How to cite: *Angew. Chem. Int. Ed.* **2023**, *62*, e202304574
doi.org/10.1002/anie.202304574

Reactive Intermediates

Diazoalkenes: From an Elusive Intermediate to a Stable Substance Class in Organic Chemistry

*Max M. Hansmann**

Dedicated to A. Stephen K. Hashmi on the occasion of his 60th birthday

Abstract: Over decades diazoalkenes ($R_2C{=}C{=}N_2$) were postulated as reactive intermediates in organic chemistry even though their direct spectroscopic detection proved very challenging. In the 1970/80ies several groups probed their existence mainly indirectly by trapping experiments or directly by matrix-isolation studies. In 2021, our group and the Severin group reported independently the synthesis and characterization of the first room-temperature stable diazoalkenes, which initiated a rapidly expanding research field. Up to now four different classes of N-heterocyclic substituted room-temperature stable diazoalkenes have been reported. Their properties and unique reactivity, such as N_2/CO exchange or utilization as vinylidene precursors in organic and transition metal chemistry are presented. This review summarizes the early discoveries of diazoalkenes from their initial postulation as transient, elusive species up to the recent findings of the room-temperature stable derivatives.

1. Elusive intermediates in reaction mechanisms—Properties, synthesis and reactivity

Diazoalkanes [$R_2C{=}N_2$ (**I**); Figure 1] as well as their cyclic isomers, diazirines (**II**), have been known for more than 100 years and have found plenty of applications as remarkable versatile building blocks in organic synthesis.[1] In contrast, the higher carbon homologs, diazoalkenes ($R_2C{=}C{=}N_2$, **III**), also known as diazoolefins, are considered as extremely unstable chemical species and fleeting intermediates in organic chemistry. Diazoalkenes can be represented by a series of Lewis structures with either cumulenic double bonds (**IIIa**), as a vinyl anion diazonium cation (**IIIb**) or by a C–C polarized Lewis structure containing a C=N=N fragment (**IIIc**). Both Lewis structures **IIIb** and **IIIc** feature a lone pair at carbon and support a bent $C{=}C{=}N_2$ moiety, while a large contribution of Lewis structure **IIIa** should favor a linear structure. Even though diazoalkenes are frequently drawn in a linear fashion, quantum chemical calculations of the parent diazoalkene $H_2C{=}C{=}N_2$ clearly favor a bent structure in which the linear compound is a transition state for the C–C–N angle inversion.[2]

The importance of Lewis-structure **IIIb** featuring a vinyl diazonium moiety likely causes the challenges associated with the characterization of diazoalkenes since dinitrogen liberation is highly favorable. Consequently, it is expected that low temperatures are required for diazoalkene detection and indeed matrix-isolation studies of $F_2C{=}C{=}N_2$ proved successful.[3] $F_2C{=}C{=}N_2$ (**2**) could be generated in nitrogen matrixes at a few Kelvin either by photochemical excitation of difluoropropadienone (**1**) under loss of CO,[3a] or via the reaction of dinitrogen with difluorovinylidene (**4**) obtained by photochemical triggered rearrangement of difluoroacetylene (**3**) (Scheme 1).[3b] Note, the difluoro substituent is required since 1,2-migration in the vinylidene intermediate is extremely facile and difluorovinylidene is kinetically stabilized towards rearrangement compared to vinylidene ($H_2C{=}C{:}$).[4]

1.1. Postulation by trapping experiments

Due to their extreme reactivity diazoalkenes are typically proposed as elusive reaction intermediates in organic synthesis. They are anticipated as key-intermediates in the Seyferth–Gilbert homologation,[5] as well as in its Ohira–Bestmann modification[6] or in the Colvin reaction (Scheme 2).[7] The established mechanism involves the formation of a highly reactive diazoalkene **8** by a Horner–Wadsworth–Emmons reaction from diazomethylphosphonate esters [Seyferth–Gilbert reagent (**5**)/Ohira–Bestmann reagent (**6**)] (Scheme 2a) or by Peterson olefination from metalated trimethylsilyl-diazomethane (**7**) (Scheme 2b).[8] In both cases a rapid dinitrogen elimination occurs to form vinylidenes **9**. The later alkylidene carbenes (**9**) quickly undergo 1,2-migration to form alkynes (**10**). Gilbert and co-workers attempted to isolate diazoalkenes but dinitrogen elimination as well as the 1,2-migration both

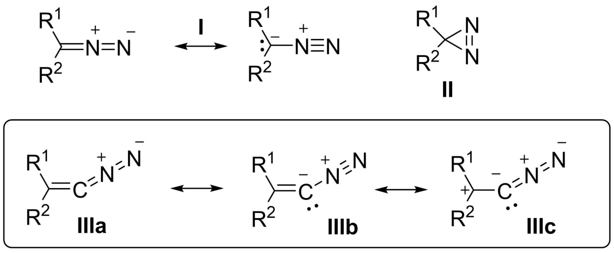
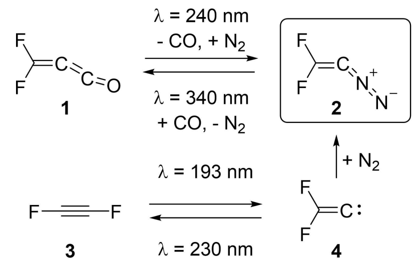


Figure 1. Comparison between diazoalkane (**I**), diazirine (**II**) and diazoalkenes (**III**).



Scheme 1. Matrix-isolation studies of a diazoalkene.

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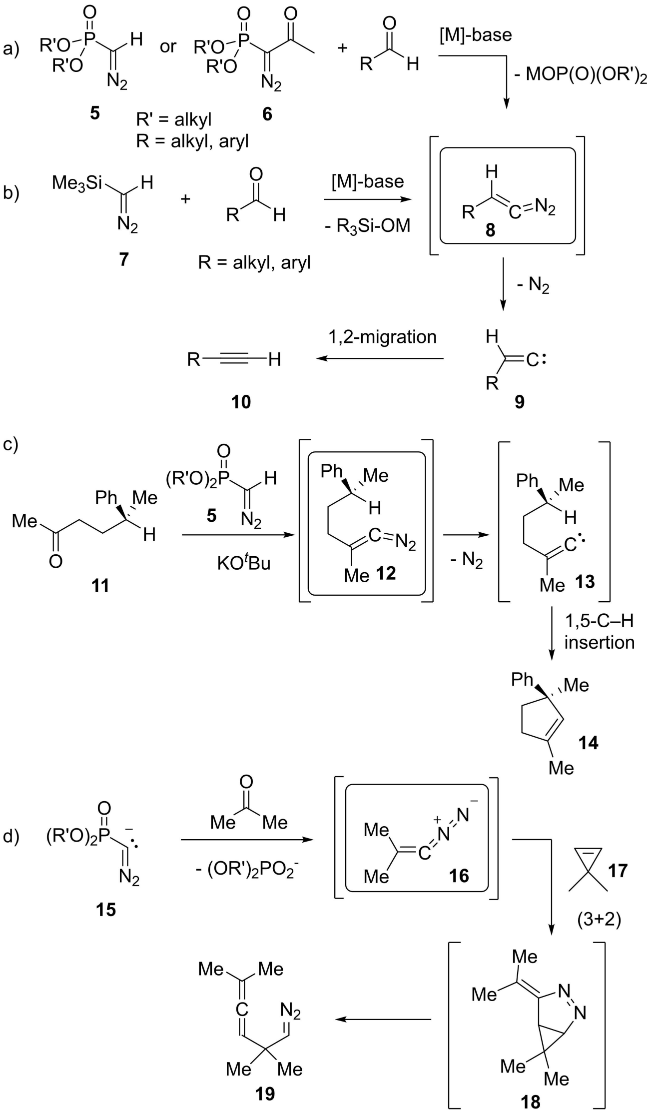

Scheme 2. Diazoalkenes as postulated intermediates generated by phosphorus or silyl diazo precursors.

