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Synthesis, Crystal and Electronic Structures of a Thiophosphinoyl- and Amino-Substituted Metallated Ylide

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On the occasion of the 60th birthday of Professor Holger Braunschweig

α -Metallated ylides have revealed themselves to be versatile reagents for the introduction of ylide groups. Herein, we report the synthesis of the thiophosphinoyl and piperidyl (Pip) substituted α -metallated ylide $[\text{Ph}_2(\text{Pip})\text{P}=\text{C}=\text{P}(\text{S})\text{Ph}_2]\text{M}$ ($\text{M}=\text{Li}, \text{Na}, \text{K}$) through a four-step synthetic procedure starting from diphenylmethylphosphine sulfide. Metallation of the ylide intermediate was successfully accomplished with different alkali metal bases delivering the lithium, sodium and potassium salts, the latter isolable in high yields. Structure analyses of the lithium and potassium compounds in the solid state with and without crown ether revealed different aggregates (monomer, dimer and hexamer) with the metals coordinated by the thiophosphoryl moiety and ylidic carbon atom. Although the piperidyl group does not coordinate to the metal, it significantly contributes to the stability of the ylide by charge delocalization through negative hyperconjugation.

Phosphorus ylides are valuable reagents in chemical synthesis and have been applied in various research directions since many years. Apart from their utilization in organic synthesis (e.g., in olefination reactions), they have also been used as ligands in coordination chemistry and as strong donor substituents in organic materials and main group compounds.^[1] Typically, ylides are synthesized from the corresponding phosphonium salts by deprotonation. However, more recently, the introduction of ylide moieties by a salt metathesis approach using α -metallated ylides has become a viable alternative.^[2] The prerequisite for this approach is the accessibility of ylide species. The first metallated ylide was already reported by Corey and Kang in 1982, who prepared lithium triphenylphosphonium methyldiide, $\text{Ph}_3\text{PC}(\text{H})\text{Li}$, by lithiation of phosphonium meth-

ylide.^[3] While this ylide was only used as an in situ-prepared reagent and its existence had also been questioned by Schlosser and co-workers,^[4] Bestmann and Schmidt succeeded in the isolation of the cyano-stabilized compound **A** (Figure 1), whose alkali metal salts were also later structurally characterized.^[5] Since then, a number of metallated ylides (compounds **B-E**) have been isolated^[6] – partly also on a gram scale – and applied in ylide transfer reactions.^[7] Our group, for example, isolated the sulfonyl-substituted compounds **D** and used them for the stabilization of low-valent main group species^[8] as well as in the synthesis of ylide-substituted phosphines, which revealed themselves to be powerful ligands for homogeneous catalysis.^[9,10]

In order to expand the portfolio of readily accessible metallated ylides for their use in main group chemistry, we became interested in the preparation of further readily isolable and storable ylide. Whereas sulfonyl and sulfinyl groups have already been proven to be suitable groups for stabilizing the high negative charge at the ylidic carbon atom, we also expected P^{V} substituents to be able to provide sufficient stabilization. Thus, we targeted the synthesis of a thiophosphoryl-substituted compound and selected compound **Y-H** (Scheme 1), since we expected the additional amino substituent at the phosphonium unit to be beneficial for metal coordination and hence for isolation of the alkali metal ylides. Here, we report our findings.

We assumed that **Y-H** should be readily prepared from **2**, which itself should be accessible from the commercially available bis(diphenylphosphino)methane (dppm). Unfortunately, initial attempts to synthesize this compound proved to

