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Tetrahedral versus Planar Four-Coordinate Carbon: A Sulfonyl-Substituted Methandiide

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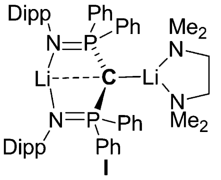
The electronic structure of compounds with main-group elements in unusual oxidation states or coordination environments has inspired research during recent decades. Differences between the second-row elements and their heavier congeners have been illustrated with many examples, such as the intensively studied differences between alkenes and alkynes compared with their heavier *trans*-bent analogues.[1] Although the chemistry of carbon belongs to the oldest and most studied fields in chemistry, new bonding modes and concepts are still being established. Some recent examples are the introduction of quadruple bonding in diatomic C_2[2] or divalent carbon(0) in carbodiphosphoranes (carbones).[3] This research is often driven by the unique reactivity of these compounds, which is based on the unusual electronic structure. As such, bond activation reactions, a research field long limited to transition-metal complexes, has started to evolve.[4]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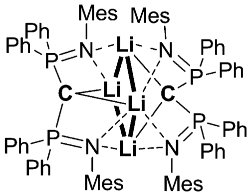
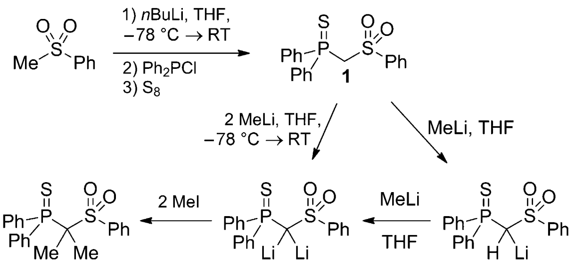

II

One of the long indisputable concepts in the chemistry of carbon compounds is that of the tetrahedral arrangement of four-coordinate carbon, as manifested in van't Hoff's proposal.[5] However, this rule has been challenged, firstly, by computation by Schleyer and co-workers predicting the stabilization of planar tetracoordinate carbon by electropositive substituents.[6] Finally, this prediction was verified experimentally in 2010 by Liddle and co-workers, who succeeded in the isolation of a compound with such a planar four-coordinate carbon in the bis(phosphonium)-stabilized methandiide **I**.[7,8] However, no other known methandiide, such as **II**, although limited in number, has been shown to feature this planar carbon conformation.[9,10,11] This provokes the question, of whether planarization is solely the result of geometric restrictions caused by the coordinating side arms or whether it results from an unknown bonding motif of carbon. To address this question, we set out to prepare new dilithio methandiides. Due to their extremely limited accessibility, investigations have so far concentrated on, but are not limited to, the readily available bis(phosphonium)-substituted compounds.[12] To clarify the influence of the Li coordination by intramolecular donor functions, further substituents at the dimetallated carbon have to be examined.[13] Herein, we describe the synthesis and structure of a sulfonyl-substituted geminal dianion and discuss its electronic structure with respect to the planarization of the four-coordinate carbon atom.

The starting α-thiophosphinoyl-substituted sulfone **1** was synthesized from methyl phenyl sulfone by a sequence of lithiation followed by trapping with Ph_2PCl and oxidation with elemental sulfur (Scheme 1). Due to competing formation of the disubstituted compound, **1** could only be obtained in moderate yields of up to 49 % as a colorless crystalline solid. To evaluate the deprotonation behavior of **1**, lithiation was first accomplished with one equivalent of methyllithium in THF solution. Storage at 0 °C gave crystals of the lithium salt **1-Li** in 81 % yield. Compounds **1** and **1-Li** were characterized by multinuclear NMR spectroscopy, single-crystal X-ray diffraction analysis (see the Supporting Information), and elemental analysis.



Scheme 1. Synthesis and lithiation of α-thiophosphinoyl-substituted sulfone **1**.

