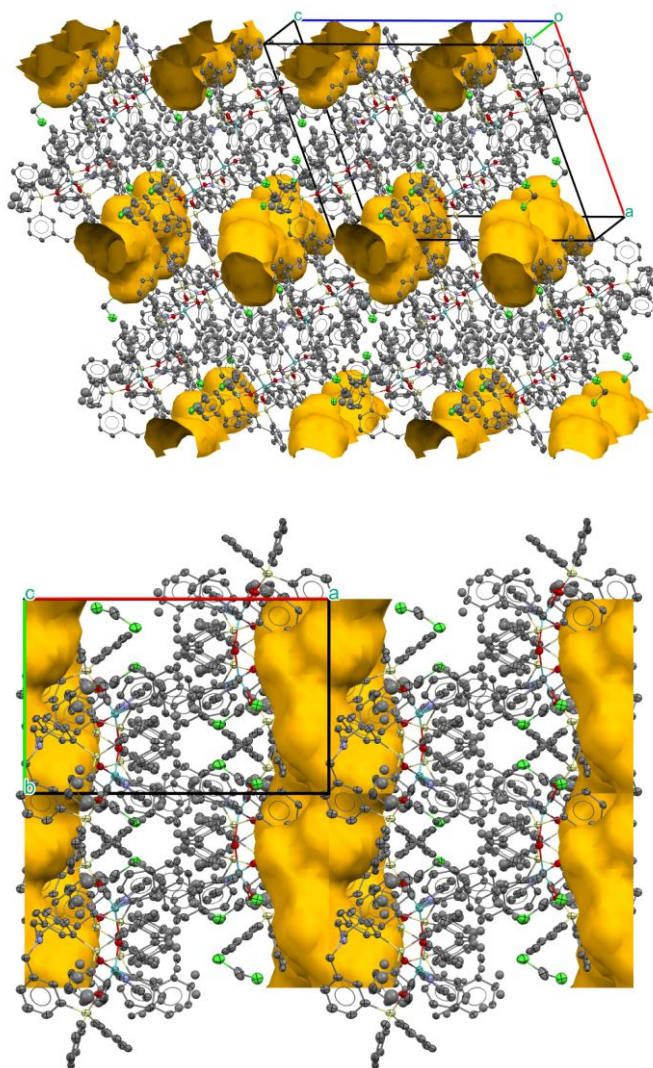


Figure S47. Solvent accessible voids (orange brown surface) in the structure of **139a•Py** dichloromethane solvate in a random orientation (top) and along the crystallographic *c* axis (bottom).

Table S22. Crystal data and structure refinement of compound **139a•Py** dichloromethane solvate.

Identification code	14544	
Empirical formula	C ₇₂ H ₆₄ Cl ₂ Mo N ₂ O ₃ Si ₃	
Color	violet	
Formula weight	1256.36 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c, (no. 14)	
Unit cell dimensions	a = 20.887(3) Å	α = 90°.
	b = 12.7056(18) Å	β = 107.864(3)°.
	c = 26.768(4) Å	γ = 90°.
Volume	6761.2(16) Å ³	
Z	4	
Density (calculated)	1.234 Mg·m ⁻³	
Absorption coefficient	0.372 mm ⁻¹	
F(000)	2608 e	
Crystal size	0.153 x 0.05 x 0.007 mm ³	
θ range for data collection	1.599 to 26.732°.	
Index ranges	-25 ≤ h ≤ 26, -16 ≤ k ≤ 16, -33 ≤ l ≤ 33	
Reflections collected	143560	
Independent reflections	14302 [R _{int} = 0.0972]	
Reflections with I > 2σ(I)	9833	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99858 and 0.97410	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14302 / 36 / 812	
Goodness-of-fit on F ²	1.021	
Final R indices [I > 2σ(I)]	R ₁ = 0.0493	wR ² = 0.1069
R indices (all data)	R ₁ = 0.0874	wR ² = 0.1216
Extinction coefficient	n/a	
Largest diff. peak and hole	0.453 and -1.027 e·Å ⁻³	

