

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 [Cy₃PCSO₂Tol]M (Cy₃I-M) (with M = Li, Na, K) are reported. In contrast to its triphenylphosphonium analogue the synthesis of Cy₃I-M revealed to be less straight forward. Synthetic routes to the phosphonium salt precursor Cy₃I-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 Cy₃I-H. Metalation to the

ylidides was finally achieved with strong bases such as *n*BuLi, 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 ylidides, have early been discussed and applied in synthesis.^[3,4] For example, Corey reported on an enhanced reactivity of ylidides 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 carbocycles.^[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.

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]

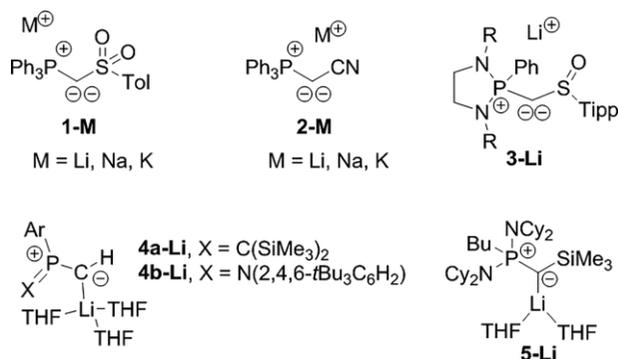


Figure 1. Isolated and structurally characterized metalated ylides.

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

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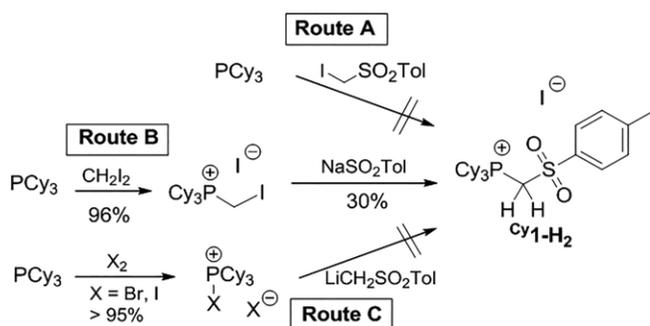
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to more stable products. Here, we report on the preparation of **Cy1-M**, the cyclohexyl derivative of **1-M**. Despite this rather small change in the molecular structure the synthesis of **Cy1-M** turned out to be surprisingly more difficult than expected.

Results and Discussion

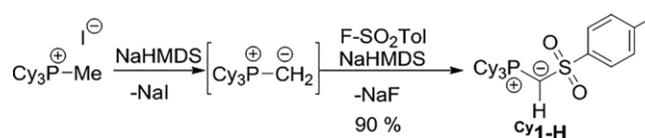
For the preparation of **Cy1-M**, we at first addressed a synthetic route analogous to that reported for the PPh_3 system.^[8] Thus, tricyclohexylphosphine and (iodomethyl)tolylsulfone were reacted at different temperatures to access the phosphonium salt **Cy1-H₂** in the first reaction step (Route A, Scheme 1). However, in contrast to the phenyl compound no selective formation of **Cy1-H₂** 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_6D_6 or without solvent; at 60 °C or room temperature). Likewise, reaction of the halo phosphonium salts $[\text{Cy}_3\text{PX}]\text{X}$ (with $\text{X} = \text{Br}, \text{I}$) with lithiated methyl(*p*-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 **Cy1-H₂**, albeit only in small quantities together with a series of by-products. Due to the low nucleophilicity of the sulfinate harsh reaction conditions in refluxing DMF or DMSO were necessary to observe detectable amounts of **Cy1-H₂**. Albeit **Cy1-H₂** 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 **Cy1-H₂** for further synthesis.



Scheme 1. Examined pathways for the synthesis of the tricyclohexyl-phosphonium salt **Cy1-H₂**.