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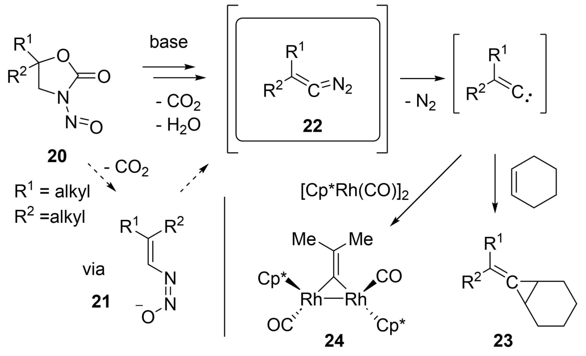
occurred rapidly even below −78 °C.[9] Recent detailed kinetic studies with ^{13}C-isotopically labeled substrates analyzed by low temperature NMR allowed the propensity of substituent migration to be determined,[10] however, the direct spectroscopic detection of either the diazoalkene or vinylidene intermediate remains so far unsuccessful.[11] DFT calculations as well as low temperature NMR studies of the Colvin reaction indicate the first step (Peterson olefination) to be rate-determining and all subsequent transition states and intermediates to be lower in energy hampering the detection of the diazoalkene.[10] The intermediacy of vinylidenes in these transformation is not limited to alkyne formation via 1,2-migration. For instance ketone **11** is proposed to generate transient diazoalkene **12** upon reaction with **5**, followed by dinitrogen loss and formation of vinylidene **13** in which 1,2-migration is intercepted by a stereospecific 1,5-C–H insertion (**13** to **14**) (Scheme 2c).[12] The reactivity of transient vinylidenes or alkylidene carbenes was summarized previously and is not the focus of this review.[13] Interestingly, in the reaction with cyclopropene **17**, the formation of diazo compound **19** was observed which was speculated to be generated by (3+2) cycloaddition (**18**) of a transient diazoalkene **16** (Scheme 2d).[14] Note, in respect to phosphorus diazo compounds Bertrand and co-workers reported the only known cumulenic diazo compounds $[R_2(Cl)P{=}C{=}N_2]$ in 1987, which also showed reactivity as a 1,3-dipole.[15]

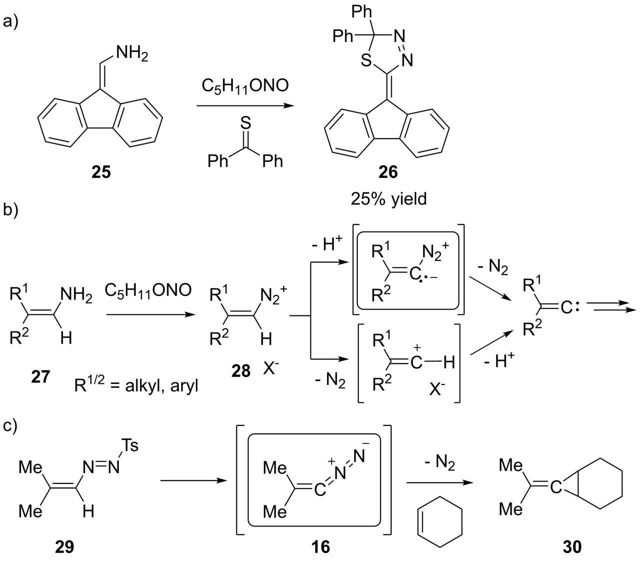
The alkaline decomposition of 5,5-disubstituted *N*-nitrosooxazolidones (**20**) is also proposed to proceed through diazoalkene (**21**) formation, which rapidly eliminate dinitrogen to form vinylidenes (Scheme 3). A series of articles by Newman and co-workers in the 1960/70ies show that the vinylidene can be trapped with olefins to afford cyclopropenation products (**23**).[16] Herrmann and co-workers employed the fragmentation of *N*-nitrosooxazolidones to generate the bridged, bimetallic rhodium vinylidene complex **24**.[17] Note, that the base mediated fragmentation of *N*-nitrosooxazolidones follows a complicated multi-step mechanism, in which both H_2O and CO_2 are step-wise eliminated presumably via **21**. The mechanism was studied in detail for instance by ^{15}N labelling,[18] and it remains questionable if other intermediates such as vinyl cations or vinyl diazonium[19] species are involved as key-intermediates.



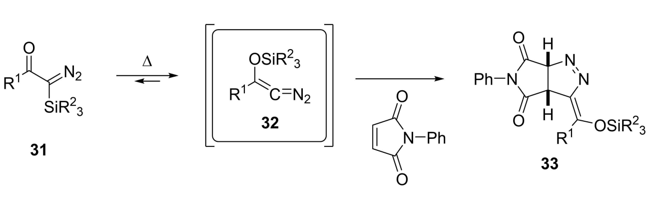
Scheme 3. Postulated diazoalkene formation from the decomposition of *N*-nitrosooxazolidones **20**.

One of the rare experiments in which the diazoalkene formation was postulated to be intercepted prior to the loss of dinitrogen, was reported in the nitrosation of vinylamine **25** in the presence of thiobenzophenone as trapping reagent (Scheme 4a).[20] 1,3,4-thiadiazoline **26** is proposed to be formed by (3+2) cycloaddition of the diazoalkene intermediate with the thioketone. Nitrosation of primary vinyl amines (**27**) should afford vinyl diazonium salts **28**, but it is not clear if vinyl cations or diazoalkenes are subsequently formed as reactive species (Scheme 4b).[21] Stang and co-workers analyzed the complex decomposition of (tosylazo)alkene **29** and could isolate the alkylidenecyclopropanes **30** presumably arising from diazoalkene **16** formation followed by alkylidene carbene generation (Scheme 4c).[22]

Another synthetic approach to access diazoalkenes was reported by Maas and co-workers by 1,3-(C→O) silyl migration. Thermal treatment of α-diazo-α-silylketones (**31**) in the presence of dipolarophiles such as *N*-phenylmaleimide lead to the 1,3-dipolar cycloaddition products **33** (Scheme 5).[23] It seems likely that a 1,3-(C→O) silyl migration leads to the highly reactive diazoalkene **32** which acts as a 1,3-dipole to form **33** and in the absence of trapping reagent generates vinylidenes upon dinitrogen liberation.[23]



Scheme 4. Diazoalkenes as postulated intermediates in the nitrosation of primary vinyl amines (a) and (b) and the decomposition of (tosylazo)alkenes (c).



Scheme 5. Diazoalkenes by 1,3-Brook rearrangement followed by trapping.

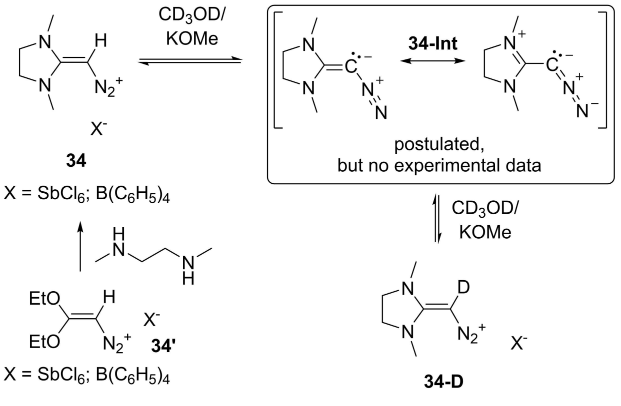
1.2. Stable diazoalkenes—An early postulation

In 1985, Bott studied the reactivity of resonance-stabilized vinyl diazonium cations **34** derived from **34′** (Scheme 6).[24] He observed that a solution of **34** in d_4-MeOH in the presence of base (KOMe) leads to deuteration of the α-position to the diazonium group (**34-D**).[24] Since no liberation of dinitrogen occurred, he postulated that the diazoalkene **34-Int** should be reasonably stable due to its resonance stabilization. Even though **34-Int** was postulated, no subsequent detection or characterization data of the diazoalkene could be found in the literature. Attempts to deprotonate vinyl diazonium salts[25] were reported to be unsuccessful,[26] and upon reaction with 1,4-diazabicyclo-[2,2,2]octane (DABCO) as base more complex heterocyclic rearrangement products arising from vinylidene intermediates were described.[27]

