Lithium Phosphinomethanides: Two Novel Structures†

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The first η^1-C–metal-bonded lithium phosphinomethanide, (PMDETA)Li[HC(SiMe$_3$)PMe$_2$] (**6**), crystallizes from solutions of $H_2C(SiMe_3)PMe_2$ and ^nBuLi in hexane/PMDETA (PMDETA = MeN(CH$_2$CH$_2$NMe$_2$)$_2$) in the orthorhombic space group $Pna2_1$ with a = 19.862 (2) Å, b = 10.551 (1) Å, c = 10.400 (1) Å, and R_w = 0.035 for 223 refined parameters and 3234 unique observed reflections. The Li atom has a distorted tetrahedral coordination geometry by the three amine functions of PMDETA and by the phosphinomethanide carbon atom with Li–C = 2.207 (5) Å. No short Li–P contacts are observed in the crystal. In the first crystallographically examined coligand free lithium phosphinomethanide, {Li[C(SiMe$_3$)$_2$PMe$_2$]}$_2$ (**7**), the two-coordinate lithium cations exhibit a bent geometry (∠CLiP′ = 128.5 (2)°) within a six-membered ring in a chair conformation formed by head-to-tail dimerization. The coordination sphere of Li is completed by additional weak Li···H$_3$C–Si interactions, both intramolecular (Li···H = 2.44 (3) Å) and, even more prominent, intermolecular to a neighboring molecule (Li···C = 2.541 (4) Å; Li···H = 2.33 (3), 2.30 (3), and 2.46 (3) Å). The compound crystallizes from a mixture of HC(SiMe$_3$)$_2$PMe$_2$ and ^nBuLi in boiling hexane within several weeks (monoclinic space group $P2_1/c$ with a = 8.971 (1) Å, b = 12.588 (2) Å, c = 12.739 (2) Å, β = 104.61 (1)°, R$_w$ = 0.031 for 205 refined parameters and 1802 observed reflections).

Introduction

Phosphinomethanides (**1**), with directly connected isoelectronic phosphorus and carbon atoms, are among the most versatile ligands in organometallic chemistry. Both

$$[R_2P\text{-}CR'_2]^-$$

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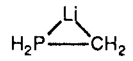
phosphorus and carbon donors may compete for a metal center, the coordination mode realized depending on the nature of the substituents and on the reaction conditions. Thus, numerous different coordination modes are possible and indeed have been observed. Moreover, variable oxidation states and coordination numbers of the metal centers are frequently encountered.[1,2]

The coordination of phosphinomethanides to lithium is especially interesting for the following reasons.

(i) Lithium is the first metal in the periodic table and thus may be regarded as the prototypal metal center. Calculations on the simplest lithium phosphinomethanide predict a monomeric three-membered ring structure (**2**) as the potential energy minimum.[3]



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(ii) The coordination mode of lithium to the bifunctional anion may serve as a probe for the actual charge distribution in a given phosphinomethanide.

(iii) Lithium phosphinomethanides are the most common and versatile reagents for the introduction of the phosphinomethanide ligand into metal complexes. Since their reactivity is strongly solvent dependent, as is their coordination to lithium, the investigation of aggregation and coordination of lithium phosphinomethanides may support the understanding of their reactivity patterns.

The role of the donor solvents (as coligands to lithium), and of the P and C substituents, on the lithium coordination has been amply demonstrated in a series of *di*phosphinomethanides.[4] Among the *mono*phosphinomethanide lithium complexes, a series of compounds with TMEDA (=Me$_2$NCH$_2$CH$_2$NMe$_2$) as the coligand to lithium and with an increasing number of Me$_3$Si substituents at the carbanionic C atom has been characterized structurally (compounds **3**–**5**). Particularly interesting in this respect are **4** and **5**, where by introduction of Me$_3$Si groups additional weak Li···P contacts (dotted lines) are observed.

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† Complexes with Phosphinomethane and Phosphinomethanide Ligands. 17. Part 16: Reference 4.