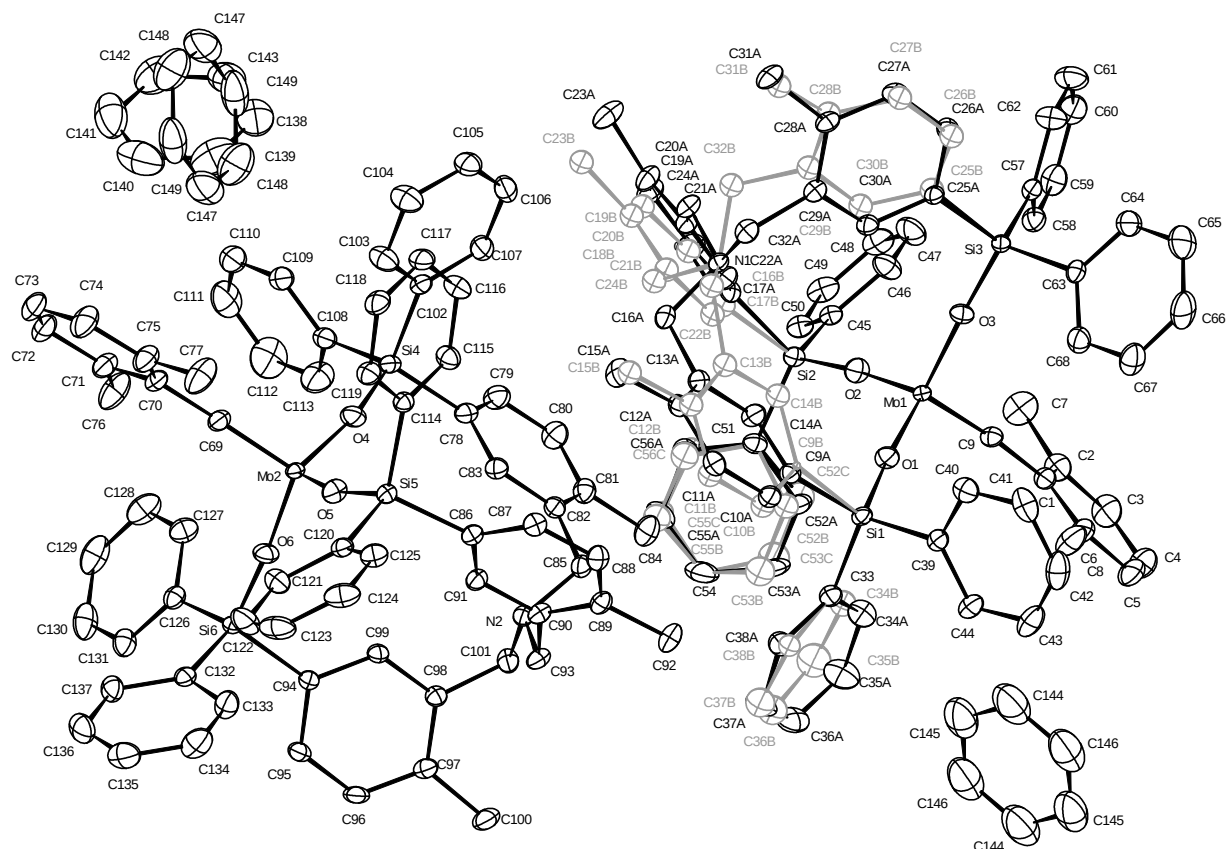
Single Crystal Structure analysis of **139b**

Figure S48. The molecular structure of **139b** benzene solvate. H atoms have been removed for clarity. Main structure shown in black and disordered parts shown in grey.

X-ray Crystal Structure Analysis of **139b** benzene solvate:

$C_{75}H_{69}MoN_2O_3Si_3$, $M_r = 1212.52 \text{ g mol}^{-1}$, yellow prism, crystal size $0.185 \times 0.141 \times 0.061 \text{ mm}^3$, triclinic, space group $P-1$ [2], $a = 14.0701(9) \text{ \AA}$, $b = 20.5423(13) \text{ \AA}$, $c = 22.8551(15) \text{ \AA}$, $\alpha = 82.019(3)^\circ$, $\beta = 78.595(3)^\circ$, $\gamma = 75.507(2)^\circ$, $V = 6241.5(7) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $D_{\text{calc}} = 1.290 \text{ g cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.317 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{\text{min}} = 0.95849$, $T_{\text{max}} = 0.98591$), Bruker-AXS Kappa Mach3 with APEX-II detector and $\text{I}\mu\text{S}$ microfocus Mo-anode X-ray source, $0.913 < \theta < 33.142^\circ$, 420731 measured reflections, 47608 independent reflections, 38271 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.0508$. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0334$ [$I > 2\sigma(I)$], $wR_2 = 0.0851$ [all data], 1584 parameters and 0 restraints.

Full .cif data for the compound are available under the CCDC number CCDC 2293664.