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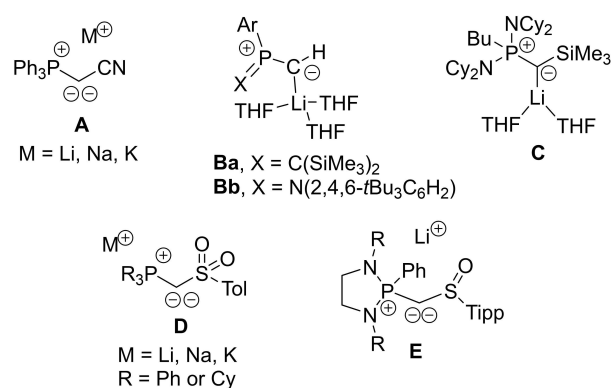
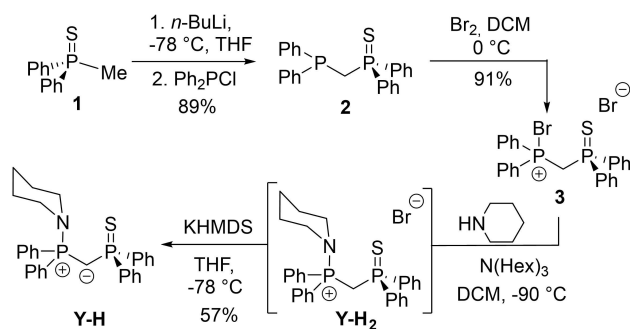


Figure 1. Isolated metallated ylides.



Scheme 1. Synthesis route for Y-H starting from chlorodiphenylphosphine sulfide (1).

be challenging, since selective oxidation of only one phosphine moiety with one equivalent of either bromine or sulfur to the respective mono-oxidized compound, despite literature evidence, could not be achieved with sufficient selectivity.^[11] We therefore decided to try an alternative synthetic procedure towards Y-H using methyl diphenylphosphine sulfide 1, which was prepared according to a literature procedure in a one-pot reaction between Ph₂P-Cl and MeMgCl and subsequent treatment with elemental sulfur.^[12] For the synthesis of 2, the phosphine sulfide 1 was reacted with a stoichiometric amount of *n*-BuLi in THF followed by addition of chlorodiphenylphosphine. Removal of the solvent and work-up gave 2 as a colourless solid in 89% yield. The product could clearly be identified by multinuclear NMR spectroscopy, the ³¹P{¹H} NMR spectrum showing two doublets at δ_p = -28.4 and 40.0 ppm with a coupling constant of ²J_{pp} = 77.3 Hz.^[13]

The next step was the bromination of 2 using stoichiometric amounts of elemental bromine in DCM at low temperatures. Thereby, bromine addition must be carried out in a controlled manner to minimize side product formation. The resulting product 3 shows low solubility in DCM, thus allowing for its isolation as colorless solid in excellent yields. Spectroscopic analysis showed doublets at δ_p = 33.7 and 49.6 ppm in the ³¹P{¹H} NMR spectrum, consistent with a transition from P^{III} to P^V.^[14] Next, amination to yield Y-H₂ was achieved through reaction with one equivalent of piperidine and two equivalents of trihexylamine. Unfortunately, this reaction was surprisingly unselective, always delivering the phosphine oxide as a by-product. At 0 °C, an approx. 1:2 ratio of aminated to oxidized product was formed as determined by ³¹P{¹H} NMR spectroscopy. Lowering the reaction temperature improved the selectivity, giving 75% of the aminated compound at -90 °C. Since separation of the compounds was found to be difficult, the mixture was directly used for the subsequent deprotonation step. Fortunately, treatment of the mixture with KHMDS (HMDS = bis(trimethylsilyl)amide) in THF led to the precipitation of the deprotonated phosphine oxide, thus allowing the isolation of ylide Y-H in a moderate 57% yield on a gram scale in a single step from 3. Ylide Y-H revealed to be highly stable, showing no decomposition upon storage in a glovebox over extended periods of time. Y-H is characterized by two doublets in the ³¹P{¹H} NMR spectrum at δ_p = 33.7 and 41.7 ppm (Table

1). In the ¹H NMR spectrum, a doublet of doublets integrating to one at δ_H = 1.84 ppm is indicative of successful deprotonation. Furthermore, the central carbon atom in Y-H appears as a doublet of doublets at δ_C = 16.9 ppm in the ¹³C{¹H} NMR spectrum, which is considerably shifted to higher field compared to the corresponding signal of 3. Single crystals of Y-H could be obtained from slow evaporation of a saturated diethyl ether solution (Figure 2).^[15] Single crystals of Y-H₂ were serendipitously obtained from a reaction solution of the metallated ylide (see Supporting Information for details), thus allowing the comparison of the bond lengths and angles of the whole compound series (see Table 2).

