Metalated Ylides: A New Class of Strong Donor Ligands with Unique Electronic Properties

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ABSTRACT: The development and design of new ligand systems with special donor properties has been essential for crucial advances made in main-group-element and transition-metal chemistry over the years. This Forum Article focuses on metalated ylides as novel ligand systems. These anionic congeners of bisylides possess likewise two lone pairs of electrons at the central carbon atom and can thus function as XL-type ligands with strong donor abilities. This article highlights recent efforts in the isolation and application of metalated ylides with a focus on work from this laboratory. We summarize structural and electronic properties and their use in organic synthesis as well as main-group-element and transition-metal chemistry.

1. INTRODUCTION

Amines and phosphines are the textbook examples of Lewis bases as electron-pair donors and ligands in main-group-element and transition-metal chemistry. The early developments in organometallic chemistry and homogeneous catalysis are strongly connected with advances made in the design of these ligand systems. In contrast, carbon-centered Lewis bases have been less important. This was historically due to the fact that carbon bases with a free pair of electrons at carbon, e.g., carbenes or carbanions, are usually highly sensitive and reactive compounds. Yet, with the remarkable developments in carbene chemistry, these bases have found increasing attention over the last decades. Like carbenes, ylides are overall neutral compounds with a carbon-centered pair of electrons and thus have potential as versatile Lewis bases in coordination and bond activation chemistry. This has been proven by the revival of research interest in bisylides, above all carbodiphosphoranes (CDPs), in the past years.

Since the first synthesis of an ylide and their use in Wittig-type reactions, these compounds have been applied in a variety of important reactions, e.g., for natural product synthesis. The most important class of ylides are phosphorus ylides (P-ylides). Their electronic structure has mostly been described by two canonical structures: ylene A and ylide A’ (Figure 1A). However, computational studies have shown that the contribution of the ylenic structure is minimal because it requires (d−p)π interaction with d orbitals at phosphorus. Recently, the canonical structure A" with a donor−acceptor interaction between phosphorus and carbon has found renewed interest. It classifies ylides as phosphane-stabilized carbenes. An analogous description has also been used for bisylidic compounds, particularly CDPs. This leads to their description either as ylides B’ or as a divalent carbon compound with carbon in the formal oxidation state of zero (carbone B") and donor−acceptor interactions between the phosphine and central carbon atom (Figure 1B). The unique electronic structure of these compounds has been studied in detail in recent years but is still under debate.

The high electron density and availability of two lone pairs at the central carbon atom of bisylides suggest new and unusual ligand properties for CDPs and related bisylidic compounds. In the case of CDPs, recent studies have proven their unique reactivity, which makes them highly attractive as carbon bases. For example, hexaphenylcarbodiphosphorane was found to undergo adduct formation with small molecules or ions such as CO2, BH3, or GeCl+ or can be used as a ligand in transition-metal complexes or in bond activation reactions. Their chemistry has been summarized in recent review articles. Likewise, bent allenes, which have also been described as carbodicarbenes, feature similar properties and can function as ligands with remarkable donor strengths. The first studies on these rather peculiar carbon(0) compounds were pioneered in particular by Bertrand and Fürstner, already demonstrating their potential in transition-metal chemistry. Later, the groups of Ong, Meek, and Stephan impressively confirmed the utility
of these ligands in transition-metal-catalyzed reactions. As such, high activities were observed in several different catalytic transformations, such as in hydrogenation and hydroamination reactions or in C−C coupling reactions.

Because of these impressive reports on the structure and applicability of carbon-centered donor bases, our group has become interested in the class of metalated ylides, the so-called yldiides. They can be viewed as the anionic congeners of bisylides, formed by the replacement of one positively charged carbon atom (e.g., a phosphonium group) by a neutral substituent (Figure 2). Comparable to bisylides, metalated ylides possess two pairs of electrons at the central carbon atom and should thus potentially act as monoaionic XL-type $\sigma$- and $\pi$-donor ligands. In this Forum Article, we highlight recent developments in the chemistry of metalated ylides. We will particularly focus on isolated systems, their electronic structure, and their donor properties.

