

MINIREVIEW

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Phosphorus-ylides: powerful substituents for the stabilization of reactive main group compounds

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Phosphorus ylides are 1,2-dipolar compounds with a negative charge on the carbon atom. This charge is stabilized by the neighbouring onium moiety, but can also be shifted towards other substituents thus making ylides strong π donor ligands and hence ideal substituents to stabilize reactive compounds such as cations and low-valent main group species. Furthermore, the donor strength and the steric properties can easily be tuned to meet different requirements for stabilizing reactive compounds and for tailoring the properties and reactivities of the main group element. Although the use of ylide substituents in main group chemistry is still in its infancy, the first examples of isolated compounds impressively demonstrate the potential of these ligands. This review summarizes the most important discoveries also in comparison to other substituents, thus outlining avenues for future research directions.

Introduction

The isolation of reactive main group compounds has been a part of extensive research activities in recent years. These research endeavors are driven by efforts to gain a better understanding of chemical bonding and structure–reactivity relations as well as by the ability of such compounds to undergo bond activation reactions. This transition metal-like behaviour has been demonstrated by a variety of main group element species that offer the prospect of applications in homogeneous catalysis.¹ While several key compounds in this chemistry were already isolated in the last decades of the 20th century,² it was only with the beginning of the new millennium that their synthetic potential was recognized. Since then, reactive species, such as heavier alkenes and alkynes and low-valent compounds have been developed from curiosities to isolable and tunable species.³

A remarkable breakthrough in this context was reported in 2005 by Power with the activation of dihydrogen by using digermynes **1** (Fig. 1a).⁴ The facile reaction was possible due to the special bonding situation in the Ge≡Ge linkage. A high-lying HOMO and low-lying LUMO allowed a transition metal-like synergistic donation and acceptance of electron density to and from the H–H bond and thus its activation and splitting (Fig. 1b). Two years later, a similar strategy was employed by Bertrand and coworkers using cyclic alkyl(amino)carbenes (CAACs) such as **2**.⁵ They demonstrated the importance of the substituents at the carbene carbon atom for tuning orbital energies. Since then, controlling the energy gap between a filled

and vacant orbital has become a general strategy to tailor main group compounds for bond activations,⁶ which lately has led to the activation of rather inert bonds. As such, Aldridge and Goicoechea reported the reversible C–C bond activation of benzene by using aluminyl complex **3**,⁷ while Braunschweig and coworkers accomplished N₂ reduction by using the transient borylene **4**.⁸

These examples impressively demonstrate the potential of reactive main group compounds, and also the importance of the molecular design, *i.e.* the choice of the substituents at the main group element for their isolation and applications. In this minireview, we focus on the use of phosphorus ylides as substituents in main group chemistry. Unlike traditional aryl or amido substituents, ylides only recently received renewed interest in main group chemistry, which already led to the discovery of unique properties and reactivities. Herein, we

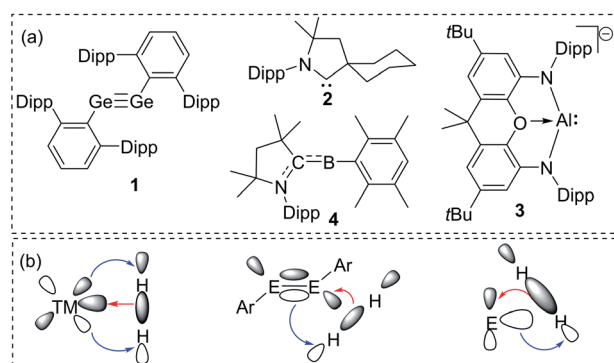


Fig. 1 (a) Landmark examples of reactive main group compounds active in bond activations (dipp = 2,6-diisopropylphenyl); (b) H₂ activation by using transition and main group element compounds.