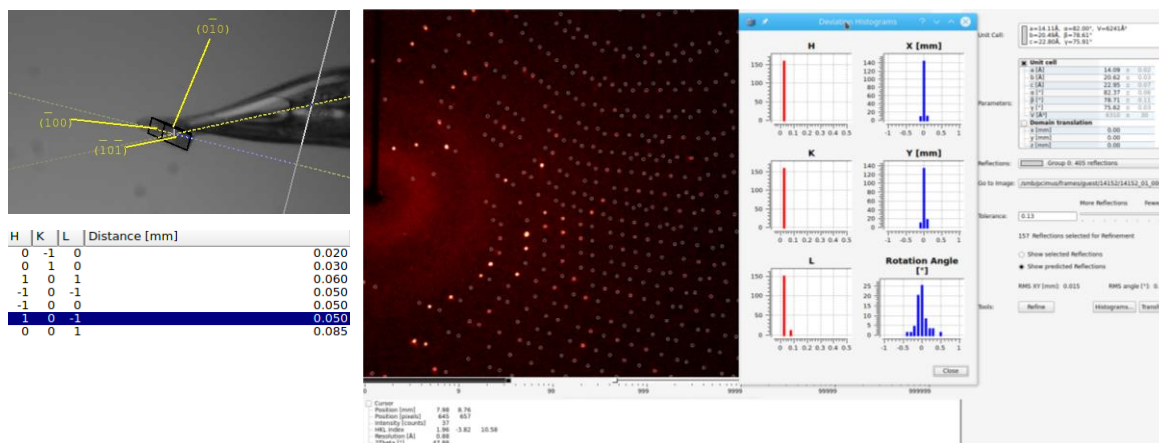


Figure S49. Crystal faces and unit cell determination/refinement of compound **139b** benzene solvate.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.57	774	774	100.0	12.76	31.08	97.77	0.0210	0.0074
2.57 - 1.72	1793	1793	100.0	14.60	13.29	82.07	0.0240	0.0085
1.72 - 1.36	2626	2626	100.0	14.74	8.99	68.07	0.0276	0.0101
1.36 - 1.19	2573	2573	100.0	14.50	7.30	56.57	0.0327	0.0120
1.19 - 1.08	2591	2591	100.0	13.29	5.16	44.40	0.0413	0.0160
1.08 - 1.00	2715	2715	100.0	10.79	4.37	34.94	0.0475	0.0209
1.00 - 0.94	2647	2647	100.0	9.45	3.42	26.82	0.0578	0.0270
0.94 - 0.89	2827	2827	100.0	8.51	3.02	23.02	0.0661	0.0323
0.89 - 0.86	2021	2021	100.0	8.04	2.94	21.27	0.0718	0.0352
0.86 - 0.82	3142	3142	100.0	7.72	2.74	19.36	0.0796	0.0394
0.82 - 0.79	2769	2769	100.0	7.40	2.44	16.89	0.0922	0.0458
0.79 - 0.77	2178	2178	100.0	7.15	2.09	14.57	0.1080	0.0547
0.77 - 0.75	2334	2334	100.0	6.92	1.78	12.28	0.1271	0.0640
0.75 - 0.73	2594	2594	100.0	6.73	1.70	11.53	0.1404	0.0702
0.73 - 0.71	2927	2927	100.0	6.51	1.62	10.51	0.1531	0.0778
0.71 - 0.69	3285	3286	100.0	6.28	1.43	9.29	0.1780	0.0910
0.69 - 0.68	1780	1782	99.9	6.07	1.32	8.46	0.1953	0.1022
0.68 - 0.66	3885	3894	99.8	5.88	1.26	7.70	0.2193	0.1118
0.66 - 0.65	2148	2157	99.6	5.69	1.11	6.68	0.2519	0.1297
0.65 - 0.64	2196	2213	99.2	5.25	1.06	6.32	0.2694	0.1445
0.64 - 0.63	1489	2518	59.1	1.57	0.83	3.33	0.3205	0.2931
0.73 - 0.63	17710	18777	94.3	5.39	1.28	7.87	0.2021	0.1145
Inf - 0.63	51294	52361	98.0	8.33	3.71	24.83	0.0505	0.0321

A resolution cut off (SHEL 999 0.7) was applied to exclude poorly determined reflections at high diffraction angles. The structure contains some disordered subunits (phenyl rings and tripodal ligand of one molecule of the asymmetric unit). These have been described as best as possible with different parts and occupancies. Isotropic atomic displacement parameters were partially applied to minor parts of the disorder. AFIX instruction was applied to force one of the aryl rings into a hexagonal shape. The correctness of the structure was also confirmed by spectroscopic methods.