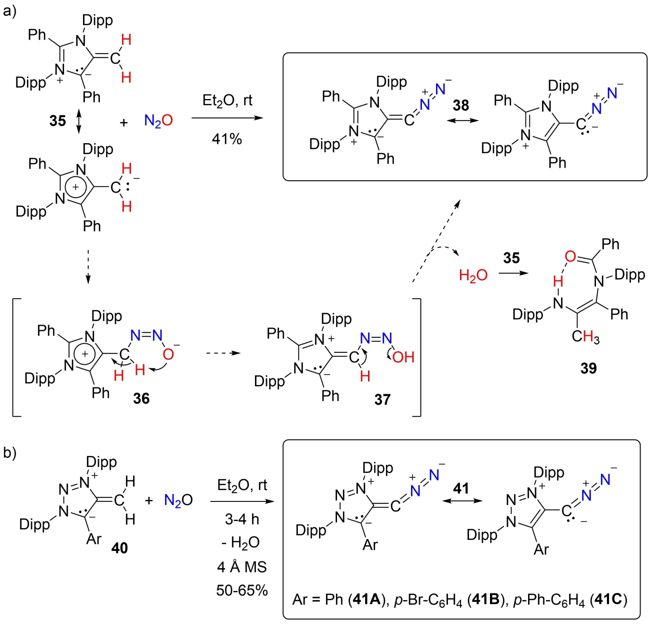
2. Room-temperature-stable diazoalkenes

2.1. Synthesis—Diazo transfer from N_2O

Since the detection of various trapping products in the 1970/80ies diazoalkenes appeared far too reactive to be isolable at room temperature. In 2021, our group and the Severin group reported the synthesis and characterization of the first room-temperature-stable diazoalkenes.[28,29] The synthesis relies on the dinitrogen transfer from nitrous oxide (N_2O) to polarized olefins. Upon reacting mesoionic N-heterocyclic olefin (mNHO) **35**[30] with N_2O the stable diazoalkene **38** could be isolated in 41 % yield (Scheme 7a). The mechanism most likely proceeds through initial addition upon N_2O (mNHOs are very strong carbon-based donors)[30] to form alkane diazotate **36**,[31] followed by intramolecular proton transfer to give diazohydroxide **37** (note the similarity to **21**). Elimination of water leads to the desired diazoalkene **38**, while the liberated water is scavenged irreversibly by the reaction of a second equivalent mNHO (**35**) to give the stoichiometric amide byproduct **39**. We later observed that this reaction is also applicable to 1,2,3-triazole



Scheme 6. Deuteration of vinyl diazonium salt **34** via a postulated diazoalkene intermediate **34-Int**.

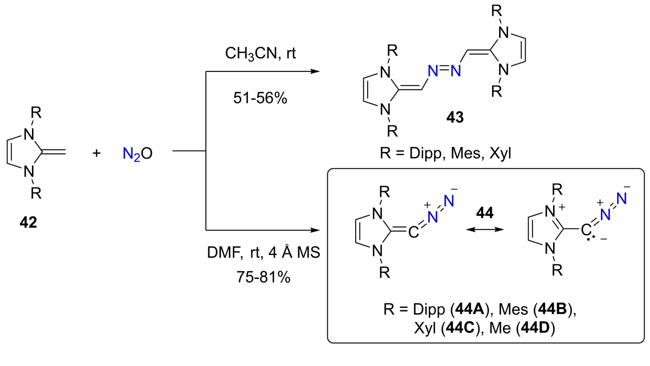


Scheme 7. Room-temperature-stable diazoalkenes based upon the reaction of mNHO **35** (a) and mNHO **40** (b) to give diazoalkenes **38** and **41**, respectively.

derived mNHOs **40**[30] to afford the corresponding stable diazoalkenes **41** (Scheme 7b).[32] In case of **41** the formed water can be trapped by molecular sieves and no stoichiometric byproduct is formed allowing isolated yields greater than 50 %.

Previously, Severin and co-workers reported the generation of azo-bridged NHO dimers **43** based upon the reaction of N-heterocyclic olefin[33] **42** with nitrous oxide (Scheme 8).[34] Since the azo-bridged NHO dimer **43** is electron-rich ($E_{1/2} \approx -1.34$ V vs. Fc/Fc$^+$), it was applied as strong stoichiometric organic reductant. In follow-up work, they discovered that by changing the solvent to DMF the dimer formation could be suppressed and instead the room-temperature-stable diazoalkenes **44** were isolated in good yields (Scheme 8).[29,35]

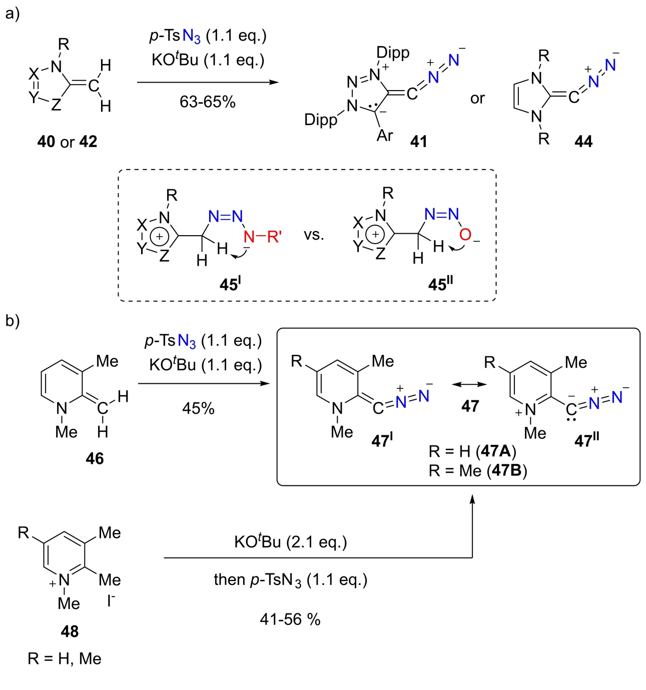
While it is still unclear how the mechanism switches between dimer (**43**) and diazoalkene (**44**) formation the authors concluded that the solvent is the crucial factor for product selectivity.[29] Interestingly, one example of a stable diazoalkene featuring N-Me groups (**44D**) was also reported. While the previous examples only contained sterically bulky N-substituents (N-Dipp; Dipp = 2,6-diisopropylphenyl), **44D** highlights that the diazoalkene stability is not due to a kinetic stabilization by sterically bulky groups, but must be the result of electronic stabilization (see below). Note the similarity of this substance class to **34-Int** postulated by Bott in 1985 (Scheme 6).



Scheme 8. Switching selectivities: Dimer **43** vs. diazoalkene **44** generation reported by Severin and co-workers.

2.2. Synthesis—Diazo transfer from azides

Recently, we could find a new route to stable diazoalkenes by dinitrogen transfer from azides such as p-TsN$_3$ (Scheme 9).[36] This finding allows a much broader synthetic access to stable diazoalkenes since only strong nucleophiles are capable of activating N$_2$O.[37] We could show that upon reaction of polarized olefins such as mNHOs (**40**) or NHOs (**42**) with p-TsN$_3$ in the presence of additional base (KO^{t}Bu) the previous diazoalkenes **41** or **44** are readily accessible (Scheme 9a). We assume the diazo transfer most likely to proceed, in analogy to the Regitz-diazo transfer,[38] via intermediate **45^{I}** which closely resembles the nitrous oxide addition intermediate (**45^{II}**) (inset, Scheme 9a). While in the reaction with N$_2$O water has to be scavenged, a tosyl amide salt is liberated. Most importantly, this new approach opens up a much larger diazoalkene scope applicable to weak nucleophiles. Pyridine derived olefin **46** is less nucleophilic than mNHOs and classical NHOs and is not capable of activating N$_2$O. Remarkably, pyridine olefin **46** reacts with



Scheme 9. Dinitrogen transfer from p-tosyl azide to give stable diazoalkenes.

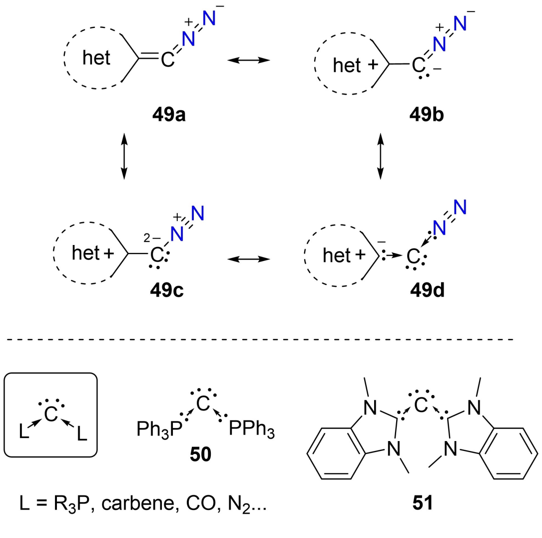
p-TsN$_3$ in the presence of KO^{t}Bu to give the diazoalkene featuring a pyridine backbone (Scheme 9b). The synthesis can also be directly performed from the lutidinium salts **48** with two equivalents KO^{t}Bu avoiding the isolation of the olefin intermediate (**46**).