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 methylenephosphorane, Cy_3PCH_2 , on a suitable sulfonyl electrophile (Scheme 2). To this end, tricyclohexylphosphonium methylide, Cy_3PCH_2 , was in situ formed from $[\text{Cy}_3\text{PMe}]\text{I}$ 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 di-

rect formation of ylide **Cy1-H** under the reaction conditions since ylide $\text{Cy}_3\text{P}=\text{CH}_2$ simultaneously acts as reagent as well as base and deprotonates the initially formed phosphonium salt **Cy1-H₂** thus yielding **Cy1-H** and $[\text{Cy}_3\text{PMe}]\text{F}$. Therefore, under optimized conditions Cy_3PCH_2 was treated with one equiv. of tosyl fluoride in the presence of a further equiv. NaHMDS to prevent the reformation of $[\text{Cy}_3\text{PMe}]\text{F}$. Thus, **Cy1-H** could be obtained in only one reaction step as colorless solid in excellent yields of 90%. **Cy1-H** was characterized by NMR and IR spectroscopy as well as XRD and elemental analysis. The ylide exhibits a singlet at $\delta_{\text{P}} = 26.8$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum and a doublet at $\delta_{\text{H}} = 1.86$ ppm with a coupling constant of $^2J_{\text{PC}} = 8.4$ Hz in the ^1H NMR spectrum. The $^{13}\text{C}\{^1\text{H}\}$ NMR signal of the ylidic carbon appears at $\delta = 26.1$ ppm with a large $^1J_{\text{PC}}$ coupling constant of 105 Hz (cf. 44.5 ppm; $^1J_{\text{CP}} = 31.3$ Hz in **Cy1-H₂**), which is in line with the increased *s*-character in the P–C bond of **Cy1-H** compared to the phosphonium salt precursor **Cy1-H₂**. This is also reflected in the larger P–C–S angle in the molecular structure (Figure 2, Table 1) of **Cy1-H** (127.63(19)°) compared to that observed in **Cy1-H₂** [117.85(9)°].



Scheme 2. Preparation of ylide **Cy1-H**.

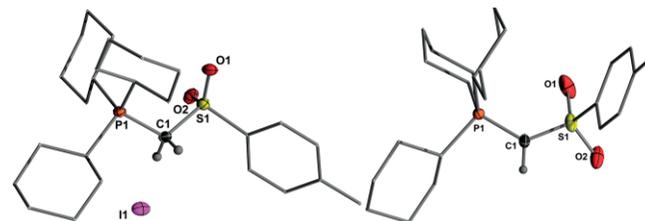


Figure 2. Molecular structures of phosphonium salt **Cy1-H₂** and ylide **Cy1-H**. Thermal ellipsoids at the 50% probability level. Selected bond lengths and angles are given in Table 1. Crystallographic details are given in the Supporting Information.

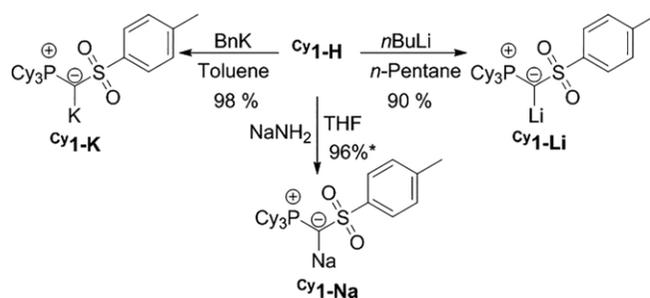
With ylide **Cy1-H** in hand, we next attempted its metalation to **Cy1-M**. At first, alkali metal HMDS bases were tested which were successfully applied to access the PPh_3 analogue **1-M**. However, no reaction was observed with **Cy1-H** even after a prolonged reaction time. This suggests, that the more electron-rich PCy_3 unit significantly lowers the CH acidity of the ylide. Accordingly, stronger metal bases were tested. Indeed, monitoring of the metalation reaction by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy revealed the successful formation of the different alkali metal ylides **Cy1-M**, when using *n*-butyllithium, benzyl potassium (BnK), and sodium amide, respectively (Scheme 3). The formation of the alkali metal ylides is evidenced by a distinct high-field shift of the signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum compared to the ylide precursor **Cy1-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 **Cy1-H**). Albeit all reactions were highly selective as judged by NMR

Table 1. Important NMR spectroscopic and crystallographic properties of **Cy1-H₂**, **Cy1-H**, and its metalated congeners **Cy1-Li** and **Cy1-K**.

