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 neighboring 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. While several key compounds in this chemistry were already isolated in the last decades of the 20th century, 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.

A remarkable breakthrough in this context was reported in 2005 by Power with the activation of dihydrogen by using digermyne 1 (Fig. 1a). 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. 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, 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, while Braunschweig and coworkers accomplished N2 reduction by using the transient borylene 4.

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...
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. The use of such ligands is beyond the scope of this review but has been covered in excellent review articles.

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, particularly with large silyl substituents as used by Lappert in the tetrylenes 5a and 5b or more recently by Yamashita in the aluminum anion 6 (Fig. 2). 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. The most popular aryl groups are mesityl (Mes), 2,6-disisopropylphenyl (Dipp) and terphenyl groups as pioneered by Power and coworkers (e.g. in 1).

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*)SiPR3 (Ar* = 2,6-[C(H)Ph2]-4-PrC6H4) such as in 7. These substituents allowed the isolation of a low-coordinate species, which activates H2 at temperatures as low as −10 °C. Because of the extreme bulk of the amide the hydrido-digermene exists in equilibrium with its monomeric metal[α] hydride 7, which catalyses hydroboration reactions. 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.

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[14,18] 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 imines[20] and their carbon[21,22] and phosphorus[23] 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[24] and tetrylenes,[25] such as germylene[9,26]

Phosphorus ylides (Fig. 2), such as the parent methylenetriphenylphosphorane 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. Recently, the canonical structure A″ 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 carbodiorganophosphoranes (CDPs).[27] However, recent studies showed that in metallated ylides the ionic ylidic structure is more important,[28] 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 ylidiides

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 ylidiides, 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 ylidiides.
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.\(^{23}\)

The first isolation of an alkali metal ylide was accomplished by Bestmann with the synthesis of the cyanido-functionalized sodium ylide 10.\(^ {23}\) 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.\(^ {24}\) 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-carbometalation of phosphino(silyl)carbene 11 with \(\text{n-BuLi}\).\(^ {25}\) 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 phosphonio groups. Similar observations were made by Niecke with phosphoranylidene ylides 13a and 13b.\(^ {26}\) 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-H\(_2\) (Fig. 4).\(^ {27}\) 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 phosphonio group. While the sodium salt of 14 featured a dimeric structure with two \(\{\text{NaO}\}_4\) cubes connected via one common 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-H\(_2\) 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 \(\sigma\) (HOMO–1) and one of \(\pi\) (HOMO) symmetry, thus confirming the strong basicity of 14 and its ability to act as a \(\sigma\) and \(\pi\) donor.

Besides 14 also its PCy\(_3\) analogue was recently reported. Introduction of the PCy\(_3\) group led to a remarkably reduced acidity of the ylide precursor, thus requiring stronger metal bases (benzyl potassium) for metallation.\(^ {28}\) Nonetheless, ylide 15 was isolable on a gram-scale (Fig. 6). A sulfinyl-stabilized ylide was reported by Maerten, Baceiredo and coworkers.\(^ {29}\) Lithium ylide 16 was synthesized by deprotonation with \(\text{n-BuLi}\) and showed a dimeric structure with a Li_2O_2 core and decreased P-C and C-S bond lengths owing to the increased negative character at the ylidic carbon center.
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 in the late 1980s by reaction of alkylidene phosphoranes with chloroboranes (Scheme 2). Also, the synthesis of the ylide-substituted lithium borate was described, but no further reactivity studies were reported. Breher and coworkers however, recently disclosed an FLP-type reactivity of sterically uncumbered ylides, which allowed their application in the activation of small molecules such as CO₂ or NH₃ and thus suggests a more versatile reactivity of these compounds.