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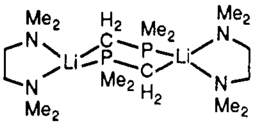

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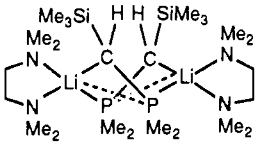

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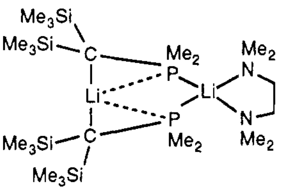

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Moreover, in **5** the Li coordination numbers of the two Li atoms are different and may be classified as 2 (ignoring the weak contacts) and 4. With the parent phosphinomethanides of **4** and **5**, i.e. $[HC(SiMe_3)PMe_2]^-$ and $[C(SiMe_3)_2PMe_2]^-$, it seemed worthwhile to study the influence of the coligand in more detail: on the one hand, a tridentate coligand ($MeN(CH_2CH_2NMe_2)_2$, PMDETA) instead of TMEDA should promote a monodentate coordination mode, while the complete absence of coligands, on the other hand, should promote a 2-fold coordination of lithium.

Experimental Section

A. Preparation and Characterization of Compounds. All compounds were handled under a dry argon atmosphere by employing vacuum line techniques. Solvents were dried with $LiAlH_4$, stored, and distilled immediately prior to their use. $MeN(CH_2CH_2NMe_2)_2$ (=PMDETA) was obtained from commercial sources, dried and distilled from potassium, and stored over molecular sieves. $H_2C(SiMe_3)PMe_2$ and $HC(SiMe_3)_2PMe_2$ were prepared as described elswhere.[5]

Synthesis of (PMDETA)Li[HC(SiMe$_3$)PMe$_2$] (6). A 15.08-mL (67-mmol) amount of PMDETA and 40.36 mL of butyllithium in hexane (1.66 M, 67 mmol) were added to 9.89 g (67 mmol) of $CH_2(SiMe_3)PMe_2$. Within 5 days, colorless crystals (17.88 g, 81.6%) formed, which are washed twice with 20 mL of hexane and dried by evaporation of the solvent. The highly air sensitive crystals were suitable for X-ray analysis but slowly decompose on storage at 5 °C (the color turns to brown). Anal. Calcd for $C_{15}H_{39}N_3LiSiP$ (mol wt 327.49): C, 55.01; H, 12.00. Found: C, 54.86; H, 12.29.

Synthesis of {Li[C(SiMe$_3$)$_2$PMe$_2$]}$_2$ (7). To 5 g of $HC(SiMe_3)_2PMe_2$ (22.68 mmol) was added butyllithium in hexane (13.66 mL, 1.66 M, 22.68 mmol), and the mixture was refluxed for 3 weeks. The colorless crystals that separated from the solution were washed twice with 20 mL of hexane and dried in vacuo. Anal. Calcd for $C_9H_{24}LiSi_2P$ (mol wt 226.38): C, 47.75; H, 10.68. Found: C, 47.21; H, 10.82.

B. X-ray Structure Determinations of (PMDETA)Li[HC(SiMe$_3$)PMe$_2$] (6) and {Li[C(SiMe$_3$)$_2$PMe$_2$]}$_2$ (7). Suitable single crystals of both compounds were sealed under argon at dry-ice temperatures into glass capillaries and examined directly on the diffractometer (Syntex P2$_1$, Mo Kα radiation, λ = 0.71069 Å, graphite monochromator). Crystal data and important numbers pertinent to data collection and structure refinement are collected in Table I. Data were corrected for Lp effects but not for those of absorption.