	Cy1-H₂	Cy1-H	[Cy1-Li]₄-LiI	[Cy1-K]₈
P–C1 /Å	1.8279(17)	1.718(3)	1.676(2)	1.669(6)
S–C1 /Å	1.7846(17)	1.662(3)	1.602(2)	1.591(6)
S–O1 /Å	1.4423(13)	1.450(3)	1.4800(18)	1.494(4)
S–O2 /Å	1.4381(13)	1.451(3)	1.4953(16)	1.471(4)
P–C _{Cy} ^{a)} /Å	1.8237(12)	1.836(8)	1.855(16)	1.850(6)
M–C1 /Å	–	–	2.159(5)	2.906(6)
P–C1–S /°	117.85(9)	127.63(19)	127.48(15)	127.20(4)
δ = ³¹ P /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 **Cy1-H** in *n*-pentane with one equiv. *n*BuLi yielded the highly soluble **Cy1-Li**, which can easily be purified by filtration from the insoluble starting materials and thus could be isolated as yellow solid in 90% yield. **Cy1-Li** was characterized by multinuclear NMR spectroscopy, elemental and XRD analysis. The ⁷Li NMR signal appears as broad singlet at 0.6 ppm, the ³¹P NMR signal at δ = 10.1 ppm and is thus the most downfield shifted signal in the whole series of the alkali metal ylidiides **Cy1-M**. The potassium compound **Cy1-K** could also be isolated as pure solid in excellent yields of up to 98%.



Scheme 3. Metalation of **Cy1-H** with alkali metal bases to **Cy1-M** (M = Li, Na, K) (* = NMR yield).

Single crystals of **Cy1-Li** were grown by slow vapor diffusion of *n*-pentane into a saturated THF solution of the ylide to form a tetramer with an additional molecule of lithium iodide (present from the synthesis of **Cy1-H** via route B).^[16] The monomeric subunit (asymmetric unit) consists of one ylide, 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 S₄ axis of the molecule.

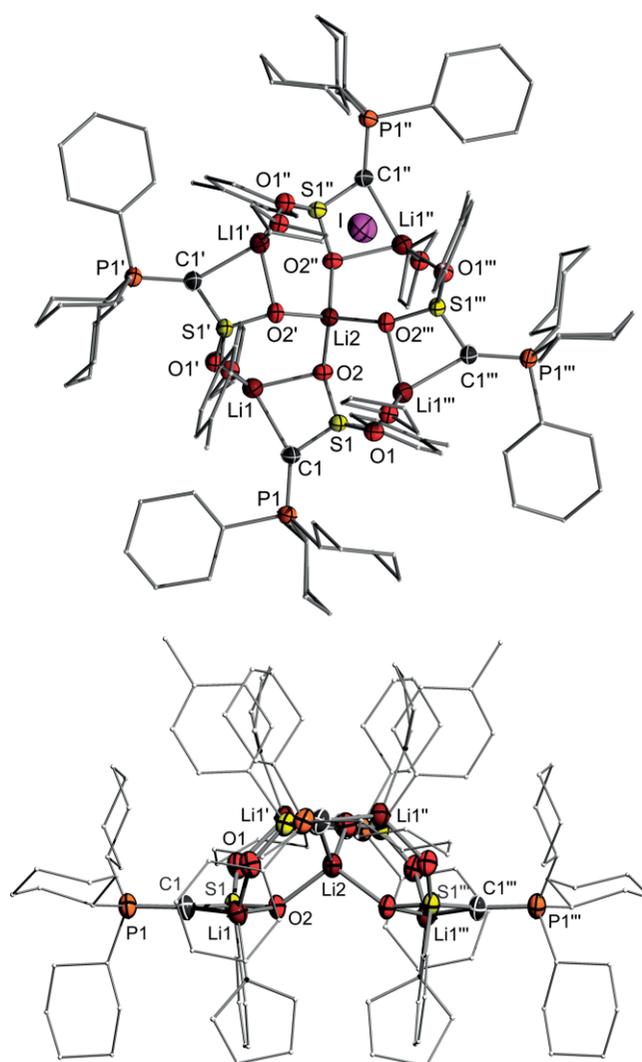


Figure 3. Molecular structure of (**Cy1-Li**)₄-LiI·4THF. (Top) Top view, (bottom) side view; the counter-anion is not shown. Ellipsoids at the 50% probability level. Selected bond lengths /Å and angles /°: Li1–C1 2.159(5) Å; Li1–O2 2.022(5), Li1–O1' 1.875(5), Li2–O2 1.9354(15), S1–C1–P1 127.48(15), S1–C1–Li1 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.