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highlight important findings and bring them in context with other substituents used in main group chemistry. It must be noted that besides anionic substituents neutral donor ligands (e.g. NHCs and bisylides) have also been used to access reactive main group species and transition metal complexes.⁹ The use of such ligands is beyond the scope of this review but has been covered in excellent review articles.¹⁰

Substituents in main group chemistry

The isolation of reactive main group compounds would not have been feasible without the appropriate choice of substituents. While many remarkable developments have recently been made, further advances are certainly necessary to reach an advanced control of the stability and activities. In order to isolate reactive main group compounds, a balance of thermodynamic and kinetic stabilization is required. In general, large substituents are needed to shield the reactive center from decomposition and other unwanted transformations. Specifically bulky alkyl, aryl and amido groups are often employed,¹¹ particularly with large silyl substituents as used by Lappert in the tetrylenes **5a** and **5b**¹² or more recently by Yamashita in the aluminum anion **6** (Fig. 2).¹³ Likewise, *ortho*-substituted aryl groups – either attached to a substituent or as plain aryl groups – provide steric protection and like all bulky substituents further stabilization through London dispersion forces.¹⁴ The most popular aryl groups are mesityl (Mes), 2,6-diisopropylphenyl (Dipp) and terphenyl groups as pioneered by Power and coworkers (e.g. in **1**).⁴

The importance of increasing the steric bulk for reactivity control was impressively demonstrated by Jones and coworkers using the extremely bulky amido substituents of type N(Ar*) Si¹Pr₃ (Ar* = 2,6-[C(H)Ph₂]₂-4-¹PrC₆H₂) such as in **7**. These substituents allowed the isolation of low coordinate species, including digermynes ¹Pr₃Si(Ar*)NGeN(Ar*)Si¹Pr₃, which activates H₂ at temperatures as low as –10 °C.¹⁵ Because of the extreme bulk of the amide the hydrido-digermene exists in equilibrium with its monomeric metal(II) hydride **7**, which catalyses hydroboration reactions.¹⁶ A very recent example of the power of steric protection for stabilizing reactive species was reported by Bertrand and coworkers. The careful design of bulky benzo[*c*]pyrrolidino heterocycles enabled the stabilization and isolation of the first monosubstituted carbene.¹⁷

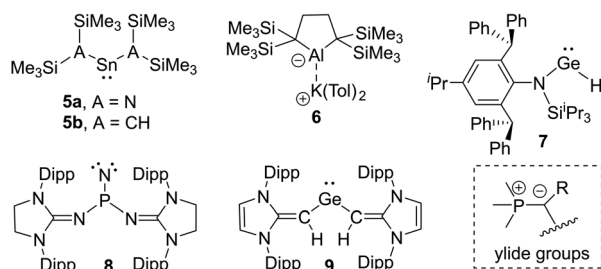


Fig. 2 Examples of low-valent main group compounds with different substituents.

Besides kinetic stabilization, thermodynamic stabilization using ligands with the “right” electronic properties is crucial to access reactive species. A large variety of different substituents have been applied, including special substituents with particular properties, e.g. boryl^{6d,18} and even metallo substituents.¹⁹ For stabilizing low-valent and electron-deficient compounds strong σ - and π -donors are particularly well suited such as aryl or amido groups, but also other σ - and π -donor substituents have emerged in recent years. Prominent examples are N-heterocyclic imines²⁰ and their carbon^{21,22} and phosphorus²³ derivatives. Due to the contribution of an ylidic form to their electronic structure they are strong donors and thus allowed the isolation of a series of reactive main group compounds, e.g. phosphino nitrene **8**²⁴ and tetrylenes,²⁵ such as germylene **9**.²⁶

Phosphorus ylides (Fig. 2), such as the parent methylene-triphenylphosphorane Ph₃PCH₂, are dipolar compounds with a carbanionic center directly bound to a phosphonium moiety. Due the lone pair at the carbon atom they can act as π -donor substituents, suitable for stabilizing electron-deficient compounds. The R group in the ylide backbone allows the tuning of the steric and electronic properties and hence an advanced control of the reactivity of the main group species. The electronic structure of ylides has been vividly discussed over the years. At first, it was mostly described by two canonical structures – ylene A' and ylide A (Fig. 3). However, computational studies have shown that the contribution of the ylenic structure A' is minimal, as it requires (d-p) π interaction with d-orbitals at phosphorus, which are however too high in energy.²⁷ Recently, the canonical structure A''²⁸ with a donor-acceptor interaction between phosphorus and carbon has found renewed interest. This structure describes ylides as phosphine-stabilized carbenes. An analogous description has also been used for bisylides, particularly carbodiphosphoranes (CDPs).²⁹ However, recent studies showed that in metallated ylides the ionic ylidic structure is more important,³⁰ so this description will be used throughout this review. Despite this unique electronic structure of P-ylides, their use as substituents in main group chemistry is still in its infancy. However, with the recent gram-scale isolation of alkali metal precursors broader applications have opened up.