2. SYNTHESIS AND ISOLATION OF METALATED YLIDES

While ylide chemistry is now well-established, only a very few reports have appeared on their metalated congeners. Such yldiides are the anionic versions of bisylides, e.g., CDPs, where one PR$_3^+$ moiety is replaced by a neutral substituent (Figure 2). Because of the high negative charge at the carbon atom, they are assumed to be highly nucleophilic species. The first synthesis of a metalated ylide [Ph$_3$P=CR-Li]$_2$C$_2$H$_2$] was proposed by Schlösser and co-workers using pentaphenylphosphane and an excess of butyllithium. However, no isolation or reactivity studies were reported at that time. Later studies by Corey and Kang in the 1980s reported an enhanced reactivity of yldiides in Wittig reactions with sterically hindered ketones. Here, the metalated ylide was prepared by direct deprotonation of the corresponding ylide at low temperatures, although again no isolation was accomplished because of the high nucleophilicity of the compounds. The first isolation and characterization of an yldiide was described by Bestmann and Schmidt in 1987 by means of the cyanido-functionalized compound 1 (Scheme 1). I was prepared by a classical deprotonation reaction of the corresponding ylide 1-H with sodium hexamethyldisilazide (NaHMDS). Although no structure elucidation was reported, they concluded on the basis of IR spectroscopic studies that resonance structure 1′ with charge stabilization by the CN moiety significantly contributes to the electronic distribution in 1. Yet, because of the observed reactivity, a structure with two pairs of electrons at the central carbon atom (1) was also suggested. Only recently, the contribution of form 1′ with a dative bond between phosphorus and carbon was considered, and thus properties analogous to those of bisylides were proposed (vide infra).

Until today, only three yldiides have been isolated and also structurally characterized: (i) the silyl-substituted yldiide 2 synthesized by Bertrand et al., 3 phosphoranyldiene ylides 3a and 3b by Niecke et al. (Figure 3), and (ii) the sulfonyl-substituted compound 4 reported by our group (Figure 4). Interestingly, the metalated ylide 2 was not prepared via a classical deprotonation reaction analogous to 1 but via a 1,2-carbometalation reaction of carbone 5 with butyllithium. The structure of the silyl-substituted compound (Figure 3, left) featured a planar geometry around the ylidic carbon atom with short P−C [1.636(11) Å] and Si−C [1.755(10) Å] distances. The latter reflects the stabilizing effect of the negative charge by the silyl group, while the short P−C bond can be explained by increased Coulombic interactions in the P$^{b+}$−C$^{b−}$ linkage or strong $\sigma$ donation from and $\pi$-back-bonding to the phosphine ligand (vide infra). The lithium atom in 2 is coordinated by the ylidic carbon atom as well as two tetrahydrofuran molecules. An analogous coordination mode was found in the structure of phosphoranyldiene ylides 3a and 3b. Likewise, short P−C bonds of 1.632(5) and 1.624(5) Å, respectively, were observed in 3a and 3b, which are comparable to 2.

In contrast to 2 and 3, the sulfonyl-substituted yldiide 4 was the first example of a metalated ylide, which is readily available also in a multigram scale by a straightforward double deprotonation sequence from the corresponding phosphonium salt 1-H$_2$ (Scheme 2). Depending on the base used in the last step, the lithium, sodium, or potassium compounds are accessible; the latter two were also characterized by single-crystal X-ray diffraction analysis (Figure 4). The molecular structure of the monomeric crown-ether-complexed potassium salt of 4 showed only a weak C−K interaction and a bent P−C−S moiety with short P−C [1.646(2) Å] and C−S [1.626(2) Å] bonds. The structure of the sodium compound is somewhat more complex but showed similar coordination modes and bond lengths compared to its potassium congener. Valuable insight into the electronics of the compound is given by a comparison of the structural parameters of 4-M with its protonated precursors, ylide 4-H and phosphonium salt 4-H$_2$.

Upon each deprotonation step, the P−R bond cleavage (R = amide, aldoxime) contributes to the electronic structure of metalated ylides. In this contribution, we focus on isolated metalated ylides of type X,L and should thus potentially act as monoanionic X,L-type $\sigma$- and $\pi$-donor ligands. In this Forum Article, we highlight recent developments in the chemistry of metalated ylides. We will particularly focus on isolated systems, their electronic structure, and their donor properties.

