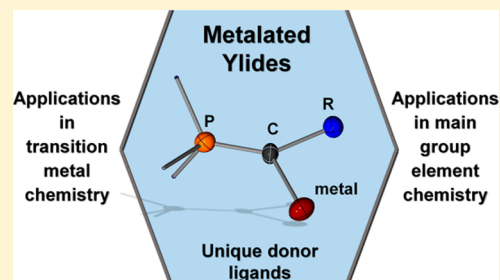


Metalated Ylides: A New Class of Strong Donor Ligands with Unique Electronic Properties

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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 X₂L-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 carbodiphosphanes (CDPs), in the past years.

Since the first synthesis of an ylide¹ and their use in Wittig-type reactions,² 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.³ Recently, the canonical structure **A''** with a donor–acceptor interaction between phosphorus and carbon has found renewed interest.⁴ It classifies ylides as phosphane-stabilized carbenes. An analogous description has also been used for bisylidic compounds, particularly CDPs.⁵ This leads to their description either as bisylides **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

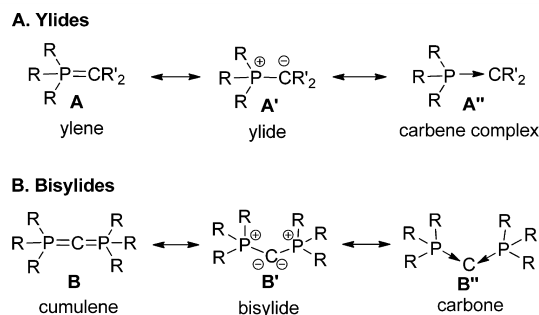


Figure 1. Comparison between ylides (A) and bisylides (B).

structure of these compounds has been studied in detail in recent years⁶ but is still under debate.⁷

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.⁸ 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⁺₉ or can be used as a ligand in transition-metal complexes¹⁰ or in bond activation reactions.¹¹ Their chemistry has been summarized in recent review articles.¹² Likewise, bent allenes,¹³ 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 Füstner, already demonstrating their potential in transition-metal chemistry.¹⁴ Later, the groups of Ong, Meek, and Stephan impressively confirmed the utility

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of these ligands in transition-metal-catalyzed reactions.¹⁵ 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 **C**, the so-called yldiides. They can be viewed as the anionic congeners of bisylides, formed by the replacement of one positively charged onium moiety (e.g., a phosphonium group) by a neutral substituent (Figure 2).¹⁶ Comparable to bisylides, metalated

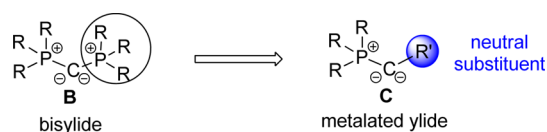


Figure 2. Comparison between metalated ylides and bisylides.

ylides possess two pairs of electrons at the central carbon atom and should thus potentially act as monoanionic X_L-type σ - and π -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 [$\text{Ph}_3\text{P}-\text{C}(\text{Li})-\text{C}_3\text{H}_7$] was proposed by Schlosser and co-workers using pentaphenylphosphane and an excess of butyllithium.¹⁷ 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.¹⁸ 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).¹⁹ **1** 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).^{12a}

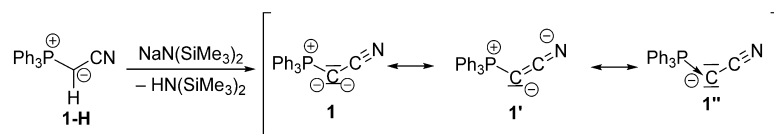
Until today, only three yldiides have been isolated and also structurally characterized: (i) the silyl-substituted yldiide **2** synthesized by Bertrand et al.,²⁰ phosphoranylidene ylides **3a** and **3b** by Niecke et al.²¹ (Figure 3), and (iii) the sulfonyl-substituted compound **4** reported by our group (Figure 4).²² Interestingly, the metalated ylide **2** was not prepared via a classical deprotonation reaction analogous to **1** but via a 1,2-carbometalation reaction of carbene **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 $\text{P}^{\delta+}-\text{C}^{\delta-}$ linkage or strong σ donation from and π -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 phosphoranylidene 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-H₂** (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-H₂**. Upon each deprotonation step, the P–C–S linkage experiences an increasing contraction. For example, the C–S bond shortens from 1.809(3) Å in **4-H₂** to 1.626(2) Å in **4**. This was explained by Coulombic interactions within the $\text{P}^{\delta+}-\text{C}^{\delta-}-\text{S}^{\delta+}$ moiety, while negative hyperconjugation effects lead to elongated P–R and S–R bonds to the β substituents. The widening of the P–C–S angle is well in line with a change in the hybridization of the ylidic carbon atom from sp^3 to sp^2 .