Alkali metal ylides

Since the first synthesis of ylides over a century ago and their use in Wittig type reactions, this class of compounds has been widely utilized in organic synthesis. In contrast, their metallated congeners, so-called yldiides, have for a long time remained unexplored, despite being ideal reagents to introduce ylide substituents *via* simple salt metathesis. Schlosser and Corey were the first who synthesized lithium yldiides.³¹

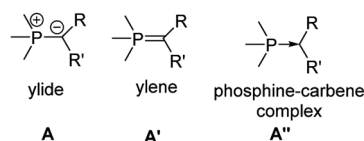


Fig. 3 Bonding situation in ylides.



However, neither any isolation nor structure elucidation was reported probably due to the high sensitivity of these compounds. Until today, only a few alkali metal ylides have been isolated. In general, strongly electron-withdrawing groups facilitate their preparation *via* direct metallation of an ylide with strong alkyl or amide metal bases and the isolation of the ylide. It is noteworthy that in general the number of metal complexes with an ylide ligand is rather limited, probably also a consequence of the few readily available ylide precursors. Nonetheless, complexes with mid- and late transition metals and actinides have been reported.³²

The first isolation of an alkali metal ylide was accomplished by Bestmann with the synthesis of the cyanido-functionalized sodium ylide **10**.³³ Spectroscopic and reactivity studies showed that due to the stabilization of the negative charge by the nitrile functionality both canonical structures **10a** and **10b** contribute to the electronic structure of the ylide (Scheme 1). XRD analyses of different alkali metal salts of **11** were later reported and revealed an astonishing structural diversity varying from coordination polymers to monomers depending on the alkali metal and the use of crown ethers as additional ligands.³⁴ The first structure elucidations were reported in the 1990s. Bertrand and coworkers reported the silyl-substituted lithium ylide **12** which was uniquely synthesized by a 1,2-carbometallation of phosphino(silyl)carbene **11** with *n*-BuLi.³⁵ In the solid state (Fig. 5), **12** formed a monomeric structure with the lithium atom coordinated by two THF molecules and the ylidic carbon atom, which featured a planar geometry. The short P–C and Si–C bonds indicated the strong stabilization of the negative charge by the silyl and phosphonium groups. Similar observations were made by Niecke with phosphoranylidene ylides **13a** and **13b**.³⁶ This bond shortening is characteristic of ylides and the charge accumulation on the ylidic carbon atom. Therefore, the P–C bond length can serve as a measure for the charge concentration and also transfer to other groups.

In 2015, our group reported a sulfonyl substituted ylide **14** which could be prepared on a gram scale by deprotonation of the phosphonium salt **14-H₂** (Fig. 4).³⁷ **14** exhibited a remarkable stability in solution and could be stored for weeks under an inert atmosphere, thus representing an ideal reagent for ylide transfer (see below). The high stability is due to the strong stabilization of the negative charge by the sulfonyl and phosphonium group. While the sodium salt of **14** featured a dimeric structure with two (NaO)₄ cubes connected *via* one common



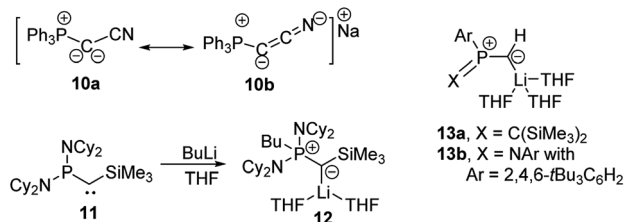
Fig. 4 (top) Synthesis and (bottom) the HOMO and HOMO–1 of **14**.



Fig. 5 Structures of the lithium ylide **12** and the sodium salt of **14**.

face (Fig. 5), the potassium analogue formed a monomer with 18-crown-6 as an additive. Again, a decrease in the bond lengths was seen in the P–C–S linkage of **14** relative to **14-H₂** and **14-H**, owing to the increased coulombic interactions with the increased charge on the ylidic carbon atom. Computational studies confirmed the presence of two lone pairs at the carbon atom, one of σ (HOMO–1) and one of π (HOMO) symmetry, thus confirming the strong basicity of **14** and its ability to act as a σ and π donor.

