Synthesis, Isolation and Crystal Structures of the Metalated Ylides [Cy₃P-C-SO₂Tol]M (M = Li, Na, K)

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Dedicated to Manfred Scheer on Occasion of his 65th Birthday

Abstract. The preparation and isolation of the metalated ylides [Cy₃P-C-SO₂Tol]M (Cy₁-M) (with M = Li, Na, K) are reported. In contrast to its triphenylphosphonium analogue the synthesis of Cy₁-M revealed to be less straightforward. Synthetic routes to the phosphonium salt precursor Cy₁-H₂ via different methods revealed to be unsuccessful or low-yielding. However, nucleophilic attack of the ylide Cy₃P=CH₂ at toluenesulfonyl fluoride under basic conditions proved to be a high-yielding method directly leading to the ylide Cy₁-H. Metalation to the ylides was finally achieved with strong bases such as nBuLi, NaNH₂, or BnK. In the solid state, the lithium compound forms a tetrameric structure consisting of a (C–S–O–Li)₄ macrocycle, which incorporates an additional molecule of lithium iodide. The potassium compound forms a C₄-symmetric structure with a (K₄O₄)₂ octahedral prism as central structural motif. Upon deprotonation the P–C–S linkage undergoes a remarkable contraction typical for metalated ylides.

Introduction

Since the first synthesis of an ylide more than one century ago and the pioneering work by Wittig, Staudinger and others,[1] ylides have become an important class of reagents. They are nowadays routinely used in organic synthesis in a variety of transformations, as well as in catalysis, e.g. as group transfer reagents, or as ligands in coordination chemistry.[2] Besides simple ylides, also their metalated congeners, the so-called yldiides, have early been discussed and applied in synthesis.[3,4] For example, Corey reported on an enhanced reactivity of yldiides in Wittig reactions with hindered ketones,[5] while Bestmann demonstrated their potential in a number of cascade reactions, such as for the syntheses of alkynes and carbacycles.[6] Despite these early reports in the 1980s, their isolation was for a long time limited to very few examples.[6a] This is mostly due to the high reactivity of metalated ylides, which is strongly connected with the high charge concentration at the ylidic carbon atom.[6]

Until today, only five metalated ylides have been isolated and also structurally characterized (Figure 1),[7] whereat only 1-M[8] and 2-M[9] (with M = Li, Na, K) have been prepared in gram-scale and applied in synthesis. For example, our group demonstrated that 1-M and 2-M are excellent reagents for ylide-functionalizations,[10] which represents a powerful tool for the electronic manipulation of main group compounds.[11,12] As such, electron-deficient species like borenium ions and tetrylenes were successfully isolated starting from 1-Na.[13] Likewise, a series of ylide-substituted phosphines were prepared which turned out to be excellent ligands for homogeneous catalysis.[14]

Figure 1. Isolated and structurally characterized metalated ylides.

During our studies on the use of 1-M in main group chemistry we observed the C–H activation at one of the phenyl groups of the phosphonium moiety as side-reaction leading to the protonation and subsequently to the cleavage of an ylide ligand from the main group metal.[13a] In order to further exploit the use of metalated ylides for the stabilization of reactive compounds we thus became interested in replacing the PPh₃ moiety by a tricyclohexyl phosphonium moiety which should less tend to undergo any CH activation processes and hence lead...
to more stable products. Here, we report on the preparation of $^{Cy}_{1}$-M, the cyclohexyl derivative of 1-M. Despite this rather small change in the molecular structure the synthesis of $^{Cy}_{1}$-M turned out to be surprisingly more difficult than expected.