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-

Scheme 1. Preparation of Yldiide **1** and Resonance Structures of **1**



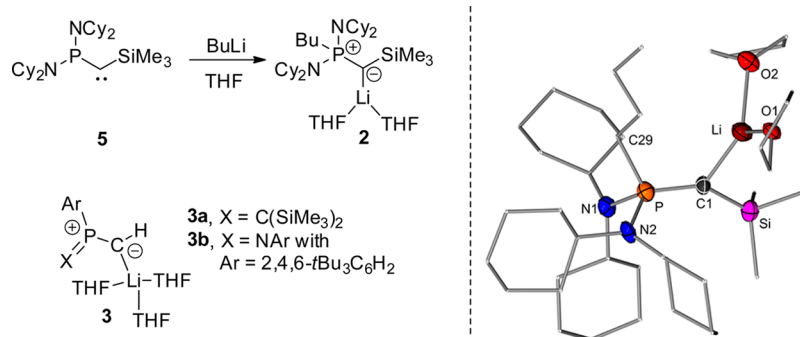


Figure 3. Isolated metalated ylides **2** and **3** (left) and molecular structure of **2** (right).

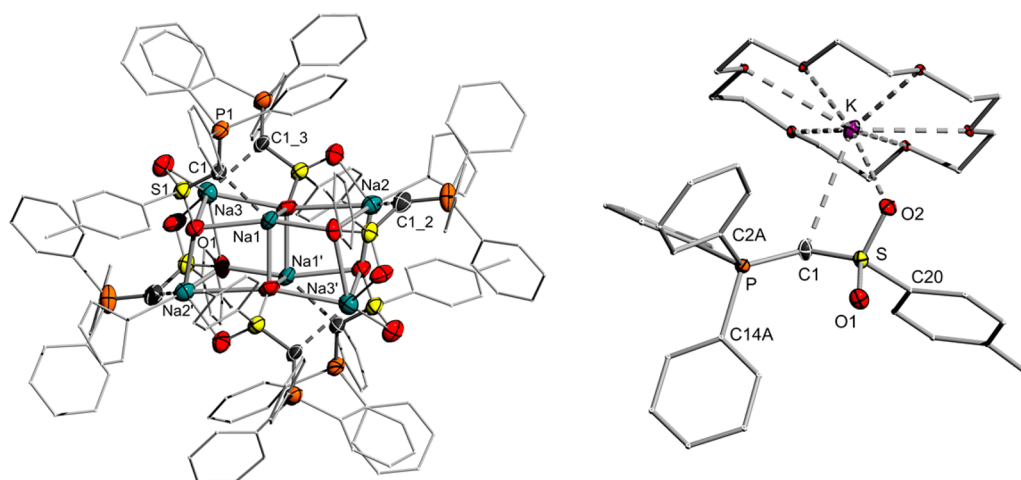
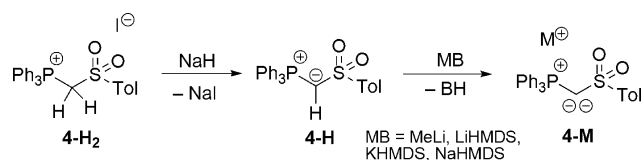


Figure 4. Molecular structures of **4-Na** and **4-K-18-crown-6**.

Scheme 2. Preparation of Ylide **4**



ray diffraction analysis²³ and the unfavorable energetic situation of the d orbitals of the phosphorus atom, as shown by computational studies.²⁴ Additionally, their reactivity (e.g., their protonation energies compared to carbenes^{6c}), their behavior in transition-metal complexes,²⁵ and their highest occupied molecular orbitals (HOMOs) and HOMOs-1^{6b} clearly prove the presence of two lone pairs at the central carbon atom. Thereby, one of these lone pairs is of σ symmetry and the other one of π symmetry, so that CDPs can act as σ - and π -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 σ donation. Depending on the substituents, also π back-donation from the p orbital (π lone pair) of the central carbon into, e.g., low-lying σ^* orbitals, plays a significant role. Nevertheless, σ donation usually exceeds π 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 organic²⁶ and main-group-element compounds²⁷ 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 π acceptor compared to PPh_3 .^{6d}