Besides **14** also its PCy₃ analogue was recently reported. Introduction of the PCy₃ group led to a remarkably reduced acidity of the ylide precursor, thus requiring stronger metal bases (benzyl potassium) for metallation.³⁸ Nonetheless, ylide **15** was isolable on a gram-scale (Fig. 6). A sulfonyl-stabilized ylide was reported by Maerten, Baceiredo and coworkers.³⁹ Lithium ylide **16** was synthesized by deprotonation with *n*-BuLi and showed a dimeric structure with a Li₂O₂ core and decreased P–C and C–S bond lengths owing to the increased negative character at the ylidic carbon center.



Scheme 1 Formation of ylides **11** and **12** by carbolithiation and metalation and the structure of lithium ylides **13**.



Fig. 6 Metalated ylides **15** and **16**.

Besides structure elucidation by XRD analysis, phosphorus ylides can easily be identified by ^{31}P NMR spectroscopy. Upon metalation, a distinct high-field shift of the ^{31}P NMR signal relative to that of the ylide precursor is usually observed. For example, an upfield shift from 14.2 ppm for **14-H** to $\delta_{\text{P}} = -11.1$ ppm for the sodium salt of **14** has been observed. Likewise, the $^1J_{\text{PC}}$ coupling constant significantly decreases due to the increased p-character in the P–C linkage, *e.g.* by $\Delta J = 40$ Hz in case of the cyano-ylide **10**³⁴ and even by $\Delta J = 121$ Hz for sulfoxide **16**.³⁹

Ylide-stabilized group 13 compounds

As strong donor substituents ylides are supposedly well suited for stabilizing electron-deficient compounds. With their inherent electron-deficiency group 13 compounds should thus be ideal target molecules. Indeed, Bestmann reported the synthesis of ylide-functionalized boranes **17** in the late 1980s by reaction of alkylidenephosphoranes with chloroboranes (Scheme 2).⁴⁰ Also, the synthesis of the ylide-substituted lithium borate **18** was described, but no further reactivity studies were reported. Breher and coworkers however, recently disclosed an FLP-type reactivity of sterically uncumbered α -borylated ylides, which allowed their application in the activation of small molecules such as CO_2 or NH_3 and thus suggests a more versatile reactivity of these compounds.^{40c,d}

The ability of ylide substituents to stabilize electron-deficient species was finally proven by means of ylide **14**. The reaction of **14** with $\text{BH}_3 \cdot \text{THF}$ delivers the di(ylide)borane **19** which yields the first ylide-stabilized boron cation **20** by hydride abstraction using trityl salts (Fig. 7). The stabilizing effect of the ylide groups was reflected in the high stability of **20** even in boiling toluene and up to 200 °C in the solid state. The molecular structure of the PF_6^- salt revealed that one of the sulfonyl groups of the ylide ligands coordinates to the boron atom, which is in plane with the two ylide ligands $(\text{S}(\text{P})\text{C})_2\text{B}$. The short B–C_{ylide} distances (*viz.* 1.481(7) and 1.510(9) Å) indicated significant π donation from the ylide center. This observation was further reiterated by longer P–C and S–C bonds in the ylide due to the decrease in the negative charge on the ylidic carbon atom. DFT studies confirmed the π interaction, but also a high polarity of the C–B–C linkage as reflected by the Wiberg bond indices, the calculated charges and the frontier orbitals. Consistent with the highly electrophilic boron center **20** reacts with a range of Lewis bases to form the corresponding adducts and with KF to form the corresponding fluoroborane. The high C–B bond polarity is expressed in the reactivity towards primary

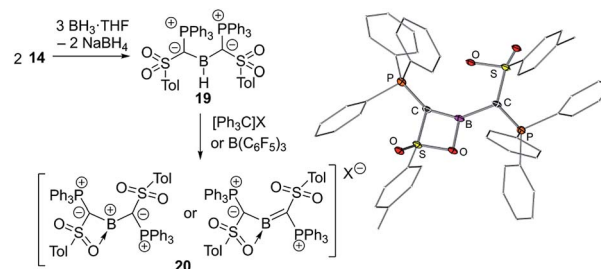


Fig. 7 Synthesis of the di(ylydyl)boron cation **20** and its molecular structure ($\text{X} = [\text{B}(3,5\text{-Cl}_2\text{C}_6\text{H}_3)_4]^-$, $[\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4]^-$, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ or PF_6^-).

and secondary amines, which leads to the formation of tris(amino)boranes by N–H activation and subsequent cleavage of the B–C bond.

