

# Ligand Exchange at Carbon: Synthetic Entry to Elusive Species and Versatile Reagents

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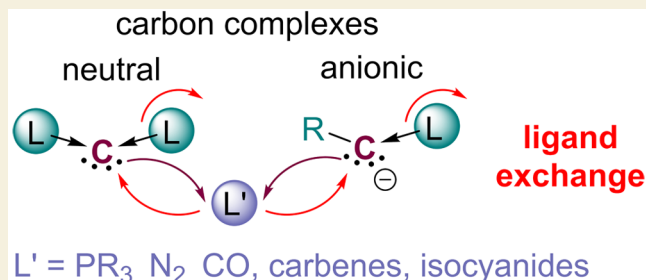
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**ABSTRACT:** How different is carbon compared to other elements in the periodic table? Can carbon compounds be regarded as coordination complexes with carbon as the central element undergoing a facile exchange of its ligands? Although carbon clearly plays a special role among the elements of the periodic table, recent studies have drawn parallels between the bonding situation and the reactivity of carbon compounds to transition metal complexes. This Perspective summarizes recent reports about ylidic and zwitterionic compounds that were shown to exhibit ambiguous bonding situations that can be interpreted as donor–acceptor interactions similar to the bond between a metal

and a neutral ligand. Based on this conception, ligand exchange reactions prototypical of transition metal complexes were realized at carbon atoms, enabling new synthetic strategies for the synthesis of reactive species and building blocks. In particular, the exchange of  $N_2$ , CO, and phosphine ligands led to the development of a mild method for accessing new compounds and reagents with unusual properties, such as vinylidene ketenes or stable ketenyl anions, that open up a diverse but still poorly explored follow-up chemistry.

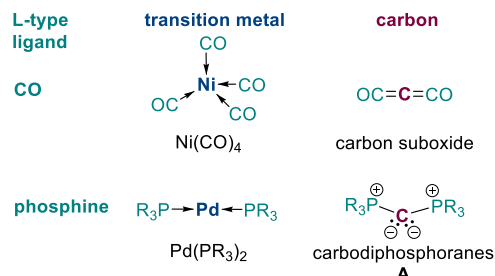
**KEYWORDS:** Ligand exchange, ylides, carbanions, carbenes, carbon monoxide, phosphines, small molecule activation



## 1. INTRODUCTION

The propensity of carbon to form four covalent bonds is fundamental to organic chemistry and has—since Kekulé’s theory of chemical structures—been considered a paradigm in chemistry.<sup>1</sup> These bonding properties of carbon, together with the generally high carbon–carbon and carbon–heteroatom bond strengths, have made carbon a unique element on the periodic table with unparalleled diversity and breadth in chemical reactivity and structures. While these properties of carbon are often considered to be the normal behavior of chemical elements, they in fact represent an abnormality: None of the other elements in the periodic table exhibit such a rich and versatile chemistry.

Due to this special behavior of carbon, it has almost been taken for granted that carbon always uses all four valence electrons in bonding interactions. However, it is nowadays well-known that this tetravalency is not a paradigm. Neutral carbon compounds with lone pairs at carbon, such as carbon monoxide, isonitriles or carbenes, are no longer laboratory curiosities, but widely applied in chemistry.<sup>2</sup> In the past decades even compounds with a zerovalent carbon center have been discussed.<sup>3,4</sup> A prime example for such compounds, which have been intensively discussed in the literature, are carbodiphosphanes **A** (CDP, Figure 1). In these compounds, the central carbon atom binds to two phosphorus substituents, keeping all four valence electrons as lone pairs, which can then



**Figure 1.** Comparison of carbon compounds with related transition metal complexes with carbon monoxide and phosphine ligands.

interact with other elements and substrates. With these properties, CDPs obviously share similarities with phosphine complexes of the transition metals. Here, phosphine ligands are considered prototypical L-type ligands that coordinate to transition metals via dative interactions. Consequently, such a bonding mode has also been proposed for carbodiphosphor-

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anes.<sup>3</sup> This concept was controversially discussed in the literature and led to a questioning of established bonding concepts. The description of compounds such as carbodiphosphoranes or carbon suboxide as coordination complexes of carbon<sup>5</sup> was coined, with this “rethinking” of carbon compounds leading to the discovery of many exciting new reactivity patterns and the isolation of unusual species.<sup>6</sup>

In this Perspective, we discuss the description of carbon compounds as coordination complexes with carbon as the central element. We start by summarizing the special quantum properties of carbon, which are responsible for its special role among the elements in the periodic table. We continue with the controversial discussion about the bonding situation in ylidic and zwitterionic carbon compounds, which led to the description of such species as coordination complexes. In the last two sections, we show how this conception led to the development of ligand exchange reactions at carbon, similar to the coordination chemistry of the transition metals. This ligand exchange represents a new synthetic strategy that provides access to novel compounds and reagents with unusual properties and reactivities. Although these exchange reactions have only recently been recognized, they have already produced a series of extraordinary species that demonstrate the potential of this approach for further applications in the future.

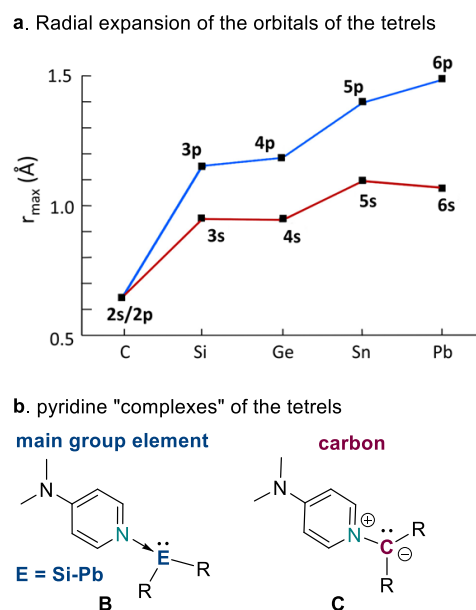
## 2. THE TRANSITION METAL-LIKE BEHAVIOR OF CARBON

### 2.1. Carbon: The Abnormal Element

The “abnormality of carbon” and its strong tendency to use its four electrons in four bonds can be explained by its exquisite position in the periodic table and its related quantum structure. Due to the lack of a core–shell with the same angular momentum ( $l = 1$ ), i.e., the lack of nodes in the 2p orbital, the radial extension of the p orbitals is very similar to that of the 2s orbital.<sup>7,8</sup> Therefore, these orbitals easily mix to hybrid orbitals, which form stronger bonds due to better orbital overlap and reduced Pauli repulsion between the C–X bonds (or the C–X bond and possibly remaining lone pair) as a consequence of increased bonding angles.<sup>9</sup>

Owing to the increasingly different radial extent of the s and p orbitals when going down the group in the periodic table (Figure 2a), “hybridization defects” occur. This was first noted by Kutzelnigg in his work on “Chemical Bonding of Higher Main Group Elements”. He in fact was the first to also conclude that “it is rather the heavy elements which behave normally and not the more familiar elements” of the second period.<sup>9</sup> These hybridization defects increase the tendency of heavier elements to keep a nonbonding lone-pair s orbital and to only form bonds with essentially unhybridized p orbitals. This ultimately leads to weaker bonds and greater reactivity of these compounds.

The origin of the diverse chemistry of carbon and the stability of its different structures stems not only from the similar expansion of the 2s and 2p orbitals but also from the involvement of all four valence electrons in bonding interactions. This leads to the formation of an electron octet and hence to highly stable compounds. Since all the other elements in the second period of the periodic table have fewer or more than four valence electrons, their compounds either possess lone pairs (NH<sub>3</sub>, H<sub>2</sub>O) or empty p-orbitals (BH<sub>3</sub>) at the central element, which ultimately results in increased



**Figure 2.** Comparison of the group 14 elements: (a) Atomic orbital radial probability function of group 14 elements. Reproduced from ref 10. Copyright 2021 American Chemical Society. (b) Structures of pyridine complexes of tetrylenes.