Both structures were solved by direct methods (SHELXS-86) and completed by subsequent Fourier syntheses. All hydrogen atoms were located in difference maps. Refinement was done with anisotropic displacement parameters for the non-H atoms. For **6**, H1 was refined isotropically, while the methyl groups were treated as rigid groups. All other H atoms were included at constant positions in structure factor calculations (U_{iso} = 0.05 Å^2). For **7**, all H atoms could be refined isotropically, except those at C13, which were treated as rigid groups. The correct polarity of the crystal structure of **6** was checked by refinement of the inverse coordinate set, which yielded significantly higher R values (Table I). Tables II and III contain the atomic coordinates and Tables IV and V important distances and angles. See the note at the end of the paper for supplementary material available.

Table I. Crystal Structure Data for 6 and 7

	6	7
cryst dimens, mm	0.4 × 0.4 × 0.55	0.3 × 0.35 × 0.5
formula	$C_{15}H_{39}LiN_3PSi$	$C_{18}H_{48}Li_2P_2Si_4$
M_r	327.497	452.753
cryst syst	orthorhombic	monoclinic
space group	$Pna2_1$ (No. 33)	$P2_1/c$ (No. 14)
a, Å	19.862 (2)	8.971 (1)
b, Å	10.551 (1)	12.588 (2)
c, Å	10.400 (1)	12.739 (1)
β, deg	90	104.61 (1)
V, Å^3	2179.5	1392.1
Z	4	2 dimers
d_{calcd}, g/cm^3	0.988	1.080
μ(Mo Kα), cm^{-1}	1.7	3.2
F(000), e	728	496
T, °C	−50	−50
$[(\sin \vartheta/\lambda]_{max}$, Å^{-1}	0.572	0.572
hkl range	+22,+12,±11	+10,+14,±14
scan type	ω	ω
scan width (in ω), deg	0.8	0.7
scan speed, deg/min	0.7–29.3	0.7–29.3
rflns measd	3734	2457
no. of unique rflns	3412	2184
R_{int}		0.02
no. of obsd, rflns	3234 ($F_o \geq 2.0\sigma(F_o)$)	1802 ($F_o \geq 4.0\sigma(F_o)$)
no. of ref params	223	205
R^a	0.038/0.039^c	0.030
$R_w{}^b$	0.035/0.036^c	0.031
$\Delta\rho_{fin}$ (max/min), e/Å^3	+0.32/−0.36	+0.29/−0.25

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$; $w = 1/\sigma^2(F_o)$; function minimized $\sum w(|F_o| - |F_c|)^2$. [c] The second value refers to the refinement of the inverse coordinate set.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 6^a

atom	x/a	y/b	z/c	U(eq), Å^2
P1	0.65321 (3)	0.70443 (6)	0.53805	0.023
Si1	0.55421 (3)	0.79920 (6)	0.33036 (9)	0.028
N1	0.7614 (1)	0.5903 (2)	0.2478 (2)	0.025
N2	0.6545 (1)	0.5049 (2)	0.0726 (2)	0.026
N3	0.6279 (1)	0.3424 (2)	0.2966 (2)	0.023
C1	0.5963 (1)	0.6674 (2)	0.4118 (3)	0.021
C2	0.6099 (1)	0.8923 (3)	0.2172 (3)	0.041
C3	0.5160 (2)	0.9271 (3)	0.4346 (3)	0.052
C4	0.4816 (1)	0.7330 (3)	0.2346 (3)	0.044
C5	0.6021 (2)	0.7455 (3)	0.6828 (3)	0.042
C6	0.6791 (2)	0.5461 (3)	0.5978 (3)	0.040
C7	0.7676 (1)	0.7298 (3)	0.2416 (3)	0.027
C8	0.8106 (1)	0.5447 (3)	0.3437 (3)	0.037
C9	0.7758 (1)	0.5344 (3)	0.1210 (3)	0.026
C10	0.7192 (1)	0.5546 (2)	0.0260 (3)	0.030
C11	0.5988 (1)	0.5580 (3)	−0.0037 (3)	0.041
C12	0.6522 (1)	0.3644 (2)	0.0651 (2)	0.026
C13	0.6057 (1)	0.3104 (3)	0.1655 (3)	0.026
C14	0.5723 (2)	0.3200 (3)	0.3865 (3)	0.028
C15	0.6855 (2)	0.2639 (3)	0.3325 (3)	0.044
Li	0.6540 (2)	0.5457 (4)	0.2789 (4)	0.023

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*a_ia_j$.