Results and Discussion

For the preparation of $^{Cy}_{1}$-M, we at first addressed a synthetic route analogous to that reported for the PPh$_3$ system.$^{[8]}$ Thus, tricyclohexylphosphine and (iodomethyl)tolylsulfone were reacted at different temperatures to access the phosphonium salt $^{Cy}_{1}$-H$_2$ in the first reaction step (Route A, Scheme 1). However, in contrast to the phenyl compound no selective formation of $^{Cy}_{1}$-H$_2$ was observed due to several competing side-reactions such as reduction of the sulfonyl group, oxidation of PCy$_3$ and deprotonation by the more basic PCy$_3$. This reaction was observed under different reaction conditions (in C$_6$D$_6$ or without solvent; at 60 °C or room temperature). Likewise, reaction of the halo phosphonium salts [Cy$_3$PX]X (with X = Br, I) with lithiated methyl(tolyl)sulfone proved to be unsuccessful (Route C). No product formation was observed by NMR spectroscopy. In contrast, treatment of the (iodomethyl)phosphonium salt with sodium sulfinate (Route B) delivered the desired phosphonium salt $^{Cy}_{1}$-H$_2$, albeit only in small quantities together with a series of by-products. Due to the low nucleophilicity of the sulfinate the halo reaction conditions in refluxing DMF or DMSO were necessary to observe detectable amounts of $^{Cy}_{1}$-H$_2$. Albeit $^{Cy}_{1}$-H$_2$ could be isolated in pure form by this method and spectroscopically as well as structurally characterized (see below), it was impossible to further improve the reaction to reliably yield sufficient amounts of $^{Cy}_{1}$-H$_2$ for further synthesis.

In order to obtain high quantities of the ylide precursor for its metalation we turned our attention towards a further synthetic pathway, the nucleophilic attack of the methylphosphonate, Cy$_3$PCH$_2$, on a suitable sulfonyl electrophile (Scheme 2). To this end, tricyclohexylphosphonium methylide, Cy$_3$PCH$_2$, was in situ formed from [Cy$_3$PMe]I and sodium hexamethyldisilazide (NaHMDS) and subsequently treated with tosyl fluoride. Sulfonyl fluorides have proven to be excellent electrophiles for the formation of C–S bonds.$^{[15,17]}$ NMR spectroscopic studies of the reaction mixture revealed the direct formation of ylide $^{Cy}_{1}$-H under the reaction conditions since ylide Cy$_3$P=CH$_2$ simultaneously acts as reagent as well as base and deprotonates the initially formed phosphonium salt $^{Cy}_{1}$-H$_2$ thus yielding $^{Cy}_{1}$-H and [Cy$_3$PMe]F. Therefore, under optimized conditions Cy$_3$PCH$_2$ was treated with one equiv. of tosyl fluoride in the presence of a further equiv. NaHMDS to prevent the reformation of [Cy$_3$PMe]F. Thus, $^{Cy}_{1}$-H could be obtained in only one reaction step as colorless solid in excellent yields of 90%. $^{Cy}_{1}$-H was characterized by NMR and IR spectroscopy as well as XRD and elemental analysis. The ylide exhibits a singlet at δ$_P$ = 26.8 ppm in the $^{31}$P{1H} NMR spectrum and a doublet at δ$_H$ = 1.86 ppm with a coupling constant of $^{2}$J$_{PC}$ = 8.4 Hz in the $^{1}$H NMR spectrum. The $^{13}$C{1H} NMR signal of the ylidal carbon appears at δ = 26.1 ppm with a large $^{1}$J$_{PC}$ coupling constant of 105 Hz (cf. 44.5 ppm; $^{1}$J$_{CP}$ = 31.3 Hz in $^{Cy}_{1}$-H$_2$), which is in line with the increased s-character in the P–C bond of $^{Cy}_{1}$-H compared to the phosphonium salt precursor $^{Cy}_{1}$-H$_2$. This is also reflected in the larger P–C–S angle in the molecular structure (Figure 2, Table 1) of $^{Cy}_{1}$-H$_2$ (127.63(19)°) compared to that observed in $^{Cy}_{1}$-H$_2$ [117.85(9)°].

With ylide $^{Cy}_{1}$-H in hand, we next attempted its metalation to $^{Cy}_{1}$-M. At first, alkali metal HMDS bases were tested which were successfully applied to access the PPh$_3$ analogue 1-M. However, no reaction was observed with $^{Cy}_{1}$-H even after a prolonged reaction time. This suggests, that the more electron-rich PCy$_3$ unit significantly lowers the CH acidity of the ylide. Accordingly, stronger metal bases were tested. Indeed, monitoring of the metatation reaction by $^{31}$P{1H} NMR spectroscopy revealed the successful formation of the different alkali metal ylidides $^{Cy}_{1}$-M, when using n-butyllithium, benzyl potassium (BnK), and sodium amide, respectively (Scheme 3). The formation of the alkali metal ylidides is evidenced by a distinct high-field shift of the signal in the $^{31}$P{1H} NMR spectrum compared to the ylide precursor $^{Cy}_{1}$-H (Table 1). For example, addition of BnK or NaNH$_2$ gave rise to a broad singlet at 3.2 ppm and 6.1 ppm, respectively (cf. 26.7 ppm for $^{Cy}_{1}$-H). Albeit all reactions were highly selective as judged by NMR
Table 1. Important NMR spectroscopic and crystallographic properties of $\text{Cy}_1\text{-H}_2$, $\text{Cy}_1\text{-H}$, and its metalated congeners $\text{Cy}_1\text{-Li}$ and $\text{Cy}_1\text{-K}$.