Table S23. Crystal data and structure refinement of compound **139b** benzene solvate.

Identification code	14152	
Empirical formula	C ₇₅ H ₆₉ Mo N O ₃ Si ₃	
Color	yellow	
Formula weight	1212.52 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1, (no. 2)	
Unit cell dimensions	a = 14.0701(9) Å	α = 82.019(3)°.
	b = 20.5423(13) Å	β = 78.595(3)°.
	c = 22.8551(15) Å	γ = 75.507(2)°.
Volume	6241.5(7) Å ³	
Z	4	
Density (calculated)	1.290 Mg·m ⁻³	
Absorption coefficient	0.317 mm ⁻¹	
F(000)	2536 e	
Crystal size	0.185 x 0.141 x 0.061 mm ³	
θ range for data collection	0.913 to 33.142°.	
Index ranges	-21 ≤ h ≤ 21, -31 ≤ k ≤ 31, -35 ≤ l ≤ 35	
Reflections collected	420731	
Independent reflections	47608 [R _{int} = 0.0508]	
Reflections with I > 2σ(I)	38271	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98591 and 0.95849	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	47608 / 0 / 1584	
Goodness-of-fit on F ²	1.016	
Final R indices [I > 2σ(I)]	R ₁ = 0.0334	wR ² = 0.0786
R indices (all data)	R ₁ = 0.0493	wR ² = 0.0851
Extinction coefficient	n/a	
Largest diff. peak and hole	0.960 and -0.920 e·Å ⁻³	

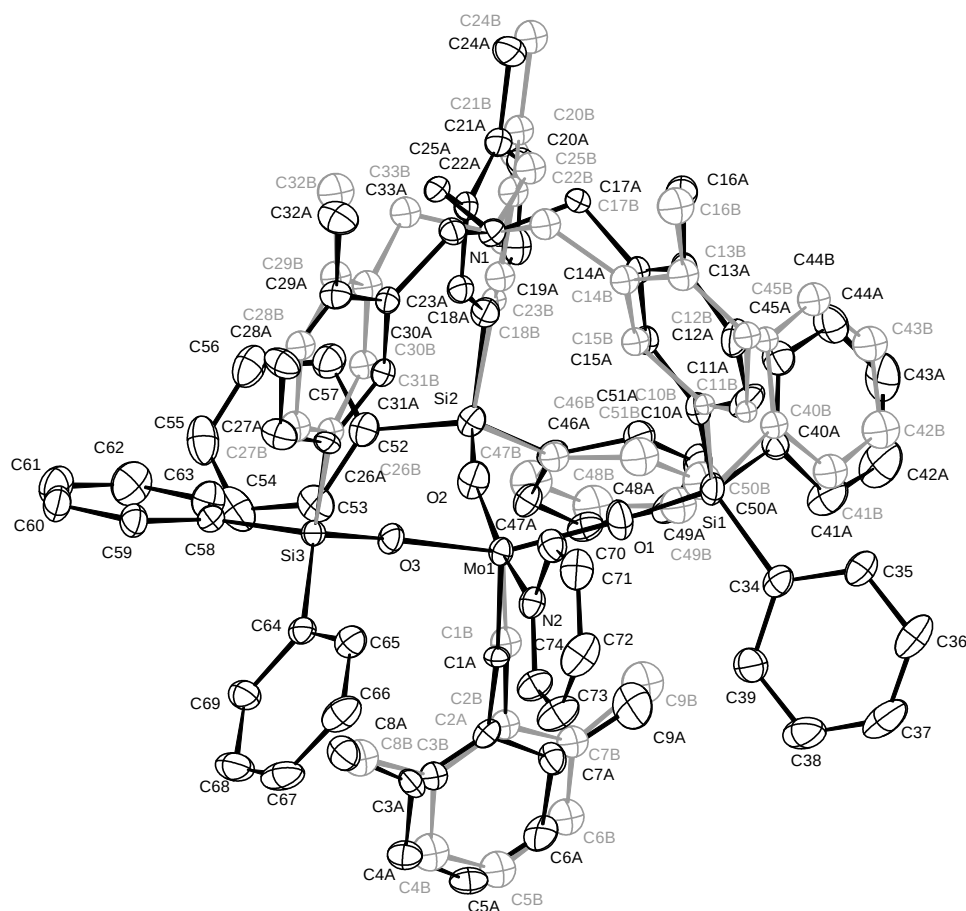
Single Crystal Structure analysis of **139b•Py**

Figure S50. The molecular structure of **139b•Py**. H atoms have been removed for clarity. Main structure shown in black and disordered parts shown in grey.