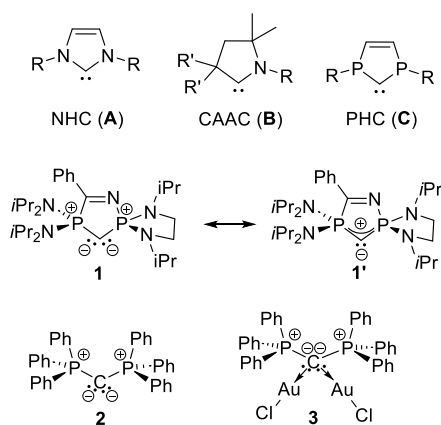
reactivity due to the presence of electrophilic and nucleophilic sites and decreased stabilities of E–E and E–R bonds due to increased repulsion between lone pairs (note the high reactivity of the F<sub>2</sub> molecule).

These quantum properties make carbon a unique element in the periodic table and have led to the development of bonding concepts and reaction mechanisms for carbon compounds almost independently of all other elements. For example, while coordination complexes of transition metals are traditionally described by dative or donor–acceptor interactions, the chemistry of carbon is characterized by covalent electron-sharing bonds (Figure 1). Notably, this differentiation is also made between carbon and other main group elements, including the heavier group 14 elements. For instance, compounds of type B are commonly described as pyridine complexes of a heavier carbene, while the corresponding carbon analogs C are referred to as nitrogen ylides (Figure 2b). However, in the last two decades, this differentiation has been called into question.

### 2.2. Carbon as Central Element in Coordination Complexes

The renewed discussion about the bonding in carbon compounds was triggered by reactivity studies on ylidic compounds and a series of landmark reports on the transition metal-like behavior of carbon and other main group element compounds,<sup>11–16</sup> which defied longstanding paradigms in chemistry. For example, singlet carbenes such as N-heterocyclic carbenes (NHCs, A)<sup>17</sup> or cyclic alkyl(amino)carbenes (CAACs, B)<sup>18,19</sup> have been established as classes of isolable low-valent carbon compounds in which carbon does not obey its usual tetravalent nature (Figure 3). Furthermore, Bertrand and co-workers demonstrated that singlet carbenes can activate dihydrogen, a reactivity that was long thought to be exclusive to transition metals.<sup>20</sup>

In 2006, Kato, Baceiredo, and co-workers reported on cyclic CDP 1, which structurally resembles carbenes, particularly

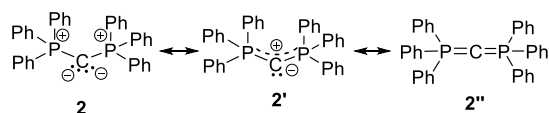


**Figure 3.** Examples of isolated carbenes and carbodiphosphanes **1** and **2** as well as CDP digold complex **3**.

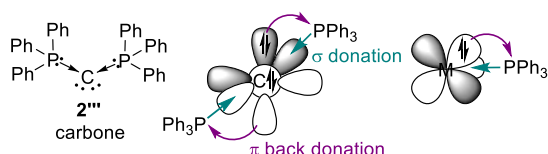
diphosphinocarbenes (PHC, **C**),<sup>21</sup> and was thus first described as a divalent carbon species but with enhanced donor strength compared to that of NHCs.<sup>22</sup> Like carbenes, CDPs are compounds with a disubstituted carbon atom but differ by virtue of the fact that they bear two lone pairs at the central carbon atom. In early reports these compounds were also described as heterocumulenes with phosphorus carbon double bonds,  $R_3P=C=PR_3$ . But already Ramirez, who first prepared the hexaphenyl system **2** in 1967,<sup>23</sup> described it as different structures among form **2** bearing two lone pairs at carbon (Figure 4). The availability of these two lone pairs was experimentally proven by Vicente in 2003 through the synthesis of the gem-dimetallated complex **3**, in which **2** served as a double Lewis base (Figure 3).<sup>24</sup>

Based on these findings, Frenking and co-workers computationally re-evaluated the electronic structure of CDPs. Analysis

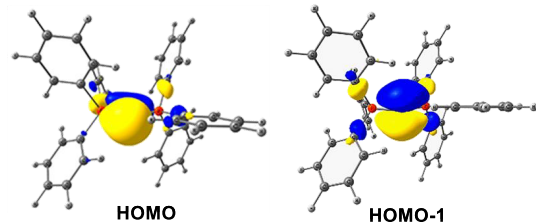
#### a. Representations of carbodiphosphorane **2**



#### b. Representation of **2** as donor–acceptor complex



#### c. Two highest occupied molecular orbitals of **2**

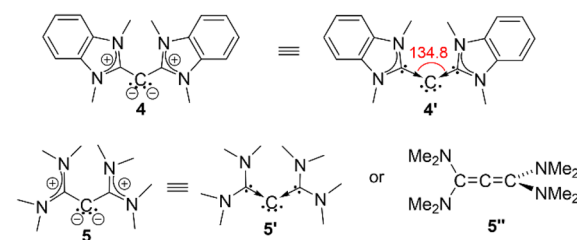


**Figure 4.** Representation of carbodiphosphorane **2** by (a) different structures, including (b) as a donor–acceptor complex. (Note that only the donation from the phosphines into the empty  $p_y$  orbital is shown.  $\sigma$  donation may also occur into the  $p_x$  orbital.) (c) Illustration of the two highest occupied molecular orbitals.

of the molecular orbitals (Figure 4c), the bonding situation and charge distribution (e.g., by quantum theory of atoms in molecules (QTAIM) and natural bond orbital (NBO) analyses), as well as the first and second proton affinities, led to the conclusion that **2** neither possesses a cumulene (**2''**) nor a carbene-like structure (**2'**). True double bonds, as in the cumulene structure, require the contribution of d-orbitals at phosphorus, which are too high in energy to engage in bonding interactions.<sup>25</sup> Energy decomposition analyses (EDA) of the different fragmentation patterns of **2** finally led to its description as a coordination complex with donor–acceptor interactions  $L \rightarrow C \leftarrow L$  between two phosphine ligands and carbon in a zero-oxidation state (Figure 4b).<sup>26,27</sup> Thus, the term “carbone” was introduced for these molecules to distinguish them from carbenes.

The captodative description of carbones resembles the typical bonding in transition metal complexes and was subsequently transferred to other compounds, in which the phosphine ligands were replaced by other L-type ligands such as carbon monoxide, isonitriles, carbenes  $CR_2$  or combinations thereof.<sup>28,29</sup> For example, the introduction of two carbenes gives rise to the class of carbodicarbenes (CDC; Figure 5),

#### carbodicarbenes



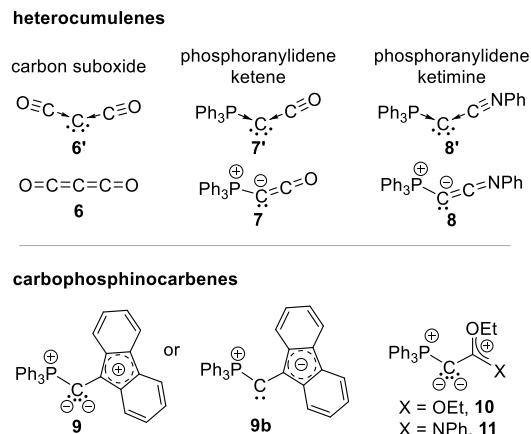
**Figure 5.** Carbodicarbenes **4** and **5** were prepared by Bertrand and Füstner.

which were first predicted by Frenking and co-workers to be stable compounds based on computational studies,<sup>30</sup> and shortly afterward experimentally confirmed by the groups of Bertrand and Füstner (**4** and **5** in Figure 5).<sup>31,32</sup> Like CDPs, carbodicarbenes are best described by the ylidic or dative form (**4** and **4'**) or, in some cases, also as “bent” allenes. For example, compound **5** was found to be linear in the solid-state but still shown to coordinate metals via the central carbon atom. In recent years, a series of further carbodicarbenes have been described which exhibit extraordinary donor strengths, similar to CDP **2**.<sup>33–36</sup> These donor properties have been exploited in various applications, such as their use as ligands in homogeneous catalysis<sup>37–40</sup> or for the stabilization of reactive main group compounds.<sup>41–43</sup>

Crystallographic analyses of CDCs revealed a bending of the central C–C–C moiety, which clearly argues against a classical allene structure with  $C=C$  double bonds but is in line with the theoretical predictions and the proposed zerovalent, ylidic (structures **4** and **5**) or carbene (structure **5'**) character. The degree of bending was explained by the acceptor properties of ligand L, with a stronger  $\pi$ -acceptor ability of L resulting in a larger angle and a more pronounced cumulene-like structure  $R_nE=C=ER_n$ . It is noteworthy, however, that all (hetero)-cumulenes investigated for their carbene character showed shallow energy potentials for the bending of the central L–C–L angle. This flexibility is reflected in the different crystal structures reported for CDP **2**,<sup>44,45</sup> which drastically vary in the

P–C–P angle (132–180°) and thus confirm the absence of classical double bonds.

