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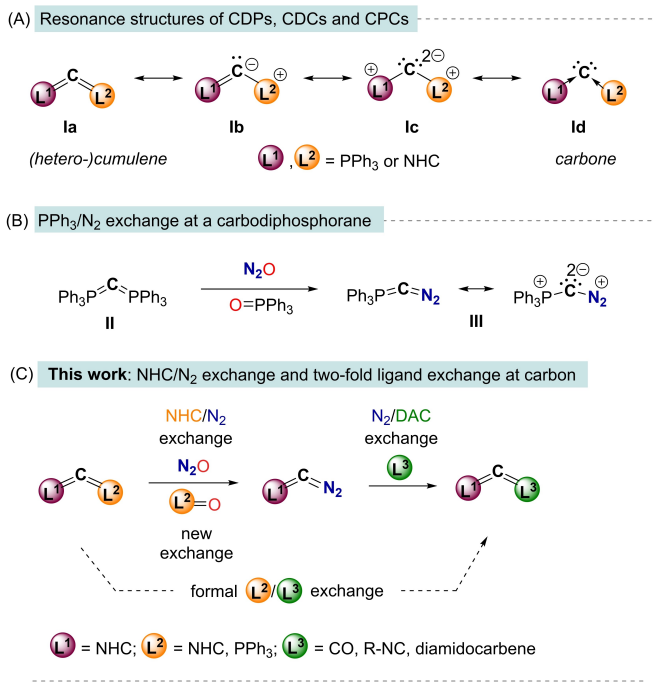
VIP **Diazoalkenes** *Very Important Paper*

Cleavage of Carbodicarbenes with N_2O for Accessing Stable Diazoalkenes: Two-Fold Ligand Exchange at a C(0)-Atom

*Yijie He, Yichong Lyu, David Tymann, Patrick W. Antoni, and Max M. Hansmann**

Abstract: The cleavage of carbophosphinocarbenes and carbodicarbenes with nitrous oxide (N_2O) leads to the formation of room-temperature stable diazoalkenes. The utility of Ph_3P/N_2 and NHC/N_2 ligand exchange reactions were demonstrated by accessing novel benzimidazole- and benzothiazole derived diazoalkenes, which are not accessible by the current state-of-the-art methods. The stable diazoalkenes subsequently allow further ligand exchange reactions at C(0) with carbon monoxide, isocyanide, or a diamidocarbene (DAC). Overall, the combination of hitherto unknown NHC/N_2 and N_2/L (L = DAC, CO, R–NC) ligand exchange reactions at a C(0) center allow the selective functionalization of the carbodicarbene ligand structure which represents a new methodology to rapidly assemble novel carbodicarbenes or cumulenic compounds.



Scheme 1. (A) Resonance structures of carbodicarbenes (CDCs) carbodiphosphoranes (CDPs) or carbophosphinocarbenes (CPCs); (B) reaction of CDP with N_2O to form Ph_3PCN_2; (C) NHC/N_2 exchange and double ligand exchange reported in this work.

In 1961 Ramírez and co-workers described the synthesis of $Ph_3P{=}C{=}PPh_3$, the first carbodiphosphorane (CDP), which can be represented by a series of zwitterionic/ylidic Lewis-structures **Ia**–**Ic** (Scheme 1A).[1] In 2006, Frenking reinterpreted the electronic structure of CDPs as carbon(0) compounds in which a C(0)-atom is flanked by two neutral donor ligands ($Ph_3P{\rightarrow}C{\leftarrow}PPh_3$; **Id**) similar to transition metal coordination compounds, coining the term carbones.[2] Based on this bonding analysis and the isolobal exchange of ligand fragments, carbodicarbenes (CDC; NHC:→C←:NHC) were postulated,[3] which soon after were experimentally verified by the Bertrand and Fürstner groups.[4,5] Since these seminal findings, carbodicarbenes developed into a well-utilized ligand class with several applications including main-group and transition metal chemistry, catalysis as well as material science.[6] Chelating carbodicarbenes,[7] and mixed carbophosphinocarbenes (CPC; $R_2C{:}{\rightarrow}C{\leftarrow}{:}PPh_3$) have been described and utilized.[8] Studies have focused on the strong σ-donor properties,[9] which is especially pronounced as the filled p-type orbital on carbon prevents M→L-backdonation but allows for redox non-innocence.[10] Frenking, Ong and co-workers have shown a "hidden π-accepting" character of CDCs alongside the strong donor abilities,[11] as a low-lying, empty p-type orbital centered on the flanking NHC can act as an acceptor in 1,2-addition reactions, reminiscent of frustrated Lewis pairs.