X-ray Crystal Structure Analysis of **139b•Py**:

$C_{74}H_{68}MoN_2O_3Si_3$, $M_r = 1213.51 \text{ g mol}^{-1}$, purple prism, crystal size $0.19 \times 0.18 \times 0.08 \text{ mm}^3$, triclinic, space group $P-1$ [2], $a = 12.196(2) \text{ \AA}$, $b = 14.638(2) \text{ \AA}$, $c = 19.3970(9) \text{ \AA}$, $\alpha = 83.076(7)^\circ$, $\beta = 76.990(6)^\circ$, $\gamma = 67.589(12)^\circ$, $V = 3116.8(8) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $D_{calc} = 1.293 \text{ g}\cdot\text{cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.318 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.92274$, $T_{max} = 0.97586$), Bruker AXS Enraf-Nonius KappaCCD diffractometer with a FR591 rotating Mo-anode X-ray source, $2.678 < \theta < 31.506^\circ$, 106119 measured reflections, 20734 independent reflections, 16516 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0461$. The structure was solved by *SHELXS* and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0337$ [$I > 2\sigma(I)$], $wR_2 = 0.0840$ [all data], 926 parameters and 0 restraints.

Full .cif data for the compound are available under the CCDC number CCDC 2293660.

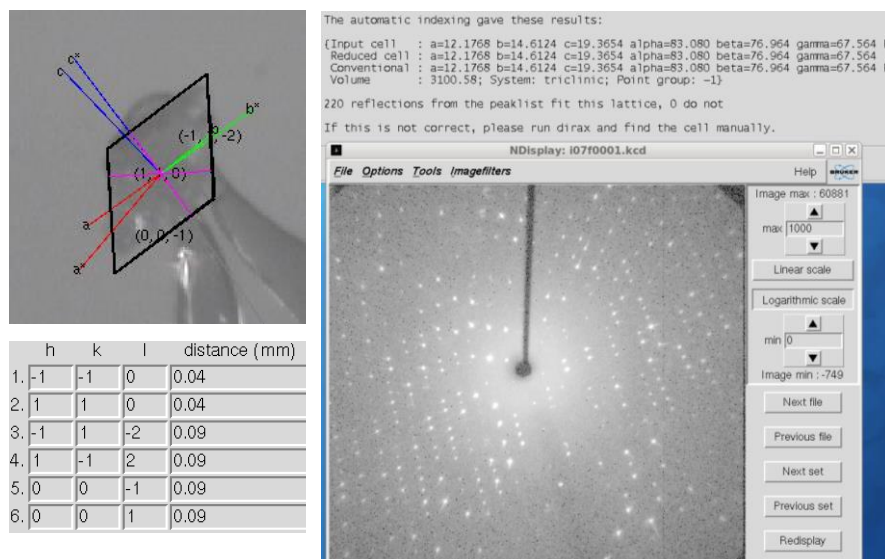


Figure S51. Crystal faces and unit cell determination/refinement of compound **139b•Py**.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.61	357	372	96.0	10.78	95.68	72.54	0.0318	0.0125
2.61 - 1.76	828	828	100.0	7.66	43.59	53.25	0.0294	0.0152
1.76 - 1.40	1182	1182	100.0	6.80	28.59	45.42	0.0308	0.0173
1.40 - 1.22	1204	1204	100.0	6.40	21.95	39.17	0.0333	0.0189
1.22 - 1.11	1188	1188	100.0	6.07	15.05	33.18	0.0371	0.0219
1.11 - 1.03	1205	1205	100.0	5.88	13.32	29.99	0.0403	0.0241
1.03 - 0.97	1174	1174	100.0	5.58	10.40	26.25	0.0472	0.0282
0.97 - 0.92	1229	1229	100.0	5.32	8.62	23.06	0.0547	0.0331
0.92 - 0.88	1193	1193	100.0	5.08	7.55	19.43	0.0623	0.0384
0.88 - 0.85	1047	1047	100.0	4.85	7.46	19.17	0.0669	0.0415
0.85 - 0.82	1212	1212	100.0	4.67	6.45	16.29	0.0749	0.0497
0.82 - 0.79	1403	1403	100.0	4.53	5.44	13.54	0.0924	0.0627
0.79 - 0.77	1049	1049	100.0	4.28	4.75	11.48	0.1026	0.0774
0.77 - 0.75	1176	1176	100.0	4.19	3.87	8.98	0.1300	0.1034
0.75 - 0.73	1322	1322	100.0	4.01	3.70	7.85	0.1416	0.1234
0.73 - 0.71	1468	1468	100.0	3.87	3.20	6.15	0.1633	0.1629
0.71 - 0.70	775	775	100.0	3.78	2.86	4.97	0.1872	0.2039
0.70 - 0.68	1724	1724	100.0	3.59	2.81	4.36	0.1932	0.2371
0.68 - 0.67	961	961	100.0	3.47	2.31	3.12	0.2357	0.3289
0.67 - 0.66	976	978	99.8	3.43	2.35	2.91	0.2446	0.3585
0.66 - 0.65	901	911	98.9	3.23	2.12	2.43	0.2744	0.4287
0.75 - 0.65	8127	8139	99.9	3.65	2.84	4.77	0.1888	0.2314
Inf - 0.65	23574	23601	99.9	4.91	10.69	19.04	0.0478	0.0447