Results and Discussion

According to Figure 1, **6** is the first example of a monomeric monophosphinomethanide lithium complex. The Li$^+$ cation in **6** is coordinated to the three N donor atoms of the PMDETA ligand in just the same way as in other

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Table III. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 7

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq), Å^2
Li	0.0256 (4)	−0.0897 (3)	0.1094 (3)	0.034
Si1	0.27206 (7)	0.03380 (5)	0.30263 (5)	0.028
Si2	−0.05964 (6)	0.11870 (5)	0.19183 (4)	0.025
P	0.17597 (6)	0.12332 (4)	0.06463 (4)	0.023
C	0.1225 (2)	0.0611 (2)	0.1769 (2)	0.024
C11	0.1846 (3)	−0.0116 (2)	0.4148 (2)	0.036
C12	0.4001 (3)	0.1501 (2)	0.3591 (2)	0.034
C21	−0.1866 (3)	0.0230 (2)	0.2413 (2)	0.043
C22	−0.1826 (3)	0.1715 (2)	0.0594 (2)	0.036
C23	−0.0362 (3)	0.2360 (2)	0.2883 (2)	0.038
C31	0.2152 (3)	0.2652 (2)	0.0963 (2)	0.030
C32	0.3743 (3)	0.0850 (2)	0.0666 (2)	0.037
C13	0.4074 (3)	−0.0767 (2)	0.2890 (2)	0.050

Table IV. Important Distances (Å) and Angles (deg) for 6 with Estimated Standard Deviations in Units of the Last Significant Figure in Parentheses

	Bond Distances		
P–C1	1.776 (3)	Si–C1	1.830 (3)
P–C5	1.866 (3)	Si–C2	1.890 (3)
P–C6	1.855 (3)	Si–C3	1.890 (3)
Li–C1	2.207 (5)	Si–C4	1.888 (3)
Li–N1	2.209 (4)	Li–N2	2.188 (4)
Li–N3	2.214 (4)	C1–H1	0.90 (3)
	Bond Angles		
P–C1–Si	117.8 (1)	P–C1–Li	105.1 (2)
Si–C1–Li	112.9 (2)	P–C1–H1	110 (2)
Si–C1–H1	109 (2)	Li–C1–H1	101 (2)
C1–Li–N1	117.9 (2)	C1–Li–N2	137.0 (2)
C1–Li–N3	113.0 (2)	N1–Li–N2	83.9 (2)
N1–Li–N3	116.4 (2)	N2–Li–N3	83.8 (2)

Table V. Important Distances (Å) and Angles (deg) for 7[a]

	Bond Distances		
P–C	1.799 (2)	Li–C	2.172 (4)
Si1–C	1.844 (2)	Li–P′	2.519 (4)
Si2–C	1.841 (2)	P–C31	1.846 (2)
P–C32	1.838 (2)	Si1–C11	1.884 (2)
Si1–C12	1.888 (2)	Si1–C13	1.882 (2)
Si2–C21	1.873 (2)	Si2–C22	1.888 (2)
Si2–C23	1.899 (2)		
	Bond Angles		
P′–Li–C	128.5 (2)		
Li′–P–C	110.5 (1)	Li′–P–C31	114.2 (1)
Li′–P–C32	116.4 (1)	C–P–C31	108.8 (1)
C–P–C32	109.1 (1)	C31–P–C32	96.9 (1)
Li–C–P	103.1 (1)	Li–C–Si1	108.2 (1)
Li–C–Si2	96.2 (1)	P–C–Si1	119.4 (1)
P–C–Si2	109.4 (1)	Si1–C–Si2	117.0 (1)
	Intermolecular Li···H_3C–Si Contacts		
Li–C23″	2.541 (4)	Li–H231″	2.33 (3)
Li–H232″	2.30 (3)	Li–H233″	2.46 (3)
Li–C23″–Si2″	170.8 (2)	C–Li–C23″	126.3 (2)
P′–Li–C23″	103.4 (1)		

[a] See Figure 1 for numbering scheme adopted. Symmetry operations: primed atoms −*x*, −*y*, −*z*; double-primed atoms, −x, −0.5 + *y*, 0.5 − *z*.