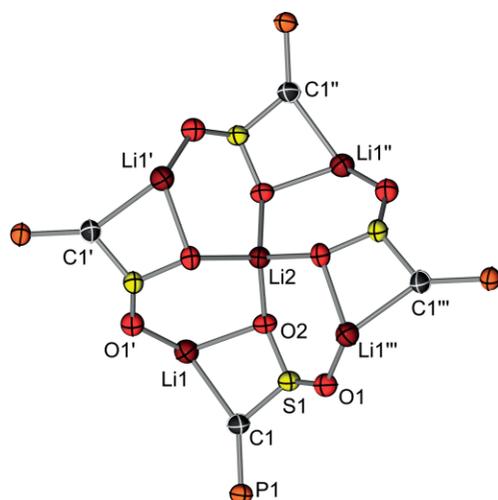


Figure 4. Drawing of the inner core of the structure of Cy1-Li .

In the molecular structure of Cy1-Li , the ylidic carbon atom C1 adopts a planar arrangement with an ideal sum of angles of $360.0(2)^\circ$. The C1–Li1 distance amounts to $2.159(5) \text{ \AA}$ 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 ylide **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 $1.828(1) \text{ \AA}$ in Cy1-H_2 to $1.602(2)$ and $1.676(2) \text{ \AA}$ in Cy1-Li . Likewise, the S–O and P–C_{Cy} bonds lengthen slightly because of negative hyperconjugation effects. Furthermore, the P–C–S angle widens from $117.9(1)^\circ$ in the phosphonium salt to $127.6(2)^\circ$ in the ylide 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 PPh_3 -substituted compounds.^[8] However, it is interesting to note that in comparison to the PPh_3 -substituted compounds, the S–C bonds in the PCy_3 -substituted compounds are shorter by approx. 20–30 pm. This can be explained by the lower ability of the PCy_3 compared to the PPh_3 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 ylide 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 C_4 -symmetric octamer in the tetragonal space group $P4/n$ with two additional THF molecules on the