The molecular structure of **1-Li** is illustrated in Figure 1. The asymmetric unit contains half a molecule, which is assembled to the dimer through inversion. The lithium atom is neither coordinated to the methanide carbon nor to the

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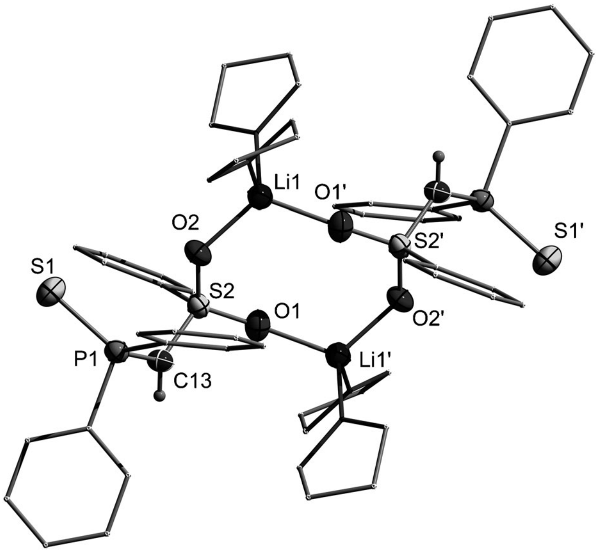

Figure 1. Molecular structure of **1-Li**. Hydrogen atoms (except for the methanide hydrogen) are omitted for clarity. Thermal ellipsoids are at 50 % probability.

thiophosphinoyl moiety.[10c] Completion of the Li coordination sphere is solely achieved by the coordination of the two sulfone oxygen atoms and two additional THF molecules. The central structural motif is an $(O\text{-}S\text{-}O\text{-}Li)_2$ eight-membered ring featuring a chair-like conformation. Compared with the neutral compound **1**, the most remarkable change in the structural parameters concerns the P-C-S backbone. The C–P and the C–S (1.740(3) and 1.651(2) Å, respectively) bond lengths are significantly shorter than those for **1** (1.839(4) and 1.801(4) Å). The carbon atom possesses a planar arrangement (sum of angles = 359.6(2)) with a widening of the P-C-S bond angle from 113.8(2) to 124.6(2)°.[14] The latter indicates a considerable change in the electronic structure and an increased s-character in the bonds to the methanide carbon (see below).

The $^{31}P\{^1H\}$ and the ^7Li NMR spectra exhibited singlets at $\delta = 32.6$ and 0.0 ppm, respectively, indicating no interaction between the methanide carbon and lithium in solution. The methanide signals appear as doublets at $\delta = 2.73$ ppm ($^2J_{HP} = 12.1$ Hz) in the ^1H NMR and at $\delta = 44.0$ ppm in the $^{13}C\{^1H\}$ NMR spectrum, with a large coupling constant of $^1J_{CP} = 109.8$ Hz compared with the **1** (59.7, $^1J_{CP} = 41.6$ Hz). This is in line with the increased bond angle around carbon and the assumed increased s-character. The ^1H and ^{13}C NMR signals were shifted upfield compared with those of **1**. It is noteworthy that **1-Li** features exclusively sharp signals indicating a rigid structure in solution or fast exchange processes. DFT calculations of dimeric **1-Li** and possible monomeric structures showed only small energetic differences, so that both species are possible in particular in coordinating solvents.[15,16]

With the monoanion **1-Li** in hand, a second deprotonation was attempted. For this purpose, compound **1** was treated with two equivalents of MeLi at room temperature. After 4 h, the $^{31}P\{^1H\}$ NMR spectrum in C_6D_6 showed the complete consumption of **1** and the formation of a single species at $\delta = 26.4$ ppm. Trapping of the reaction mixture with iodomethane gave the dimethylated compound **2** nearly quantitatively (Scheme 1 and the Supporting Information). After work-up, **2** could be isolated in 88 % yield.[17] For isolation of the intermediate dilithio species, a THF solution of sulfone **1** was treated with two equivalents MeLi at −30 °C. Storage at room temperature gave the dilithiated species as a crystalline solid in 73 % isolated yield.

X-ray diffraction analysis confirmed the double lithiation and revealed an unusual dimeric structure (Figure 2 a and the Supporting Information). The asymmetric unit contains half a molecule, which is assembled to the dimer through inversion. The structure consists of four methandiides and six coordinating THF molecules. In contrast to many oligomeric