A resolution cut off (SHEL 999 0.68) was applied to exclude poorly determined intensities at high diffraction angles. The missing low angle reflections were presumably shadowed by the primary beam stop. Two reflections (OMIT -3 6 3; 0 0 6) with high $I\sigma(I)$ were excluded before the final refinement cycles. The structure contains some disordered subunits (alkylidyne ligand, phenyl rings and tripodal ligand). These have been described as best as possible with different parts and occupancies. Isotropic atomic displacement parameters were partially applied to minor parts of the disorder. AFIX instruction was applied to force one of the aryl rings into a hexagonal shape.

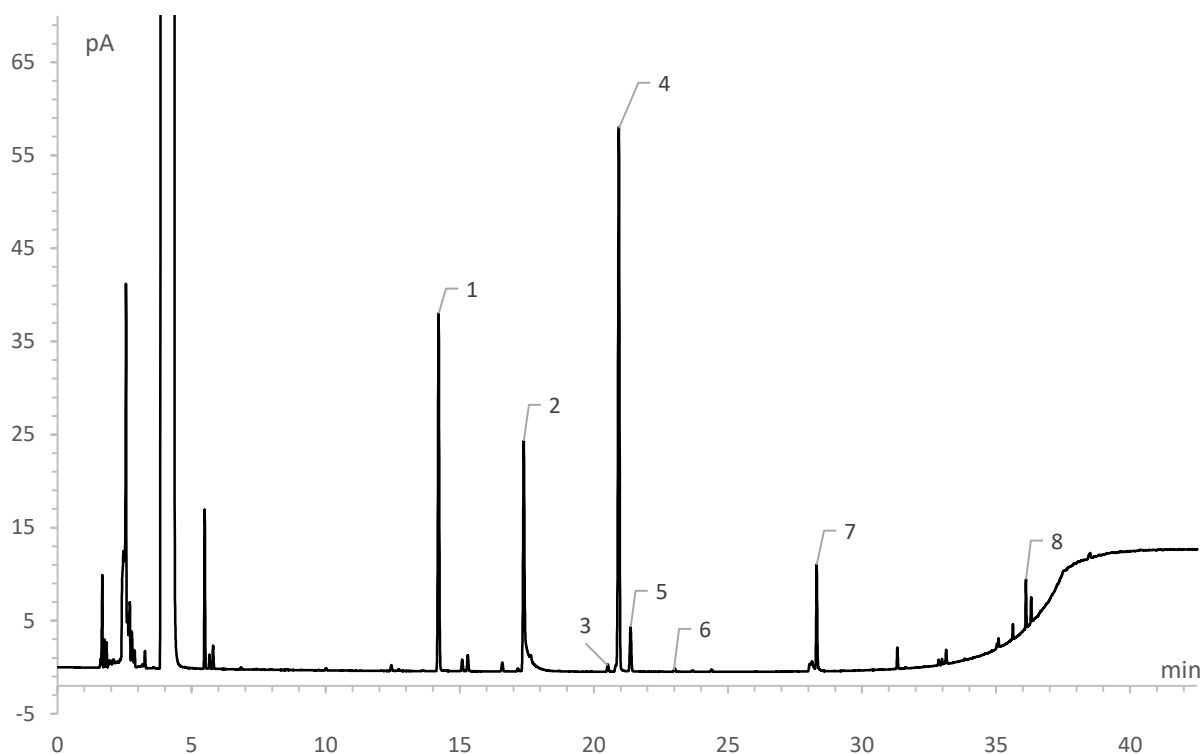
Table S24. Crystal data and structure refinement of compound **139b•Py**.