PMDETA–lithium compounds.[7] The central Li–N2 bond is slightly shorter (2.188 (4) Å) than the Li–N1/Li–N3 bonds (2.209 (4)/2.214 (4) Å). A distorted-tetrahedral coordination geometry is completed by the carbanionic C atom of the phosphinomethanide. The Li–C1 bond is significantly shorter (2.207 (5) Å) than the Li–C bonds in 4 (2.249 (9)/2.26 (1) Å). This reflects the generally observed trend that additional weak interactions of Li, as in 4 (Li···P contacts), reduce the bonding interactions of Li with the other donor atoms. Nevertheless, the Li–C1 bond is longer than the Li–C bonds in 3 (2.150 (8)/2.141 (6) Å) and in (PMDETA)Li[HC(SiMe$_3$)$_2$] (2.13 (5) Å).[8] A comparison of 6 with the latter is highly desirable, as it would allow the direct evaluation of the effect of phosphino vs silyl substitution at the carbanionic C atom upon the Li–C bond lengths. This in turn would enable an estimation of the anionic charge localization at the carbanionic C atom. It looks as if the phosphino substituent in 6 would actually reduce the charge at C1 when compared with that for the disilylmethanide [HC(SiMe$_3$)$_2$]$^-$ (presumably due to the higher electronegativity of P vs that of Si), but the extremely large standard deviations in the latter structure determination render a direct comparison problematic. The most interesting aspect of the structure of 6 concerns the PMe$_2$ group. The intramolecular Li–P1 distance is long (3.174 (6) Å) and clearly nonbonding, as is also evident from the conformation of the PMe$_2$ group with the lone pair pointing *away* from the Li center (Figure 1). Thus, three-membered ring formation as in 2 can be definitely excluded. Therefore, 6 represents the first example of a lithium phosphinomethanide without Li–P bonding, i.e.,

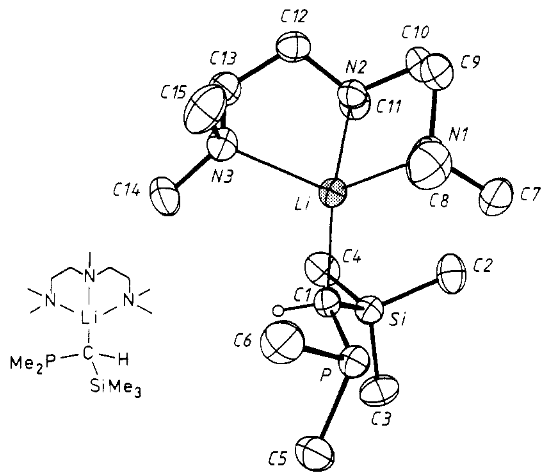

Figure 1. Molecular structure of 6 in the crystal and atomic numbering scheme used (ORTEP; displacement ellipsoids at the 50% probability level, H atoms omitted for clarity with the exception of H1).

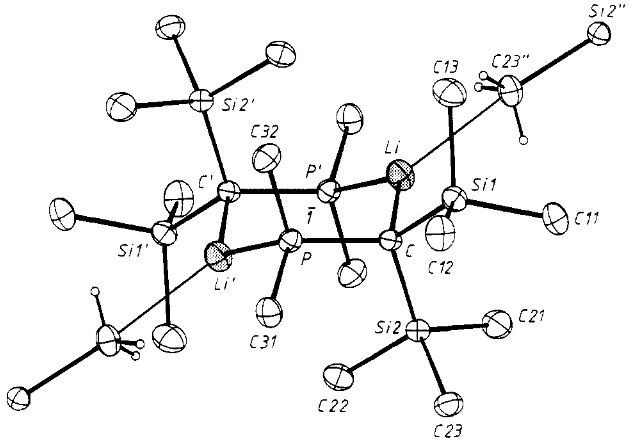

Figure 2. Molecular structure of 7 (without H atoms), including the additional Li···H_3C–Si interactions to neighboring molecules.