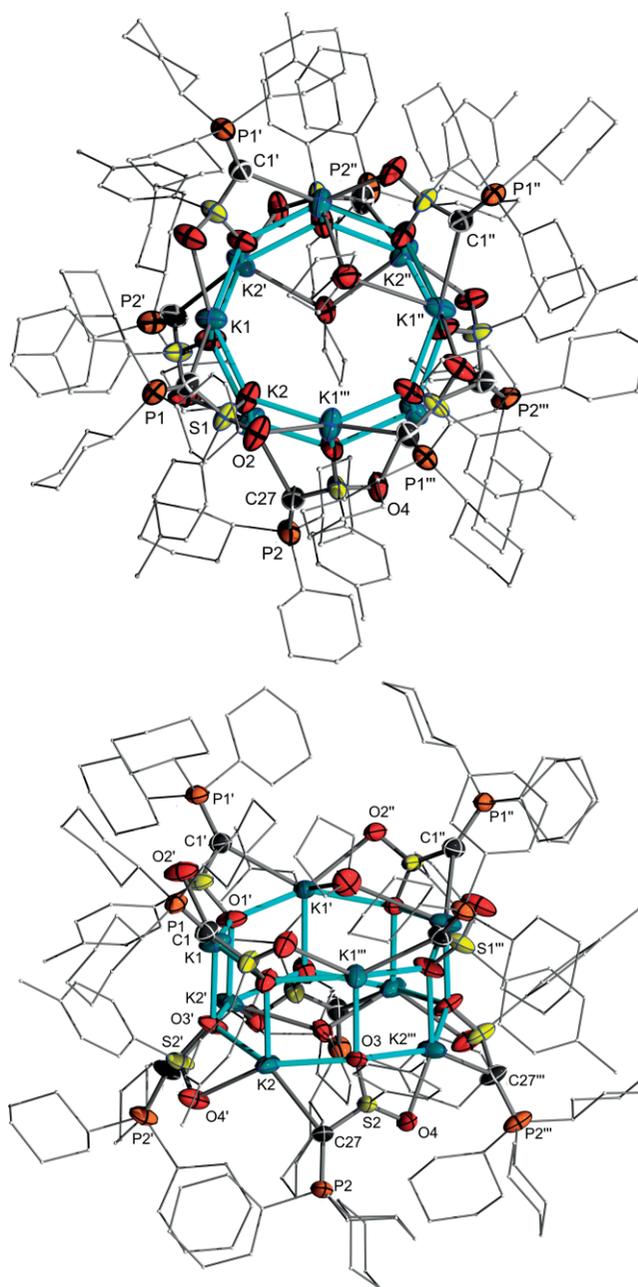


Figure 5. Molecular structure of $[(\text{Cy1-K})_8 \cdot 2\text{THF}]$. (Top) side view, (bottom) top view. Ellipsoids at the 50% probability level. Non-coordinating THF solvent molecules as well as disordered moieties are omitted for clarity. Selected bond lengths / \AA and angles / $^\circ$: K1–C1 $2.906(6)$, K2–C27 $2.906(6)$, K1–O3 $2.672(4)$, K1–O1 $2.709(4)$, K1–O1' $2.764(4)$, K1–O2' $2.767(5)$. Further structure parameters are provided in Table 1, crystallographic details are given in the Supporting Information.

C_4 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 K₂O₂ 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 **Cy1-Li**.

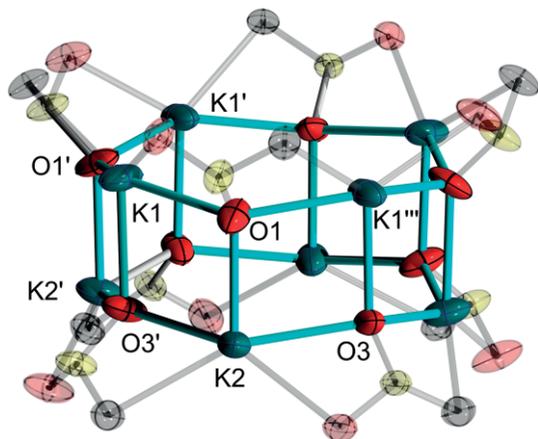


Figure 6. Drawing of the inner core of the structure of **Cy1-K**.

Conclusions

In conclusion, we have successfully developed a synthetic protocol for the high-yielding isolation of the tricyclohexylphosphonium-substituted metalated ylides [Cy₃PCSO₂Tol]M (**Cy1-M**) (with M = Li, Na, K). The synthesis was accomplished by reaction of tricyclohexylphosphonium methylene with tosyl fluoride under basic conditions thus directly forming the ylide precursor **Cy1-H**, which was subsequently deprotonated with strong metal bases. This deprotonation was found to be considerably less facile than in case of the PPh₃ analogue thus demonstrating the pronounced acidifying properties of a PPh₃ moiety compared to the PCy₃ unit. The molecular structures of the lithium and potassium ylide could be elucidated by XRD analysis. In the solid state, **Cy1-Li** forms a S₄-symmetric tetrameric structure with one additional lithium iodide molecule, while **Cy1-K** exhibits a C₄ 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 **Cy1-H₂** 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, Et₂O, DCM, *n*-Pentane, *n*-Hexane) or dried in accordance with standard procedures. ¹H, ¹³C{¹H}, ³¹P{¹H}, ⁷Li 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). To display multiplicities and signal forms correctly the following abbreviations were used: s = singlet, d = doublet, m = multiplet, br = broad signal. Signal assignment was supported by DEPT, APT, HSQC and HMBC experiments. Elemental analyses were performed on an Elementar vario MICRO-cube elemental analyzer.