|            | $\text{Cy}_1\text{-H}_2$ | $\text{Cy}_1\text{-H}$ | $\text{[Cy}_1\text{-Li}]_4\text{LiI}$ | $\text{[Cy}_1\text{-K}]_8$ |
|------------|---------------------------|-------------------------|--------------------------------------|---------------------------|
| $\text{P-C1} / \ang$ | 1.8279(17)                | 1.718(3)                | 1.676(2)                             | 1.669(6)                  |
| $\text{S-C1} / \ang$ | 1.7846(17)                | 1.662(3)                | 1.602(2)                             | 1.591(6)                  |
| $\text{S-O1} / \ang$ | 1.4423(13)                | 1.450(3)                | 1.490(18)                            | 1.494(4)                  |
| $\text{S-O2} / \ang$ | 1.4381(13)                | 1.451(3)                | 1.495(16)                            | 1.471(4)                  |
| $\text{P-Cc}^a / \ang$ | 1.8237(12)                | 1.836(8)                | 1.855(16)                            | 1.850(6)                  |
| $\text{M-C1} / \ang$ | —                         | —                       | 2.159(5)                             | 2.906(6)                  |
| $\text{P-C1-S}^\circ$ | 117.85(9)                 | 127.63(19)              | 127.48(15)                           | 127.20(4)                 |
| $\delta = \text{^31P} / \text{ppm}$ | 35.4                      | 26.8                    | 10.1                                 | 3.1                       |

$^a$ Average values.

studies, isolation turned out to be most facile for the lithium and the potassium compound. Reaction of a suspension of $\text{Cy}_1\text{-H}$ in $n$-pentane with one equiv. $n$-BuLi yielded the highly soluble $\text{Cy}_1\text{-Li}$, which can easily be purified by filtration from the insoluble starting materials and thus could be isolated as yellow solid in 90% yield. $\text{Cy}_1\text{-Li}$ was characterized by multinuclear NMR spectroscopy, elemental and XRD analysis. The $^7\text{Li}$ NMR signal appears as broad singlet at 0.6 ppm, the $\text{^31P}$ NMR signal at $\delta = 10.1$ ppm and is thus the most downfield shifted signal in the whole series of the alkali metal yldiides $\text{Cy}_1\text{-M}$. The potassium compound $\text{Cy}_1\text{-K}$ could also be isolated as pure solid in excellent yields of up to 98%.

Scheme 3. Metalation of $\text{Cy}_1\text{-H}$ with alkali metal bases to $\text{Cy}_1\text{-M}$ ($M = \text{Li, Na, K}$) (* = NMR yield).

Single crystals of $\text{Cy}_1\text{-Li}$ were grown by slow vapor diffusion of $n$-pentane into a saturated THF solution of the yldiide at –30 °C and analyzed by XRD techniques. The yldiide crystallizes in the tetragonal space group $P4_2/n$ (Figure 3) as a $S_4$ symmetric tetramer with an additional molecule of lithium iodide (present from the synthesis of $\text{Cy}_1\text{-H}$ via route B).

The monomeric subunit (asymmetric unit) consists of one yldiide, in which the lithium ion is coordinated by the ylidic carbon atom, one oxygen of the sulfonyl group and a THF molecule. Aggregation of the monomers to the tetramer is realized through the coordination of the second oxygen atom of the sulfonyl moiety, which bridges the lithium ions of monomeric subunits. Thus, a highly symmetric ($C$–$S$–$O$–$Li$)$_4$ macrocycle is formed (Figure 4), whose outer sphere is fully covered by the coordinating THF molecules and phosphonium groups. This structure is most probably responsible for the high solubility of the compound also in hydrocarbon solvents, since the polar moieties of the complex are well covered in the inner core of the structure. In this context it is interesting to note that the macrocycle itself adopts not a planar but a bowl-like geometry. The additional lithium ion Li2 is complexed in the center of the resulting pocket and lies on the $S_4$ axis of the molecule.