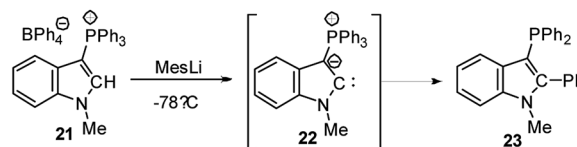
Besides **20** no further low-valent group 13 compounds with ylide substituents have been reported to date. However, the potential of ylide substituents in this chemistry was picked up in recent computational studies by Phukan and coworkers.⁴¹ They suggested that the use of ylide substituents leads to an improved stability of borylenes and thus could be a promising strategy to access these reactive species.

Ylide-stabilized group 14 compounds

Cyclic amino(ylyde)carbenes (CAYCs) (for example **22**) have been known for some time, but only stabilized in the coordination sphere of transition metals.⁴² These complexes were synthesized by cyclization of transition-metal isocyanide complexes and thus limited to few examples. As the donor ability of an ylide exceeds that of an amino substituent, CAYCs were expected to exhibit increased electron-releasing capacities compared to NHCs. In 2008, Kawashima reported the first attempts to isolate a CAYC derived from phosphonium salt **21** (Scheme 3).⁴³ Although the free carbene **22** could not be isolated even at low temperatures, trapping reactions and transfer to transition metals confirmed its formation. IR spectroscopy of the complex $[\text{22} \cdot \text{Rh}(\text{CO})_2\text{Cl}]$ proved the superior donor strength of **22** compared with diamino or alkyl(amino)carbenes. This was also confirmed by Fürstner by means of a series of sulphur- and phosphorus-ylide functionalized CAYCs⁴⁴ and by computational studies.⁴⁵ Despite several further attempts no stable ylide-substituted carbene has been reported so far.⁴⁶ This lack is probably due to the high nucleophilicity, which results in decomposition pathways, such as by transfer of aryl substituents at the phosphonium group (*e.g.* to **23**) or intramolecular deprotonations in the α - or β -position of the onium group.⁴⁷



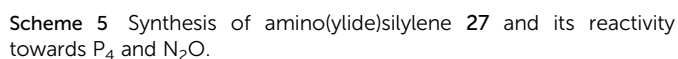
Scheme 2 Synthesis of ylide-substituted boranes (hexyl = $-\text{C}(\text{CH}_3)_2-\text{C}(\text{CH}_3)_2\text{H}$; TMP = 2,2,6,6-tetramethylpiperidino) and the structure of **18**.



Scheme 3 Attempted isolations of CAYC **22**.



A further stability increase compared to that of diylidesilylenes **25** was realized by Kato and co-workers by synthesizing a cyclic amino(ylide)silylene. **27** was accessible by reduction of dichlorosilane **26** with elemental potassium in toluene at 80 °C (Scheme 5).⁵¹ ²⁹Si NMR spectroscopy of **27** showed a resonance



Germynes **31** analogous to **27** could also be isolated (Scheme 6), but *via* an unusual isomerization of the phosphine-stabilized germyne **30** which was generated by photolysis of a diazo precursor.⁵³ Both germynes **31** were stable at room temperature, but no further reactivity studies were reported. Kato, Baceiredo and co-workers further exploited the potential of ylidic donor substituents by studying variants of **27** and **31** with phosphorus and boron instead of carbon as donor atoms.⁵⁴ This led to a further increase in the electron density at the group 14 elements. Consequently, silylene **32a** is a stronger donor than **27** and allowed the generation of the corresponding silanone that exhibited a higher stability than **29**.⁵⁵ Germylene **33a** showed an interesting multi-site reactivity. While the neutral Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ preferred the coordination to the germanium centre, the silylium cation SiEt_3^+ favoured the binding to the phosphorus atom. This bifunctional activity could also be applied in the hydrosilylation of carbon dioxide with triethylsilane using the $\text{B}(\text{C}_6\text{F}_5)_3$ adduct as the catalyst.⁵⁶