Synthesis of [Cy₃P-Me]I: Tricyclohexylphosphine (16.00 g, 57.05 mmol, 1.00 equiv.) was dissolved in toluene (200 mL). Methyl iodide (3.8 mL, 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 Et₂O (3 × 10 mL). The solid was dried in vacuo (1 × 10⁻³ mbar) for 4 h, giving [Cy₃P-Me]I as a white, amorphous powder (98 %, 23.50 g). ¹H NMR (CD₂Cl₂, 400 MHz): δ = 2.5 (m, 3 H, PCy-CH), 2.0–1.9 (m, 11 H, PCy-CH₂), 1.9 (d, *J* = 12.1 Hz, 3 H, CH₃), 1.8–1.8 (m, 3 H, PCy-CH₂), 1.6–1.2 (m, 16 H, PCy-CH₂) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 161.9 MHz): δ = 33.7 (s) ppm. The obtained signals are in accordance with literature values.^[19]

Synthesis of Cy1-H: [Cy₃P-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*-toluenesulfonyl 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). ¹H NMR (CD₂Cl₂, 400 MHz): δ = 7.69 (d, ²*J*_{HH} = 8.2 Hz, 2 H, *o*-CH), 7.18 (d, ²*J*_{HH} = 7.9 Hz, 2 H, *m*-CH), 2.36 (s, 3 H), 2.27–2.09 (m, 3 H, PCy₃-CH), 1.86 (d, ²*J*_{PH} = 8.4 Hz, 1 H, PCHS), 1.85–1.75 (m, 11 H, PCy₃-CH₂), 1.73–1.65 (m, 3 H, PCy₃-CH₂), 1.47–1.32 (m, 6 H, PCy₃-CH₂), 1.31–1.06 (m, 10 H, PCy₃-CH₂). ¹³C{¹H} NMR (CD₂Cl₂, 100.6 MHz): δ = 149.7 (*ipso*-C), 140.2 (*p*-C), 129.5 (*m*-CH), 125.5 (*o*-CH), 33.1 (d, ²*J*_{CP} = 50.8 Hz, PCy₃-CH), 27.8 (d, ³*J*_{CP} = 3.1 Hz, PCy₃-CH₂), 27.6 (d, ²*J*_{CP} = 12.3 Hz, PCy₃-CH₂), 26.5 (d, ⁴*J*_{CP} = 1.6 Hz, PCy₃-CH₂), 26.1 (d, ²*J*_{PH} = 105 Hz, PCS), 21.6 (*p*-Tol-CH₃). ³¹P{¹H} NMR (CD₂Cl₂, 161.9 MHz): δ = 26.8 (s) ppm. EA: calcd: C: 69.61, H: 9.21, S: 7.15 %, found C 69.26, H: 9.04, S: 7.38 %.

Synthesis of Cy1-Li: **Cy1-H** (3.63 g, 8.09 mmol, 1.0 equiv.) was suspended in *n*-pentane (100 mL). *n*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 **Cy1-Li** as a yellow powder (90 %, 3.33 g). ¹H NMR ([D₈]THF, 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-CH₃),

1.95–1.84 (m, 10 H, PCy-CH+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). ¹³C{¹H} NMR ([D₈]THF, 100.6 MHz): δ = 155.5 (*ipso*-C), 137.1 (*p*-C) 128.4 (*m*-CH), 126.9 (*o*-CH), 36.9 (d, *J* = 52.8; PCy₃-CH), 28.7 (PCy₃-CH₂), 28.6 (d, *J* = 8.4, PCy₃-CH₂), 27.5 (PCy₃-CH₂), 21.4 (*p*-Tol-CH₃). The signal for the PCS bridge could not be observed. ³¹P{¹H} NMR ([D₈]THF, 162 MHz): δ = 10.1 (s) ppm. ⁷Li NMR ([D₈]THF, 155.6 MHz): δ = 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%