3. ELECTRONIC STRUCTURE OF METALATED YLIDES

The bonding situation in CDPs has continuously been the subject of discussions. In general, it has been described in three different ways (Figure 5). Thereby, the cumulene structure B′ can be neglected because of the bent structure confirmed by X-
ray diffraction analysis\textsuperscript{23} and the unfavorable energetic situation of the d orbitals of the phosphorus atom, as shown by computational studies.\textsuperscript{24} Additionally, their reactivity (e.g., their protonation energies compared to carbenes\textsuperscript{6c}), their behavior in transition-metal complexes,\textsuperscript{25} and their highest occupied molecular orbitals (HOMOs)\textsuperscript{−16b} clearly prove the presence of two lone pairs at the central carbon atom. Thereby, one of these lone pairs is of $\sigma$ symmetry and the other one of $\pi$ symmetry, so that CDPs can act as $\sigma$- and $\pi$-donor ligands.

Thus, for a long time, the bisylidic structure B with ylidic electron-sharing bonds between the phosphorus and carbon atoms had been considered to be the best description of the electronic structure. However, a few years ago, Frenking and co-workers showed by means of energy decomposition analysis (EDA) that the carbene structure $B''$ has a significant contribution to the bonding situation.$^{6,7}$ Similar to the bonding situation in transition-metal complexes, the two phosphine ligands form dative interactions to stabilize the carbon(0) center by $\sigma$ donation. Depending on the substituents, also $\pi$ back-donation from the p orbital ($\pi$ lone pair) of the central carbon into, e.g., low-lying $\sigma^*$ orbitals, plays a significant role. Nevertheless, $\sigma$ donation usually exceeds $\pi$ back-donation, thus explaining the typically high negative partial charge at the central carbon atom. Overall, the concept of a dative bonding situation in $B''$ applied the Dewar–Chatt–Duncanson model often used for the bonding situation in transition-metal complexes to organic\textsuperscript{26} and main-group-element compounds\textsuperscript{27} and allowed an explanation of the properties of similar compounds, such as the large bonding angle in carbon suboxide, in which CO serves as stronger $\pi$ acceptor compared to PPh$_3$.\textsuperscript{6d}

While first computational studies on bisylides only considered symmetrical bonding situations, recent studies also demonstrated that the unsymmetrical bonding situation [R$_2$P=P=C$\equiv$PR$_3$] with one ylidic and one dative bond has to

![Diagram](image1.png)
be considered for the description of the electronic structure of B. Thus, the carbene structure $B^\sigma$ and the unsymmetrical structure $B^\pi$ are, from an EDA perspective, the best canonical structures to describe the bonding situation in CDPs. Other unsymmetrical bonding situations [e.g., $R_1P^\sigma\rightarrow C\equiv PR_2$] were found to be negligible.

Recently, our group focused on the bonding situation in metalated ylides particularly in comparison with related bisylidic compounds. Both the influence of the substituent $L$ (anion-stabilization vs charge delocalization) and the total charge of the molecule (metalated ylide vs bisylide) on the bonding situation were studied (Figure 6). Thereby, also unsymmetrical bonding situations, such as $B^\pi$ in Figure 5, were considered.

Comparable to bisylides, the two highest canonical molecular orbitals, HOMO and HOMO−$1$ of the metalated ylides, are mainly localized at the central carbon atom and are indicative for two lone-pair orbitals, one of $\sigma$ symmetry and one of $\pi$ symmetry. This clearly confirms their potential as $\sigma$- and $\pi$-donor ligands. Figure 7 exemplarily depicts these orbitals for the sulfonyl system 6. The systems with carbon-based ligands 8, 9, and 13, however, also showed a significant contribution of delocalization of the electron density: for the imidazole 8 and imidazolate 9 moieties, the HOMO is delocalized over the ligands, while for the cyanido moiety in 13, both the HOMO and HOMO−$1$ are delocalized. This suggests a significant $\pi$-acceptor strength of these substituents that has not been observed for the phosphorus and silyl and sulfonyl ligands.