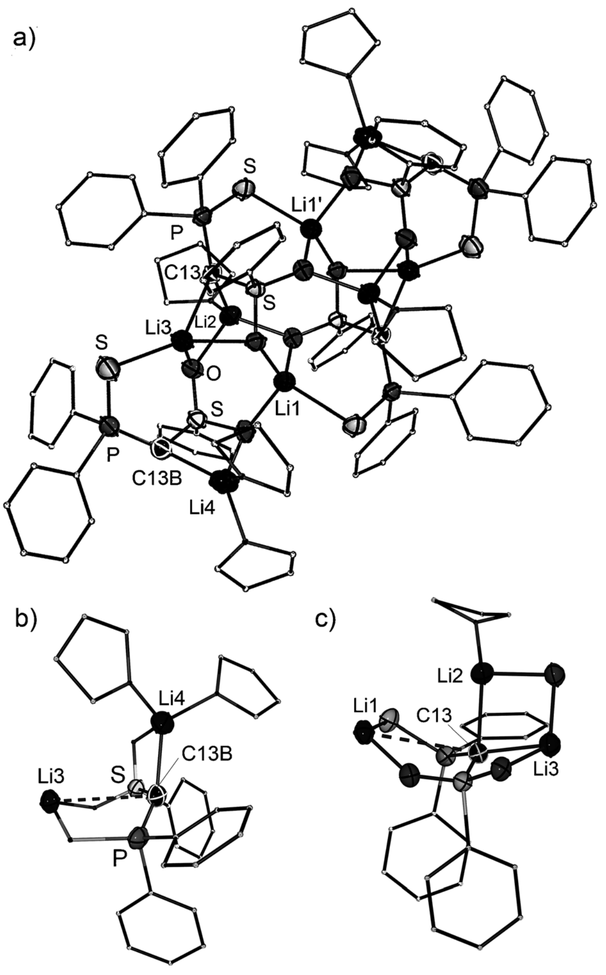

Figure 2. a) Molecular structure of **1-Li₂**. Hydrogen atoms and noncoordinating THF molecules in the unit cell are omitted for clarity. Thermal ellipsoids are at 50 % probability. Selected bond lengths [Å] and angles [°]: C1–P1 1.831(3), C7–P1 1.836(2), C13–S2 1.620(3), C13–P1 1.720(3), C13–Li3 2.138(7), C13–Li2 2.332(7), C14–S2 1.801(4), P1–S1 2.008(2), O1–S2 1.498(2), O2–S2 1.500(2), C1B–P1B 1.833(4), C7B–P1B 1.837(4), C13B–S2B 1.605(4), C13B–P1B 1.700(4), C13B–Li4 2.202(8), C13B–Li3 3.227(7), C14B–S2B 1.804(4), P1B–S1B 2.028(2), O1B–S2B 1.505(3), O2B–S2B 1.501(3); S2-C13-P1 120.9(2), S2B-C13B-P1B 121.9(2), Li3-C13-Li2 74.1(2), Li3-C13B-Li4 97.8(2). b), c) Coordination environments of the methandiide carbon atoms.

organolithium compounds and previously reported dialkali metal methandiides, no regular Li polyhedron is formed, rather a peculiar structure, in which the Li atoms form four-, six-, or eight-membered rings with the donor atoms, which are connected with each other by one common side.[11,18] In contrast to **1-Li**, the Li atoms in **1-Li$_2$** show contacts to the methandiide carbon atom and the thiophosphinoyl moiety. In comparison with the neutral compound **1** and anion **1-Li**, the double deprotonation resulted in a further contraction of the P-C-S backbone. In comparison to **1**, the C–P bond lengths are shortened by 7 % (**1**: 1.839(4) Å; **1-Li$_2$**: 1.700(4) and 1.720(3) Å) and the C–S bond lengths by 10 % (**1**: 1.801(4) Å; **1-Li$_2$**: 1.620(3) and 1.605(3) Å). The P–S and S–O bond lengths exhibited a lengthening of 4 %. These bond length changes continue the tendencies observed for **1-Li** (Table 1).

Table 1. Comparison of the structural parameters (average values for **1-Li$_2$** and the P–C$_{Ph}$ bond lengths) and NMR data ([D$_8$]THF (**1** and **1-Li**), [D$_8$]toluene (**1-Li$_2$**)) for the P-C-S moiety in **1**, **1-Li**, and **1-Li$_2$**.