While first computational studies on bisylides only considered symmetrical bonding situations, recent studies also demonstrated that the unsymmetrical bonding situation $[\text{R}_3\text{P}^+-\text{C}^-\leftarrow\text{PR}_3]$ with one ylidic and one dative bond has to

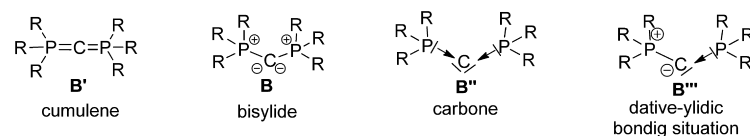


Figure 5. Canonical structures of CDPs.

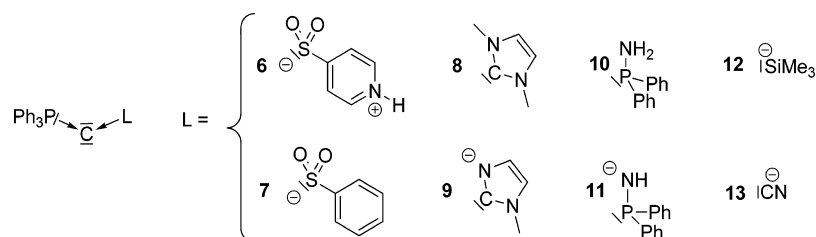


Figure 6. Metalated ylides and bisylides.

be considered for the description of the electronic structure of **B**.²⁸ Thus, the carbene structure **B''** and the unsymmetrical structure **B'''** are, from an EDA perspective, the best canonical structures to describe the bonding situation in CDPs. Other unsymmetrical bonding situations [e.g., $R_3P^+-C=PR_3$] 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'''** in Figure 5, were considered.²⁸

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 σ symmetry and one of π symmetry. This clearly confirms their potential as σ - and π -donor ligands. Figure 7 exemplarily depicts these orbitals for

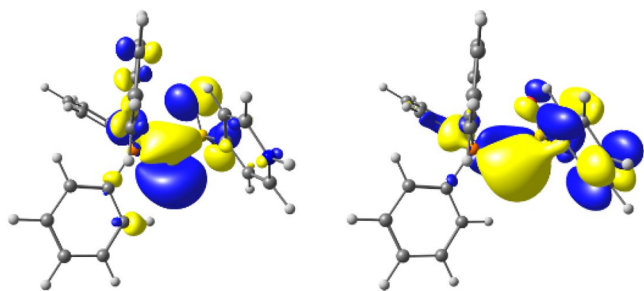


Figure 7. HOMO (left) and HOMO–1 (right) for 6.

the sulfonamide 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 π -acceptor strength of these substituents that has not been observed for the phosphorus and silyl and sulfonamide 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 π -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

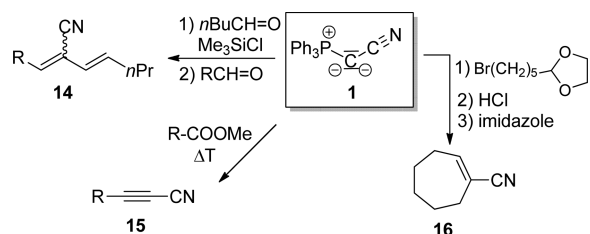
and anionic compound pairs showed that the negative charge of the central carbon atom does not change significantly upon the introduction of a negative charge at the periphery of the ligand. For example, the sulfonamide systems **6** and **7** and the isoelectronic compound pair with $L=CN^-/CO$ showed 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 π -acceptor strength of the ligand. For the carbon-based ligands, which also showed π delocalization in HOMO and HOMO–1 (see above), the charge at the central carbon is lower (usually around $-1.0 e$) than that for the weaker π acceptors ($>-1.1 e$). The charge increases further with higher σ -donor strength (for example, a trimethylsilyl moiety, $-1.5 e$). 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 sulfonamide 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 bisylide 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 π acceptor (carbon-based ligands). Consequently, an unsymmetrical bonding situation, $P\rightarrow C-L^+$, contributes to the bonding situation in all structures, while a carbene-like bonding situation, $P\rightarrow C\leftarrow L$, is only relevant for certain bisylides. This is especially interesting for hexaphenylcarbodiphosphorane, for which the carbene structure **B''** as well as the unsymmetrical structure **B'''** 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**.