Natural bond orbital analysis was found to be ambiguous in providing clear insight into the bonding situation because of the fact that it is impossible to distinguish between $\pi$-back-bonding, negative hyperconjugation and electron-sharing double bonds as well as between dative and ylidic electron-sharing bonds by this method. Furthermore, several, mostly unsymmetrical, resonance structures showed equally high residual densities, indicating that different bonding situations are suitable for the description of the electron distribution within the molecule. However, an interesting observation concerned the partial charge at the ylidic carbon atom. A comparison of the neutral and anionic compound pairs showed that the negative charge of the central carbon atom does not change significantly upon the introduction of a negative charge at the periphery of the ligand. For example, the sulfonyl systems 6 and 7 and the isoelectronic compound pair with $L=\text{CN}^-/\text{CO}$ showed only a small or even no increase in the negative charge despite the fact that the overall molecular charge becomes negative. Instead, the partial charge at the central carbon atom allowed an estimation of the $\pi$-acceptor strength of the ligand. For the carbon-based ligands, which also showed $\pi$ delocalization in HOMO and HOMO−$1$ (see above), the charge at the central carbon is lower (usually around −$1.0\text{ e}$) than that for the weaker $\pi$ acceptors (>$−1.1\text{ e}$). The charge increases further with higher $\sigma$-donor strength (for example, a trimethylsilyl moiety, $−1.5\text{ e}$). Thus, the donor strength of the central carbon atom does not depend on the total charge but much more on the ligands acceptor and donor strengths. Additionally, the position of the positive charge in the backbone of compound 6 was found to have a significant effect. Shifting the positive charge in the pyridyl unit to the ortho position of the ligand shortens the C−S bond, which is even further pronounced if, instead, the oxygen of the sulfonyl moiety is protonated. This suggests that the distance of the positive charge in the backbone of bisylides has a strong effect on their properties.

An extensive EDA study revealed that introducing a negative charge to a bisylyde to form a metalated ylide results in the preference of an ylidic electron-sharing bond between the central carbon atom and the ligand $L$ over a dative interaction. Double bonds are only of relevance if the ligand $L$ is a strong $\pi$ acceptor (carbon-based ligands). Consequently, an unsymmetrical bonding situation, $P\rightarrow C\rightarrow L^-$, contributes to the bonding situation in all structures, while a carbene-like bonding situation, $P\rightarrow C\rightarrow L$, is only relevant for certain bisylides. This is especially interesting for hexaphenylcarbodiphosphorane, for which the carbene structure $B^\pi$ as well as the unsymmetrical structure $B^\pi$ are valid descriptions of the bonding situation (Figure 5), with a slight preference of the carbene structure. Altogether, these findings suggest that the bonding situation, and with it the reactivities and donor properties of these compounds, in metalated ylides can be carefully tailored by the design of the ligand $L$.

4. Reactivity and Coordination Ability of Metalated Ylides

Applications in Organic Synthesis. For a long time, the Bestmann system 1 had been the best studied metalated ylide. This ylide was used in a series of tandem reactions, which made use of 1 as a strong nucleophile as well as a highly reactive Wittig-type reagent. This intrinsic double reactivity was elegantly employed in cyclization reactions such as to 16 or the formation of alkynes like 15 or conjugated olefins (e.g., 14; Scheme 3).
In the case of the other isolated metalated ylides 2−4, reactivity studies mostly focused on the nucleophilicity of these systems. Reactions with different electrophiles allowed facile access to functionalized ylides, such as with halogen or phosphinyl moieties. Scheme 4 summarizes a series of reactions performed with 4. Here, a remarkable reactivity was observed when 4 was treated with aldehydes. In contrast to simple ylides and earlier reports by Corey and Kang, the Wittig-type reaction was only observed in traces, while the acylated compounds 19 were the main products formed. Mechanistically, this was explained by formation of the alcoholato intermediate analogous to classical Wittig reactions. However, because of the high donor ability of the ylide ligand, this intermediate formally eliminates a hydride (to 19a) or an aryl anion (to 19b) in the next step to form the carbonyl compounds.

Applications in Main-Group-Element Chemistry. The use of metalated ylides in the coordination of main-group-element species and compounds has only scarcely been studied until today. The first studies were performed with boranes and chloroboranes, although initially the ylide substituent was introduced after borane functionalization and no metalated ylide was used as a ligand precursor.50 The only direct use of a metalated ylide to stabilize reactive main-group-element compounds was only reported recently by our group, employing the sulfonyl-substituted yldiide 4-Na. The direct treatment of 4-Na with borane Lewis base adducts selectively delivered the bisylide-functionalized borane 20 in high yields (Figure 8).52 Here, the electron deficiency in the monomeric borane species is compensated for because of the high donor capacity of the yldiide and its ability to function as σ- and π-donor ligands. This was confirmed by the short C−B distances as well as the π bonding obvious in the molecular orbitals of 20. Furthermore, the high donor strength of the ylide ligand was demonstrated by the stabilization of boron cations.50 These were found to be readily available by hydride abstraction from 20 using trityl salts with weakly coordinated anions31 or the highly Lewis acidic B(C₆F₅)₃.32 Cation 21 and Lewis base adducts thereof were revealed to be thermally highly stable. The stability was referred to the special donor properties of the ylide ligand, which results, on the one hand, in strong electrostatic interactions and, on the other hand, in π delocalization within the whole C−B−C linkage (cf. the HOMO−1 in Figure 7).