2.3. Structural and spectroscopic data

Stable N-heterocyclic diazoalkenes can be described by a series of resonance structures: Either a cumulenic Lewis structure (**49a**), a polarized structure with a C–C single bond (**49b**), with two negative charges on carbon (**49c**), or as a carbone in which carbon is coordinated by two neutral donor ligands ($L^1 \rightarrow C \leftarrow L^2$; L = carbene and N$_2$; **49d**) (Scheme 10).

The latter dative description was motivated by the interpretation of carbodiphosphoranes (**50**)[39] and carbodicarbenes (**51**)[40] as divalent carbon(0) compound postulated by Frenking and co-workers,[41] and also analyzed computationally for the case of two mixed ligand classes L^1 = NHC and L^2 = N$_2$.[42] Computations of (NHC)C(N$_2$) indicate a bent structure (127°) with a N–N bond length of 1.164 Å and a natural charge of $-0.25\,e^-$ at carbon. The calculated first and second proton affinities for (NHC)C(N$_2$) (244 and 111 kcal mol^{-1}) are much lower than of carbodiphosphoranes (280 and 186 kcal mol^{-1}) and carbodicarbenes (ca. 290 and 170 kcal mol^{-1}) disfavoring a $L^1 \rightarrow C \leftarrow L^2$ description. Especially in case of pyridine derived diazoalkene **47**, which was not computationally investigated in this study, the $L^1 \rightarrow C \leftarrow L^2$ description appears unlikely since the 2-pyridine carbene should act as a rather strong π-acceptor ligand.[43] NRT calculations indicate a high degree of electron delocalization.[28,29] Even though Lewis structure **49d** appears to contribute only minor to the electronic description of diazoalkenes (see below for experimental data support), the dative description cannot be fully neglected and has advantages for instance to explain reactivity such as ligand exchange reactions (see below). NBO analysis of simplified diazoalkene **38** indicates 1.56 e in a C(sp^2) orbital as well as 1.6 e and 1.8 e in C=C and C=N bonds, respectively.[28] Note, NBO analysis indicates a three center-four-electron π-bonding in the CN$_2$ fragment which is likely increasing the stability of the CN$_2$ moiety disfavoring N$_2$ dissociation.[28] Interestingly, the frontier molecular orbitals throughout the diazoalkene series strongly resemble (Figure 2). The HOMO is centered on the CN$_2$ fragment and has π-type character at carbon while the HOMO-1 has σ-type character at carbon reminiscent of the frontier molecular orbitals typically encountered in carbon(0) compounds[41,42] and in general to base-supported zero-oxidation state main group species.[44]

So far ten stable diazoalkenes have been reported featuring the 4-imidazole (**38**),[28] the 1,2,3-triazole (**41**),[32] the 2-imidazole (**44**),[29] and pyridine (**47**)[36] heterocyclic cores. Their characterization data are summarized in Table 1. Unique to the stable diazoalkene substance class is a characteristic IR band in a range of ca. 1944–1984 cm^{-1} arising from the CN$_2$ asymmetric vibrational stretch, which is positioned in an unusual cumulenic IR wavenumber range. Typically, diazoalkanes (≈2000–2200 cm^{-1}) and diazonium (≈2100–2300 cm^{-1}) compounds are shifted to larger wavenumbers.[45] In fact, there are very few diazo compounds with IR bands below 2000 cm^{-1}, nearly all derived from metalated diazo compounds such as (Me$_3$Pb)$_2$CN$_2$ or HgCN$_2$.[46] These compounds support a high electron density at the CN$_2$ moiety leading to a decrease in the N–N and increase in C–N bond order. Note, the wavenumbers for metalated diazo compounds decrease on average by 50 cm^{-1} for M: Si > Ge > Sn > Pb and have also be interpreted by an increase in the effective mass,[46,47] which cannot be the case for diazoalkenes. The carbon atom (CN$_2$) appears at $\Delta(^{13}C) \approx 28.6$ to 35.1 ppm for diazoalkene classes **38**, **41** and **44**, while **47** [$\Delta(^{13}C) \approx 65$ ppm] is uniquely



Scheme 10. Possible Lewis-structures of diazoalkenes **49a–d** (top) and the concept of carbon(0) L→C←L compounds (bottom).

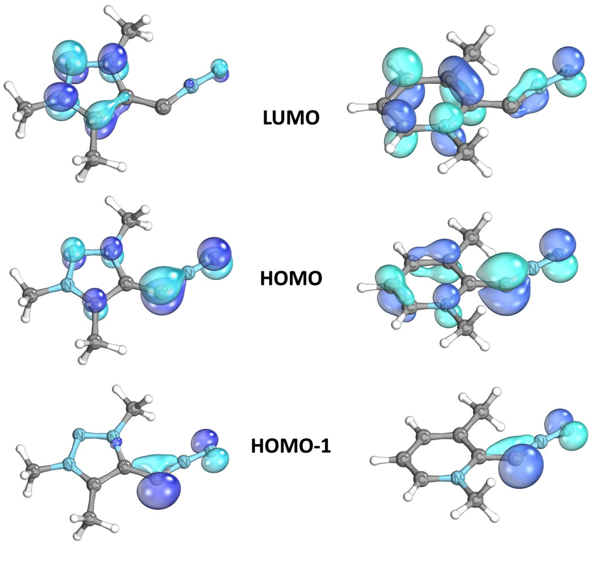
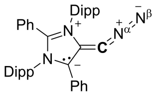
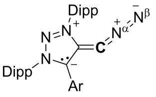
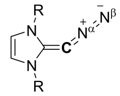
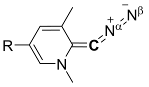


Figure 2. Molecular orbitals for diazoalkenes **41-Me**[32] and **47A**.[36]

Table 1: Characterization data for all so far reported room-temperature-stable diazoalkenes.

	 **38**	 **41** Ar = Ph (**41A**) *p*-Br-C_6H_4 (**41B**) *p*-Ph-C_6H_4 (**41C**)	 **44** R = Dipp (**44A**) Mes (**44B**) Xyl (**44C**) Me (**44D**)	 **47** R = H (**47A**) Me (**47B**)
	4-imidazole (38)	**1,2,3-triazole (41)**	**2-imidazole (44)**	**pyridine (47)**
IR [cm^{-1}]	1944	1956 (**41A**) 1953 (**41B**) 1953 (**41C**)	1984 (**44A**) 1961 (**44B**) 1963 (**44C**) 1954 (**44D**)	1971/1955 (**47A**) 1951 (**47B**)
^{13}C [ppm]	31.1 (C_6D_6)	34.5 (**41A**; C_6D_6) 35.2 (**41B**; C_6D_6) 34.8 (**41C**; C_6D_6)	35.1 (**44A**; C_6D_6) 33.3 (**44B**; C_6D_6) 33.5 (**44C**; C_6D_6) 28.6 (**44D**, d_8-THF)	66.0 (**47A**; C_6D_6) 63.2 (**47B**; C_6D_6)
^{13}C–^{13}C [Hz]	65.6	60.0 (**41A**)	n. d.	75.8 (**47A**)
^{15}N [ppm]	256.7 (α) 282.4 (β)	255.0 (α; **41A**) 288.7 (β; **41A**)	n. d.	256.6 (α; **47A**) 279.7 (β; **47A**)
C–C [Å]	1.391(8)	1.401(2) (**41A**) 1.399(1) (**41C**)	1.397(5) (**44A**) 1.377(3) (**44C**) 1.412(6) (**44D**)	1.402(4)/1.398(4) (**47A**)
C–N [Å]	1.257(7)	1.274(2) (**41A**) 1.276(1) (**41C**)	1.285(5) (**44A**) 1.274(3) (**44C**) 1.264(6) (**44D**)	1.273(4)/1.287(4) (**47A**)
N–N [Å]	1.184(7)	1.157(2) (**41A**) 1.154(1) (**41C**)	1.147(5) (**44A**) 1.169(3) (**44C**) 1.156(6) (**44D**)	1.171(4)/1.163(4) (**47A**)
< CCN [°]	124.3(5)	121.6(1) (**41A**) 123.5(1) (**41C**)	121.3(3) (**44A**) 119.6(2) (**44C**) 123.2(4) (**44D**)	125.9(3) (**47A**)

Data for **38** obtained from Ref. [28]; **41** from Ref. [32]; **44** from Ref. [29] and **47** from Ref. [36]; n.d. = not determined.