The ability of ylide substituents to stabilize electron-deficient species was finally proven by means of ylide 14. The reaction of 14 with BH₃·THF delivers the dilyl)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 PF₆⁻ salt revealed that one of the silyl groups of the ylide ligands coordinates to the boron atom, which is in plane with the two ylide ligands (S[P(η)]C₃). B. The short B-Cylide distances (viz. 1.481(7) and 1.510(9) Å) indicated significant π interaction 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 ylide 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 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. 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(ylide)carbenes (CAYCs) (for example 22) have been known for some time, but only stabilized in the coordination sphere of transition metals. 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, Kawasaki reported the first attempts to isolate a CAYC derived from phosphonium salt 21 (Scheme 3). 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 [22-Rh(CO)₂Cl] proved the superior donor strength of 22 compared with diamino or alkyl(ylide)carbenes. This was also confirmed by Fürstner by means of a series of sulphur- and phosphorus-ylide functionalized CAYCs and by computational studies. Despite several further attempts no stable ylide-substituted carbene has been reported so far. 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.
The unique properties of ylide-substituted tetrylenes have impressively been demonstrated by means of heavier carbene analogues. Driess and coworkers reported the synthesis of the cyclic diylidesilylenes 25 by treatment of α,α′-dibromo-orthoxylene in the presence of KHMDMS (HMDS = hexamethyldisilazide) with SiBr₄ (Scheme 4) and subsequent reduction of the dibromosilane 24 with KC₈ or Jones’ Mg(I) reagent. Although 25b could not be structurally characterized, solutions of the silylene were stable up to three months. The ²⁹Si NMR signal of 25a (δₛᵢ = 213.3 ppm) and the signal of the ylidic carbon atom (approx. 90 ppm) appeared to be significantly downfield shifted compared to those of NHSis and carbanionic compounds, respectively. This was explained by DFT calculations, which revealed an aromatic character and an electron-rich silicon center in 25 as reflected by the resonance structure 25B. The cyclic diylide|stannylene analogous to 25a was already reported by Schmidpeter in 1998 by the reaction of the diylide precursor with Sn(HMDS)₂ (Scheme 5). It also featured a monomeric structure in solution with a ¹²⁵Sn NMR signal appearing as a triplet at δ = 880.0 ppm.

A further stability increase compared to that of diylidesilylenes 25 was realized by Kato and co-workers by synthesizing a cyclic amino|ylidesilylene. 27 was accessible by reduction of dichlorosilane 26 with elemental potassium in toluene at 80 °C (Scheme 5). ²⁹Si NMR spectroscopy of 27 showed a resonance at δₛᵢ = 202.2 ppm, whereas the ylide carbon signal appeared as a doublet at 137.7 ppm in the ¹³C NMR spectrum, thus suggesting a strong π donation from the ylide to the divalent silicon centre. This was confirmed by the short Si–C bond length [1.798 (2) Å] in the solid-state structure, which featured a planar six-membered ring and an increased Si–N bond length compared to that of diaminosilylenes. Thus, it was concluded that 27 is best described by the canonical structure 27B with a π interaction between the ylide and the silicon center. Accordingly, the silylene exhibited a stronger donor ability compared to NHSis and even NHCs and for example readily reacted with P₄ at room temperature through silylene insertion into a P–P bond to give the SiP₄ cage 28. Moreover, the high electron density at the silicon atom was used to access the first base-free silanone 29 by simple reaction of 27 with N₂O. ²⁹Si NMR spectroscopy of 27 showed an interesting multi-site reactivity. While the neutral compound 27A was accessible by reduction of 27 with KC₈ or Jones’ Mg(I) reagent, 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. 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. ³¹Germylene 33a showed an interesting multi-site reactivity. While the neutral Lewis acid B(C₆F₅)₃ preferred the coordination to the germa-nium centre, the silylium cation SiEt₃⁺ favoured the binding to the phosphorus atom. This bifunctional activity could also be applied in the hydrosilylation of carbon dioxide with triethylsilane using the B(C₆F₅)₃ adduct as the catalyst.
Ylide-functionalized tetrylenes, the ylide groups (P–C–S plane) in 34 and 35 arranged perpendicularly to the C–E–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 Sn–C and Ge–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/C01) 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 C–H activation of one of the PPh3 phenyl groups to form cyclotetramerane 36. DFT studies suggested that the C–H activation occurs across the Ge–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), ylide substituents were found to cause a marked polarization of the P–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). 59 Spontaneous dissociation was for example observed in diylide and amino(ylide) functionalized systems. For all other halophosphines, elongated P–Cl bonds were observed, and the halide could easily be abstracted e.g. by addition of AlCl3. Crystallographic studies of YPHal2 revealed that one of the P–Cl bonds is roughly perpendicularly arranged to the P–C–(R)–P plane which leads to a parallel orientation of the p orbital at the ylidic carbon atom and the s* orbital of the P–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 dylide-substituted cations such as 39, 40 and 41 which feature a delocalization of the charge within the C–E–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-functionalized phosphorus compounds.
substituted phosphines (YPhos, Fig. 7). Although these phosphines have been known for quite some time, 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). 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 o-haloaryl substituents are well suited for stabilizing reactive compounds and heterocyclic vinyl substituents demonstrate that these substituents as well as by Dieckmann and coworkers using imidazolidin-2-imino substituents [IAPs] and by Sundermeyer and coworkers using phosphazenyl groups (PAPs). 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 activities 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 (boreniun 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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