Carbon suboxide (**6**, Figure 6) was long considered a prime example of a linear cumulene, but later shown to have a bent



**Figure 6.** Examples of additional compounds discussed as coordination complexes of carbon.

minimum structure, which was thus also described as a CO complex of carbon (**6'**).<sup>46–48</sup> Owing to the stronger acceptor ability of CO than of PPh<sub>3</sub>, the C–C–C angle in **6** is larger than that in phosphoranylidene ketene **7**. Fürstner and colleagues explored the properties of **7** and related compounds of the Ph<sub>3</sub>P → C ← L type with L being phenyl isonitrile (**8**)<sup>49</sup> or a carbene ligand (**9–11**).<sup>5</sup> While carbophosphinocarbene **10** reacted as a double Lewis base to form the corresponding digold complex, all the other systems only formed monoaurated species. The unavailability of the second lone pair was explained by its stronger involvement in back-donation to ligand L. Compound **9** even predominantly exists in carbene form **9b** since fluorenyl-9-ylidene is an excellent π acceptor, which enables the complete escape of one lone pair at the central carbon atom due to the favorable aromatization gained by the fluorenyl system. Besides the compounds shown in Figure 6, various other systems have been described as carbenes, including diazo compounds (vide infra) and heavier group 14 element systems.<sup>50–53</sup>

The description of carbon compounds by a captodative bonding model analogous to transition metal complexes led to a “rethinking”<sup>6</sup> of carbon and inspired researchers to search for further examples of carbon coordination complexes and explore the synthetic potential of these unique double Lewis bases. Nonetheless, this concept has also been criticized, mainly because it allegedly presents molecules more interesting than they might be in reality and because it suggests the presence of weak dative interactions between carbon and the respective substituent/ligand, which is usually not the case.<sup>54,55</sup> In fact, the ylidic (or zwitterionic) bonding model (e.g., **2'**), which has been used for decades for the description of phosphorus ylides, is just as suitable as the captodative model for explaining important features, such as short C–L bonds, bent structures, or the presence of two lone pairs at the central carbon atom. Therefore, this “traditional” model also retains its validity. An unequivocal, experimental distinction between the two models is difficult, as it requires a distinction between electron-sharing and dative bonds. According to the definition by Haaland, a differentiation lies in the way the bonds are

cleaved, with an electron-sharing bond cleaving in a homolytic way and a dative bond in a heterolytic way.<sup>56</sup> In transition metal chemistry, this heterolytic cleavage of bonds to L-type ligands is commonly observed and often expressed in the reversibility of ligand binding. The exchange of one ligand by another ligand, therefore, represents a prototypical reaction in transition metal complexes. However, such a reactivity of CDPs and related compounds, which would ultimately support the analogy of carbon species with transition metal complexes, has been established only in recent years.

It is important to keep in mind that compounds with ambiguous bonding situations are, in general, insufficiently described by a single Lewis structure. Several structures are often necessary to describe not only the actual connectivity of the atoms but also their bonding properties. These different structures often do not equally contribute to the “true” electronic structure but may still be important to explain the often-diverse chemical reactivity of such systems. In general, representations that best describe the reactivity of compounds should be used. Extreme Lewis structures, which are based only on arrow pushing but do not reflect reactivity, should be discarded or questioned until they are proven experimentally.

### 3. LIGAND EXCHANGE AT NONMETAL CENTERS

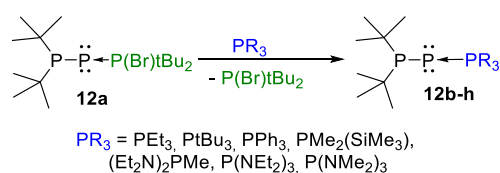
#### 3.1. Ligand Exchange at Phosphorus

Early investigations on the reactivity of carbenes focused on exploring their coordination chemistry to evaluate their potential as exceptionally strong Lewis bases. A possible ligand exchange at carbon, in analogy to transition metal compounds, was not examined but had been described before for other elements of the p-block. Owing to the diagonal relationship between phosphorus and carbon, we will focus on phosphorus-centered ligand exchange reactions here. However, group 13 and 14 compounds, particularly those with low-valent boron and silicon centers, have also been shown to undergo exchange of Lewis basic ligands similar to transition metals.<sup>57–61</sup>

Ligand exchange reactions at phosphorus have been investigated in phosphine-phosphinidene complexes.<sup>62</sup> Phosphinidenes (R–P) are isoelectronic with nitrenes (R–N) and carbenes but remained elusive species until the first isolation reported by Bertrand in 2016 (vide infra). Prior stabilization of phosphinidenes was achieved through coordination of Lewis bases, such as phosphines. The first indication of the coordination-like chemistry of these phosphine-phosphinidene complexes came from Cowley and Cushner, who observed the exchange of PMe<sub>3</sub> in (CF<sub>3</sub>)P←PMe<sub>3</sub> via concentration-dependent NMR experiments.<sup>63</sup> Similar observations were made by Fritz, Protasiewicz, and other groups, who were also able to displace phosphines such as *t*Bu<sub>2</sub>PBr from **12** by other phosphines (Scheme 1).<sup>64–67</sup>

Systematic studies on ligand exchange were possible with the first stable singlet phosphinidenes, which were shown to form

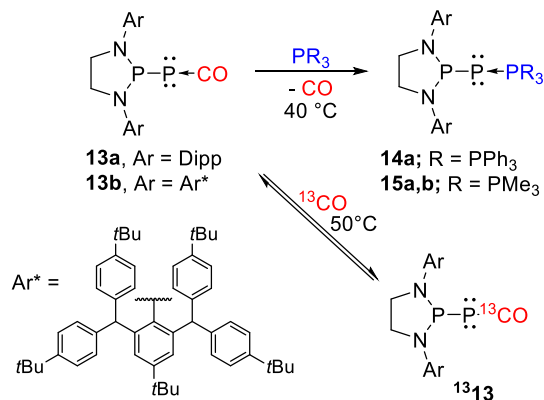
#### Scheme 1. Phosphine Exchange in Phosphine–Phosphinidene Complexes Reported





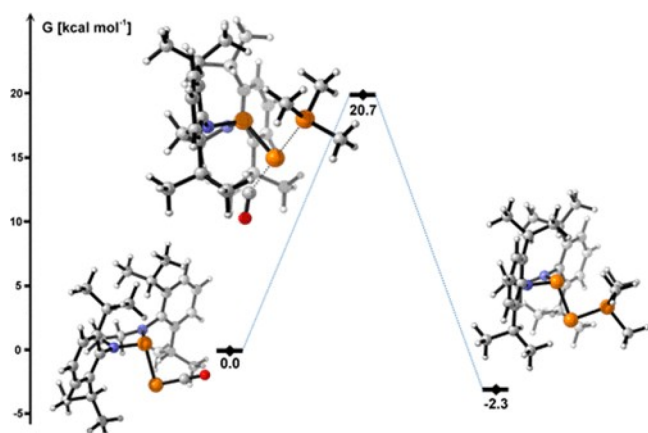
complexes not only with phosphines but also with CO, isonitriles and carbenes.<sup>68,69</sup> In 2016, Bertrand and Hansmann investigated the exchange of the CO ligand in (phosphino)-phosphaketenes **13a** and **13b** (Scheme 2), resulting in the CO

**Scheme 2. Ligand Exchange at a Stable Phosphinidene (Dipp = 2,6-Diisopropylphenyl)**



displacement by more donating phosphines.<sup>70</sup> Notably, such a CO by phosphine exchange is a prime example of ligand exchange in transition metal chemistry and has been proven to occur at the phosphinidene center in **13**. At 40 °C, PPh<sub>3</sub> and PMe<sub>3</sub> displaced the CO ligand to form phosphine complexes **14a** and **15a**, while the more sterically congested phosphinidene **13b** only reacted with the smaller PMe<sub>3</sub> to form **15b**.