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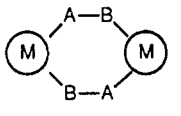
(7) See for instance: (a) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1987**, 716. (b) Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Stamper, J. G.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 949. (c) Raston, C. L.; Shelton, B. W.; Whitaker, C. R.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1988**, 987.

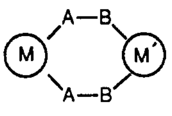
(8) Lappert, M. F.; Engelhardt, L. M.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1982**, 220.

with an η^1-C-bonded phosphinomethanide. The angle P1–C1–Li is slightly smaller (105.1 (2)°) than the angle Si1–C1–Li (112.9 (2)°), but this cannot be attributed to any appreciable Li···P interaction, since the lone pair at P1 obviously does not point toward the metal. Presumably this observation solely reflects steric interactions. As frequently found in related structures, the P1–C1 bond is somewhat shorter (1.776 (3) Å) than the P1–C5 (1.866 (3) Å) and P1–C6 (1.855 (3) Å) bonds, as is Si–C1 (1.830 (3) Å) compared to Si–C2 (1.890 (3) Å), Si–C3 (1.890 (3) Å), and Si–C4 (1.888 (3) Å), which reflects the very special stabilization of carbanionic C atoms by silyl and/or phosphino substituents.[6]

In Figure 2, the centrosymmetric structure of the dimeric **7** is clearly seen. The six-membered ring formed by head-to-tail dimerization is in a chair conformation. The type I connectivity observed in **7** is in marked contrast to its mono-TMEDA adduct **5** (type II), which shows a head-to-head arrangement. In **5**, the two lithium cations are different due to the TMEDA coordination to only one of the metals. Different metal centers obviously lead to the type II arrangement, which is also found in (TMEDA)Li$(PMe_2CH_2)_2AlMe_2$.[9] There is only one exception: in $[Me_2Al(CH_2PMe_2)_2]Mg$, a type I arrangement is observed.[10] Type I generally is favored when the metal centers M are identical, as is the case in **7** and **3**. Indeed, the structures of **7** and **3** are very similar, the main difference being the coordination number of lithium: 4 in **3** and, at least to a first approximation (see below), 2 in **7**.



I



II

Although coordination number 2 at lithium is not uncommon for organolithium compounds, the situation in **7** deserves further comment. In two other cases (e.g., **5** and $[Li(THF)_4]\{Li[C(SiMe_3)_3]_2\}$[11]) lithium is coordinated by two identical donor atoms and adopts a (nearly) linear geometry (in organoamido lithium chemistry dicoordinate lithium atoms are known as part of four-, six-, and eight-membered rings[12,13]). In contrast in **7**, the primary donor set is made up by one phosphorus and one carbon atom and the angle C–Li–P amounts to not more than 128.5 (2)°.

This angle is particularly surprising, as a true 2-fold coordination at Li should rather result in bonding angles close to linear, as is indeed observed in the above-mentioned compounds. Closer inspection of the intermolecular interactions reveals, however, that in **7** the coordination sphere of Li is augmented by a weak interaction to a neighboring Si methyl group (Li···C23 (−*x*, −0.5 + *y*, 0.5 − *z*) = 2.541 (4) Å, Figure 2). Most noteworthy, this interaction to a good approximation is along the 3-fold axis of the methyl group (Li···C23–Si2 = 170.8 (2)°), thus resulting in about equal Li···H distances to all three H atoms at C23 (at distances of 2.33 (3), 2.30 (3), and 2.46 (3) Å). Quite remarkably, the Li coordination including C23 is virtually planar (sum of the angles 358.2°; Table V).