Identification code	14313	
Empirical formula	C ₇₄ H ₆₈ Mo N ₂ O ₃ Si ₃	
Color	purple	
Formula weight	1213.51 g·mol ⁻¹	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1, (no. 2)	
Unit cell dimensions	a = 12.196(2) Å	α = 83.076(7)°.
	b = 14.638(2) Å	β = 76.990(6)°.
	c = 19.3970(9) Å	γ = 67.589(12)°.
Volume	3116.8(8) Å ³	
Z	2	
Density (calculated)	1.293 Mg·m ⁻³	
Absorption coefficient	0.318 mm ⁻¹	
F(000)	1268 e	
Crystal size	0.19 x 0.18 x 0.08 mm ³	
θ range for data collection	2.678 to 31.506°.	
Index ranges	-17 ≤ h ≤ 17, -21 ≤ k ≤ 21, -28 ≤ l ≤ 28	
Reflections collected	106119	
Independent reflections	20734 [R _{int} = 0.0461]	
Reflections with I > 2σ(I)	16516	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.97586 and 0.92274	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	20734 / 0 / 926	
Goodness-of-fit on F ²	1.024	
Final R indices [I > 2σ(I)]	R ₁ = 0.0337	wR ² = 0.0779
R indices (all data)	R ₁ = 0.0510	wR ² = 0.0840
Extinction coefficient	n/a	
Largest diff. peak and hole	0.477 and -0.828 e·Å ⁻³	

4.3 Selected GC Chromatograms

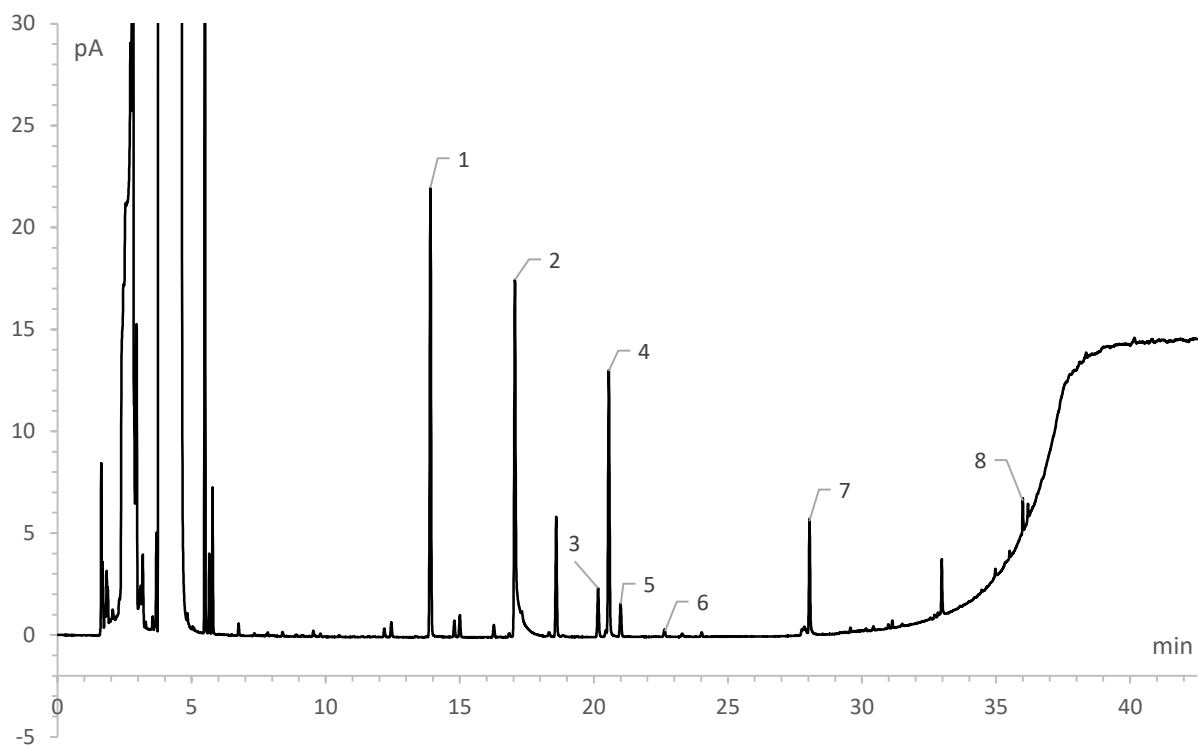
A response factor ($0.91 \pm 5\%$) was determined for the internal standard cyclohexanol in reference to isopulegol through triple measurements at different concentrations.