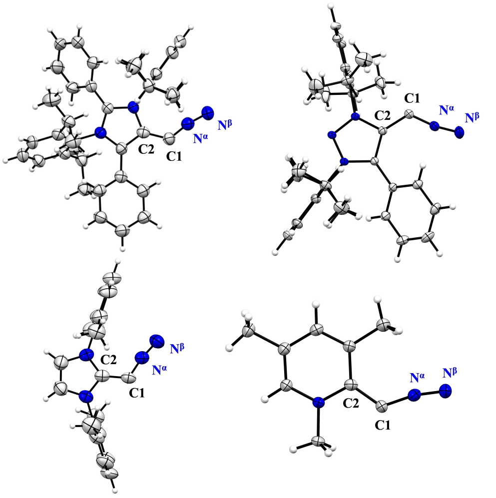


Figure 3. Representative X-ray solid-state structures of **38**,[28] **41 A**,[32] **44 B**[29] and **47 B**.[36] Thermal ellipsoids are shown with 50 % probability.

positioned outside of this range. Note, as reference the ^{13}C NMR resonance of the central ylidic carbon atom of $Ph_3P{=}C{=}PPh_3$ appears at 13 ppm,[48] and diazomethane ($H_2C{=}N_2$) at 23.1 ppm.[45] The ^{13}C–^{13}C coupling constants of the stable diazoalkenes are in a range of 60–76 Hz (Table 1), which is indicative for a bonding between a C(sp^2)–C(sp^2) bond. The two N-atoms of the diazo moiety can be assigned by ^{15}N NMR and are positioned in a rather narrow range of 256–288 ppm. The outer nitrogen atom is unusually high-field shifted; as comparison diazoalkanes typically appear in the ^{15}N NMR in a range of 330–440 ppm.[45] In case of diazoalkene classes **38**, **41** and **47** two *E* and *Z* isomers should be discriminable, but the analytical data show only one set of signals in solution, most likely since rotation of the C–CN_2 bond is fast on the NMR timescale.

Up to date seven X-ray solid-state structures of stable diazoalkenes have been reported (Table 1). Representative solid-state structures of the four classes are shown in Figure 3. Most strikingly in all cases the CCN fragment is bent with angles in a range of 119.6(2)° to 125.9(3)°. This data agrees with computations that show an activation energy of ca. 10 kcal mol^{-1} being required to bent diazoalkene **41** into a linear fashion.[32]

A search on the Cambridge Crystallography Database (CCD) of all X-ray solid-state structures deposited containing a terminal CN_2 group reveals the bond lengths in diazoalkenes to belong to some of the shortest C–N [1.257(7)–1.287(4) Å] and longest N–N [1.147(5)–1.184(7) Å] bond lengths (Figure 4).[49] In fact, there are few compounds being positioned in this unusual area (bottom right corner in Figure 4). Similar bond parameters are obtained by metalated diazo compounds of the structure $[M]{-}C(N_2)R$, for instance $[M]{=}Pd(PPh_3)_2Cl$,[50] $Rh(PEt_3)_3$,[51] or ArSn.[52,53] This data agrees with an electron rich carbon center, a strong C–N bond and weakened N–N bond consistent with the IR data. The structural data clearly

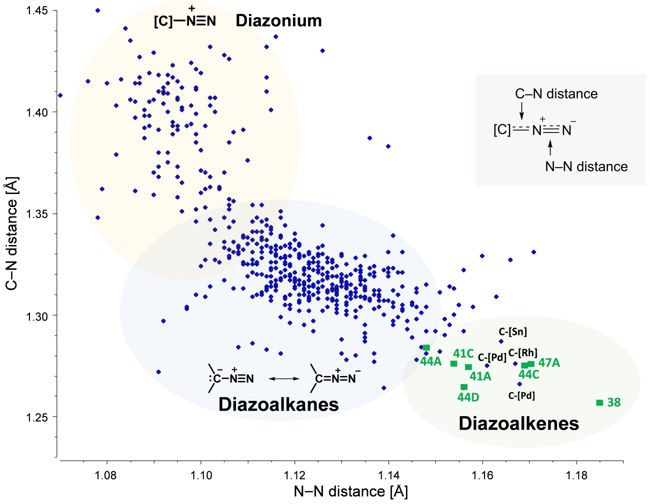


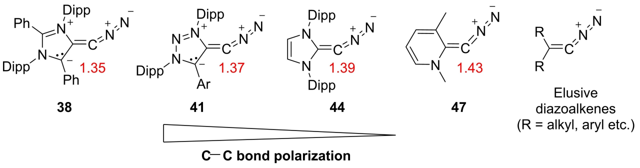
Figure 4. Analysis of the X-ray data deposited in the CCD containing the CN_2 fragment as a function of the C–N and N–N bond lengths. Top left area: typical for diazonium, middle: diazoalkanes; green dots represent all deposited X-ray structures of diazoalkenes.

disfavor resonance structures **49c** and **49d** with N–N triple bond (diazonium) contributions; in such cases long C–N and short N–N distances should be observed (Figure 4, area top left). In conclusion, the experimental data agree best with Lewis structures **49b** and **49a** (Scheme 10).

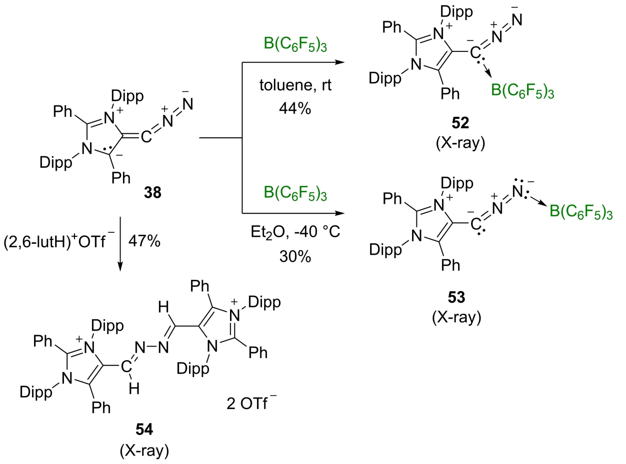
Why have stable diazoalkenes been overlooked for decades? Clearly, steric shielding is not a requirement since imidazole **44D** (N-Me) as well as pyridine derived diazoalkenes **47A/B** (N-Me) are room-temperature-stable compounds under inert conditions. We believe that both strong resonance-stabilization and polarization of the C–C bond of the diazoalkene strongly contribute to the stabilization of the CCN_2 moiety. C–C bond polarization leads to an electron rich CN_2 fragment with short C–N and long N–N bond lengths. The experimental data suggests that the current diazoalkene classes can be sorted according to their bond polarization: **38** < **41** < **44** < **47** (Scheme 11). This trend is supported by the calculated Wiberg-bond indices for the C–C bond to increase from 1.35 (**38**), 1.37 (**41**), 1.39 (**44**) and 1.43 (**47**).[36] No C–C bond polarization leads to elusive and extremely reactive diazoalkenes, prone to N_2 loss, which are the same intermediates postulated in organic reaction mechanisms (see above). Note, the thermal stability of the reported diazoalkenes also appear to correlate with this trend. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements show that **38**, **41** and **44** are thermally stable compounds (decomposition $>150\,°C$), while **47** decomposes rapidly and highly exergonically [decomposition enthalpies ($\Delta H_D \approx -1600\,J\,g^{-1}$)] at ca. 90 °C in a typical energy range for small energetic diazo compounds.[36,54]

2.4. Reactivity of stable diazoalkenes—Reactivity with electrophiles and dienophiles

In agreement with the pronounced negative natural charges of the CN_2 fragment at C ($-0.26\,e^-$) and N ($-0.20\,e^-$) for **38**, diazoalkenes react with electrophiles either at carbon or the outer nitrogen atom.[28] In the reaction with the Lewis acid $B(C_6F_5)_3$ both possible Lewis acid/base adducts **52** and **53** could be confirmed by X-ray solid-state structures (Scheme 12).[28] Note, from a structural point of view a similarity could be drawn between **53** and recently reported CN_2^{2-} bridged platinum complexes.[55] It is interesting to point out that CN_2^{2-} is isoelectronic to the azide anion (N_3^-). Simple protonation with lutidinium triflate leads to a more complex azine dimer **54**.