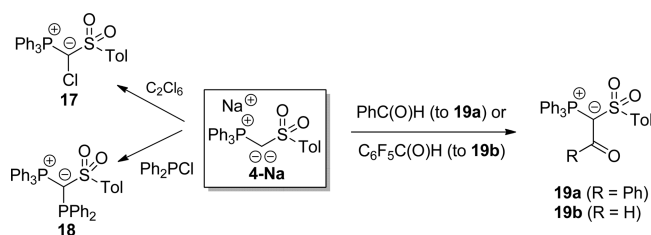
4. REACTIVITY AND COORDINATION ABILITY OF METALATED YLIDES

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.¹⁹ 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).

Scheme 3. Reactivity of the Metalated Ylide 2



Scheme 4. Reactivity of the Ylide 4-Na



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.²⁹ 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 ylide **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).²² Here, the electron deficiency in the monomeric borane species is compensated for because of the high donor capacity of the ylide 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.³⁰ These were found to be readily available by hydride abstraction from **20** using trityl salts with weakly coordinated anions³¹ or the highly Lewis acidic $B(C_6F_5)_3$.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 phosphonium cations such as **22**.³³ These cations were

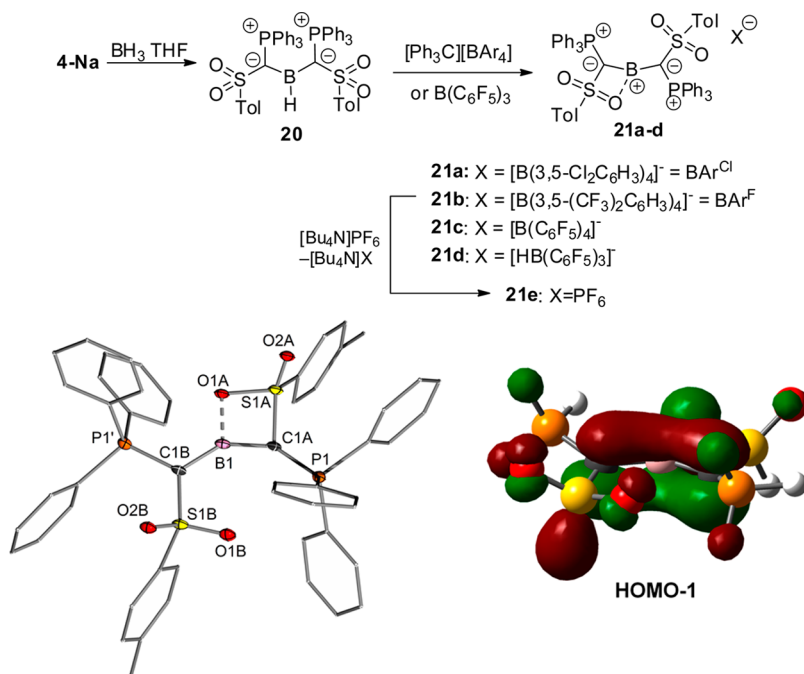


Figure 8. (Top) Synthesis of borane **20** and borenium cations **21**. (Bottom) Molecular structure of **21e** (PF₆⁻ not shown) and HOMO–1 of a hydrogen-substituted model system of **21**.