	1	**1-Li**	**1-Li$_2$**
C–S [Å]	1.801(4)	1.651(2)	1.613(3)
C–P [Å]	1.839(4)	1.740(3)	1.710(3)
P–S [Å]	1.949(1)	1.982(1)	2.018(2)
S–O [Å]	1.439(3)	1.459(2)	1.501(2)
S–C$_{Ph}$ [Å]	1.771(4)	1.792(3)	1.803(4)
P–C$_{Ph}$ [Å]	1.844(4)	1.835(2)	1.834(3)
P-C-S [°]	113.8(2)	124.6(2)	121.4(2)
δ_H, $^2J_{HP}$ [ppm, Hz]	4.80, 10.5	2.73, 12.1	–
δ_C, $^1J_{CP}$ [ppm, Hz]	58.4, 44.1	44.0, 109.8	50.6 (br)

Concerning the question of planarization, the coordination sphere of the two different methandiide carbon atoms has to be discussed in more detail. Both coordination spheres strongly deviate from the ideal tetrahedral environment. Atom C13B (Figure 2 b) exhibits a strangely distorted fourfold coordination with an approximately planar C-P-S-Li4 unit (least square plane, deviation: 0.17 Å). Atom Li3 coordinates almost perpendicularly to this plane with an torsion angle (Li4-C-P-Li3) of 97.6(2)°. The coordination sphere around C13 (Figure 2 c) contains a third Li atom and is best described by a plane consisting of Li3-C13-P-S-Li1, on top of which Li2 is coordinated. This bonding motif of C13 resembles that of the planar four-coordinate carbon atom in **I**. Neglecting the contact to Li2, C13 exhibits a quasi-planar arrangement with a short contact to Li3 (2.138(7) Å) and rather long contact to Li1 (3.309(6) Å). Nevertheless, no planar four-coordinate carbon as in compound **I** was detected in **1-Li$_2$**, but rather an intermediate coordination form.

Multinuclear NMR studies of **1-Li$_2$** at room temperature revealed broadened signals, especially in the ^{1}H and ^{7}Li NMR, in nonpolar (C$_6$D$_6$, [D$_8$]toluene) and coordinating solvents ([D$_8$]THF). Variable temperature studies from room temperature to −80 °C showed no significant change in the ^{31}P{^{1}H} NMR, but a clear splitting to two sharp singlets in the ^{7}Li NMR spectrum at around 0 °C (see the Supporting Information). Because the structure of **1-Li$_2$** has four different Li and two different phosphorous environments, these NMR data indicate either a breaking of the aggregate in solution to a monomeric species or further exchange processes, which could not be resolved by cooling to −80 °C. Due to these processes and ^{7}Li–^{13}C coupling, the ^{13}C{^{1}H} NMR signal of the methanide carbon ($\delta = 50.6$ ppm) is broad. This signal is downfield by $\Delta\delta = 14.6$ ppm compared with **1-Li**, which is in line with studies on related sulfonyl-substituted methandiides by Gais and co-workers.[12]

The observed changes in the bond lengths and angles together with the NMR data suggested a rehybridization by deprotonation of **1** to **1-Li** and **1-Li$_2$** from sp^3 to sp^2. To fully rationalize the electronic structure of dianion **1-Li$_2$** and to evaluate the differences between the planar and distorted tetrahedral coordination, DFT calculations were performed.[15] At first, a monomeric model system **A** was chosen, featuring the environment around C13B (Figure 2 a) with THF and the contacts to the second methandiide replaced by the coordination of dimethyl ether. The energy-optimized structure of model system **A** is in good agreement with the molecular structure (see the Supporting Information). The calculated atomic charges and the Wiberg bond indices (Figure 3 b) suggest a highly ionic resonance structure for methandiide **A** with a highly negatively charged carbon atom ($q_C = -1.51$). This suggests little π-type electron delocalization in the P-C-S backbone, and that two lone pairs are essentially localized on the central carbon atom. Thus, the contracted C–P and C–S bond lengths observed in the crystal structure result from electrostatic attractions in P$^+$-C^{2-}-S^{2+}.[19] It is noteworthy that the shortening of the C–P bond length is more pronounced in the bis(phosphonium) substituted dianions, such as **I** and **II**.[11] This is the result of stronger interactions of the lone pairs at carbon with the sulfonyl moiety compared with the thiophosphinoyl unit. This high anion-stabilizing ability of the