Although 4 is the only metalated ylide, which has been used as an isolated ligand to stabilize low-valent or electron-deficient main-group-element species, the potential of these ligands as strong donor ligands has indirectly been proven by the use of ylide functionalization, in which the ylide moiety was constructed in the course of the compound synthesis. One example was reported by Schmidpeter and co-workers in 1997, who showed that ylide functionalization efficiently stabilizes phosphenium cations such as 22.33 These cations were

Figure 8. (Top) Synthesis of borane 20 and borenium cations 21. (Bottom) Molecular structure of 21e (PF₆⁻ not shown) and HOMO−1 of a hydrogen-substituted model system of 21.
prepared by a one-pot synthesis from phosphonium salts using phosphorus trichloride and trimethylamine as bases or from silyl-substituted ylides by chlorosilane elimination (Scheme 5).

Most interestingly, the ylide substituents affected the spontaneous dissociation of the corresponding chlorophosphines to the ionic phosphenium halides in solution as well as in the solid state. Hence, no use of weakly coordinating anions was necessary. The phosphenium cations showed the typical low-field-shifted signals in the $^{31}$P NMR spectra and a bent $\text{C} \cdots \text{P} \cdots \text{C}$ moiety with an angle of 113.9(3)$^\circ$. The stability of the cationic species was referred to as the charge delocalization on the two ylide moieties, as shown by the resonance formulas $22'$ and $22''$.

Besides stabilizing cationic compounds, ylide functionalization was also used to stabilize low-valent species, such as carbenes and silylenes. This was demonstrated by Driess, Kawashima, and Fürnster by means of the preparation of 23–25 (Figure 9) as well as by computational studies by Borthakur and Phukan. The ylide-functionalized carbenes were shown to be exceptionally strong electron-releasing ligands, surpassing the traditional N-heterocyclic carbenes in this regard.

**Applications in Transition-Metal Chemistry.** The use of metalated ylides in transition-metal chemistry has first been demonstrated by Niecke and co-workers. The ylide 3b was employed in a salt metathesis reaction to form the bisylide-functionalized mercury compound 26 (Scheme 6). In the molecular structure, 26 featured a linear $\text{C} \cdots \text{Hg} \cdots \text{C}$ arrangement and short $\text{P} \cdots \text{C}$ distances comparable to those found in the ylide 3b suggesting a still present high negative charge at the ylidic carbon atom.

Because of the lack of readily available ylides, no other direct conversions to their transition-metal complexes have been reported. However, their potential has been demonstrated by the introduction of ylide ligands via other synthetic routes. One of the most interesting applications certainly concerns the potential access of phosphonium alkylidene complexes $[\text{M} \cdots \text{C(\text{R})Pr}_3]$. These complexes have mostly been synthesized from ylides and subsequent $\alpha$-H abstraction or $\text{H}_2$ elimination.

![Scheme 6. Synthesis of a Bisylide-Substituted Mercury(II) Complex](image)

Figure 9. Carbenes and silylenes stabilized by ylide functionalization.

![Scheme 5. Preparation of Ylide-Stabilized Phosphenium Cations](image)

Figure 10. Examples of phosphonium alkylidene complexes.
5. CONCLUSIONS AND PERSPECTIVES

Although the number of metalated ylides is still extremely limited, their unique electronic properties and donor abilities have been demonstrated by a series of impressive examples. Their unique donor capacity and their potential to function as low-valent main-group-element species seems to be far underdeveloped. Given the recent developments in this field of research, which have especially been stimulated by the design of new supporting ligand systems, many more exciting results can be expected by ylide functionalization. This will immensely benefit from the preparation of new stable and readily available ylides, which allow for a more facile and versatile application.

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Notes

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■ REFERENCES

(1) Michaelis, A.; Gimborn, H. V. Ueber das Betain und Cholin des Triphenylphosphins. Ber. Dtsch. Chem. Ges. 1894, 27, 272.

(2) Staudinger, H.; Meyer, J. Ueber neue organische Phosphorverbindungen II. Phosphazine. Helv. Chim. Acta 1919, 2, 619.

(3) Lischka, H. Electronic structure and proton affinity of methylenephosphorane by ab initio methods including electron correlation. J. Am. Chem. Soc. 1977, 99, 3533.