The reversibility of the CO coordination in **13** was also demonstrated through an exchange with carbon-13 labeled CO. Mechanistically, the reaction was found to proceed via an associative pathway by attack of the ligand at the phosphinidene phosphorus atom with concomitant elimination of CO (Figure 7). A dissociative mechanism via initial



**Figure 7.** Reaction profile for the exchange of CO by a phosphine with a phosphinidene. Reprinted from ref 70. Copyright 2016 American Chemical Society.

decarbonylation was energetically less favorable. Ligand exchange was also possible from the PPh<sub>3</sub> complex **14a** with stronger  $\sigma$ -donating ligands, including PMe<sub>3</sub>, adamantyl isonitrile (CNR), NHC and CAAC ligands. DFT studies confirmed that all exchange reactions proceeded toward increasing phosphinidene–complex stability in the order CO < PR<sub>3</sub> < CNR < NHC < CAAC.

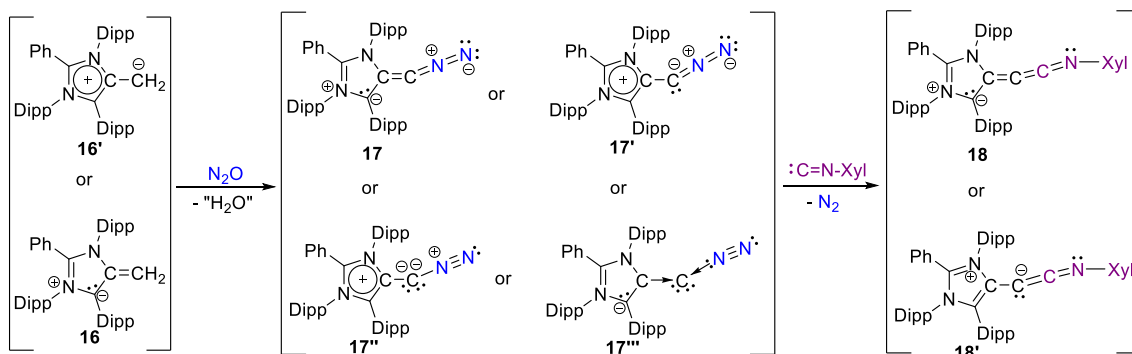
### 3.2. Ligand Exchange at Carbon

The first ligand exchange reaction at carbon<sup>71</sup> was accomplished by Hansmann and co-workers in 2021 by means of the isolable diazoalkene **17**.<sup>72</sup> This diazo compound was prepared from the corresponding mesoionic N-heterocyclic olefin **16** with nitrous oxide and can be described through a series of zwitterionic Lewis structures as well as carbon complex **17'''** with a carbene and dinitrogen ligand (Scheme 3). Crystal structure analysis of **17** revealed short C–C and C–N bonds ranging between typical single and double bonds with a strongly bent C–C–N linkage [124.3(5)°]. Despite these short bonds, diazoalkene **17** and its triazole analog **19** (Scheme 4) undergo exchange of the N<sub>2</sub> ligand upon addition of 2,6-dimethylphenyl isocyanide (Xyl–NC) to form vinylidene ketenimine **18** and **20**, respectively. Like the N<sub>2</sub> complex, vinylidene ketenimines can be represented by a series of resonance structures and exhibit a bent C–C–C unit with a large angle of 163.9(1)° and short C–C distances of 1.2324(16) and 1.3815(15) Å. Therefore, the authors suggested a preference for the cumulene structures **18** and **18'**.

Shortly after this initial report, the Hansmann<sup>73</sup> and Severin<sup>74</sup> groups independently presented a N<sub>2</sub>/CO ligand exchange in diazoalkenes with mesoionic triazoles as well as normal and mesoionic imidazoles as substituents. The carbonylation reaction proceeded readily at room temperature and furnished the corresponding alkylidene ketenes **21** in good to excellent yields. The solid-state structures of **21** exhibited C–C bond lengths between a single bond and a double bond for the C3–C1 bond (approximately 1.38 Å) and between a double bond and a triple bond for the ketenyl C1–C2 bond (1.23 Å), thus indicating the presence of a resonance hybrid between a zwitterion with a C–C triple bond (**21'**) and a cumulenic structure (**21**). Like ketenimines **18** and **20**, the ketenes possess a bent C–C–CO linkage with low barriers for the bending, as reflected by the different angles ranging from 136.1(1)° to 160.1(12)° observed in the solid state. The signal for the central carbon atom C1 of **21** appeared at 34.5 ppm in the <sup>13</sup>C NMR spectrum, i.e., considerably high field shifted compared to “normal” ketenes, thus suggesting an increased negative partial charge at this position. A comparison of the <sup>1</sup>J(<sup>13</sup>C1–<sup>13</sup>C2) coupling constants in the series of compounds **19**–**21** revealed an increase from 60 Hz in compound **19a** to 107 Hz in compound **20a** and 120 Hz in compound **21a**. This trend is in line with the increasing s-character in the order CCN<sub>2</sub> < CCCO < CCCNXyl, which corroborated well with the widening of the angle at C1 calculated for methyl-substituted model systems of the triazole compounds (Figure 8).

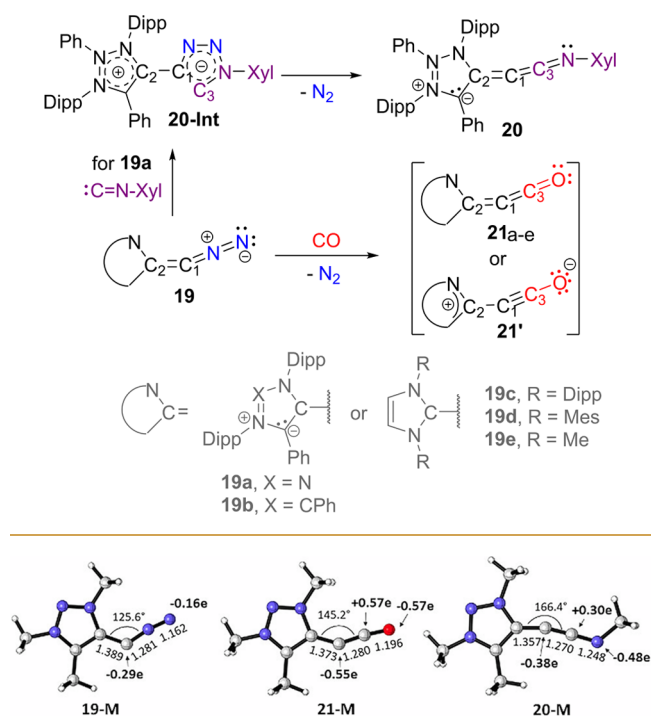
DFT calculations on the mechanism of the N<sub>2</sub>/CO exchange suggested that the reaction proceeded via a single transition state.<sup>73</sup> Nucleophilic attack of **19** at the CO leads to the release of dinitrogen without the formation of any acyl intermediate. It is important to note that this reactivity is different from that of regular S<sub>N</sub>2 reactions, in which the polarization is opposite, with the carbon center being attacked by a nucleophilic partner. This unique reactivity of diazoalkenes **17** and **19** toward ligand exchange is thus based on the strong donor ability of the (mesoionic) carbene, which renders the C1 atom highly nucleophilic and thus favors the binding of ligands with stronger acceptor properties. Interestingly, the N<sub>2</sub>/isocyanide reaction was calculated to proceed via a slightly different mechanism, proceeding via the formation of intermediate **20**–

**Scheme 3. Synthesis of the Stable Diazoalkene 17 from Mesoionic N-Heterocyclic Olefin 16 and Exchange of the N<sub>2</sub> Ligand by Xylyl Isocyanide (Xyl = 2,6-Dimethylphenyl Isocyanide)<sup>a</sup>**



<sup>a</sup>Note that only selected resonance forms of 17 and 18 are shown.

**Scheme 4. Exchange of N<sub>2</sub> by Xylylisocyanide and CO in 19**



**Figure 8.** Calculated properties of a model system of the isoelectronic series 19–21 (BP86/def2TZVPP). Reprinted from ref 73. Copyright 2021 American Chemical Society.