Considering the dative bonding description NHC:→C←:NHC a question raises if it is possible to perform a direct exchange of the NHC ligand, which was so far not reported. The concept of ligand exchange at carbon is an emerging field. N_2/R–NC,[12,13a] N_2/CO,[13] and PPh_3/CO[14] exchange reactions at both neutral and metalated carbon centers were recently reported.[15]

Our group just described the reaction of carbodiphosphoranes with N_2O to undergo a formal PPh_3/N_2 exchange to access Ph_3PCN_2 (Scheme 1B).[16] We wondered if carbophosphinocarbenes and carbodicarbenes could react with N_2O to enable ligand exchange reactions. Here we present a new ligand exchange reaction, the NHC/N_2 exchange which

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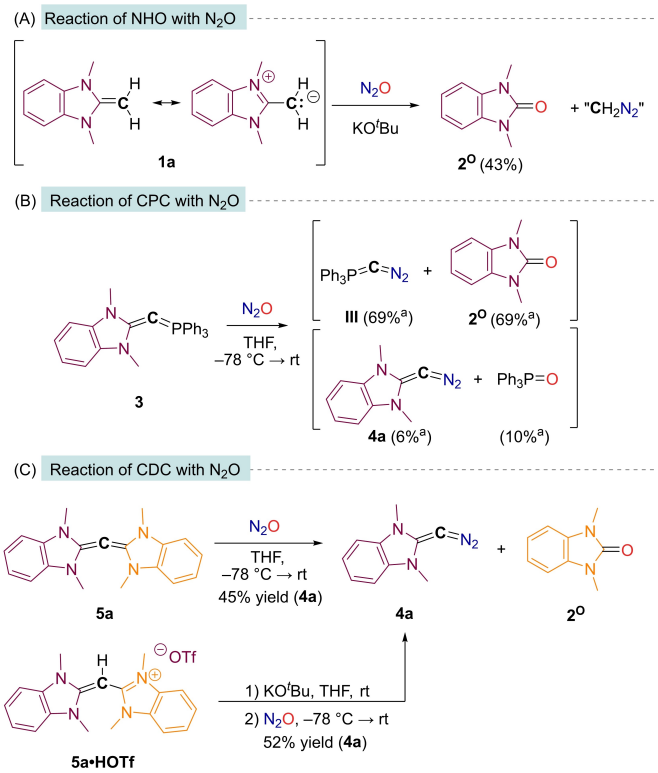
gives direct access to several new classes of stable diazoalkenes,[12,17] as well show that exchange reactions can be subsequently coupled to obtain cumulenes (Scheme 1C). Our initial motivation to find new synthesis pathways to diazoalkenes was driven by targeting the unknown benzimidazole derived diazoalkene **4a** (Scheme 2).

So far, the only reported methods to obtain stable diazoalkenes are diazo-transfer from N_2O,[12,17] or azides[18] to *N*-heterocyclic olefins (NHOs).[19] While Severin and coworkers reported a clean conversion of structurally related imidazole-based NHOs to the respective diazo compounds,[17a] in the case of benzimidazole-NHO **1a**, only the formation of urea **2°** (43 % yield) was observed (Scheme 2A). This process most likely involves a (3+2)/retro-(3+2) cycloaddition mechanism, accompanied by the cleavage of diazomethane, similar to the reactivity observed for pyridine-NHOs[18] and substituted imidazole NHOs.[20,21] The inverted regioselectivity in the (3+2) cycloaddition mechanism can be rationalized by the higher electrophilicity of the C2-atom as well as the lower aromaticity of the benzimidazole compared to the imidazole heterocycle. Applying our recently described tosyl azide N_2-transfer strategy resulted in a mixture of products with traces of the desired diazoalkene. Detected major side reactions were C_1-loss and the formation of a *N*-tosyl guanidine,[22] as well as nucleophilic substitution by attack on sulfur and not nitrogen of the tosyl azide moiety.