In 2019, our group reported the first acyclic diylide-substituted stannylene and germylene formed by simple reaction of yldiide **14** with half an equivalent of $\text{GeCl}_2 \cdot \text{dioxane}$ and SnCl_2 , respectively (Fig. 8).⁵⁷ The ease of this synthesis demonstrated the utility of group 1 yldiides in accessing ylidesubstituted main group species. XRD analyses revealed unusual structures of both compounds. In contrast to all other





Fig. 8 (Top) Synthesis of the diyliide germylene and stannylene **34** and **35**. (Bottom left) Bonding situation in **34** and **35** and (bottom right) the molecular structure of **34**.

ylide-functionalized tetrylenes, the ylide groups ($\text{P}-\text{C}-\text{S}$ plane) in **34** and **35** arranged perpendicularly to the $\text{C}-\text{E}-\text{C}$ linkage, thus preventing any π -donation from the ylide to the empty p-orbital at Sn/Ge . This results in an unusual bonding situation, in which three lone pairs at the two carbon atoms and the central element are in plane and located next to each other (Fig. 8). Accordingly, the $\text{Sn}-\text{C}$ and $\text{Ge}-\text{C}$ bond lengths (2.23 and 2.04 Å, respectively) were found to be in the range of single bonds. This unusual structure was explained by the ability of the sulfonyl group to stabilize the negative charge on the ylidic carbon atom and its coordination to the metal, which demonstrates the impact of the substituents in the ylide backbone on the electronic properties and thus on the reactivity of the tetrylene. A comparison of the HOMO–LUMO energies and calculated Tolman electronic parameter (2032.3 cm^{-1}) of germylene **34** with those of other acyclic germylenes suggested that **34** is the germylene with the highest donor capacity reported so far. The same holds true for stannylene **35**. While the stannylene is stable in solution at room temperature, **34** showed limited stability and undergoes $\text{C}-\text{H}$ activation of one of the PPh_3 phenyl groups to form cyclotetragermene **36**. DFT studies suggested that the $\text{C}-\text{H}$ activation occurs across the $\text{Ge}-\text{C}$ linkage, implying a bifunctional reactivity of ylide-substituted tetrylenes.

Ylide-stabilized group 15 compounds

Ylide-functionalized phosphorus compounds have been intensively studied in the 1990s particularly by Schmidpeter and coworkers who for example focused on the impact of ylide substitution in halophosphines.⁵⁸ Due to the π -donation (negative hyperconjugation),⁵⁹ ylide substituents were found to cause a marked polarization of the $\text{P}-\text{Hal}$ bond. Depending on the other substituents this polarization even results in the spontaneous dissociation of the halide to form phosphonium cations of type **38** (Fig. 9).⁶⁰ Spontaneous dissociation was for example observed in diylide and amino(ylide) functionalized

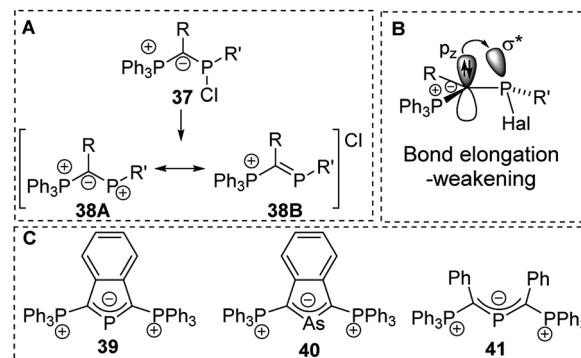


Fig. 9 (A) Dissociation of ylide-substituted chlorophosphines to phosphonium cations, (B) orbital interactions in ylide-substituted halophosphines and (C) diylide-substituted group 15 cations.

systems. For all other halophosphines, elongated $\text{P}-\text{Cl}$ bonds were observed, and the halide could easily be abstracted *e.g.* by addition of AlCl_3 . Crystallographic studies of YPhal_2 revealed that one of the $\text{P}-\text{Cl}$ bonds is roughly perpendicularly arranged to the $\text{P}-\text{C}(\text{R})-\text{P}$ plane which leads to a parallel orientation of the p_z orbital at the ylidic carbon atom and the σ^* orbital of the $\text{P}-\text{Cl}$ bond and hence results in an effective charge transfer (Fig. 9B). The same π -donation effects were observed in analogous arsenic compounds and allowed the isolation of di(ylide)-substituted cations such as **39**, **40** and **41** which feature a delocalization of the charge within the $\text{C}-\text{E}-\text{C}$ linkage.^{58b,61,62}