Figure 3. Molecular structure of $\text{[Cy}_1\text{-Li}]_4\text{LiI}+\text{THF}$. (Top) Top view, (bottom) side view; the counter-anion is not shown. Ellipsoids at the 50% probability level. Selected bond lengths /Å and angles $\beta$: Li1–C1 2.159(5) Å; Li1–O2 2.022(5); Li1–O1 1.875(5); Li2–O2 1.9354(15); S1–C1–P1 127.48(15); S1–C1–Li1 86.07(15); P1–C1–Li1 146.41(18). Further structure parameters are provided in Table 1, crystallographic details are given in the Supporting Information.
In the molecular structure of Cy1-Li, the ylidic carbon atom C1 adopts a planar arrangement with an ideal sum of angles of 360.0(2)°. The C1–Li1 distance amounts to 2.159(5) Å and is thus in the typical range for organolithium aggregates.[17] A comparison of the important bond lengths and angles in Cy1-Li in comparison to its protonated precursors is given in Table 1. As already observed for yldiide 1-K, the central P–C–S linkage undergoes a remarkably contraction upon each deprotonation step due to increased electrostatic attractions with increasing charge at the central carbon atom. The S–C and P–C bonds thus shorten from 1.785(2) and 1.828(1) Å in Cy1–H2 to 1.602(2) and 1.676(2) Å in Cy1-Li. Likewise, the S–O and P–CCy bonds lengthen slightly because of negative hyperconjugation effects. Furthermore, the P–C–S angle widens from 117.9(1)° in the phosphonium salt to 127.6(2)° in the yldiide indicating an increase of s-character upon deprotonation, which is retained after the second deprotonation.

Overall, the changes in the bond lengths and angles in Cy1-Li relative to its protonated precursors is similar to the trends observed for the PPh3-substituted compounds.[8] However, it is interesting to note that in comparison to the PPh3-substituted compounds, the S–C bonds in the PCy3-substituted compounds are shorter by approx. 20–30 pm. This can be explained by the lower ability of the PCy3 compared to the PPh3 group to stabilize the negative charge at the ylidic carbon atom by electrostatic and negative hyperconjugation effects. Therefore, the electrostatic attraction in the C–S linkage increases and hence the bond shortens.

Besides the structure of the lithium yldiide we also attempted the elucidation of structure of the potassium and sodium compound. While no crystals of sufficient quality could be obtained for Cy1-Na, single-crystals of Cy1-K could be obtained by storage of a saturated THF solution at –30 °C. Cy1-K crystallizes as C4-symmetric octamer in the tetragonal space group P4/n with two additional THF molecules on the C4 axis (only one orientation shown in Figure 5).[18] Unfortunately, the quality of the crystals was rather low due to highly disordered solvent molecules (see ESI). However, the trends in the bond lengths are similar to those observed for the lithium compound discussed above (Table 1).

The central structural motif of Cy1-K consists of an octagonal prism formed by the potassium and oxygen atoms of the
sulfonyl group with K–O distances between 2.672(4) and 2.767(5) Å (Figure 6). The O–K–O angles amount to approx. 83.4(1)° within each K$_2$O$_2$ face and to approx. 133° between the faces. Each potassium atom is coordinated by the ylidic carbon atom, four oxygens of the sulfonyl groups as well as by the two loosely bound THF molecules on top and below the octahedral prism and weak C–H interactions with the cyclohexyl moieties (not shown in Figure 4). The P–C and S–C bonds are shortened compared to the ylide and the phosphonium salt and in the range of those found in the lithium compound Cy$_1$-Li.