Int through a [3 + 2] cycloaddition reaction (Scheme 4). Subsequent retrocycloaddition with elimination of N<sub>2</sub> finally leads to ketenimine 20.

Overall, the ligand exchange reactions in diazoalkenes allowed for the atom-economic synthesis of alkylidene ketenes and ketimines and thus provided access to unique types of compounds with fascinating follow-up chemistry, which promises further applications in synthetic chemistry in the future. For example, the reaction of triazole-substituted alkylidene ketene 21a with carbon disulfide allowed formal CO/CS exchange and the generation of the first stable alkylidene thioketene via the release of COS<sup>73</sup> and elimination of the N<sub>2</sub> ligand from 19a the first stable triplet vinylidene.<sup>75</sup>

**4. LIGAND EXCHANGE AT METALATED SPECIES**

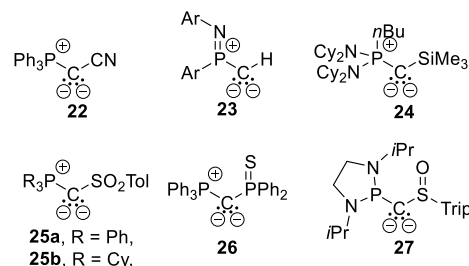
**4.1. Phosphine/CO Ligand Exchange in Metalated Ylides**

The ligand exchange reactions of diazoalkenes 17 and 19 are based on the high nucleophilicity of carbon in these compounds. Such high nucleophilicities are difficult to reach in neutral compounds but should be easily realized in carbanionic systems.  $\alpha$ -Metalated ylides (also referred to as metal yliides; Figure 9A) can be regarded as anionic

**A. Comparison between yliides and bisylides**



**B. Examples of isolated yliides**

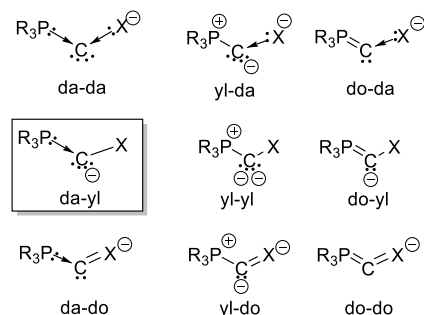


**Figure 9.** (A) Comparison of the structures of metalated ylides (yliides) with those of carbodiphosphoranes (bisylides) and (B) examples of isolated yliides.

congeners of carbodiphosphoranes. In the former, a phosphine ligand is formally replaced by an anionic ligand X, thus rendering a different bonding description necessary (vide infra). Over the past few years, several metalated ylides have been isolated and applied in different research directions (Figure 9B), particularly as ylide-transfer reagents.<sup>76–82</sup>

In the conventional Lewis structure of yliides, the central carbon is involved in an ylidic bond to the phosphorus atom and a single bond to ligand X (Figure 9). This bonding description is supported by crystallographic data that show short C–P bond lengths indicative of an ylidic bond. Furthermore, DFT calculations revealed that the HOMO and HOMO-1 reside on the central carbon atom, in line with the presence of two lone pairs. The sole exception is 22, in which  $\pi$ -delocalization into the cyano group is observed due to

its stronger acceptor properties. To obtain a deeper understanding of the bonding situation in metalated ylides, Gessner and Frenking carried out computational studies (e.g., NBO, EDA).<sup>83</sup> Nine possible representations were considered, which included a dative (“da”), an ylidic/electron-sharing (“yl”), or a double (“do”) bond to describe the bond between the central carbon and the two ligand fragments (Figure 10).

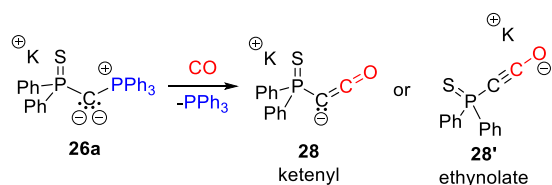


**Figure 10.** Possible resonance structures for ylides (da = dative bond, yl = ylidic bond, do = double bond).

In contrast to CDPs, the carbene description “da-da” does not significantly contribute to the bonding situation in the ylides. Instead, the carbynyl “da-yl” structure with a dative bond between the phosphine ligand and the central carbon atom in combination with an electron-sharing bond to X becomes more relevant. This can be attributed to the stronger  $\sigma$ -electron donation of the anionic ligand. Importantly, the study further revealed that there is no clear picture of the bonding in metalated ylides. Instead, these compounds are best described by a combination of representations shown in Figure 10, which vary depending on the anionic ligand X.

Since the calculations suggested a dative bonding between the phosphine ligand and the central carbon atom, metalated ylides provide an intriguing platform for testing ligand exchange at carbon in anionic species. Indeed, such a ligand exchange reaction was demonstrated by our group in 2022. The reaction between the metalated ylide **26a** and carbon monoxide resulted cleanly in the formation of ketenyl anion **28** with concomitant loss of  $\text{PPh}_3$  (Scheme 5).<sup>84</sup> While the

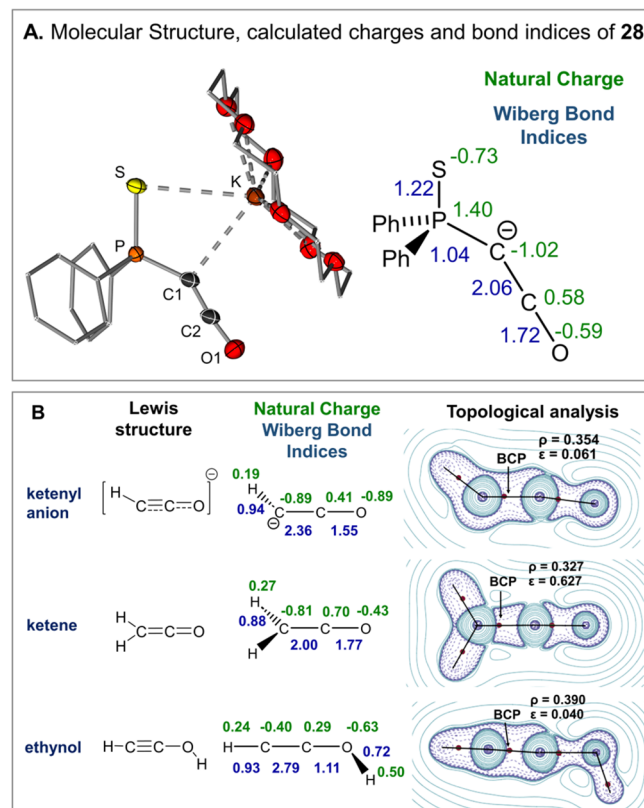
#### Scheme 5. Synthesis of the First Isolable Ketanyl Anion **28** via $\text{PPh}_3/\text{CO}$ Ligand Exchange at an Anionic Carbon and Its Resonance Form, Ethynolate **28'**



reaction mechanism is still under investigation, it likely proceeds through an initial nucleophilic attack of the metalated ylide at carbon monoxide, followed by back-donation from CO, which ultimately leads to the extrusion of the phosphine.

The selective phosphine/CO exchange in **26a** enabled the first gram-scale isolation and structural elucidation of a ketenyl anion, which has previously been observed only as a reaction intermediate. Structure elucidation was thus of particular importance since these anions have often been described as

ynolate anions in the literature.<sup>85</sup> XRD analysis of potassium salt **28**, both as a THF-containing coordination polymer and as an 18-crown-6 complexed monomer (Figure 11A), revealed an



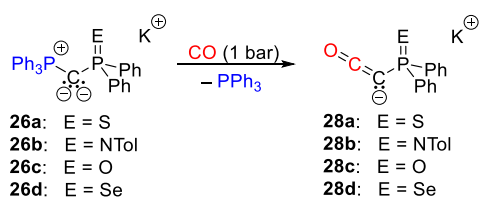
**Figure 11.** Molecular structure and bonding analysis of **28** as well as of the parent ketenyl anion, ketene, and ethynol. Adapted with permission from ref 84. Copyright 2022 The American Association for the Advancement of Science.

almost linear  $\text{C}=\text{C}=\text{O}$  but a bent  $\text{P}-\text{C}=\text{C}$  linkage, supporting the ketenyl description **28**. Nevertheless, the short  $\text{C}-\text{C}$  bond length of 1.245 Å and the elongated  $\text{C}-\text{O}$  distance of 1.215 Å argue for a contribution of the ynolate form **28'**. The computationally derived, energy-optimized structure resembles the solid-state structure of the ketenyl anion with a bent  $\text{P}-\text{C}-\text{C}$  angle of  $155^\circ$ . However, the Wiberg bond indices (WBIs) for the  $\text{C}-\text{C}$  and  $\text{C}-\text{O}$  distances of 2.06 and 1.72, respectively, fall between the expected values for both structures **28** and **28'**, suggesting that the description of the bonding situation by one of them is not correct. This was confirmed by computations on the parent anion,  $[\text{HCCO}]^-$ , ketene  $[\text{H}_2\text{CCO}]$  and ethynol  $[\text{HCCOH}]$  carried out at the coupled cluster level of theory (Figure 11B), which likewise revealed an electronic structure of the ketenyl anion between that of ketene and ethynol. The intermediate bonding situation and thus the delocalization of the negative charge result in remarkable stability of these anions in solution and in the solid state. In contrast to small ketenes, no dimerization was observed.