Table VI. Distances (Å) and Angles (deg) in Six-Membered Rings of Lithium Phosphinomethanides

	7	5	4	3
C–P–Li	110.5 (1)	121.5 (3) 120.7 (3)	108.1 (2) 110.8 (2)	114.4 (2) 112.7 (2)
P–Li–C	128.5 (2)		114.6 (4) 114.2 (4)	110.7 (2) 108.2 (3)
P–C–Li	103.1 (1)	92.9 (4) 94.8 (4)	96.9 (3) 97.6 (3)	113.2 (3) 111.8 (3)
P–C	1.799 (2)	1.780 (5) 1.790 (5)	1.772 (5) 1.773 (5)	1.751 (3) 1.754 (5)
Li–P[a]	2.519 (4)	2.716 (9) 2.72 (1)	2.680 (7) 2.661 (8)	2.593 (7) 2.615 (6)
Li–C	2.172 (4)	2.18 (1) 2.17 (1)	2.249 (9) 2.26 (1)	2.150 (8) 2.141 (6)

[a] The shortest distances in **5** and **4** are selected.

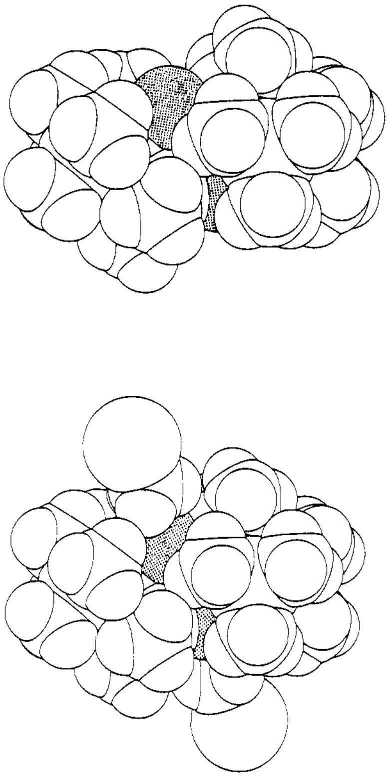


Figure 3. Space-filling representations of **7** (SCHAKAL; lithium atom dotted): (top) without Li···H_3C–Si contacts; (bottom) with intermolecular contacts.

This peculiar intermolecular Li···H_3C contact, which might be considered as a 3-fold agostic Li–H interaction, is not novel, however. Actually, it is also observed in the well-known classic structure of tetrameric methyllithium by Weiss.[14,15] In the latter, the contact serves to expand the coordination number of Li from 3 to 4, while in **7**, the coordination number of Li is 3, if the additional methyl contact is included. As compared to that in $(LiMe)_4$, the Li···H_3C interaction in **7** is slightly longer (Li···H_3C = 2.36 Å in $(LiMe)_4$[14]). It should also be noted that tight inter-

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(13) For dicoordinate compounds see also: (a) Hitchcock, P. B.; Lappert, M. F.; Power, P. P.; Smith, S. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1669. (b) Olmstead, M. M.; Power, P. P.; Sigel, G. *Inorg. Chem.* **1986**, *25*, 1027. (c) Murray, B. D.; Power, P. P. *J. Am. Chem. Soc.* **1984**, *106*, 7011.

(14) Weiss, E.; Hencken, G. *J. Organomet. Chem.* **1970**, *21*, 265. See also: Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, U.K., 1986; p 113.

(15) A similar Li···H_3C–B interaction has also been reported: Rhine, W. E.; Stucky, G.; Peterson, S. W. *J. Am. Chem. Soc.* **1975**, *97*, 6401.

molecular association, as observed in 7 and in $(LiMe)_4$, renders the solubility of organolithium compounds in nonpolar solvents very low, and it is only due to the large, nonpolar $SiMe_3$ groups in 7 that its solubility in unpolar aromatics is high enough to allow the slow crystallization of single crystals suitable for X-ray diffraction.