Scheme 11. Correlating C–C bond polarization and stability. Wiberg bond indices of the C–C bond indicated in red.

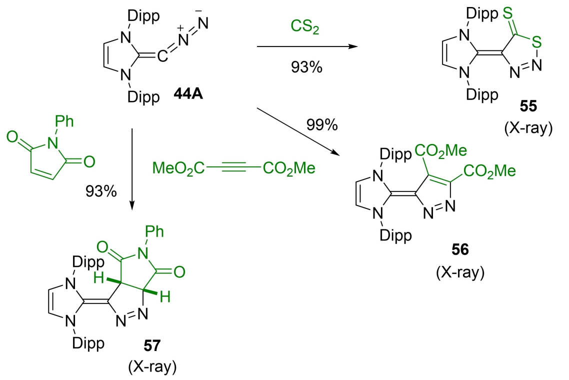


Scheme 12. Dual-site nucleophilicity and protonation of diazoalkene **38**.

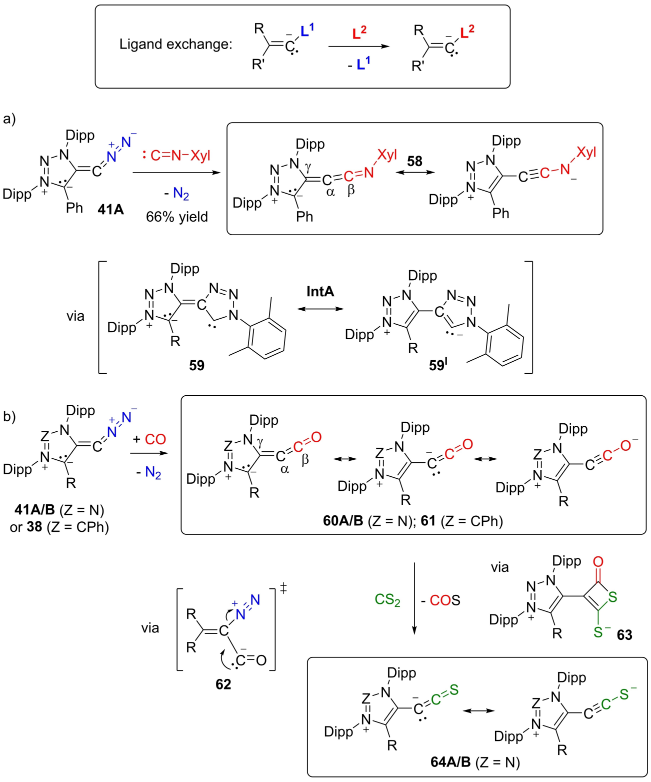
Resonance-stabilized diazoalkenes can react as 1,3-dipoles similar to diazoalkanes.[56] In the reaction of **44A** with polarized dienophiles such as carbon disulfide, dimethyl acetylenedicarboxylate and *N*-phenylmaleimide the cycloaddition products **55**, **56** and **57** could be isolated in excellent yields respectively (Scheme 13).[29]

2.5. Reactivity of stable diazoalkenes—N_2 ligand exchange

Stable diazoalkenes react with ambiphiles such as isocyanides or carbon monoxide via N_2/isocyanide[28] or N_2/CO exchange (Scheme 14).[32,57] The resulting stable hetero cumulenes, namely vinylidene ketenimines (**58**) and vinylidene ketenes (**60/61**), can be described through a series of Lewis-structures (Scheme 14). Large ^{13}C–^{13}C coupling constants indicate a multi-bonded species with C–C double/triple bond contribution. The mechanism of this transformation was calculated in the case of the isocyanide to proceed through a stepwise (3+2) cycloaddition to give intermediate **59/59I**, followed by a (3+2) cycloreversion under release of dinitrogen.[32] Interestingly, in the case of carbon monoxide a concerted mechanism occurs in which the diazoalkene adds to the LUMO of CO followed by a



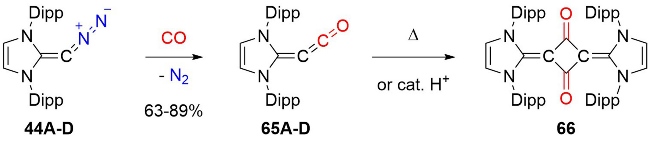
Scheme 13. Examples for the reactivity of diazoalkenes as 1,3-dipoles.



Scheme 14. Ligand exchange reactions at a vinylidene center.

concerted "backflip" of electron density via transition state **62** (Scheme 14b). Note, recently such analogous isoelectronic ligand exchange reactions with carbon monoxide raised significant interest.[58]

The chemistry of stable vinylidene ketenes[59] has been scarcely investigated presumably since such compounds are typically prepared by flash vacuum pyrolysis and hence are challenging to access.[60] We could show that resonance stabilized vinylidene ketenes **60 A/B** react with carbon disulfide to give the vinylidene thio-ketenes **64 A/B** via the structurally characterized (2+2) cycloaddition intermediate **63** and elimination of COS. Excess of CS_2 leads to subsequent cycloaddition products. Severin and co-workers also demonstrated the N_2/CO exchange with imidazole derived **44** to give vinylidene ketenes **65** which show high thermal stability (Scheme 15).[57] Upon heating (120 °C) or the addition of catalytic amounts of acid the formation of dimer **66** was observed. Compound **65 A** (N-Dipp) was shown to form stable, monomeric coordination complexes with (dms)AuCl, $[Rh(CO)_2Cl]_2$ or $GaCl_3$.[57]



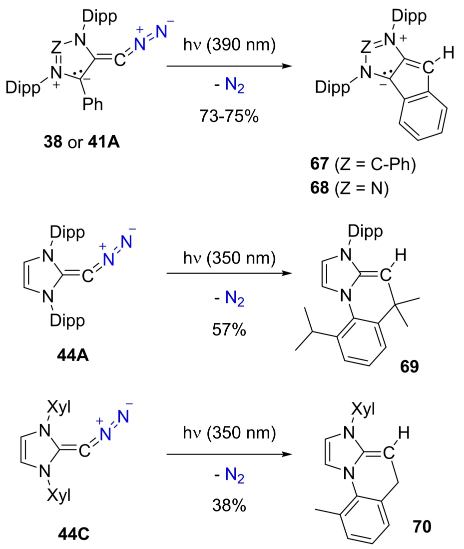
Scheme 15. N_2/CO exchange and subsequent reactivity.