Scheme 5. Preparation of Ylide-Stabilized Phosphenium Cations

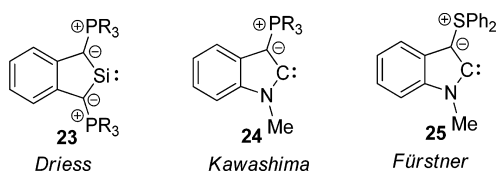
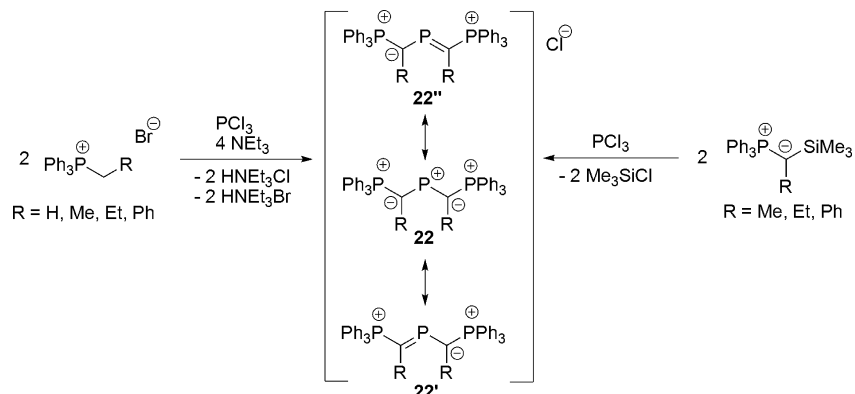
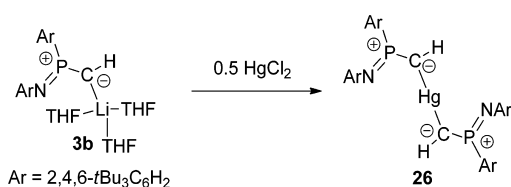


Figure 9. Carbenes and silylenes stabilized by ylide functionalization.

Scheme 6. Synthesis of a Bisylide-Substituted Mercury(II) Complex



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 effected the spontaneous dissociation of the corresponding chlorophosphines to the ionic phosphonium halides **22** in solution as well as in the solid state. Hence, no use of weakly coordinating anions was necessary. The phosphonium cations showed the typical low-field-shifted signals in the ^{31}P NMR spectra and a bent C–P–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 Fürstner by means of the preparation of **23**–**25**³⁴ (Figure 9) as well as by computational studies by Borthakur and Phukan.³⁵ 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 C–Hg–C arrangement and short P–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 $[\text{M}=\text{C}(\text{R})\text{PR}_3]$.³⁶ These complexes have mostly been synthesized from ylides and subsequent α -H abstraction or H_2 elimination.

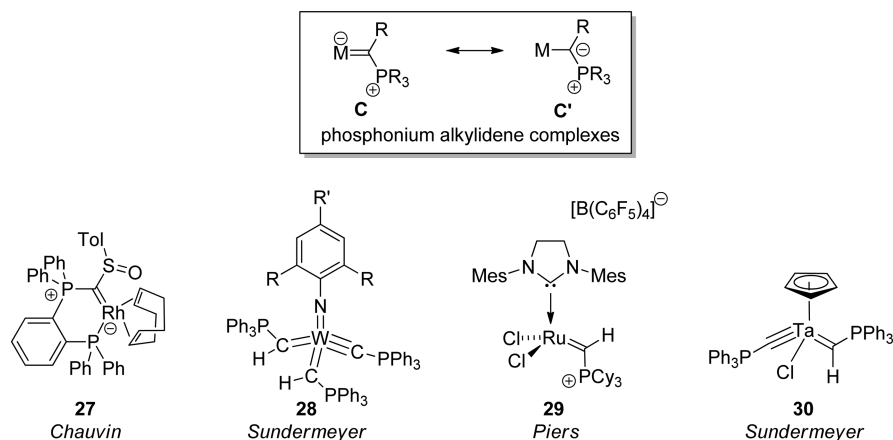


Figure 10. Examples of phosphonium alkylidene complexes.

Figure 10 shows selected examples of isolated complexes. These alkylidene complexes feature a unique electronic structure that is described by different resonance structures C and C'. Accordingly, the complexes typically show short M–C distances in the range of metal carbon double bonds. In the case of the ruthenium complex **29**, these special properties revealed to be beneficial to support high catalytic activities in ring-closing metathesis reactions. The high activity of **27** was explained by the fact that the phosphonium alkylidene allowed stabilization of the low-coordinate ruthenium center, which, in contrast to Grubbs-type systems, does not need to dissociate a ligand for the ruthenium complex to enter the catalytic cycle.

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 strong X- and L-type donor ligands have been confirmed by computational studies as well as experimental work in organic, main-group-element, and transition-metal chemistry. Particularly their use in the stabilization of electron-deficient and low-valent main-group-element species seems to be by 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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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. The authors contributed equally.

Notes

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REFERENCES

- (1) Michaelis, A.; Gimborn, H. V. Ueber das Betaïn 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*, 353.
- (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)₃PCP(C₆H₅)₃. *J. Am. Chem. Soc.* **1961**, *83*, 3539.