Scheme 2. Attempted synthesis of benzimidazole diazoalkene **4a**. (A) Unsuccessful N_2-transfer from N_2O to NHO **1**; (B) Reaction of CPC **3** with N_2O; (C) Reaction of CDC **5a** or in situ generated **5a** with N_2O leading to the desired benzimidazole diazoalkene **4a**. a) yield based on ^{1}H NMR analysis with 1,3,5-trimethoxybenezene as an internal standard.

Based on our recent finding that CDP **II** reacts with N_2O under P–C bond cleavage to form **III** (Scheme 1B),[16] we envisioned that Ong's unsymmetrical CPC **3**[8a] could serve as an ideal precursor to **4a** driven by Ph_3PO elimination.[23] Indeed, NMR monitoring of the reaction of **3** with N_2O in THF shows the expected formation of Ph_3PO and the unknown diazoalkene **4a**, although only in low quantities, while the main products (69 %) are diazophosphorus ylide **III**[16] and urea **2°** which are each formed in a 1:1 ratio (Scheme 2B; Figure S1). DFT calculations (PBE0-D3(BJ)/def2-TZVP/SMD(THF) show that the cleavage of the C–C bond in **3** is kinetically favored (Figure S143). The rate determining transition states for the (3+2) cycloaddition to the C–C bond is slightly lower in energy compared to the C–P bond (22.7 kcal/mol vs. 24.1 kcal/mol; Figure S143), explaining the preferential formation of diazo compound **III** over **4a** (Scheme 2B). To circumvent the formation of a **III**/**4a** mixture, the symmetrical CDC **5a** was selected. Upon addition of N_2O, NMR analysis of the reaction showed a clean and quantitative formation of **4a** and **2°** (1:1 ratio; Figure S2). **4a** can be purified from **2°** by precipitation from cold (−40 °C) THF and washing with Et_2O. Importantly, the new strategy excludes the possibility of diazomethane formation compared to the NHO route, avoiding safety hazards. To simplify the reaction procedure and to skip the isolation of CDC **5a**, both the deprotonation of **5a•HOTf** and the NHC/N_2 exchange were combined in a one-pot transformation yielding diazoalkene **4a** in a similar yield (52 %) as for isolated CDC **5a** (Scheme 2C).

Computational analysis showed the N_2O addition to the CDC to be rate-determining [$\Delta G^{\ddagger}$(TS1) = 23.1 kcal/mol] (Figure 1). However, unlike for **III**,[16] it is best described as a step-wise (3+2) cycloaddition (via **Int1**) rather than a concerted process. The formation of **Int2** by O-attack onto C2 is in good agreement with the observation of Ong's hidden π-accepting properties of CDCs.[11] **Int2** undergoes partial cycloreversion to afford adduct **Int3**, followed by a barrierless cleavage of the central C–C bond (−45.1 kcal/mol), yielding **4a** and **2°**. Note, the overall mechanistic similarity to the ozonolysis reaction of olefins in which a C=C bond is cleaved via a (3+2)/retro-(3+2) cycloaddition mechanism.

To explore the scope and selectivity of the NHC/N_2 exchange, two heteroleptic CDCs (**5b** and **5c**) were studied in the reaction with N_2O (Scheme 3). We hypothesized that selectivity in the N_2-transfer could be achieved by using the benzimidazole heterocycle as a sacrificial π-acceptor carbene entity.

Indeed, the reaction of benzimidazole/imidazole CDC **5b**,[8a] leads selectively to the diazoalkene **4b**[17] and **2°** with no detection of diazoalkene **4a** (Figures S6). Again, the isolation of the CDC **5b** is not required and **5b** can also conveniently be generated in situ and treated with N_2O to give the isolated diazoalkene **4b** in 69 % yield. The high selectivity of the N_2O cycloaddition reaction matches with the previous observed selectivity for [B]–H addition onto **5b** in which the hydride migrates to the benzimidazole but not