The generality of this phosphine/CO exchange reaction was subsequently extended to other metalated ylides. Successful carbonylation to the ketenyl anions **28a-d** was proven for a series of phosphinoyl-substituted metalated ylides **26**, allowing for the investigation of the influence of the substituents on the electronic structure (Scheme 6).<sup>86</sup> Although all of the ketenyl



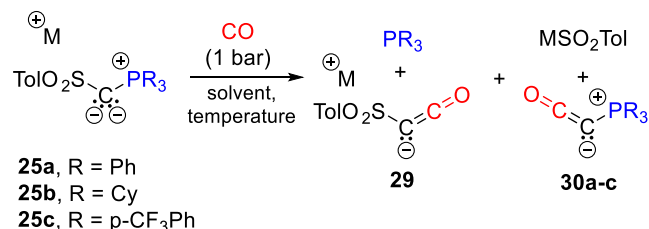
### Scheme 6. Synthesis of a Series of Phosphinoyl Ketenyl Anions 28a–d



anions were accessible in high yields and could be crystallographically characterized, no obvious trends could be observed in the solid-state structures. This was explained by the flat energy potential for the bending of the P–C–C unit, which is presumably influenced by packing effects or disorders in the crystal and thus also affects bond lengths. However, the anions exhibited systematic trends in solution. The observed decrease of the C=C=O stretching frequency for the heavier group elements (e.g., 2083 cm<sup>-1</sup> for 28d vs 2096 cm<sup>-1</sup> for 28c) indicated that less electron-withdrawing substituents favor the ketenyl form.

Access to ketenyl anions with substituents with better leaving group ability proved to be more challenging since carbonylation can also result in the formation of the competing phosphoranylidene ketene 30 with the loss of the corresponding metal salt. This competition in the displacement of the phosphine or the X ligand was first noted for the sulfonyl system 25 (Scheme 7).<sup>49,87</sup> Thus, a systematic study was

### Scheme 7. Competing Phosphine or Metal Sulfinate Elimination in the Carbonylation of the Metalated Ylide 25



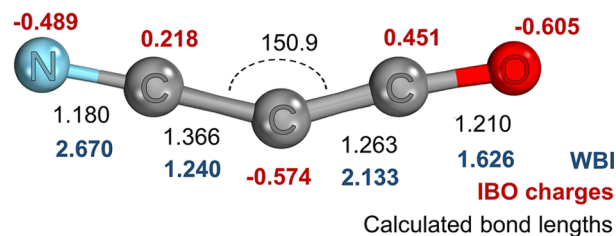
conducted to probe the influence of the phosphine, the metal cation, the solvent and temperature, as well as additional coligands, on the selectivity.<sup>88</sup> While the lithiated ylide with an electron-rich tricyclohexylphosphonium group 25b exclusively yielded phosphoranylidene ketene C<sub>6</sub>H<sub>5</sub>P–C=C=O 30b,<sup>87</sup> the PPh<sub>3</sub> analog 25a gave a mixture of products with a 4:1 ratio of 29:30a. This ratio could be further improved to 9:1 when the cation was exchanged for potassium due to its lower oxophilicity, weakening its binding to the tosyl leaving group. Further weakening of this interaction through the use of polar, coordinating solvents and cation-encapsulating coligands such as crown ethers or cryptands enabled the selective phosphine/CO exchange and the isolation of the tosyl-substituted ketenyl anion 29.

With [2,2,2]cryptand and 12-crown-4, the sodium salt of 29 forms a ligand-separated ion pair with the first “free” ketenyl anion, whose structure is thus not disturbed by interactions with the metal cation. The anion features an almost linear S–C–C–O unit, which argues for a pronounced ynoate character, although the reactivity selectively occurs at the ketenyl carbon (vide infra). DFT calculations again revealed a

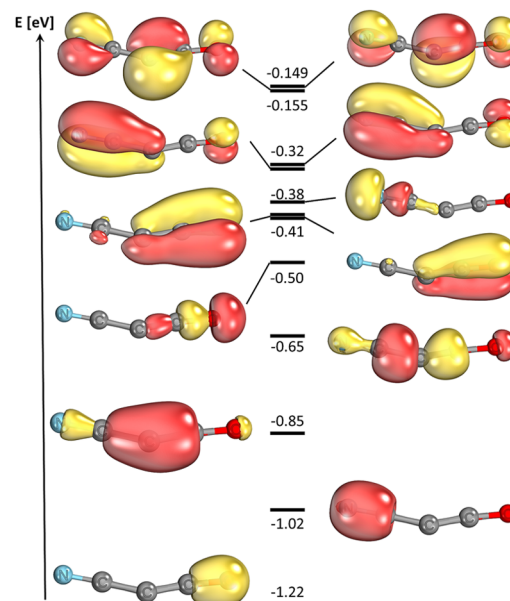
flat energy potential for bending, confirming that the angle is not a good indicator of the bonding situation.

Capitalizing on the efficiency of phosphine/CO exchange, this method could be transferred to the cyano-substituted ylide 22 to access the elusive cyanoketenone anion 31 (Figure 12).<sup>89,90</sup> Cyanoketenone itself has been prepared only in matrix

#### a Calculated structure of [NC<sub>3</sub>O]<sup>-</sup>



#### b Molecular orbital diagram of [NC<sub>3</sub>O]<sup>-</sup>



**Figure 12.** (a) Structure and bonding parameters of the energy-optimized structure of 31 at the CCSD(T)/ma-def2-TZVPP level of theory. (b) Molecular orbital diagram for the  $\pi$ -symmetric orbitals of 31. Reused with permission from ref 89. Copyright 2024 Wiley-VCH.

isolation experiments and discussed as a potential interstellar molecule, important due to its potential role in prebiotic chemistry.<sup>91–93</sup> Thus, the isolation of the anion represents an important discovery since it allows not only its use as synthetic building block but also reactivity studies with other interstellar molecules. In the solid state structure of [K([2,2,2]cryptand)]<sup>+</sup> complex of 31, the cyanoketenone anion shows a bent geometry around the central carbon atom with a large C2–C1–C3 angle of 166.4(2)°, contradicting earlier calculations that reported the anion to be linear (31' or 31'').<sup>94–97</sup> This is further evidenced by the IR spectrum of the anion, which displays three distinct signals in the region corresponding to the primary asymmetric and symmetric stretching vibrations.