- (6) (a) Tonner, R.; Öxler, F.; Neumüller, B.; Petz, W.; Frenking, G. Carbodiphosphorane: die Chemie von zweibindigem Kohlenstoff(0). *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.; Schnepf, 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.; Saffon-Merceron, N.; Branchadell, V.; Baceiredo, A. Synthesis and Characterization of a Stable Cyclic gem-Bis(phosphaylide): a 4 π -Electron Three-Membered Heterocycle. *Inorg. Chem.* **2011**, *50*, 7949. (b) Dellus, N.; Kato, T.; Bagán, X.; Saffon-Merceron, N.; Branchadell, V.; Baceiredo, A. An Isolable Mixed P,S-Bis(ylide) as an Asymmetric Carbon Atom Source. *Angew. Chem., Int. Ed.* **2010**, *49*, 6798. (c) Pascual, S.; Asay, M.; Illa, O.; Kato, T.; Bertrand, G.; Saffon-Merceron, N.; Branchadell, V.; Baceiredo, A. Synthesis of a Mixed Phosphonium–Sulfonium Bisylide R₃P=C=SR₂. *Angew. 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 Carbenes. *Angew. Chem., Int. Ed.* **2014**, *53*, 9569. (e) Morosaki, C.; Wang, W.-W.; Nagase, S.; Fujii, T. Synthesis, Structure, and Reactivities of Iminosulfane- and Phosphane-Stabilized Carbenes 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*, 5644. (b) Petz, W.; Kutschera, 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 S₂CC(PPh₃)₂, O₂CC(PPh₃)₂, and [(CO)₄MS₂CC(PPh₃)₂] (M = Cr, Mo, W). *Inorg. Chem.* **2005**, *44*, 1263. (c) Tay, M. Q. Y.; Lu, Y.; Ganguly, R.; Vidovic, D. A Carbene-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 dihydrido borenium cation. *Angew. Chem., Int. Ed.* **2011**, *50*, 8400. (e) Petz, W.; Öxler, F.; Neumüller, B.; Tonner, R.; Frenking, G. Carbodiphosphorane C(PPh₃)₂ as a Single and Twofold Lewis Base with Boranes: Synthesis, Crystal Structures and Theoretical Studies on [H₃B{C(PPh₃)₂}] and [{"(μ -H)H₄B₂}]{C(PPh₃)₂}]⁺. *Eur. J. Inorg. Chem.* **2009**, *2009*, 4507.

- (10) (a) Alcarazo, M.; Radkowski, K.; Mehler, G.; Goddard, R.; Fürstner, A. Chiral heterobimetallic complexes of carbodiphosphoranes and phosphinidene–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.; Weller, F.; Uddin, J.; Frenking, G. Reaction of Carbodiphosphorane Ph₃P=C=PPh₃ with Ni(CO)₄. Experimental and Theoretical Study of the Structures and Properties of (CO)₃NiC(PPh₃)₂ and (CO)₂NiC(PPh₃)₂. *Organometallics* **1999**, *18*, 619. (d) 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 Carbodicarbenes and Direct Detection of Boron Activation in the Methylation of Amines with CO₂. *Angew. Chem., Int. Ed.* **2015**, *54*, 15207. (e) 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.

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

(12) (a) Schmidbauer, H.; Schier, A. Coordination Chemistry at Carbon: The Patchwork Family Comprising $(\text{Ph}_3\text{P})_2\text{C}$, $(\text{Ph}_3\text{P})\text{C}(\text{C}_2\text{H}_4)$, and $(\text{C}_2\text{H}_4)_2\text{C}$. *Angew. Chem., Int. Ed.* **2013**, *52*, 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 carbon, CL_2 , 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.; Seichter, 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: Room-Temperature Stabilization inside a Hemiacerand. *Angew. Chem., Int. Ed.* **2000**, *39*, 1117. (d) Hofmann, M. A.; Bergstrasser, U.; Reiss, G. J.; Nyulaszi, L.; Regitz, M. Synthesis of an Isolable Diphosphaisobenzene and a Stable Cyclic Allene with Six Ring Atoms. *Angew. Chem., Int. Ed.* **2000**, *39*, 1261.