GC chromatogram for entry 12, table S2



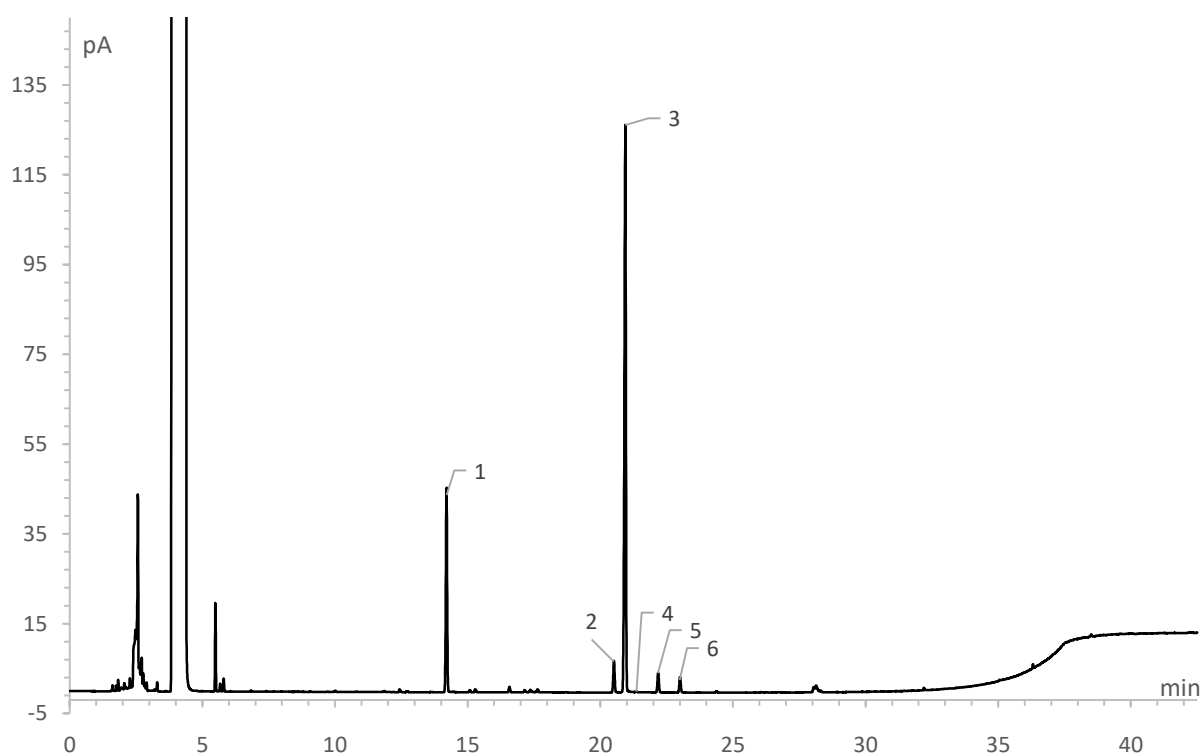
No.	Ret. Time [min]	Area [pA*min]	Amount [mg]	Factor	Peak Name
1	14.21	2.204	69.11	1.00	Cyclohexanol
2	17.39				Citronellal
3	20.52				Neo-Isopulegol
4	20.93	3.698	105.51	0.91	Isopulegol
5	21.37				Isopulegone
6	23.02				Iso-Isopulegol
7	28.31				Citronellol
8	36.11				Citronellyl ester

GC chromatogram for entry 13, table S2



No.	Ret. Time [min]	Area [pA*min]	Amount [mg]	Factor	Peak Name
1	13.91	1.267	69.07	1.00	Cyclohexanol
2	17.06				Citronellal
3	20.16				Neo-Isopulegol
4	20.56	0.832	41.28	0.91	Isopulegol
5	21.00				Isopulegone
6	22.63				Iso-Isopulegol
7	28.04				Citronellol
8	36.00				Citronellyl ester

GC chromatogram for entry 15, table S2



No.	Ret. Time [min]	Area [pA*min]	Amount [mg]	Factor	Peak Name
1	14.20	2.618	69.11	1.00	Cyclohexanol
2	20.52				Neo-Isopulegol
3	20.94	8.388	201.49	0.91	Isopulegol
4	21.37				Isopulegone
5	22.18				Neo-Iso-Isopulegol
6	23.01				Iso-Isopulegol

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