With the ylide precursor in hand, we next addressed the deprotonation to the desired ylide. Examination of different metal bases revealed that *n*-butyllithium, sodium amide and benzyl potassium gave best results to access the different alkali metal salts, with the lithium and potassium compounds being more easily formed (Scheme 2). THF and benzene, respectively, were found to be the best solvents depending on the solubility of the reagents and products and reactions with the respective solvents. The lithium and sodium ylides could both unambiguously be spectroscopically identified. However, they were found to be unstable in solution, showing facile re-formation of Y-H after only one hour and thus preventing isolation in pure form. This contrasts with the potassium derivative, which shows a higher degree of solution stability (the first signs of protonation appearing only after a 24 hour period), thus allowing for a full spectroscopic characterization (see Supporting Information).

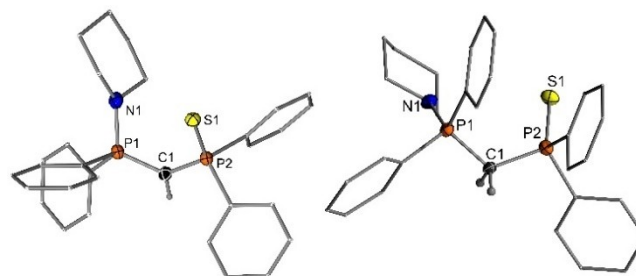
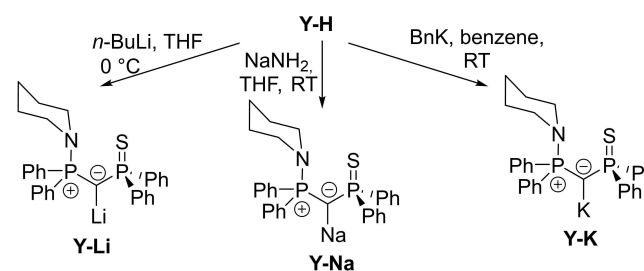


Figure 2. Molecular structures of Y-H₂ (anion omitted) and Y-H. Hydrogen atoms, except for the two H atoms bound to the central carbon atom have been omitted for clarity; thermal ellipsoids are displayed at the 50% probability level. Selected bond lengths (Å) and angles (°): For Y-H₂: P1–C1 1.803(5), P2–C1 1.831(5), P1–N1 1.647(4), S1–P2 1.9502(16), P1–C1–P2 119.4(2). For Y-H: P1–C1 1.694(2), P2–C1 1.723(2), P1–N1 1.6589(18), S1–P2 1.9743(7), P1–C1–P2 125.39(12).



Scheme 2. Synthesis pathway for individual alkali metal ylides.

From the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic data of **Y-M**, a few key trends can be seen for the different alkali metal salts (Figure 3, Table 1). The first is that, as group 1 is descended, an increasing shift to higher field in comparison to the ylide can be seen. This is in line with successful deprotonation and the resulting increase of electron density at the bridging carbon atom. At the same time, the $^2J_{\text{PP}}$ coupling constant increases, which indicates a widening of the P–C–P angle probably as a consequence of