(14) For carbodicarbenes, see: (a) Dyker, C. A.; Bertrand, G. Rethinking Carbon. *Nat. Chem.* **2009**, *1*, 265. (b) Dyker, C. A.; Lavallo, V.; Donnadiu, B.; Bertrand, G. Synthesis of an Extremely Bent Acyclic Allene (A "Carbodicarbene"): A Strong Donor Ligand. *Angew. Chem., Int. Ed.* **2008**, *47*, 3206. (c) Lavallo, V.; Dyker, C. A.; Donnadiu, B.; Bertrand, G. Synthesis and Ligand Properties of Stable Five-Membered-Ring Allenes Containing Only Second-Row Elements. *Angew. Chem., Int. Ed.* **2008**, *47*, 5411. (d) Pranckevicius, C.; Liu, L.; Bertrand, G.; Stephan, D. W. Synthesis of a Carbodicyclopropenyliene: A Carbodicarbene 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-diamines and a Prototype "Carbodicarbene. *Angew. Chem., Int. Ed.* **2008**, *47*, 3210.

(15) (a) Pranckevicius, C.; Fan, L.; Stephan, D. W. Cyclic Bent Allene Hydrido-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.; Ching, W.-M.; Yap, G. P. A.; Hsu, C.-P.; Ong, T.-G. Synthesis and Isolation of an Acyclic Tridentate Bis(pyridine)carbodicarbene and Studies on Its Structural Implications and Reactivities. *Angew. Chem., Int. Ed.* **2015**, *54*, 2420. (c) Goldfogel, M. J.; Roberts, C. C.; Meek, S. J. Intermolecular Hydroamination of 1,3-Dienes Catalyzed by Bis-(phosphine)carbodicarbene–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 Carbodicarbene 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 tertiary and N-substituted quaternary stereogenic centers by catalytic hydroalkylation of dienes. *Chem. Sci.* **2016**, *7*, 4079.

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

(17) Schlosser, M.; Kadibelban, 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 -Lithiomethylenetriphenylphosphorane, a highly reactive ylide equivalent. *J. Am. Chem. Soc.* **1982**, *104*, 4724.

(19) Bestmann, H. J.; Schmidt, M. Synthesis of Nitriles via the Ylide Anion of Sodium Cyanotriphenylphosphoranylidene methane. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 79.

(20) Goumri-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.; Nieger, M.; Niecke, E. Lithium Phosphoranylidene Ylides $\text{Mes}^*\text{-P}(=\text{E})=\text{C}(\text{H})\text{Li}(\text{THF})_3$ (E = NMe_3^* , $\text{C}(\text{SiMe}_3)_2$): Synthesis, Crystal Structure, and Transmetalation. *J. Am. Chem. Soc.* **1997**, *119*, 12410.

(22) Scherpf, T.; Wirth, R.; Feichtner, K.-S.; Molitor, S.; Gessner, V. H. Bridging the Gap between Bisylides and Methandiides: Isolation, Reactivity, and Electronic Structure of an Ylide. *Angew. Chem., Int. Ed.* **2015**, *54*, 8542.

(23) Hardy, G. E.; Zink, J. L.; Kaska, W. C.; Baldwin, J. C. Structure and triboluminescence of polymorphs of hexaphenylcarbodiphosphorane. *J. Am. Chem. Soc.* **1978**, *100*, 8001.

(24) Lischka, H. Electronic structure and proton affinity of methylenephosphorane by ab initio methods including electron correlation. *J. Am. Chem. Soc.* **1977**, *99*, 353.

(25) Petz, W.; Frenking, G. Carbodiphosphoranes and Related Ligands. *Top. Organomet. Chem.* **2010**, *30*, 49.

(26) (a) Tonner, R.; Frenking, G. $\text{C}(\text{NHC})_2$: Divalent Carbon(0) Compounds with N-Heterocyclic Carbene Ligands – Theoretical Evidence for a Class of Molecules with Promising Chemical Properties. *Angew. Chem., Int. Ed.* **2007**, *46*, 8695. (b) Klein, S.; Tonner, R.; Frenking, G. Carbodicarbenes and Related Divalent Carbon(0) Compounds. *Chem. - Eur. J.* **2010**, *16*, 10160. (c) Frenking, G.; Tonner, R. Carbodicarbenes—divalent carbon(0) compounds exhibiting carbon–carbon donor–acceptor bonds. *WIREs Comput. Mol. Sci.* **2011**, *1*, 869.

(27) Takagi, N.; Tonner, R.; Frenking, G. Carbodiphosphorane Analogues $\text{E}(\text{PPh}_3)_2$ with $\text{E}=\text{C}-\text{Pb}$: A Theoretical Study with Implications for Ligand Design. *Chem. - Eur. J.* **2012**, *18*, 1772.