Conclusions

In conclusion, we have successfully developed a synthetic protocol for the high-yielding isolation of the tricyclohexylphosphonium-substituted metalated ylides [Cy$_3$PCSO$_2$Tol][M (Cy$_1$-M) (with M = Li, Na, K). The synthesis was accomplished by reaction of tricyclohexylphosphonium methyldide with tosyl fluoride under basic conditions thus directly forming the ylide precursor Cy$_1$-H, which was subsequently deprotonated with strong metal bases. This deprotonation was found to be considerably less facile than in case of the PPh$_3$ analogue thus demonstrating the pronounced acidifying properties of a PPh$_3$ moiety compared to the PCy$_3$ unit. The molecular structures of the lithium and potassium ylide could be elucidated by XRD analysis. In the solid state, Cy$_1$-Li forms a $S_4$-symmetric tetrameric structure with one additional lithium iodide molecule, while Cy$_1$-K exhibits a $C_4$ symmetric structure with an octahedral prism as central structural motif. In the structures, the central P–C and S–C bonds are shortened compared to the ylide precursor due to electrostatic interactions. Current studies are focusing on the application of the ylide in main group chemistry.

Experimental Section

Experimental Details: Details regarding the synthesis of Cy$_1$-H$_2$ via route A, B and C are given in the Supporting Information.

General Methods: All experiments were carried out in a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Involved solvents were dried using an MBraun SPS-800 (THF, Toluene, Et$_2$O, DCM, n-Pentane, n-Hexane) or dried in accordance with standard procedures. $^1$H, $^{13}$C($^1$H), $^{31}$P($^1$H), $^7$Li NMR spectra were recorded on Avance-500 or Avance-400 spectrometers at 25 °C if not stated otherwise. All values of the chemical shift are in ppm regarding the δ-scale. All spin-spin coupling constants (J) are printed in Hertz (Hz).

Synthesis of [Cy$_3$P-Me]I: Tricyclohexylphosphine (16.00 g, 57.05 mmol, 1.00 equiv.) was dissolved in toluene (200 mL). Methyl iodide (3.83 g, 61.05 mmol, 1.07 equiv.) was added dropwise to the solution at room temp. During the addition, a white solid precipitated out of the solution. The reaction mixture was stirred at room temperature until full precipitation was achieved (2 h). Next, the suspension was filtered and washed with Et$_2$O (3 × 10 mL). The solid was dried in vacuo (1 × 10$^{-3}$ mbar) for 4 h, giving [Cy$_3$P-Me]I as a white, amorphous powder (98%, 23.50 g). $^1$H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 2.5 (m, 3 H, PCy-CH$_3$), 2.0–1.9 (m, 11 H, PCy-CH$_2$), 1.9 (d, J = 12.1 Hz, 3 H, CH$_3$), 1.8–1.8 (m, 3 H, PCy$_3$–CH$_2$), 1.6–1.2 (m, 16 H, PCy$_3$–CH). $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 161.9 MHz): δ = 33.7 (s) ppm. The obtained signals are in accordance with literature values.[19]

Synthesis of Cy$_1$-H: [Cy$_3$P-Me]I (10.00 g, 23.68 mmol, 1.00 equiv.) and NaHMDS (8.77 g, 47.82 mmol, 2.02 equiv.) were placed in a 500 mL Schlenk flask. THF (150 mL) was added, giving a white suspension which was stirred for 30 min at room temp. In a second Schlenk flask, p-toluene sulfonyl fluoride (4.12 g, 23.68 mmol, 1.00 equiv.) was dissolved in THF (25 mL) and this solution was slowly added to the suspension via cannula, upon which a color change from white to a deep brown occurred. The reaction mixture was stirred overnight, and the solvent was removed in vacuo. The residue was taken up in a dichloromethane/toluene mixture (50 mL/250 mL) and the resulting suspension was subsequently filtered over celite to obtain a clear yellow solution. Removal of the solvent under reduced pressure yielded an off-white solid, which was washed with n-hexane (5 × 25 mL). After drying in vacuo (1 × 10$^{-3}$ mbar) for 4 h at 70 °C, the pure product was obtained as a white solid (90%, 9.80 g). $^1$H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 7.69 (d, $^1$J$_{HH}$ = 7.9 Hz, 2 H, o-CH), 7.18 (d, $^1$J$_{HH}$ = 7.9 Hz, 2 H, m-CH), 2.36 (s, 3 H, 2.27–2.09 (m, 9 H, PCy$_3$-CH), 1.86 (d, $^2$J$_{HH}$ = 8.4 Hz, 1 H, PCH$_2$), 1.85–1.75 (m, 11 H, PCy$_3$-CH$_2$), 1.73–1.65 (m, 3 H, 3 H, PCy-CH$_3$), 1.47–1.32 (m, 6 H, PCy-CH$_3$), 1.31–1.06 (m, 10 H, PCy-CH$_3$). $^{13}$CP($^1$H) NMR (CD$_2$Cl$_2$, 100.6 MHz): δ = 149.7 (ips-o-C), 140.2 (p-C), 129.5 (m-C), 125.5 (o-CH), 33.1 (d, $^2$J$_{CP}$ = 50.8 Hz, PCy$_3$-CH$_3$), 27.8 (d, $^2$J$_{CP}$ = 31.1 Hz, PCy$_3$-CH$_2$), 27.6 (d, $^2$J$_{CP}$ = 12.3 Hz, PCy$_3$-CH), 26.5 (d, $^2$J$_{CP}$ = 1.6 Hz, PCy$_3$-CH$_3$), 26.1 (d, $^2$J$_{HH}$ = 105 Hz, PCy$_3$-CH$_2$), 21.6 (d, p-C, 7.7 Hz, 2 H, m-CH). $^{31}$P($^1$H) NMR (CD$_2$Cl$_2$, 161.9 MHz): δ = 26.8 (s) ppm. EA: calcd: C: 69.61, H: 9.21, S: 7.15%, found 69.26, H: 9.04, S: 7.38%.