The preference of certain conformers due to the repulsion between the lone pair at the ylidic carbon atom and the neighbouring phosphorus atom was also found in ylide-

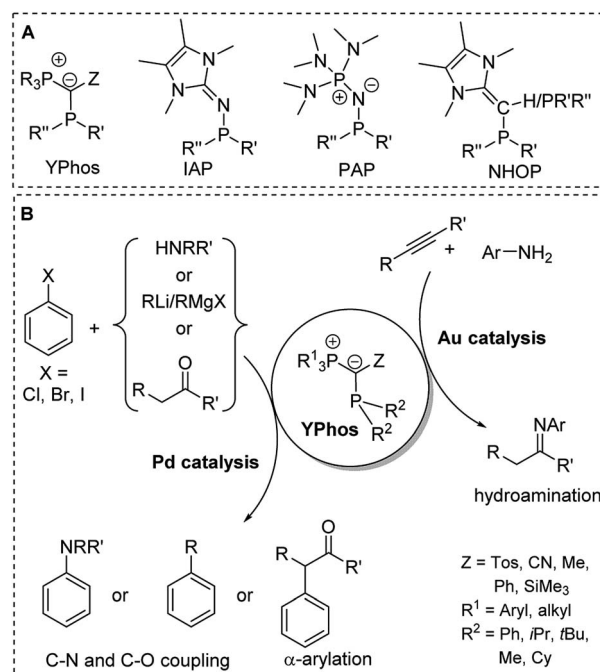


Fig. 10 (A) Structures of electron-rich phosphines. (B) Applications of YPhos ligands in homogeneous catalysis ($\text{R}, \text{R}', \text{R}'' = \text{alkyl}$).

substituted phosphines (YPhos, Fig. 7).⁶³ Although these phosphines have been known for quite some time,^{64,65} their strong donor properties owing to the electron donation from the ylide to the phosphorus centre were only recently recognized. Our group used YPhos ligands as electron-rich phosphines in homogeneous catalysis, which led to highly active gold and palladium catalysts *e.g.* for hydroamination and C–N as well as C–C coupling reactions at room temperature (Fig. 10).⁶⁶ The donor strength and the steric properties of the YPhos ligands were found to be highly tunable depending on the nature of the Z substituent in the ylide-backbone. Thus, while offering steric protection through the large phosphonium moiety, donor strengths similar to those of NHCs, which are usually considered to be stronger donors, could be reached.^{63a} Electron-rich phosphines were also reported by Beller, Rivard and Ruiz when using N-heterocyclic olefins (NHOPs)⁶⁷ as substituents as well as by Dielmann and coworkers using imidazolidin-2-imino substituents (IAPs)⁶⁸ and by Sundermeyer and coworkers using phosphazanyl groups (PAPs).⁶⁹ The latter exhibited even higher donor strengths than the YPhos ligands.

Conclusions and outlook

Overall, the use of phosphorus ylides as substituents in main group chemistry is still in its infancy. However, the survey of compounds presented in this review article and the breadth of the remarkable results achieved with the structurally related N-heterocyclic vinyl substituents demonstrate that these substituents are well suited for stabilizing reactive compounds and offer a further possibility for tailoring the properties and reactivities of main group metal compounds. Owing to their strongly electron-donating character ylides have particularly been used to stabilize electron-deficient compounds above all cations (borenium and phosphenium) and low-valent species. Specifically the reported group 14 chemistry demonstrates the true potential of these substituents not only for the stabilization of otherwise elusive species (*e.g.* Si=O), but also for imparting new reactivities including ligand-centered reactivity. Therefore, the variation of the substituent in the ylide backbone offers a further opportunity for fine-tuning the donor properties. This concept has been lately used to tailor electron-rich ylide-substituted phosphines for catalysis, which express the electronic and steric flexibility of ylide-substituents. These findings clearly demonstrate the potential of phosphorus ylides as substituents in main group chemistry. The tailoring of the ylide properties for stabilizing reactive compounds is far from being well explored but offers many possibilities for future studies.

Conflicts of interest

There are no conflicts to declare.

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