(28) Scharf, L. T.; Andradá, D. M.; Frenking, G.; Gessner, V. H. The Bonding Situation in Metalated Ylides. *Chem. - Eur. J.* **2017**, DOI: 10.1002/chem.201605997.

(29) (a) Bestmann, H.-J.; Röder, T.; Bremer, M.; Löw, D. Darstellung, Struktur und Reaktionen von Lithium-cyan(triphenylphosphoranylidene)methyl]trihydroborat(–1). *Chem. Ber.* **1991**, *124*, 199. (b) Bestmann, H.-J.; Arenz, T. Umsetzung von Phosphoniumyliden mit Alkyldichlorboranen. *Angew. Chem.* **1986**, *98*, 571.

(30) Scherpf, T.; Feichtner, K.-S.; Gessner, V. H. Using Ylide-Functionalization to Stabilize Boron Cations. *Angew. Chem.* **2017**, DOI: 10.1002/ange.201611677.

(31) (a) Krossing, I.; Raabe, I. Noncoordinating Anions - Fact or Fiction? A Survey of Likely Candidates. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066. (b) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. $[(3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3)_4\text{B}]\text{-}[\text{H}(\text{OEt})_2]^+$: a convenient reagent for generation and stabilization of cationic, highly electrophilic organometallic complexes. *Organometallics* **1992**, *11*, 3920. (c) Engesser, T. A.; Lichtenthaler, M. R.; Schleep, M.; Krossing, I. Reactive p-block cations stabilized by weakly coordinating anions. *Chem. Soc. Rev.* **2016**, *45*, 789.

(32) Erker, G. Tris(pentafluorophenyl)borane: a special boron Lewis acid for special reactions. *Dalton Trans.* **2005**, 1883.

(33) Schmidpeter, A.; Jochem, G.; Klinger, C.; Robl, C.; Nöth, H. Bis(ylide)-substituted phosphonium and phosphonium halides. *J. Organomet. Chem.* **1997**, *529*, 87.

(34) (a) Asay, M.; Inoue, S.; Driess, M. Aromatic Ylide-Stabilized Carbocyclic Silylene. *Angew. Chem., Int. Ed.* **2011**, *50*, 9589. (b) Fürstner, A.; Alcarazo, M.; Radkowski, K.; Lehmann, C. W. Carbenes Stabilized by Ylides: Pushing the Limits. *Angew. Chem., Int. Ed.* **2008**, *47*, 8302. (c) Nakafuji, S.; Kobayashi, J.; Kawashima, T. Generation and Coordinating Properties of a Carbene Bearing a Phosphorus Ylide: An Intensely Electron-Donating Ligand. *Angew. Chem., Int. Ed.* **2008**, *47*, 1141.

(35) Borthakur, B.; Phukan, A. K. Moving toward Ylide-Stabilized Carbenes. *Chem. - Eur. J.* **2015**, *21*, 11603.

(36) For examples, see: (a) Chauvin, R. Zwitterionic Organometalates. *Eur. J. Inorg. Chem.* **2000**, *2000*, 577. (b) Berno, P.; Gambarotta, S.; Kotila, S.; Erker, G. Novel vanadium and titanium phosphorus ylide complexes. *Chem. Commun.* **1996**, 779. (c) Li, X.; Schopf, M.; Stephan, J.; Harms, K.; Sundermeyer, J. Heavily π -Bond-Loaded Tungsten Phosphonio–Alkylidyne Complexes via a Domino Transylidation Cascade at (Organoimido)tungsten Tetrachlorides. *Organometallics* **2002**, *21*, 2356. (d) Romero, P. E.; Piers, W. E.; McDonald, R. Rapidly Initiating Ruthenium Olefin-Metathesis Catalysts. *Angew. Chem., Int. Ed.* **2004**, *43*, 6161. (e) Li, X.; Wang,

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 $\text{Cp}^*\text{TaCl}_4(\text{CH}_2\text{PPh}_3)$. *Organometallics* **2007**, *26*, 3456. (f) Zurawinski, R.; Lepetit, C.; Canac, Y.; Mikolajczyk, M.; Chauvin, R. From Neutral to Anionic η^1 -Carbon Ligands: Experimental Synthesis and Theoretical Analysis of a Rhodium-Ylidyne 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.