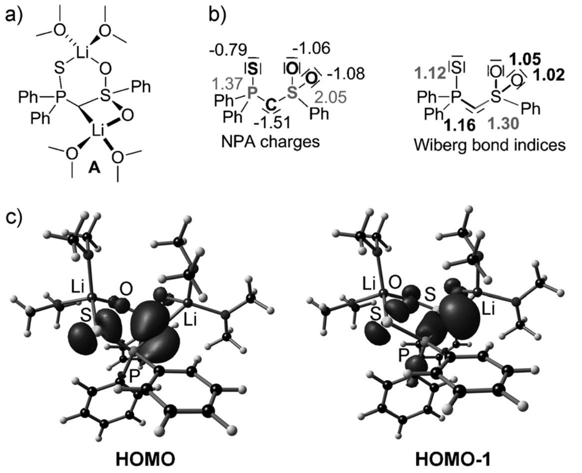

Figure 3. a) Model system **A**; b) natural atomic charges and Wiberg bond indices; c) orbital representations of the HOMO and HOMO-1 (isosurface contour value: 0.05 e Å^3).

sulfonyl unit was also confirmed by the lower charge concentration at the methanide carbon ($q_C = -1.51$) compared with the bis(thiophosphinoyl) system ($q_C = -1.77$)[11b] and by the viability of the dilithiation, which is reflected by a remarkably low reaction barrier of only 26.2 kJ mol^{-1}.

Concerning the planarization of the carbon atom, the orbital properties are of particular interest. The HOMO and HOMO-1 of **A** (Figure 3c) represent the two lone pairs at the methandiide carbon atom. The HOMO is essentially nonbonding, whereas the HOMO-1 points towards one of the lithium atoms. Natural bond orbital (NBO) analyses suggests an approximately sp^2 hybridized methanide carbon with two nonequivalent lone pairs differing in their energy and hybridization (LP(1)/HOMO-1: sp^2-hybrid orbital (sp$^{1.99}$); LP(2)/HOMO: p-orbital (sp$^{99.9}$)].[20,21] This orbital representation is close to that of the planar bis(phosphonium) system **I**. The energy-optimized structure of **I** also exhibits two different NBOs for the lone pairs, however, with a slightly higher p-character for LP(1) and thus a higher s-character in the C–P bonds (sp$^{1.45}$, sp$^{2.10}$ for **A**). This is in line with the observed broadened P-C-P angle (132.1°) compared with the P-C-S angle (121.4°) in **1-Li$_2$**. To evaluate if a higher p-character of the two lone pairs may also favor a planar arrangement in **1-Li$_2$**, variations of model system **A** were calculated: **A'** with a constrained planar Li-P-C-S-Li moiety and **A-131** and **A-135** with P-C-S bond angles fixed at 131 and 135°, respectively. Energy optimization revealed an energetic preference of the model system **A** by 21.6 kJ mol^{-1} over its planar analogue and most importantly a preference of a nonplanar arrangement in **A-131** and **A-135**. Interestingly, NBO analyses of these derivatives, including the planar system **A'**, showed no significant changes in the orbital interactions, so that in general all structures can be described by a sp^2-hybridized methanide carbon atom. However, this orbital setting has been used to explain the planar geometry at the methanide carbon in compound **I**. Next question is: how is this then in line with the structure of **1-Li$_2$**, especially given the nonplanar coordination and the strongly distorted arrangement around C13 (Figure 2c).

Overall, the calculations indicate two borderline cases for the bonding in methandiides shown in Figure 4: a) The four substituents are exclusively bound to the sp^2-hybrid orbitals through two 2e,2c bonds (C–X bonds) and one 2e,3c bond (Li-C-Li) giving way to a planar four-coordinate carbon atom (compound **I**). b) All substituents form 2e,2c bonds, whereas one of the lithium atoms is bound to the p-orbital at the carbon. This results in a strongly distorted tetrahedral arrangement with a small Li-C-Li angle (Li3-C13B-Li4 97.8(2)° in **1-Li$_2$**). Although the planar system **I** is described by bonding mode a), for the description of the structure of **1-Li$_2$** both bonding modes have to be applied. This can easily be seen from the environments of C13 and C13B in Figure 2 and was confirmed by NBO analysis of model system **B** for the environment around C13 (Figure 4b and the Supporting Information).