(4) Schmidbaur, H. Phosphorus Ylides in the Coordination Sphere of Transition Metals: An Inventory. Angew. Chem., Int. Ed. Engl. 1983, 22, 907.

(5) Ramirez, F.; Desai, N. B.; Hansen, B.; McKelvie, N. Hexaphenylcarbodiphosphorane, (C6H5)2PC(PC6H5)2, J. Am. Chem. Soc. 1961, 83, 3539.

(6) (a) Tonner, R.; Öxler, F.; Neumüller, B.; Petz, W.; Frenking, G. Carbodiphosphorane: die Chemie von zweibindung Kohlenstoff(I). Angew. Chem. 2006, 118, 8206. (b) Tonner, R.; Frenking, G. Divalent Carbon(0) Chemistry, Part 1: Parent Compounds. Chem. - Eur. J. 2008, 14, 3260. (c) Tonner, R.; Frenking, G. Divalent carbon (0) chemistry, part 2: protonation and complexes with main group and transition metal Lewis acids. Chem. - Eur. J. 2008, 14, 3273. (d) Frenking, G.; Tonner, R. Divalent carbon(0) compounds. Pure Appl. Chem. 2009, 81, 597.

(7) For a discussion about dative bonds in main-group-element chemistry, see: (a) Frenking, G. Dative Bonds in Main-Group Compounds: A Case for More Arrows. Angew. Chem., Int. Ed. 2014, 53, 6040. Angew. Chem. 2014, 126, 6152. (b) Himmel, D.; Krossing, I.; Schnepp, A. Dative Bonds in Main-Group Compounds: A Case for Fewer Arrows. Angew. Chem., Int. Ed. 2014, 53, 370; Angew. Chem. 2014, 126, 378.

(8) For further bisylides, see: (a) Dellus, N.; Kato, T.; Saffen-Merceron, N.; Branchadell, V.; Baceiredo, A. Synthesis and Characterization of a Stable Chyclic gem-Bis(phosphaylide): a 4rElectron Three-Membered Heterocycle. Inorg. Chem. 2011, 50, 7949. (b) Dellus, N.; Kato, T.; Bagán, X.; Saffen-Merceron, N.; Branchadell, V.; Baceiredo, A. An Isolated Mixed P,S-Bis(ylide) as an Asymmetric Carbon Atom Source. Angew. Chem., Int. Ed. 2010, 49, 6798. (c) Pascual, S.; Assay, M.; Illa, O.; Kato, T.; Bertrand, G.; Saffen-Merceron, N.; Branchadell, V.; Baceiredo, A. Synthesis of a Mixed Phosphonium–Sulfonium Bisylide R3P==C==SK+. Inorg. Chem. Int. Ed. 2007, 46, 9078. (d) Morosaki, C.; Suzuki, T.; Wang, W.-W.; Nagase, S.; Fujii, T. Syntheses, Structures, and Reactivities of Two Chalcogen-Stabilized Carbones. Angew. Chem., Int. Ed. 2014, 53, 9569. (e) Morosaki, C.; Wang, W.-W.; Nagase, S.; Fujii, T. Synthesis, Structure, and Reactivities of Inminosulfane- and Phosphen-Stabilized Carbones Exhibiting Four-Electron Donor Ability. Chem. - Eur. J. 2015, 21, 15405.

(9) (a) Khan, S.; Gopakumar, G.; Thiel, W.; Alcarazo, M. Stabilization of a Two-Coordinate [GeCl]+ Cation by Simultaneous σ and π Donation from a Monodentate Carbodiphosphorane. Angew. Chem., Int. Ed. 2013, 52, 6544. (b) Petz, W.; Kutschina, C.; Heitbaum, M.; Frenking, G.; Tonner, R.; Neumüller, B. Experimental and Theoretical Studies of Carbodiphosphorane−CX2 Adducts with Unusual Bonding Situations: Preparation, Crystal Structures, and Bonding Analyses of S(C2(CP3)2), O2CC(PPh3)2, and [(CO)M2(CPPh3)], (M = Cr, Mo, W). Inorg. Chem. 2005, 44, 1263. (c) Tay, M. Q. Y.; Lu, Y.; Ganguly, R.; Vidovic, D. A Carbon-Stabilized Two-Coordinate Phosphorus(III)-Centered Dication. Angew. Chem., Int. Ed. 2013, 52, 3132. (d) Inés, B.; Patil, M.; Carreras, J.; Goddard, R.; Thiel, W.; Alcarazo, M. Synthesis, structure, and reactivity of a dihydroboron cation. Angew. Chem., Int. Ed. 2011, 50, 8400. (e) Petz, W.; Öxler, F.; Neumüller, B.; Tonner, R.; Frenking, G. Carbodiphosphorane C(PPh3)3 as a Single and Twofold Lewis Base with Boranes: Synthesis, Crystal Structures and Theoretical Studies on [H2B(C(PPh3))2] and [(μ-H)2H2B(C(PPh3))2]+. Eur. J. Inorg. Chem. 2009, 2009, 4507.