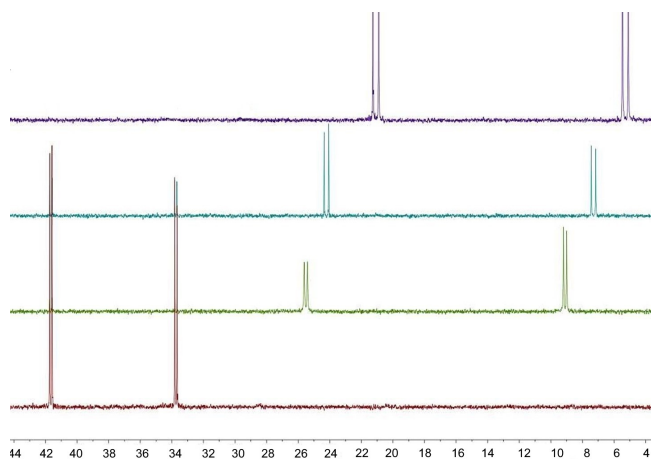


Figure 3. Comparison of $^{31}\text{P}\{^1\text{H}\}$ spectra of **Y-H** (red), **LiY** (green), **NaY** (blue) and **KY** (purple) in THF-d_8 (shifts are given in ppm).

Table 1. $^{31}\text{P}\{^1\text{H}\}$ NMR shifts and coupling constants of the parent ylide **Y-H** and the lithium, sodium and potassium ylide in THF-d_8 .

Species	δ_{P} [ppm]	$^2J_{\text{PP}}$ [Hz]	Δ_{C} [ppm]	$^1J_{\text{CP}}$ [Hz]
Y-H₂	44.7, 32.9	6.7	–	–
Y-H	41.6, 33.8	23.3	16.9	134.6 + 107.7
Y-Li	25.4, 9.2	32.5	–	–
Y-Na	24.1, 7.4	48.7	–	–
Y-K	20.9, 5.5	62.4	29.1	102.0 + 81.9

the weaker carbon metal interaction when moving down the group. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, a low-field shift of the central carbon signal is observed, moving from 16.9 ppm in **Y-H** to 29.1 ppm in **Y-K**, as well as a concomitant decrease in coupling constants from $^1J_{\text{CP}} = 134.6$ and 107.7 Hz to 102.0 and 81.9 Hz respectively. These trends have also previously been observed for other ylidiides.^[6]

Despite the instability of the ylidiides in solution, it was possible to obtain crystals of the lithium and potassium salts, both with and without addition of crown ether. The structures of all complexes are shown in Figures 4 and 5, and important bond lengths are given in Table 2. Crystallization of **Y-Li** from THF solution gives the dimer $(\text{Y-Li}\cdot\text{THF})_2$, in which the coordination sphere of lithium is composed of one carbon center from the ylide, two sulfur atoms and one solvating THF molecule. The ylidic carbon atom exhibits a trigonal planar coordination environment. No contact between the piperidyl moiety and the metal is observed. The same holds true for the corresponding 12-crown-4 (12-C-4) complex $[\text{Y}_2\text{Li}][\text{Li}(12\text{-C-4})_2]^{[16]}$. To our surprise, the addition of crown ether to the THF solvated dimer did not lead to the formation of a monomeric structure as anticipated. Instead, only one lithium cation is complexed by the crown ether, while the second Li ion is coordinated by two ylidiides, with the coordination sphere of the lithium center being completed by the sulfur atoms of the two ylidiides. Due to this coordination between sulfur and lithium, the Li1–C1–P2 bond angle of $91.90(13)^\circ$ and Li1–C1–P1 bond angle of $132.09(15)^\circ$ differ significantly from each other. The C1–Li1–C31 bond angle of $139.11(19)^\circ$ shows a high discrepancy from linearity, hence the lithium center is in a distorted tetrahedral environment. The Li–C distances of 2.131(4)–2.215(4) Å in both lithium ylidiides are comparable to previously studied dimeric lithium compounds.^[17] It is noteworthy that the Li–C distances in $[\text{Y}_2\text{Li}][\text{Li}(12\text{-C-4})_2]$ are slightly longer than those in the THF-solvated dimer. This elongation can probably be attributed to increased steric bulk and reduced