DFT calculations resulted in a linear energy-optimized structure of 31 irrespective of the functional and basis set. However, coupled cluster calculations (CCSD(T)/ma-def2-tzvp) confirmed the bent structure found in the crystal structure of 31 with a slightly narrower C–C–C bond angle of



150.9°, but with less than 2 kJ/mol being required for its widening to 180° (Figure 12a). Analysis of the electronic structure by various analysis methods revealed an ambiguous bonding situation, which is best expressed by a combination of different resonance structures. Natural resonance theory (NRT) calculations showed that the three structures **31** (33.2%), **31'** (24.0%), and **31''** (40.0%) contribute to the actual bonding situation, with the cumulene structure being the predominant structure (Figure 13). The molecular orbital

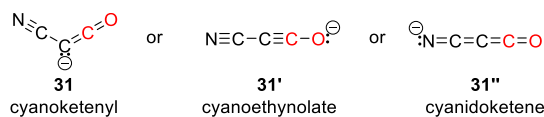


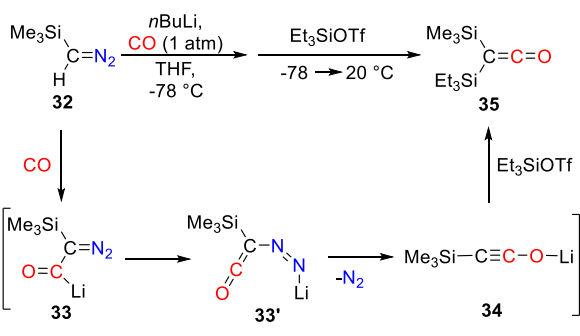
Figure 13. Possible resonance structures for the anionic cyanoketene.

(MO) diagram of the anion comprises six  $\pi$ -symmetric orbitals, which are split into three pairs with similar energies (Figure 12b). The HOMO and HOMO-1 are delocalized across the whole anion with the largest orbital coefficient at the central carbon, thus indicating a high nucleophilicity at this site.

#### 4.2. $\text{N}_2/\text{CO}$ Ligand Exchange in Metalated Diazomethanes

In 1996, Murai and co-workers reported the formation of silylketenes **35** by reaction of silyldiazomethane **32** with carbon monoxide after metalation with *n*-butyllithium. The reaction was proposed to proceed through the formation of an unstable diazoacyllithium intermediate **33**, which, upon loss of  $\text{N}_2$ , was proposed to form ynolate **34**, which can then be further functionalized to obtain ketenes, lactones, and lactams (Scheme 8).<sup>85</sup> Similar reaction intermediates have been

#### Scheme 8. Formal $\text{N}_2/\text{CO}$ Ligand Exchange in Metalated Diazomethane **32** through the Formation of Diazoacyllithium **33** to Yield Ketene **35**



observed for the reaction of strong amide or phosphide bases with CO, suggesting that the formation of a diazoacyllithium intermediate is plausible.<sup>98–101</sup>

Despite this early report, no further mechanistic investigations on this ligand exchange were conducted until Liu and co-workers reported on the direct  $\text{N}_2/\text{CO}$  ligand exchange in a (phosphino)diazomethyl anion **36** to yield the isolable (phosphino)ketenyl anion **37**.<sup>102</sup> In contrast to Murai's report, the computed reaction pathway revealed an associative pathway similar to that reported by Hansmann for diazoalkenes (Scheme 4) with an energy barrier of only 10.0 kcal/mol (Figure 14).

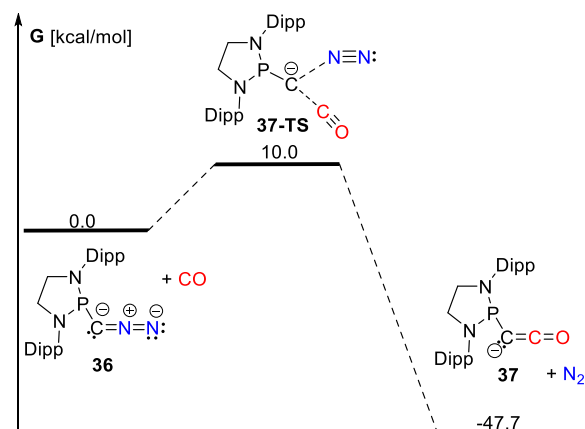


Figure 14. Calculated reaction pathway for the ligand exchange reaction in anion **36**.

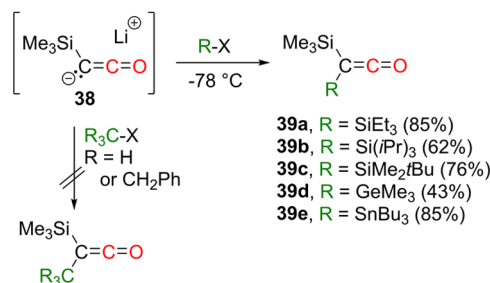
## 5. APPLICATIONS OF LIGAND EXCHANGE IN ANIONIC SYSTEMS IN SYNTHETIC CHEMISTRY

The ligand exchange at anionic carbon compounds enabled mild access to isolable ketenyl anions. These species have previously been generated in situ and have already been shown to be valuable reagents. Some of these early reports have already been summarized in other reviews.<sup>103–105</sup> Here, we will thus mainly focus on the reactivity of isolable ketenyl anions, which enable more controlled applications.

### 5.1. Salt Metathesis and Protonation

The synthesis of unsymmetrical ketenes is challenging due to the often-required harsh reaction conditions, the unavailability of suitable starting materials, or the low selectivity of the reactions. With the isolation of ketenyl anions through the carbonylation of metalated ylides, another synthetic method has become available that generally proceeds more selectively and with higher yields than traditional ketene syntheses. Murai trapped in situ generated trimethylsilylketenyl **38** with silyl chlorides and triflates,  $\text{Me}_3\text{GeBr}$ , and  $n\text{Bu}_3\text{SnCl}$  to access substituted ketenes **39a–e** in moderate yields (Scheme 9).<sup>85</sup> However, the reaction with carbon electrophiles did not result in the formation of alkyl- or benzyl-substituted ketenes.

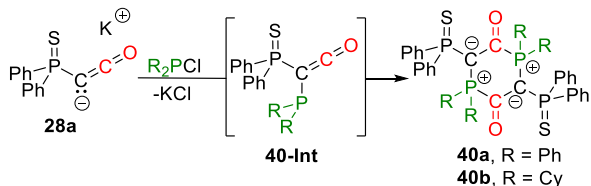
#### Scheme 9. Reaction of Ketenyl Anion **38** with Tetrel Halides to Ketenes **39** and Unsuccessful Reaction with Alkyl Halides



The reaction with chlorosilanes was shown to be more selective and high-yielding when isolated ketenyl anions **28a** and **29** were used. Furthermore, our group expanded the scope toward alkyl and trityl halides, resulting in the formation of new C–C bonds in the resulting ketenes.<sup>84</sup> Interestingly, the reaction of **28a** with chlorophosphines resulted in the formation of phosphorus heterocycles **40a,b** through the

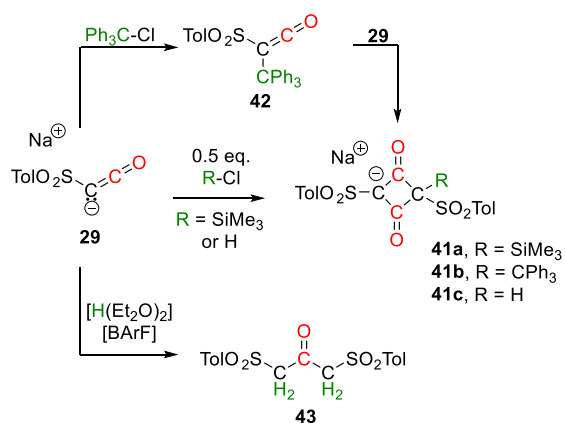
dimerization of the intermediate (phosphino)ketene **40-Int** (Scheme 10).<sup>84</sup>

**Scheme 10. Reaction of Thiophosphinoyl Ketenyl **28a** with Chlorophosphines**



Although the isolated ketenyl anions are stable toward dimerization, their respective neutral ketenes are very susceptible to direct reactions, with the ketenyl anion still present in the reaction mixture. In particular, tosyl-substituted ketenes tend to react in this way to form anionic cyclobutadiones (Scheme 11). Notably, dimerization to form

**Scheme 11. Synthesis of Anionic Cyclobutadiones **41** from Ketenyl Anion **29** and Protonation with Brookhart's Acid to Ketone **43****



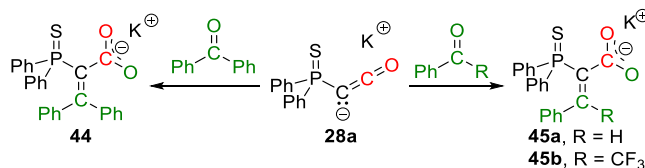
cyclobutadiones appears to be faster than elimination of salt to form ketenes. This was demonstrated by the reaction of anion **29** with trimethylsilyl chloride. Regardless of the chosen reaction conditions, only silylated cyclobutadione **41a** was isolated. Surprisingly, this compound does not undergo further salt elimination with chlorosilane because of the efficient charge delocalization within the OCCCO fragment. Direct reaction of the ketene with its ketenyl anion can be prevented through steric bulk. By reacting **29** with trityl chloride, it was possible to isolate ketene **42**. Surprisingly, ketene **42** is stable in solution and in the solid-state and does not dimerize. However, upon the addition of another equivalent of **29**, a rapid reaction to the cyclobutadione **41b** occurs.<sup>88</sup>

Due to the direct reaction of uncongested ketenes with their ketenyl anion, the isolation to H-substituted ketenes via this method remains a challenge. In the case of the tosyl-substituted ketenyl anion **29**, treatment with HCl only yields the monoprotonated cyclobutadione **41c**. For the other ketenyl anions, no selective reactions with acids were reported. Interestingly, however, when Brookhart's acid  $[H(Et_2O)_2][BARF]$  is used for the protonation of **29**,<sup>106</sup> compound **43** can be isolated. Although the exact mechanism is unknown, **43** formally forms through dimerization of the ketene and subsequent loss of carbon monoxide.