The remarkable $Li\cdots H_3C$ interaction is not confined to the structural chemistry of lithium but it is also observed with other highly Lewis-acidic metal centers, as, for example, the metals from the lanthanide series. Thus, $Cp^*_2Ln-CH_3$ ($Cp^* = Me_5C_5^-$) was found to be dimeric due to a similar, almost linear $Ln-CH_3\cdots Ln$ interaction ($Ln-C\cdots Ln = 170\ (4)°$[16]), and Cp^*BeCH_3 likewise coordinates to Cp^*_2Yb along the $Be-CH_3$ vector.[17] In the latter case the peculiar methyl coordination via the three H atoms was considered a model for methane coordination.[17]

A comparison of the angles and the distances within six-membered rings of dimeric lithium phosphinomethanides (Table VI) clearly demonstrates the structure-determining effect of the coordination number of lithium and of the steric bulk of the substituents in those rings. Figure 3 gives space-filling representations of 7, which show that the bulky $SiMe_3$ groups together with the methyl groups at P and the additional $Li\cdots H_3C-Si$ contact shield the lithium atoms quite effectively. In this respect also the methyl group C22′ deserves comment. Its position above the six-membered ring leads to a distance for Li–H221′ of only 2.44 (3) Å, which is directly comparable to the above-mentioned $Li\cdots H_3C$ agostic interactions (Li–C22′ = 3.033 (4) Å). This shielding is certainly important in determining the overall structure, as TMEDA coordination to lithium can only be achieved in a head-to-head six-membered ring (compound 5). Furthermore, Li–P in 7 with three-coordinate lithium is small, whereas the other bond lengths (Li–C, P–C), which are more affected by steric interactions, are longer than, for example, in 3. Most noteworthy, Li–C lengths in 7 and 5 are similar and the endocyclic P–C bonds in 7 (as well as Si–C1) are again shorter than the other respective P–C and Si–C bonds. The smaller values of the C1–P–Li and P–C1–Li angles, as compared to those in 3, balance the larger valence angles at lithium. Nevertheless, the larger angle P–C1–Li in 7, as compared to those in 4 and 5, reflect the absence of substantial $Li\cdots P^*$ secondary interactions observed in the latter.

The structures of the monophosphinomethanides 6 and 7, as compared to those of 3–5, clearly demonstrate that the coordination of the lithium atom as well as the overall geometry of the compounds is dominated by the presence and the nature of the coligand to lithium. In the complete absence of a strong lithiophilic donor, as, for example, TMEDA, lithium even coordinates additionally to Si-standing methyl groups. This is in perfect accord with the findings in a series of diphosphinomethanides.[4] Steric and electronic effects of the C and P substituents are less important but certainly contribute to the overall geometry. In both 6 and 7, there are no additional weak $Li\cdots P$ interactions. This is particularly surprising in the case of 7, where the low coordination number of lithium seems to be an ideal prerequisite for additional interactions, as is found in 4 and 5 and in various lithium diphosphinomethanides. As already pointed out, this $Li\cdots P$ interaction requires a small Li–C–P angle within the six-membered ring. This is most easily achieved by adopting a twist conformation as exemplified in 4. The higher degree of silyl substitution in 7 prevents this conformation for steric reasons, however, and the steric unsaturation of lithium is relieved by the additional intermolecular $Li\cdots H_3C-Si$ interaction. It thus emerges that the actual geometry found in phosphinomethanides reflects a subtle balance of steric and electronic interactions, which are not easily predictable. Even more, the study of small variations at the substituents or coligands of lithium phosphinomethanides remains a worthwhile undertaking and promises further insight into the coordination chemistry of lithium. These studies are equally important for the evaluation of weak interactions and reactivity patterns, which seem to be drastically influenced by only small changes in the substituents.

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Supplementary Material Available: Complete tables of the atomic positional and displacement parameters (8 pages); listings of observed and calculated structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

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