2.6. Photochemical excitation—Free vinylidene precursors

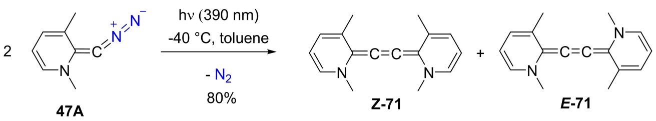
It is well known from diazoalkanes that photochemical excitation leads to loss of dinitrogen and formation of carbenes.[61] In 1978, Stang highlighted that diazoalkenes would be the ideal progenitors for unsaturated carbenes since only dinitrogen should be liberated.[62] Photochemical excitation of **38** or **41 A** with a 390 nm LED leads to the C–H insertion products **67** and **68** respectively (Scheme 16).[28,32] In case of imidazole derived diazoalkenes **44** a series of intramolecular C–H insertion products (**69** and **70**) could be isolated and structurally verified by X-ray solid-state structures.[29]

In stark contrast, photochemical excitation of diazoalkene **47 A** does not lead to C–H activation but the formation of a mixture of *E*/*Z* dimers of C4-cumulene **71** (Scheme 17).[36] Note, donor substituted C4-cumulenes or (NHC)CC(NHC) compounds are rare.[63] The dimerization of vinylidenes has been postulated in the past,[62] however, it is questionable if mechanistically free vinylidenes or metalated carbenoids are involved in such transformations.[62,64]

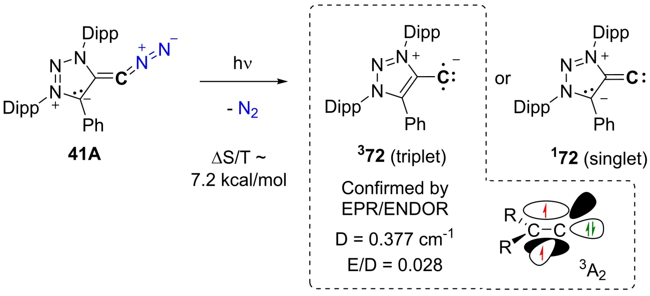
N_2 loss from diazoalkene **41 A** should deliver either singlet (^{1}**72**) or triplet (^{3}**72**) ground state vinylidenes (Scheme 18). Typically the ground state of vinylidenes is singlet; for instance calculations of $H_2C{=}C$ ($^1A_1$)→$H_2C{=}C$ ($^3B_2$) predict a large S/T gap of 48.3 kcal mol^{-1}.[65,66] However, in case of **41 A** calculations predict that the ground state of the vinylidene formed is triplet at the DFT (B3LYP/def2-TZVP $\Delta S/T$ ca. 7.2 kcal mol^{-1})[67] and CAS-SCF level of theory.[68] It seems very likely that the reason for the



Scheme 16. C–H insertion products upon photochemical excitation.



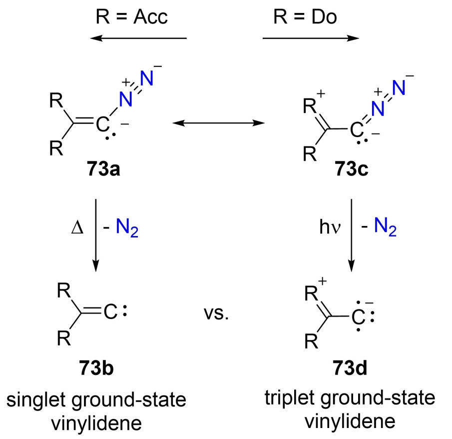
Scheme 17. Dimerization upon photochemical excitation.



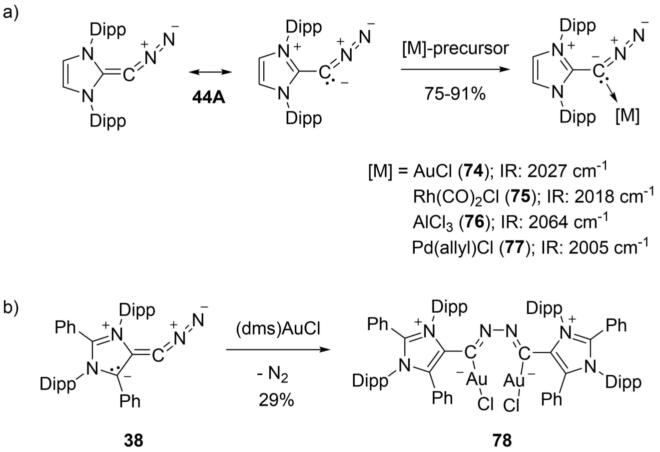
Scheme 18. EPR characterization of a triplet ground state vinylidene.

dramatic change in S/T gaps arises from the polarization of the C–C bond as outlined above favoring a zwitterionic contribution of ^{3}**72**. EPR measurements of an irradiated sample of **41 A** at 6 K clearly confirms the generation of a ground state triplet vinylidene with zero-field splitting parameters ($D = 0.377$ cm^{-1} and $|E|/D = 0.028$) in agreement with computations.[68] Additionally, the Curie-plot supports a triplet ground state, which is to the best of our knowledge the first representative of this fundamental substance class. Additionally, ENDOR measurements with a ^{13}C labeled sample of **41 A** show that the isotropic hyperfine coupling (a_{iso}) value (50 MHz) of ^{3}**72** is significantly smaller than the values associated with the divalent carbon in triplet carbenes (≈175 MHz up to ≈260 MHz).[68] The low a_{iso} value indicates that the two unpaired electrons at carbon are located in pure p-orbitals in agreement with theory (Scheme 18). One of the electrons is localized in a carbon centered p-orbital orthogonal to the heterocyclic plane, while the second electron is in a carbon based p-orbital which overlaps with the π-orbitals of the heterocyclic system delocalizing spin density into the heterocyclic core. The delocalization leads to a calculated total spin density of ca. 1.5 e on the outer carbon atom.[68] While singlet and triplet carbenes have been studied over decades,[69] vinylidenes in a triplet ground state have been overlooked, presumably since no suitable precursors were available.

It seems likely that fleeting diazoalkenes (**73 a**) presented in the first chapter rapidly eliminate dinitrogen to form ground-state singlet vinylidenes (**73 b**; Scheme 19). In contrast, donor substitution favors Lewis-structure **73 c** containing a C–N double bond resulting into increased stability towards N_2 loss. Photochemically triggered loss of N_2 from **73 c** leads to ground-state triplet vinylidenes **73 d**, which was demonstrated for ^{3}**72**. Currently, the discrimination between these extreme descriptions are part of ongoing investigations in our group.



Scheme 19. Comparison between diazoalkene representations and the formation of singlet/triplet ground-state vinylidenes.

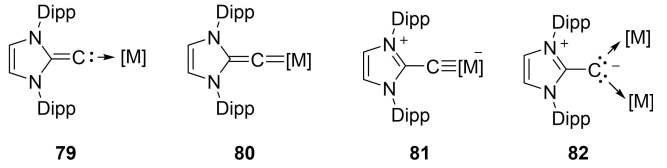


Scheme 20. Coordination complexes with the intact diazoalkene (a) and dimerization (b).

2.7. Metal vinylidene precursors

Late transition metals such as Au, Rh, Pd but also p-block elements such as aluminum (Lewis acid $AlCl_3$) coordinate to the intact diazoalkene without loss of dinitrogen (**74**–**77**; Scheme 20a).[29] The C–CN_2 and C–N bond lengths are elongated upon coordination triggering a shift into a more typical diazoalkane region. This is supported by the IR data shifting to larger wavenumbers (for instance the $AlCl_3$ adduct **76** appears at 2064 cm^{-1}). The LRh(CO)$_2$Cl complex **74** allows derivation of the donor properties of **44 A** with $\nu(CO)_{\mathrm{average}} = 2024$ cm^{-1} being a stronger overall donor than standard five-membered NHCs [$\nu(CO)_{\mathrm{average}} = 2035$–2046 cm^{-1}].[29] In case of diazoalkene **38** we observed dimerization to give the bis-gold azine complex **78** similar to the protonation attempt (**54**; Scheme 12).[28]

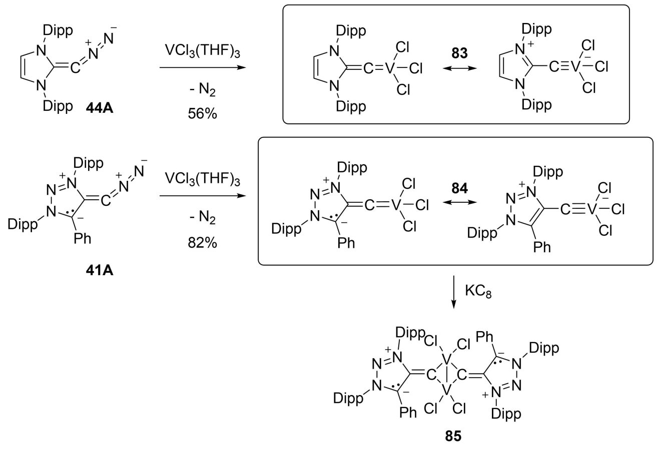
Diazoalkenes can also be utilized as vinylidene precursors for metal-vinylidene complexes. While metal carbenes are routinely accessed from diazo precursors,[70] metal vinylidenes are typically prepared by (alkyne) rearrangement chemistry and not diazo precursors.[71] Several coordination modes can be envisioned with the resulting N-heterocyclic vinylidene ligand: a neutral two-electron donor (**79**), in combination with π-backbonding to form C–M doubled complexes (**80**), or due to the C–C bond polarization even C–M triple bonded complexes (**81**) (Scheme 21). Additionally the ligand could act as four-electron donor for two metal centers (**82**).