Synthesis of Cy$_1$-Li: Cy$_1$-H (3.63 g, 8.09 mmol, 1.0 equiv.) was suspended in n-pentane (100 mL). BuLi (1.53 M in hexanes, 5.29 mL, 1.0 equiv.) was added dropwise to the suspension at 0 °C. The reaction mixture was warmed to room temp. and stirred for 1 h. The suspension was filtered via cannula furnishing a yellow solution. Removal of the solvent under reduced pressure and drying in vacuo (1 × 10$^{-3}$ mbar) for 4 h at 40 °C afforded Cy$_1$-Li as a yellow powder (90%, 3.33 g). $^1$H NMR (D$_2$)$_2$TFH, 400 MHz): δ = 7.85 (d, $^2$J$_{HH}$ = 7.7 Hz, 2 H, m-CH), 6.96 (d, $^2$J$_{HH}$ = 7.7 Hz, 2 H, o-CH), 2.28 (s, 3 H, p-Tol-CH$_3$),
1.95–1.84 (m, 10 H, PCy-CH2), 1.70–1.65 (m, 6 H, PCy-CH2),
1.61–1.57 (m, 3 H, PCy-CH2), 1.43–1.38 (m, 4 H, PCy-CH2),
1.20–1.10 (m, 10 H, PCy-CH2). \(^{31}\)C\(^{[\text{H}]}\) NMR (\(\text{D}_2\text{THF}\), 100.6 MHz): \(\delta = 155.5 \text{ (ipso-C), 137.1} \text{ (p-C) 128.4 (m-CH), 126.9} \text{ (o-CH), 36.9} \text{ (d, J = 52.8 Hz, PCy-CH)}, \)
28.7 (PCy-CH2), 28.6 (d, J = 8.4 Hz, PCy-CH2), 27.5
(PCM-CH2), 21.4 (p-Tol-CH3). The signal for the PCS bridge could
not be observed. \(^{31}\)P\(^{[\text{H}]}\) NMR (\(\text{D}_2\text{THF};162 MHz): \(\delta = 10.1 \) (s) ppm. \(^{7}\)Li NMR
(\(\text{[D}_8\text{THF,162 MHz}) : \(\delta = 0.6 \) (s) ppm. EA: calcd.: C: 68.70, H: 8.87, S: 7.05 %; found: C: 68.73, H: 8.84, S: 7.03 %.

Supportive Information (see footnote on the first page of this article):
Synthesis, Isolation and Crystal Structure of the Metalated Ylide
\(\text{[Cy}_3\text{P-C-SO}_2\text{Tol]}\).

## Acknowledgements
This project has received funding from the European Research Council under the European Union’s Horizon 2020 research and innovation program (Starting grant no 677749). Open access funding enabled and organized by Projekt DEAL.

## Keywords
Alkali metals; Ylides; Carbanions; Structure elucidation; Phosphorus ligands

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Received: December 12, 2019
Published Online: May 26, 2020