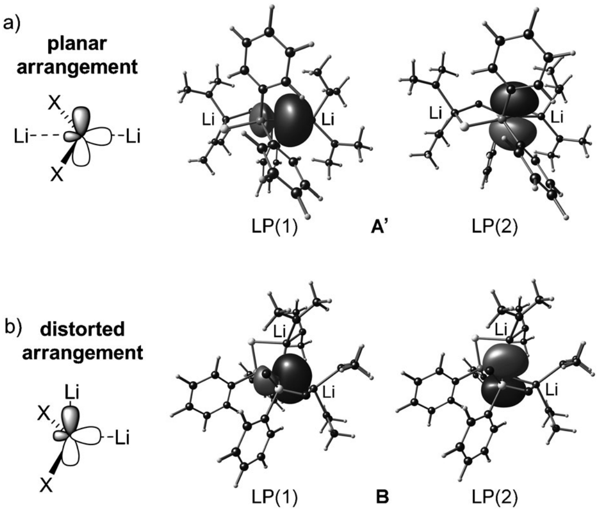

Figure 4. Bonding modes of two lithium atoms with a sp^2-hybridized carbon atom and NBOs of LP(1) and LP(2) in a) planar arrangement (**A'**) and b) distorted arrangement (**B**).

One always has to keep in mind that the interactions in dilithio methandiides are essentially electrostatic in nature (e.g., Wiberg bond indices for Li–O and Li–C: $n_{\text{Wiberg}} < 0.1$), which means that structure formation is dominated by the interaction of charges and less by the overlap of orbitals. This suggests that the isolation of further methandiides with a planar four-coordinate carbon should be possible by careful selection of the coordinating side arms and the reaction conditions (additives). It will be interesting to see, if these new bonding modes of carbon are maintained in complexes with transition metals with carbon–metal bonds of more covalent character, and if this influences the reactivity of these compounds.

In conclusion, the synthesis and characterization of mono- and dilithiated sulfonyl-substituted phosphine sulfide **1** was presented. Upon metalation, dramatic changes in bond lengths and angles of the methanide carbon were observed, which resulted from rehybridization and electrostatic interactions in the P-C-S backbone. The dilithio methandiide features a distorted carbon environment, which crucially differs from the tetrahedral arrangement. This geometry is caused mainly by geometrical restriction of the donor functions and can be described by two different bonding modes of the lithium atoms with the sp^2 hybridized carbon atom.

Acknowledgements

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Keywords: alkali metals · carbanions · lithium · planar four-coordinate carbon · structure elucidation

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[14] The methanide hydrogen has been found in the difference Fourier map and refined independently.

[15] All calculations were performed with the Gaussian 03 (Revision E.01) set of programs and the B3PW91 functional. The 6-31+G* basis set was used for hydrogen and lithium, 6–311+G** for all other atoms. NBO analyses were carried out on the optimized systems using the NBO 5.G program implemented in the Gaussian 03 package.

[16] Dimeric **1-Li** is enthalpically favoured by 44.8 $kJ\,mol^{-1}$, but entropically disvafoured ($\Delta G = 12.8\ kJ\,mol^{-1}$) compared with a monomeric derivative (see the Supporting Information).

[17] Although the dilithiation proceeds quantitatively, trapping with other, more sterically demanding electrophiles (e.g., Me_3SiCl and BnCl) resulted in the monosubstituted compound due to the high stability of the resulting monoanionic intermediate.

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[21] Both LPs are involved in negative hyperconjugation mainly into the antibonding $\sigma^*(P{-}S)$ and $\sigma^*(S{-}O)$ orbitals, but also into the $\sigma^*(P{-}C_{Ph})$ and $\sigma^*(S{-}C_{Ph})$, see the Supporting Information. These interactions resulted in significant stabilization and in the observed lengthening of the respective bonds.

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Alkali-Metal Complexes

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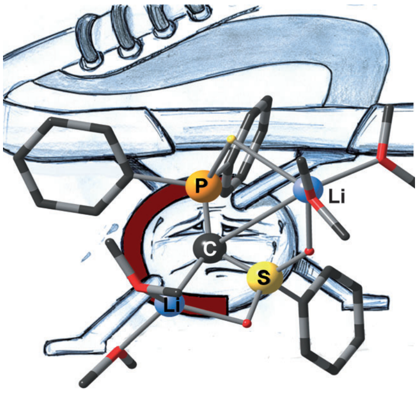
Tetrahedral versus Planar Four-Coordinate Carbon: A Sulfonyl-Substituted Methandiide



Flattened! The mono- and dilithiation of a sulfonyl-substituted phosphane sulfide is reported. The new dilithio methandiide features a distorted carbon environment between the typical tetrahedral and planar arrangement (see figure). This geometry results from geometrical restrictions of the donor functions and can be described by two unusual bonding modes of the lithium atoms with the sp^2-hybridized methanide carbon.