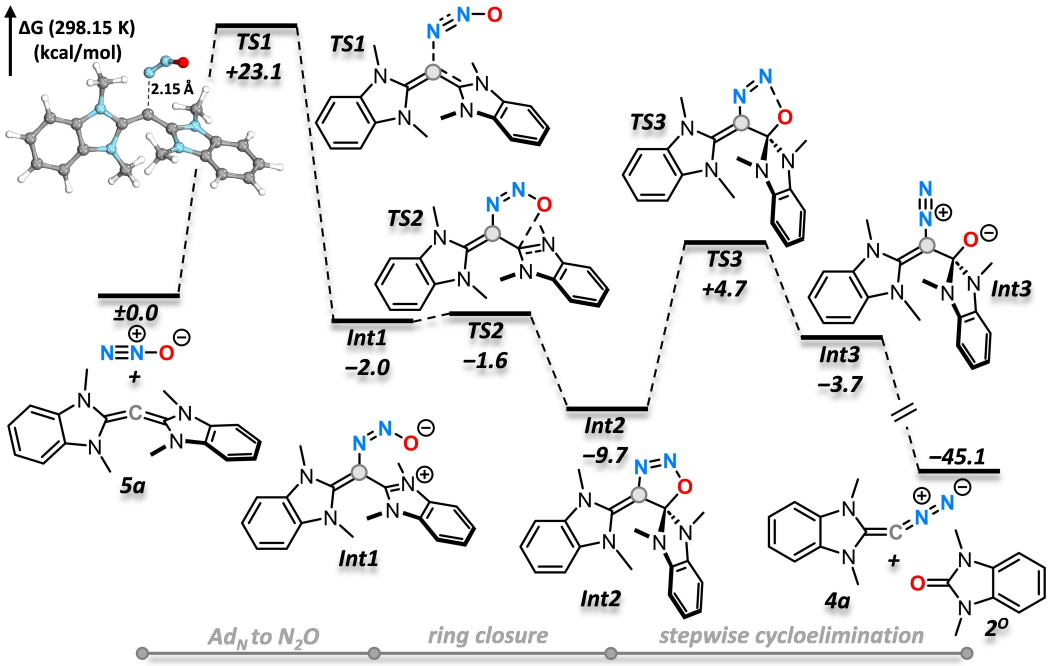
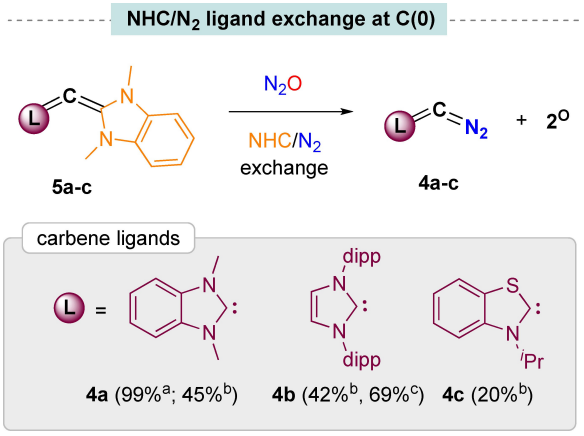


Figure 1. Computational energy profile for the formation of **4a** by C≡C-bond cleavage of **5a** with N_2O [PBE0-D3(BJ)/def2-TZVP/SMD(THF)].



Scheme 3. NHC/N_2 exchange of symmetrical (**5a**) and unsymmetrical (**5b**/**5c**) CDCs. a) yield based on ^{1}H NMR analysis with an internal standard. b) isolated yield; c) isolated yield starting with in situ generated **5b** by deprotonation with 2 equiv. of KO^{t}Bu.

imidazole C2-position.[8a] Next, the exchange methodology was tested with the literature unprecedented, stable CDC **5c** featuring mixed benzothiazole/benzimidazole[24] entities (for the synthesis, see the SI). Reaction of **5c** with N_2O affords selectively a 1:1 mixture of the hitherto unknown diazoalkene **4c** and **2°**. The in situ NMR shows **4c** being quantitatively formed (Figure S8), but the pure compound was isolated in a moderate yield (20 %) due to its loss during the washing process required to separate the urea side product. Interestingly, attempts to access the new diazoalkene **4c** using the established methods failed; the corresponding benzothiazole-derived NHO was unable to activate N_2O, while the TsN_3 strategy gave a mixture of products, clearly demonstrating the advantage of the selective NHC/N_2 exchange.