(10) (a) Alcarazo, M.; Radkowski, K.; Mehler, G.; Goddard, R.; Fürstner, A. Chiral heterobimetallat complexes of carbodiphosphoranes and phosphinide−carbene adducts. Chem. Commun. 2013, 49, 3140. (b) Alcarazo, M.; Lehmann, C. W.; Anoop, A.; Thiel, W.; Fürstner, A. Coordination chemistry at carbon. Nat. Chem. 2009, 1, 295. (c) Petz, W.; Wells, F.; Uddin, J.; Frenking, G. Reaction of Carbodiphosphorane Ph3P==C==Ph3 with Ni(CO)4. Experimental and Theoretical Study of the Structures and Properties of CO)NC(PPh3)2 and (CO)NC(PPh3)2. Organometallics 1999, 18, 619.

(11) Chen, W.-C.; Shen, J.-S.; Jurca, T.; Peng, C.-J.; Lin, Y.-H.; Wang, X.-P.; Shih, W.-C.; Yap, G. P. A.; Ong, T.-G. Expanding the Ligand Framework Diversity of Carbodicarbonates and Direct Detection of Boron Activation in the Methylation of Amines with CO2. Angew. Chem., Int. Ed. 2015, 54, 15207. (d) Dobrovetsky, R.; Stephan, D. W. Catalytic Reduction of CO2 to CO Using Zinc(II) and In Situ Generated Carbodiphosphoranes. Angew. Chem., Int. Ed. 2013, 52, 2516.
Inorganic Chemistry

(11) (a) Alcarazo, M.; Gomez, C.; Holle, S.; Goddard, R. Exploring the Reactivity of Carbon (0)/borane-based Frustated Lewis Pairs. Angew. Chem., Int. Ed. 2010, 49, 5788.

(12) (a) Schmidbaur, H.; Schier, A. Coordination Chemistry at Carbon: The Patchwork Family Comprising (Pr,P)C(C=C), (Ph,P)C(C=C), and (C,H)C. Angew. Chem., Int. Ed. 2012, 51, 176.

(b) Alcarazo, M. On the metallic nature of carbon in allenes and heterocumulenes. Dalton Trans. 2011, 40, 1839. (c) Petz, W. Addition compounds between carbones, CL2, and main group Lewis acids: A new glance at old and new compounds. Coord. Chem. Rev. 2015, 291, 1.

(13) Early work on bent allenes: (a) Weber, E.; Seichert, W.; Hess, B.; Will, G.; Dasting, H. J. A remarkably bent allene. X-Ray crystal structure and ab initio calculations. J. Phys. Org. Chem. 1995, 8, 94.

(b) Johnson, R. P. Strained cyclic cumulenes. Chem. Rev. 1989, 89, 1111. (c) Warmuth, R.; Marvel, M. A. 1,2,4,6-Cycloheptatetraene: An unprecedented structure and ab initio calculations. J. Am. Chem. Soc. 1999, 121, 7074.

(14) (a) Bartlett, G. Rethinking carbon. Nat. Rev. Chem. 2017, 1, 265. (b) Dyker, C. A.; Lavallo, V.; Donnadieu, B.; Bertrand, G. Synthesis of an Extremely Bent Acyclic Allene (A “Carbodibacene”): A Strong Donor Ligand. Angew. Chem., Int. Ed. 2008, 47, 5206. (c) Lavallo, V.; Dyker, C. A.; Donnadieu, B.; Bertrand, G. Synthesis and Ligand Properties of Stable Five-Membered-Ring Alkenes Containing Only Second-Row Elements. Angew. Chem., Int. Ed. 2008, 47, 5411. (d) Frankevich, C.; Liu, L.; Bertrand, G.; Stephan, D. W. Synthesis of a Carbodicycloprenyldiene: A Carbodibacene based Solely on Carbon. Angew. Chem., Int. Ed. 2016, 55, 5536–5540. (e) Fürstner, A.; Alcarazo, M.; Goddard, R.; Lehmann, C. W. Coordination Chemistry of Ene-1,1-diynes and a Prototype “Carbodibacene.” Angew. Chem., Int. Ed. 2008, 47, 3210.