Synthesis of ^{Cy}1-K: Benzyl potassium (0.32 g, 2.45 mmol, 1.1 equiv.) and ^{Cy}1-H (1.00 g, 2.22 mmol, 1.0 equiv.) were placed into a Schlenk tube and toluene (25 mL) was added. The red reaction mixture was stirred for 5 min at room temp. and was subsequently filtered via a filter cannula. A dark yellow solution was obtained. The solvent was removed under reduced pressure and the residue was dried in vacuo (1 × 10⁻³ mbar) for 3 h at 40 °C to yield ^{Cy}Y₅-K as a dark yellow powder (98 %, 532 mg). Single crystals of ^{Cy}1-K were grown by storage of a saturated THF solution at -30 °C. ¹H NMR ([D₈]THF, 400 MHz): δ = 7.79 (br., 2 H, *m*-CH), 6.91 (br., 2 H, *o*-CH), 2.28 (s, 3 H, *p*-Tol-CH₃), 1.87–1.75 (m, 8 H, PCy-CH+CH₂), 1.71–1.66 (m, 6 H, PCy-CH₂), 1.61–1.57 (m, 3 H, PCy-CH₂), 1.42–1.31 (m, 6 H, PCy-CH₂), 1.17–1.02 (m, 10 H, PCy-CH₂). ¹³C{¹H} NMR ([D₈]THF, 100.6 MHz): δ = 157.3 (*ipso*-C), 136.2 (*p*-C) 128.6 (*m*-CH), 126.3 (*o*-CH), 37.4 (d, *J* = 52.5 Hz; PCy₃-CH), 28.9 (PCy₃-CH₂), 28.8 (PCy₃-CH₂), 27.7 (PCy₃-CH₂), 21.5 (*p*-Tol-CH₃). The signal for PCS bridge could not be observed. ³¹P{¹H} NMR ([D₈]THF, 162 MHz): δ = 3.2 (s, br) ppm. EA: calcd.: C: 64.16, H: 8.28, S: 6.59%; found: C: 64.50, H: 8.30, S: 6.88%

Synthesis of ^{Cy}1-Na: Sodium amide (5 mg, 128 μmol, 1.01 equiv.) and ^{Cy}1-H (57 mg, 127 μmol, 1.0 equiv.) were placed into a J. Young NMR tube and [D₈]THF (0.5 mL) was added. The tube was shaken on an IKA® ROCKER 3D digital at room temp. overnight. ³¹P-NMR spectroscopy revealed full conversion of ^{Cy}1-H and the formation of ^{Cy}1-Na (ca. 96%). Attempts to purify ^{Cy}1-Na resulted in the instant protonation of the ylidic carbon atom. ¹H NMR ([D₈]THF, 400 MHz): δ = 7.80 (br., 2 H, *m*-CH), 6.90 (br., 2 H, *o*-CH), 2.27 (s, 3 H, *p*-Tol-CH₃), 1.86–1.78 (m, 8 H, PCy-CH+CH₂), 1.71–1.64 (m, 6 H, PCy-CH₂), 1.61–1.56 (m, 3 H, PCy-CH₂), 1.43–1.34 (m, 6 H, PCy-CH₂), 1.18–1.04 (m, 10 H, PCy-CH₂) ppm. ³¹P{¹H} NMR ([D₈]THF, 162 MHz): δ = 6.1 (s, br) ppm.

Single-crystal X-ray Diffraction Analyses: Data collection of all compounds was conducted with Rigaku XtaLAB Synergy (^{Cy}1-H, ^{Cy}1-H, ^{Cy}1-Li-LiI, ^{Cy}1-K). The structures were solved by direct methods, refined with the Shelx software package and expanded using Fourier techniques. The crystals of all compounds were mounted in inert oil (perfluoropolyalkylether). Crystal structure determinations were affected at 100 K. The structures were solved by direct methods, refined using full-matrix least-squares techniques on *F*² with the Shelx software package^[20] and expanded using Fourier techniques. Data collection parameters are given in Tables S1 and S2 (Supporting Information).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1971569, CCDC-1971570, CCDC-1971571, and CCDC-1971572. (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Supporting Information (see footnote on the first page of this article): Synthesis, Isolation and Crystal Structure of the Metalated Ylide [Cy₃P-C-SO₂Tol]M.

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