We next investigated the electronic properties of the two new stable diazoalkene classes **4a** and **4c**. Single crystals suitable for X-ray diffraction analysis were obtained for both **4a** and **4c** (Figure 2).[25] Both diazo compounds show short C1–C2 bond lengths [1.3897(11) Å (**4a**); 1.375(3) Å (**4c**)], with **4c** featuring the shortest reported C–C bond length of all known stable diazoalkenes, indicating a high C–C double bond character. Simultaneously, the C–N bond is slightly elongated, while the N–N bond of **4c** [1.144(2) Å] is significantly shorter than previously reported diazoalkenes, corroborating a pronounced contribution of a vinyl anion/diazonium cation resonance structure (for a structural comparison of diazoalkenes, see Table S1). DFT calculations support the *Z* isomer of **4c** to be thermodynamically favored over the *E*-isomer (ΔG = +5.0 kcal/mol; see Figure S144).

The findings observed by X-ray diffraction are supported by IR spectroscopy, showing a strong characteristic CNN-stretching vibration at 1968 cm^{-1} (**4a**) and 1985 cm^{-1} (**4c**). The ^{13}C NMR signal of the =CN_2 carbon of **4c** is significantly downfield-shifted [$\delta(^{13}C)$ = 69.6 ppm (C_6D_6)], even compared to the least polarized 2-pyridine diazoalkenes [$\delta(^{13}C)$ = 66.0 ppm–63.2 ppm;[18] for a comparison, see Table S1].

The unusual bonding situation is reflected in the ^{15}N NMR resonance of the outer *N*-atom [$\delta(^{15}N)$ = 338.8 ppm] strongly low-field shifted compared to all other diazoalkenes [$\delta(^{15}N)$ ~280–289 ppm; Table S1].[17b] The unusual ^{15}N NMR shift was supported by GIAO calculations $\delta(^{15}N)$ = 347 ppm (calc.) at the B3LYP/6-311+G(2d,p) level matching with the experimental data (see Figure S139). Computational analysis of the C–CN_2 bond shows a slightly higher Wiberg bond index for **4c** (1.48) than for **4a** (1.42)

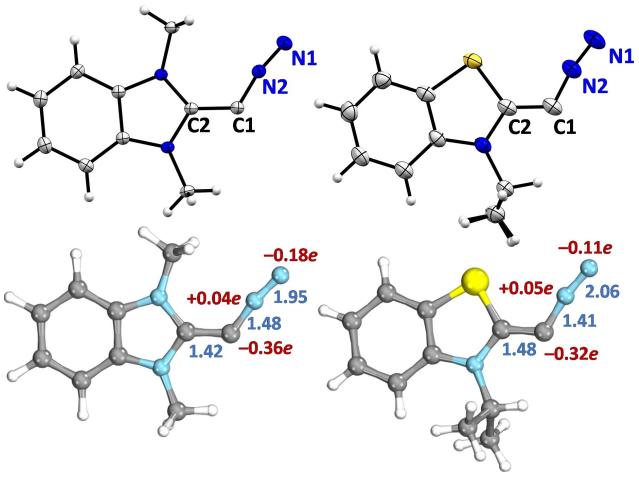
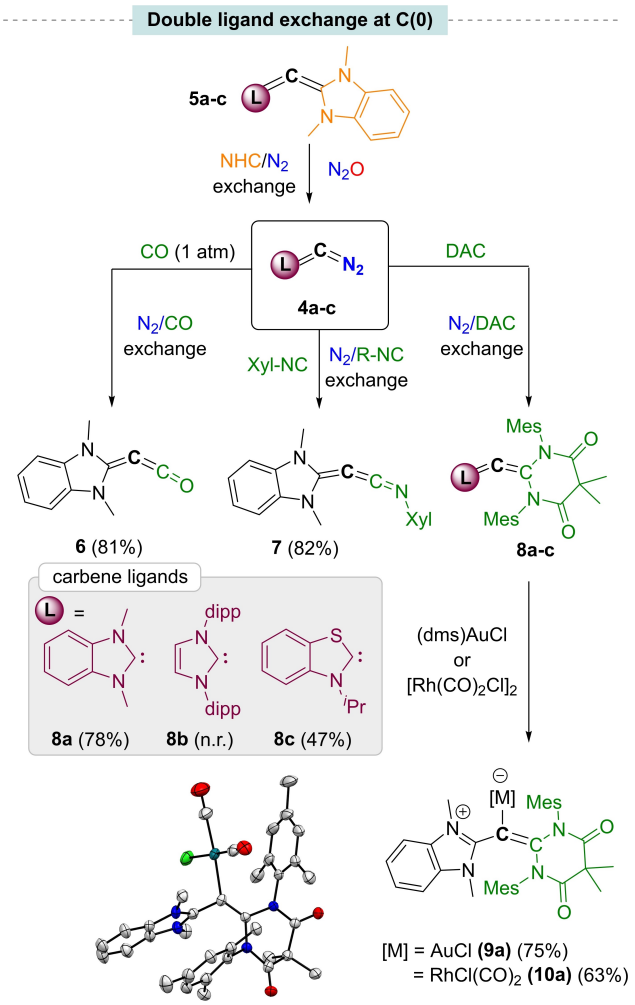