(15) (a) Frankevich, C.; Fan, L.; Stephan, D. W. Cyclic Bent Allene Hydroxy-carbonyl Complexes of Ruthenium: Highly Active Catalysts for Hydrogenation of Olefins. J. Am. Chem. Soc. 2015, 137, 5582. (b) Hsu, Y.-C.; Shen, J.-S.; Lin, B.-C.; Chen, W.-C.; Chan, Y.-T.; Chang, Y.-M.; Yap, G. P. A.; Hsu, C.-P.; Ong, T.-G. Synthesis and Isolation of an Acyclic Tridentate Bis[pyridine]carbodibacene and Studies on its Structural Implications and Reactivities. Angew. Chem., Int. Ed. 2015, 54, 4320. (c) Goldfogel, M. J.; Roberts, C. C.; Meek, S. J. Intermolecular Hydroamination of 1,3-Dienes Catalyzed by Bis(phosphinate)carbodibacene-Rhodium Complexes. J. Am. Chem. Soc. 2014, 136, 6227. (d) Roberts, C. C.; Matías, D. M.; Goldfogel, M. J.; Meek, S. J. Lewis Acid Activation of Carbodibacene Catalysts for Rh-Catalyzed Hydroarylation of Dienes. J. Am. Chem. Soc. 2015, 137, 6488. (e) Goldfogel, M. J.; Meek, S. J. Diastereoselective synthesis of vicinal tertial and N-substituted quaternary stereogenic centers by catalytic hydroarylation of dienes. Chem. Sci. 2016, 7, 4079.

(16) Alternatively, the formation of metatalated ylides can be interpreted as replacing a neutral ligand (for example, triphenylphosphine) in hexaphenylcarbodiphosphorane) by an anionic ligand.

(17) Schlosser, M.; Kadielban, T.; Steinhoff, G. Nucleophilic Ligand Exchange by Phosphoranes. Angew. Chem. 1966, 78, 1018; Angew. Chem., Int. Ed. Engl. 1966, 5, 968.

(18) Corey, E. J.; Kang, J. α-Lithiomethylene(triphenylphosphorane), a highly reactive ylide equivalent. J. Am. Chem. Soc. 1982, 104, 4724.

(19) Bestmann, H.-J.; Röder, T.; Bremer, M.; Löw, D. Bonding in Metalated Ylides and Reaction of Lithium Cyan(triphenylphosphorane)ysodium(−) with N-Heterocyclic Carbene Ligands. J. Am. Chem. Soc. 1997, 119, 12410.

(20) Gounmi-Magnet, S.; Gornitzka, H.; Baceiredo, A.; Bertrand, G. Synthetic Utility of Stable Phosphanylcarbenes: Synthesis and Crystal Structure of an α-(Lithiomethylene)phosphorene. Angew. Chem., Int. Ed. 1999, 38, 678.

(21) Baumgartner, T.; Schinkels, B.; Gudat, D.; Niegler, M.; Niecke, E. Lithium Phosphoranyldiene Ylides Mes*-P(==E)==C(H)Li(THF), (E = NMes*, C(SiMe3)2-): Synthesis, Crystal Structure, and Transmetalation. J. Am. Chem. Soc. 1997, 119, 12410.
A.; Sun, H.; Wang, L.; Schmidt, S.; Harms, K.; Sundermeyer, J. Effect of Different Bases and Phosphorus Ylide on the Selective Deprotonation of Phosphorus Ylide Adduct Cp*TaCl4(CH2PPh3).
*Organometallics* 2007, 26, 3456. (f) Zurawinski, R.; Lepetit, C.; Canac, Y.; Mikolajczyk, M.; Chauvin, R. From Neutral to Anionic η1-Carbon Ligands: Experimental Synthesis and Theoretical Analysis of a Rhodium-Yldide Complex. *Inorg. Chem.* 2009, 48, 2147. (g) Li, X.; Wang, A.; Wang, L.; Sun, H.; Harms, K.; Sundermeyer, J. Phosphorus Ylide as a Precursor for the Formation of New High-Valent Tantalum Phosphonio Methylidyne Complexes. *Organometallics* 2007, 26, 1411.