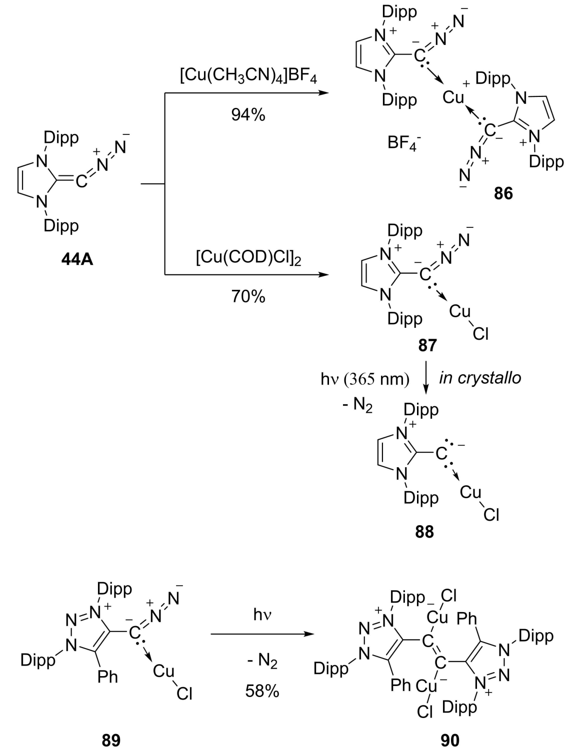
Scheme 21. Coordination modes of N-heterocyclic vinylidene ligands.

The Severin group showed that diazoalkenes **44A** and **41A** react with vanadium trichloride to afford vinylidene complexes **83** and **84**, respectively (Scheme 22).[72] The intact diazoalkene coordination cannot be observed but proceeds directly with the liberation of dinitrogen. Theoretical data support the description of **83** to be best described by a M–C double and even triple bond. Crystallographic data reveals a very short V–C bond length in agreement with vanadium alkylidyne complexes. Considering the organic exchange reactivity shown above for the N_2/CNR and N_2/CO exchange this reactivity could be classified in an analogous fashion as N_2/[M] exchange at a vinylidene center. The metal vinylidene complexes proved to be highly stable opening up the possibility to use this ligand as a new spectator ligand class for instance in catalysis. Interestingly, KC_8 reduction of **84** leads to the generation of the dimer **85** in which the vinylidene ligand acts as a bridging ligand between two vanadium centers. Note, such bridging ligands were previously accessed in a stepwise fashion starting from the N-heterocyclic olefins.[73]

While early transition metals such as vanadium spontaneously trigger N_2 loss upon diazoalkene coordination, late transition metals such as copper coordinate to the intact diazoalkene moiety, either as dimer **86** or monomer **87** (Scheme 23). Powers, Severin and co-workers reported the in crystallo photochemistry (crystal-to-crystal transformation) of single crystals of **87** to give the structurally characterized Cu-vinylidene complex **88** (Scheme 23).[74] DFT calculations predict a triplet ground state for **88** with a linear structure, while the X-ray crystallographic data shows a bent structure. It is possible that the X-ray solid-state structure is not fully relaxed, additionally the bending of the CuCl fragment occurs on a flat potential energy surface. Irradiation of the Cu-diazo complexes in solution led to a range of compounds such as a $L(Cu_8Cl_4)L$ (cube) cluster capped by two N-heterocyclic vinylidene ligands or C–H activation products.



Scheme 22. Synthesis of terminal N-heterocyclic vinylidene ligand complexes of vanadium from diazoalkenes.

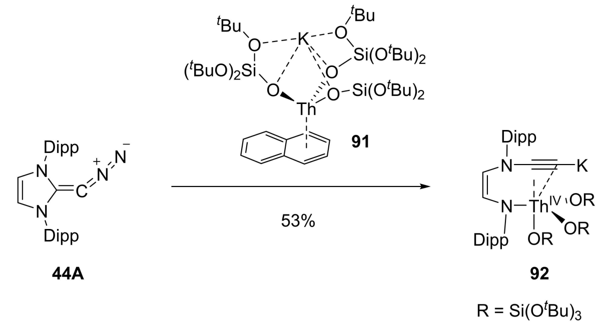


Scheme 23. Copper complexes of diazoalkenes and their irradiation products.

Interestingly, in case of diazo complex **89** irradiation in solution affords the dimer **90** (Scheme 23), which could be considered as (NHC)CC(NHC) coordinated by two CuCl fragments. It should be pointed out that related (NHC)CC(NHC) dimers were previously unsuccessful in their preparation,[75] and the presence of the Cu-fragments seems to be crucial to remove electron density. Note, without the copper coordination the system undergoes intramolecular C–H activation (**68**; Scheme 16).[68] Note, in case of diazoalkene **47 A** we were able to obtain the dimer **71** without transition metal coordination (Scheme 17).[36]

Recently, diazoalkenes have even been utilized in f-block chemistry. Maron, Mazzanti and co-workers attempted to access thorium vinylidene complexes. Upon reaction of diazoalkene **44A** with the thorium arene precursor **91** the Th^{IV} amido acetylido complex **92** could be isolated (Scheme 24).[76]

The unusual cleavage of the imidazole heterocyclic backbone was computationally investigated and is likely to be a result of the reduction of the diazoalkene by the Th-precursor. A Th-vinylidene intermediate is computationally proposed as transient intermediate, but could not be spectroscopically identified.



Scheme 24. Ring-opening of the imidazole heterocycle of diazoalkene **44 A** upon reaction with Th-complex **91**.

3. Conclusion

Over several decades, diazoalkenes have been postulated as highly reactive intermediates in organic chemistry, representing challenging fleeting targets to investigate. Only in the case of $F_2C{=}C{=}N_2$ the direct detection in matrix-isolation studies was possible while the majority of work was dedicated to indirect trapping experiences. In 1985, Bott postulated fairly stable diazoalkenes but attempts to isolate such compounds failed or were not followed-up. After more than two decades, in 2021, our group and the Severin group reported independently the first room-temperature-stable diazoalkenes based upon the diazo transfer from N_2O. Since then, ten stable diazoalkenes with four different N-heterocyclic backbones were reported. Such compounds show unique reactivity for instance as 1,3-dipoles, undergo N_2/CO or N_2/CNR exchange and serve as vinylidene precursors for free vinylidenes and metal vinylidene complexes. Since this field just initiated, it remains to be seen if the chemistry represents a niche area or develops into a very useful field for synthesis. Based upon the recent findings it is apparent that diazoalkenes offer plenty of new reactivity modes in organic chemistry, for instance to access unusual substance classes for instance hetero cumulenes such as vinylidene ketenes, but also offer new possibilities to access heterocyclic compounds via (3+2) cycloaddition reactions. Additionally, it paves an efficient and clean synthetic pathway into vinylidene chemistry, not relying on previous strategies such as metalated carbenoids, which have triggered controversial discussions. While triplet carbenes have been studied in great detail, triplet vinylidenes are virtually unknown in organic chemistry. The first examples for the application of diazoalkenes in coordination chemistry with p-, d- and even f-block elements are just emerging and it seems likely that diazoalkenes should be highly versatile precursors for future studies in main-group, transition metal and even actinide chemistry.

Acknowledgements

Support by the faculty of chemistry and chemical biology is greatly acknowledged. I thank my co-workers for their work on this topic, support by the Fonds of the chemical industry (FCI), the German Research Foundation (DFG) and the European Research Council (ERC-StG "CC-CHARGED" grant number 101077332) for financial support. Sascha Grusche is thanked for the design of the cover picture. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Diazo Compounds · Diazoalkenes · Metal Complexes · Reactive Intermediates · Vinylidenes

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Manuscript received: March 30, 2023
Accepted manuscript online: April 24, 2023
Version of record online: June 6, 2023