Figure 2. Top: X-ray solid-state structures of **4a** (left) and **4c** (right). Thermal ellipsoids are shown with 50% probability. Selected bond lengths and angles of **4a**/**4c** in [Å] and [°]: C1–C2: 1.3897(11)/1.375(3); C1–N2: 1.2811(10)/1.293(2); N1–N2: 1.1520(10)/1.144(2); N2–C1–C2: 121.58(8)/118.53(17); C1–N2–N1: 168.69(9)/169.55(19); C2–C1–N2–N1: 178.6(4)/171.1(9). Bottom: Computed structures at PBE0-D3(BJ)/def2-TZVP/SMD(THF) with Wiberg bond indices (blue) and natural atomic charges (red).



Scheme 4. Sequence of two-fold ligand exchange reactions at C(0). Xyl: 2,6-dimethylphenyl; dms: dimethylsulfide.

and C1 still bears a significant allocation of negative charge (NPA: **4a**: −0.36*e*; **4c**: −0.32*e*). The frontier molecular orbitals show π-lone pair character at C1 for the HOMO and σ-lone pair character for HOMO-1 similarly distributed as for previously reported diazoalkene classes (Figure S140–141).

Differential Scanning Calorimetry (DSC) measurements were carried out to assess the stabilities of the new diazoalkenes. **4a** features a sharp decomposition peak in the DSC measurement with an onset temperature of around 160 °C with a decomposition enthalpy of ca. 910 J/g (Figure S16–17). Heating a solution of **4a** in d_5-bromobenzene above the onset temperature (165 °C for 1.5 h) leads to unselective decomposition. **4c** is the first example of a diazoalkene with a clear melting point in the DSC at 57 °C. It shows a pronounced decomposition with an onset at ca. 90 °C (Figure S18–19), rendering it comparably unstable, similar to the weakly polarized pyridine derived diazoalkenes.[18,26]

Next, we were interested in coupling two exchange reactions at a C(0) center (Scheme 4). After the first NHC/N_2 exchange to give the diazoalkenes **4a–c**, a clean N_2/CO and N_2/R–NC exchange could be performed giving access to the unknown cumulenes, vinylidene ketene **6** (81%) and vinylidene ketenimine **7** (82%), respectively. In case of vinylidene ketene **6** X-ray diffraction shows a strongly widened C–C–C angle [145.1(2)°] compared to the diazoalkene **4a** [121.6(1)°].[13] Note, a direct ligand exchange such as NHC/R–NC is not possible on the carbodicarbene. Importantly, we investigated the possibility to perform a N_2/NHC exchange and selected diamidocarbene (DAC) as exchange partner, which has a sufficiently strong π-acceptor character.[27] Indeed, the diazoalkenes **4a** and **4c** react cleanly at room temperature with DAC to give under N_2 release the new polarized carbodicarbenes **8a** and **8c** (Scheme 4). In case of diazoalkene **4b** no reaction occurred at room temperature, presumably due to the high steric demand of both the *N*-dipp and *N*-mesityl groups. The central C-atoms in **8a** and **8c** appear in the ^{13}C NMR at $\delta(^{13}C) = 121.6$ ppm and 123.2 ppm, low-field shifted compared to CDC **5a** [$\delta(^{13}C) = 110.2$ ppm][4] (for a comparison on CDCs, see Table S2).[28] X-ray solid state structures were obtained for the new carbodicarbenes **8a** and **8c** (Figure 3). In all cases the carbene units are tilted towards each other [angle (NCCC): **8a**: 89.5(2)°; **8c**: 138.1(2)°] as well show a pronounced bending of the C1–C2–C3 fragment [**8a**: 142.00(11)°; **8c**: 135.94(19)°] which supports a carbodicarbene and not classical allene description. The X-ray solid-state structures (**8a** and **8c**) display a significantly shorter C1–C2 bond length [1.312(2)–1.360(3) Å] than the C2–C3 bond [1.358(2)–1.443(2) Å] in accordance with the π-acceptor properties of the respective carbenes.[28]