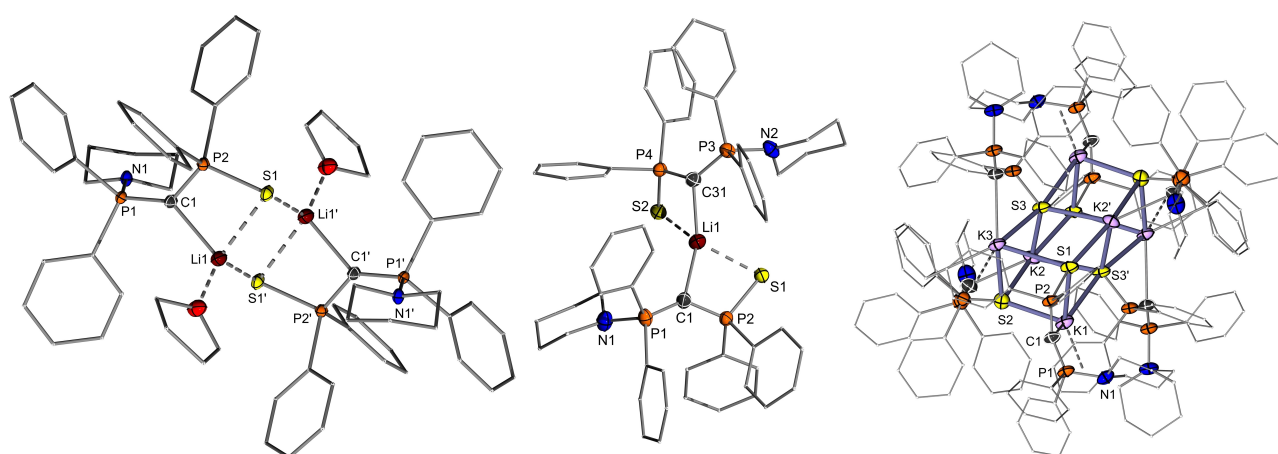


Figure 4. Molecular structures of $(\text{Y-Li}\cdot\text{THF})_2$, $[\text{Y}_2\text{Li}][\text{Li}(12\text{-C-4})_2]$ and $(\text{Y-K})_6$. Hydrogen atoms, disorder and $\text{Li}([12\text{-C-4})_2]^+$ have been omitted for clarity. Thermal ellipsoids are displayed at the 50% probability level. Selected bond lengths (Å) and angles ($^\circ$): $(\text{Y-Li}\cdot\text{THF})_2$: P1–C1 1.6391(17), P2–C1 1.6671(18), N1–P1 1.6976(15), S1–P2 2.0332(6), Li1–C1 2.132(4), S1–Li1 2.531(3), S1–Li1' 2.487(3), P1–C1–P2 134.91(11); $[\text{Y}_2\text{Li}][\text{Li}(12\text{-C-4})_2]$: P1–C1 1.639(2), P2–C1 1.658(2), N1–P1 1.725(2), S1–P2 2.0141(7), C1–Li1 2.215(4), S1–Li1 2.499(3), P1–C1–P2 135.95(13), C1–Li1–C31 139.11(19). $(\text{Y-K})_6$: P1–C1 1.585(2), P2–C1 1.674(3), N1–P1 1.708(2), S1–P2 2.0337(8), C1–K1 2.872(3), S1–K1 3.1413(9), P1–C1–P2 138.93(17). Transformations used to generate symmetry-equivalent atoms: $-x, -y, -z$ (for $(\text{Y-Li}\cdot\text{THF})_2$) and $-x, y+1/2, -z+1/2; -x, -y, -z$ and $x, -y-1/2, z-1/2$ for $(\text{Y-K})_6$.

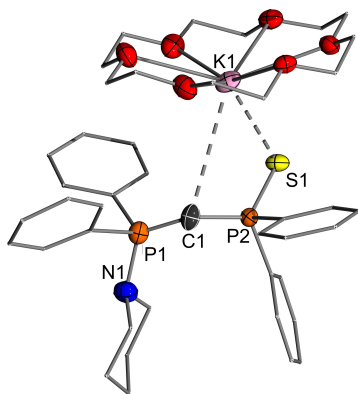


Figure 5. Molecular structure of $[\text{Y-K} \cdot (18\text{-C-6})]$. Hydrogen atoms and disorder omitted for clarity. Ellipsoids are displayed at the 50% probability level. Selected bond lengths (Å) and angles ($^\circ$): P1–C1 1.609(3), P2–C1 1.660(2), K1–C1 3.857(4), N1–P1 1.729(2), S1–P2 2.0192(8), S1–K1 3.1573(12), P1–C1–P2 139.59(16).