## 5.2. 1,2-Addition Reactions of Ketenyl Anions

The 1,2-dipolar nature of ketenyl anions renders them suitable starting materials for cycloaddition reactions. However, reactions with ketones or aldehydes lead to the formation of acrylates via the cleavage of the C=O double bond. For example, the reaction of ketenyl anion **28a** with benzophenone selectively proceeds to diphenyl acrylate **44** (Scheme 12). The

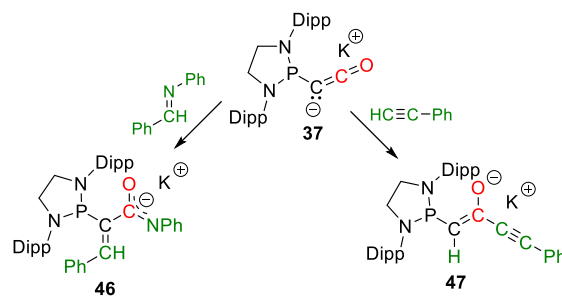
**Scheme 12. Synthesis of Acrylates **44** and **45** through the Reaction of Ketenyl Anion **28a** with Ketones and Aldehydes**



reaction likely proceeded through an initial [2 + 2]-cycloaddition to yield a  $\beta$ -lactone, which released the ring strain. Notably, reactions with asymmetric ketones and aldehydes proceed stereoselectively, and aldehydes always yield (*E*)-acrylates **45a** and **45b**.<sup>84</sup> Such C=O bond cleavage reactions were earlier investigated by Kowalski and Shindo<sup>107–110</sup> with *in situ* generated ketenyl anions and the observed selectivity explained by the torquoselectivity of the ring-opening of  $\beta$ -lactone enolate intermediates.<sup>111</sup>

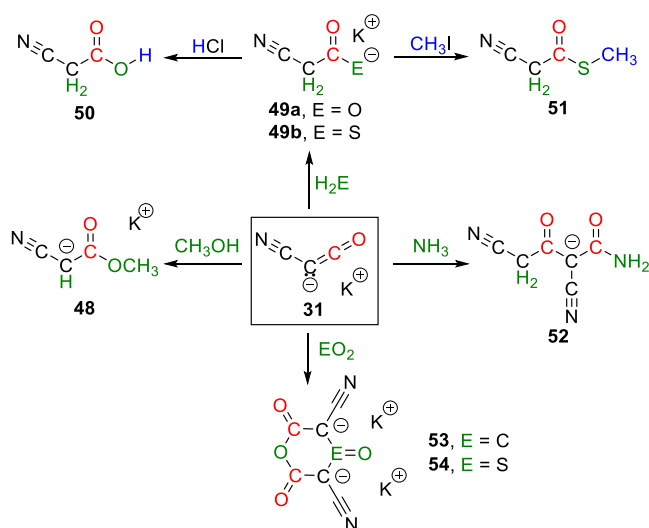
Liu and co-workers extended this reaction protocol to imines, which afforded the acrylimidate **46** with the same (*E*)-stereoselectivity, indicating a reaction pathway similar to the acrylate formation (Scheme 13). The same group attempted to

**Scheme 13. Reaction of Ketenyl Anion **37** with *N*-Benzylideneaniline to Acrylimidate **46** and with Phenylacetylene to **47****



expand the 1,2-addition reactions to alkynes. The reaction with phenylacetylene resulted in the formation of compound **47** via formal addition of the C–H bond across the C=C bond.<sup>102</sup>

This reactivity can be further extended to various compounds with protic E–H bonds (Scheme 14), which has been impressively demonstrated for cyanoketene **31**. For example, the reaction between **31** and methanol gives access to methyl cyanoacetate **48**, whereas hydrolysis leads to the formation of cyanoacetate **49a**, which can be protonated by HCl to yield neutral cyanoacetic acid **50**. Cyanoacetic acid is an important chemical for polymer synthesis but also a precursor to numerous drugs and also the nucleobase guanine. This reactivity showcases the applicability of anion **31** as functional synthetic building block to also yield compounds of industrial importance, but also important for life on earth, which further supports the relevance of the cyanoketene anion for prebiotic chemistry.

**Scheme 14. Reactivity of Cyanoketene Anion 31 toward E–H Bonds and CO<sub>2</sub> as well as SO<sub>2</sub>**


Similar to water and methanol, thio analogues **49b** and **51** can be obtained by the reaction of the anion with hydrogen sulfide, H<sub>2</sub>S. Furthermore, the cyanoketene anion is able to deprotonate ammonia, NH<sub>3</sub>, to presumably form a cyanoimide intermediate, which then reacts with another equivalent of the ketenyl anion to afford compound **52**.<sup>89</sup> In addition to the EH addition reactions, polar double bonds can be added across the ketene moiety. Exposure of cyanoketenyl **31** with CO<sub>2</sub> leads to the formation of the planar heterocycle **53** by cleavage of one C=O double bond through addition to two cyanoketene anions. The C–C bond lengths of 1.399 – 1.427 Å within the six-membered ring are indicative of an aromatic ring system without any significant delocalization of electron density toward the exocyclic oxygen atoms. The reaction with SO<sub>2</sub> results in an analogous heterocycle **54** with similar structural parameters. However, due to the trigonal pyramidal geometry around sulfur, the ring deviates slightly from ideal planarity.

## 6. CONCLUSIONS AND FUTURE DIRECTIONS

Although the representation of carbon compounds as coordination complexes is still unfamiliar and represents only an extreme representation of the actual bonding situation for most compounds, the above examples demonstrate that this captodative bonding model is becoming more important for ylidic and zwitterionic structures and is consistent with the observed reactivities. Regardless of the applicability of this bonding concept to other carbon compounds, it encourages chemists to look at compounds from a different perspective and to search for new reactivity patterns. The ligand exchange reactions observed thus far showcase the usefulness of this approach and suggest the discovery of further applications in the future.

Within only a few years, the exchange of neutral ligands at carbon atoms has opened up a synthetic pathway to previously inaccessible compounds that exhibit unique properties and reactivities. Since this ligand exchange operates under mild conditions, elusive and reactive species become synthetically accessible and hence usable for synthetic applications. Thus, this strategy is a valuable addition to the existing toolbox of synthetic chemistry, while also enabling the use of sustainable,

abundant molecules as building blocks. This has thus far been demonstrated primarily for carbon monoxide, which makes the use of elemental nitrogen the holy grail of this method.

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Both authors have written the manuscript. CRediT: **Felix Krischer** writing-original draft; **Viktoria H. Gessner** resources, writing-original draft, writing-review & editing.

### Notes

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## ABBREVIATIONS

AIM, atoms in molecules calculations; CAAC, cyclic alkyl-(amino)carbenes; CDC, carbodicarbene; CDP, carbodiphosphorane; DFT, density functional theory; EDA, energy decomposition analysis; HOMO, highest occupied molecular orbital; IR, infrared; NBO, natural bond orbital analysis; NHC, N-heterocyclic carbene; NMR, nuclear magnetic resonance; NRT, natural resonance theory; PHC, P-heterocyclic carbene; WBI, Wiberg bond index

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