Interestingly, Severin and co-workers recently described a synthesis of metalated carbodicarbenes by the reaction of diazoalkenes with a Cr-based Fischer carbene complex.[29] The here reported metal-free N_2/DAC exchange strategy

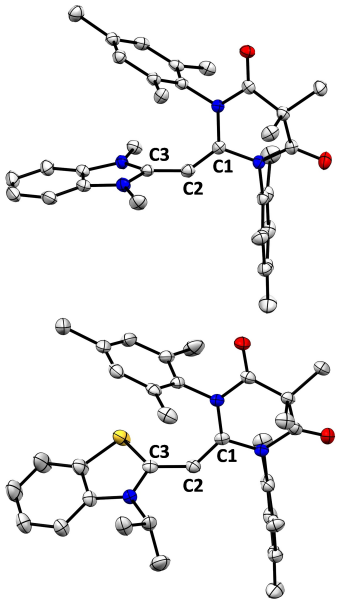


Figure 3. X-ray solid-state structure of **8a** (top) and **8c** (bottom). H atoms omitted for clarity. Thermal ellipsoids are shown with 50% probability. Selected bond lengths and angles of **8a**/**8c** in [Å] and [°]: C1–C2: 1.3115(15)/1.360(3); C2–C3: 1.3576(15)/1.443(3); C1–C2–C3: 142.00(11)/135.94(19).

allows the reaction of the free carbodicarbene ligand with any metal of choice. As proof of concept the reaction of the new CDC **8a** with either (dms)AuCl or $[RhCl(CO)_2]_2$ cleanly afforded the corresponding coordination complexes **9a** (75%) and **10a** (63%), the latter supported by X-ray diffraction. In **10a** the DAC C–C bond length [1.351(5)/1.362(5) Å; two independent molecules in the unit cell] is pronounced shorter than the elongated benzimidazole C–C bond [1.459(5)/1.447(5) Å] supporting a stronger donor influence of the benzimidazole fragment (for a comparison, see Table S3). Interestingly, upon coordination to Rh the rotational flexibility of the new CDC is lost leading to separate NMR signals of otherwise identical moieties of the CDC ligand. The solution phase (CH_2Cl_2) IR bands of the CO ligands in complex **10a** appear at 2060 cm^{-1} and 1979 cm^{-1}. The averaged IR frequency (ν_{av} = 2020 cm^{-1}; TEP = 2035.8 cm^{-1})[30] is larger than CDC **5a** (ν_{av} = 2014 cm^{-1})[4] in agreement with a lower overall donor ability, demonstrating the tunability of the electronic properties. Note, **5a** is still a significant stronger donor compared to typical five-membered NHCs (ν_{av} ~2058–2036 cm^{-1}).[4]

In summary, we have demonstrated the first PPh_3/N_2 and NHC/N_2 ligand exchange reactions of a carbophosphinocarbene and carbodicarbenes to afford novel diazoalkenes. Similar to the ozonolysis reaction, N_2O engages in a (3+2)/retro-(3+2) cycloaddition mechanism to cleave the C–C bond which was supported by DFT calculations. Notably, the newly obtained benzothiazole-based diazoalkene shows the so far shortest C–C bond and shortest N–N triple bond supported by the most low-field shifted ^{13}C NMR and ^{15}N NMR resonances for stable diazoalkenes. Such diazoalkenes are not accessible by the previous established synthesis routes and thus, the NHC/N_2 exchange method expands the chemical space of stable diazoalkenes. In addition, we demonstrated the utility of the combination of ligand exchange reactions at a C(0) atom. If coupled with a second ligand exchange, vinylidene ketenes and vinylidene ketenimines as well as polarized carbodicarbenes can be obtained which all can serve as new ligand classes. The two-step exchange reaction (NHC/N_2 and N_2/L) affords overall a formal NHC/L (L = CO, R–NC, DAC) exchange which opens up a new field of carbodicarbene chemistry.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: diazoalkenes · carbodicarbenes · ligand exchange · nitrous oxide · diazo compounds

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