Species	P1–C1 P2–C1 [Å]	P–S [Å]	P1–N [Å]	P1–C _{ph} [Å]	P–C–P [$^\circ$]
Y-H	1.694(2) 1.723(2)	1.997(1)	1.659(2)	1.812(2) 1.803(2)	125.4(1)
(YLi·THF)₂	1.638(1) 1.668(1)	2.034(1)	1.696(1)	1.825(2) 1.822(2)	135.0(1)
[Y₂Li][−]	1.639(2) 1.657(2)	2.014(7)	1.725(2)	1.802(2) 1.790(8)	136.0(1)
(Y-K)₆	1.626(2) 1.658(2), 1.610(5)	2.034(1)	1.707(2)	1.827(3) 1.826(3) 1.845(3)	136.6(2)
KY	1.661(4)	2.019(1)	1.733(4)	1.830(3)	139.5(3)

electrostatic attractions, due to one lithium cation being shared by two ylide ligands.

In addition to the structures of the lithium complexes, we were also able to obtain two structures of the potassium ylide: the solvent-free aggregate $(\text{Y-K})_6$ and the 18-crown-6-coordinated monomer $[\text{Y-K}(18\text{-C-6})]$. $(\text{Y-K})_6$ crystallizes as an C_2 -symmetric aggregate of six ylide units. The central core is comprised of two face-linked distorted K_6S_4 cubes, with the corners of the cubes alternately occupied by sulfur and potassium atoms. Each potassium atom features an additional contact with the central carbon atom of the ylide. Furthermore, the potassium ions on the corners of the $(\text{KS})_6$ core additionally interact with one aryl group of the thiophosphoryl group, thus resulting in a strongly distorted trigonal bipyramidal coordination sphere. The C–K distances range from 2.872(3) to 2.990(2) Å, which is relatively short compared to literature distances from comparable compounds, suggestive of a relatively strong bond.^[18]

In contrast to the lithium ylide $(\text{Y-Li} \cdot \text{THF})_2$, addition of stoichiometric amounts of 18-crown-6 (18-C-6) to $(\text{Y-K})_6$ allowed the formation of a monomeric structure (Figure 5). The potassium center is coordinated to both the sulfur atom and the central ylidic carbon atom, with its coordination sphere completed by crown ether oxygen atoms. It is worth noting

that the interaction between potassium and the central carbon atom is the weakest of all the ylide structures studied here, with a distance of 3.857(4) Å compared to the sum of the van der Waals radii of 4.45 Å.^[19] This presumably leads to a higher charge concentration at C1 and the shortest P1–C1 bond (1.609(3) Å) within the whole series of metallated ylides (Table 2).

A comparison of the structural features of the lithium and potassium ylides with the ylide and phosphonium salt precursor (Table 2) reveals that – as expected – the ylides exhibit shorter P–C distances than **Y-H** and particularly **Y-H₂** due to increased electrostatic attractions within the P–C–P linkage. At the same time, the bonds between the phosphorus atoms and their substituents (P–N, P–S and P–C_{ph}) elongate because of negative hyperconjugation effects. Interestingly, this elongation is more pronounced for the P–N bond than for the P–C_{ph} bond in the phosphonium group, suggesting that the amino group – although not coordinating to the metal – significantly contributes to the stability of the ylide by electronic stabilization of the charge at the ylidic carbon atom. Furthermore, the P–C–P bond angle increases in both the lithium and the potassium ylides when compared to the parent **Y-H** and **Y-H₂** compound, which implies an increasing s-character in the phosphorus-carbon bond. The larger angles are found for the potassium compounds, which is well in line with the increasing $^2J_{\text{pp}}$ coupling constant when descending the group (Figure 3).

To gain insight into the bonding situation and charge distribution in the metallated ylides, natural bond orbital analysis (NBO)^[20] studies of the dimeric THF complex of **Y-Li** and monomeric **Y-K** with crown ether compared with the ylide precursor **Y-H** were performed. The calculations reflect a moderate increase of electron density at the central carbon atom C1 upon metallation, with an increase of the negative charge from $q_{\text{C}} = -1.367$ e in **Y-H** to $q_{\text{C}} = -1.624$ e and -1.553 e in the lithium and potassium ylide, respectively. A further increase of electron density is observed for the sulfur atom ($\Delta q_{\text{S}} \approx -0.15$ e), whereas the changes in charges at all other atoms are only small ($\Delta q < 0.1$). The increase of negative charge at the sulfur atom is also accompanied by a higher occupation of the antibonding $\sigma^*(\text{P2-S})$ orbital, which is in line with substantial negative hyperconjugation effects, also expressed by a weakening of the P–S bond, that is, a reduced Wiberg bond index (WBI). This supports the strong anion-stabilizing ability of the thiophosphinoyl moiety, which decisively contributes to the overall stability of the ylide. Although the WBI of the P1–N and P1–C_{ph} bonds in the ylides barely change compared with those of **Y-H**, the negative hyperconjugation into the phosphonium group becomes evident from the changes in the occupancy of the corresponding σ^* orbitals.^[21] As can be seen from Table 3, the change in the occupancy is more pronounced for the P–N bond compared with the P–C_{ph} bond, suggesting that the piperidine moiety accepts more electron density and hence contributes to the stability of the ylide. This is well in line with the crystallographic data (see above). It is also noteworthy that the overall changes are more pronounced for the potassium compound than for the lithium

Table 3. Results of the NBO analyses of Y-H, (YLi·THF)₂ and [Y-K(18-C-6)] at the PW6B95-D3/defTZVP level of theory.^[23]

	Y-H	(YLi·THF) ₂	[Y-K(18-C-6)]
WBI (P2=S)	1.306	1.044	1.122
WBI (P1-C _{Ph}) ^[a]	0.865	0.914	0.813
q(C1)	-1.367	-1.624	-1.553
q(S)	-0.650	-0.796	-0.793
q(N)	-0.874	-0.869	-0.876
occ σ*(P2-S)	0.030	0.085 (Δ = 0.055) ^[b]	0.116 (Δ = 0.086) ^[b]
occ σ*(P1-N1)	0.145	0.186 (Δ = 0.042) ^[b]	0.206 (Δ = 0.061) ^[b]
occ σ*(P1-C _{Ph}) ^[a]	0.101	0.129 (Δ = 0.028) ^[b]	0.144 (Δ = 0.043) ^[b]

[a] average values; [b] change in occupation relative to Y-H.

compound which corroborates the more covalent character of organolithium compounds.^[22]

In conclusion, we successfully isolated and characterized a series of stable thiophosphinoyl- and amino-substituted metallated ylides. The lithium and potassium salts formed different structures in the solid state (monomer, dimer and hexamer), including a monomeric potassium crown ether complex. The structures reflect the increasing electrostatic attractions within the P–C–P linkage upon metallation, expressed by the shortening of the P–C bonds. Negative hyperconjugation effects mirrored by the lengthening of the bonds to the β-substituents contribute to the stability of the compound and demonstrate the strong anion-stabilizing ability of the P=S moiety. Interestingly, the lengthening of the bonds in the phosphonium group was more pronounced for the P–N than the P–C_{Ph} bond, demonstrating its importance for stabilizing the metallated ylide by negative hyperconjugation. This stabilizing effect was also confirmed by NBO analyses, showing a considerable increase in the occupancy of the σ*(P–N) orbital. Current studies are focusing on the application of the metallated ylides Y–M in main group chemistry.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: alkali metals · lithium · potassium · structure elucidation · ylide ligands

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