Pergamon

PII: S0277-5387(97)00285-4

Polyhedron Vol. 17, No. 2–3, pp. 351–355, 1998

0277–5387/98 $19.00+0.00

Synthesis and structure of (*P*,*P*-diphenylphosphino)methyl lithium-tetrahydrofuran

Dirk Steinborn,* Olaf Neumann, Horst Weichmann, Frank W. Heinemann and Jens-Peter Wagner

Institut für Anorganische Chemie der Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Str. 2, D-06120 Halle (Saale), Germany

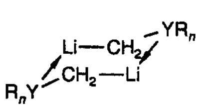
(Received 30 April 1997; accepted 25 June, 1997)

Abstract—$Bu_3SnCH_2PPh_2$, prepared by reaction of Bu_3SnCH_2I with $NaPPh_2$ in liquid ammonia and by reaction of Bu_3SnCl with $LiCH_2PPh_2$/tmeda, reacts with BuLi in hexane as solvent in the presence of a small amount of THF to give $[\{Li(CH_2PPh_2)(thf)\}_\infty]$ (**4**). An X-ray structure analysis revealed that the (*P*,*P*-diphenylphosphino)methyl ligands are arranged in a μ_3-1 : $2\kappa^2C$: $3\kappa P$ fashion. Thus, compound **4** exhibits a polymeric ladder-like structure in which six-membered $Li_2C_2P_2$ rings with a chair conformation and planar four-membered Li_2C_2 rings are arranged alternately. The interplanar angle between the Li_2C_2 rings and the planar Li_2C_2 units belonging to the neighbored six-membered rings amounts to 145.0(4)°. The Li—C bonds within the six-membered rings are shorter than those within the four-membered rings [2.21(1) *vs* 2.39(1) Å]. The distorted tetrahedral donor set of Li is made up by one phosphorus, one oxygen (tetrahydrofuran) and two methylene carbon atoms. © 1997 Elsevier Science Ltd

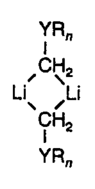
Keywords: phosphinomethyl lithium; functionalized methyl lithium compounds; tin–lithium transmetallation; crystal structure.

Structures of functionalized methyl lithium compounds of the type $LiCH_2YR_n$ with Lewis-basic heteroatoms Y are strongly dependent (i) on the nature of the heteroatom Y, (ii) on the type of the substituents R (alkyl, aryl) and (iii) on co-ligands which might be present. To date there have been found two common structural types: $[Li_2(CH_2SPh)_2(tmeda)_2]$ (**1a**) [1], $[Li_2(CH_2PMe_2)_2(tmeda)_2]$ (**2a**) [2], $[Li_2(CH_2PPhMe)_2(tmeda)_2]$ (**2b**) [2], $[Li_2(CH_2PPhMe)_2(sparteine)_2]$ (**2c**) [2], and $[Li_2(CH_2PPh_2)_2(tmeda)_2]$ (**2d**) [3] crystallize as dimers with six-membered rings $[Li_2C_2Y_2]$ in which the heteroatom Y is coordinated to lithium (type **A**). $[Li_2(CH_2SMe)_2(tmeda)_2]$ (**1b**) [1], $[Li_2(CH_2SPh)_2(thf)_4]$ (**1c**) [4], and $[Li_2(CH_2NPh_2)_2(thf)_3]$ (**3a**) [5] are dimeric complexes with four-membered rings $[Li_2C_2]$ in which the heteroatom is not coordinated to lithium (type **B**). $[\{Li(CH_2SMe)(thf)\}_\infty]$ (**1d**) [4] is the only example where the six-membered $Li_2C_2Y_2$ and the four-membered Li_2C_2 rings are arranged alternately giving a polymeric ladder-like structure. Furthermore, there is one example of a tetrameric structure, namely $[Li_4(CH_2NC_5H_{10})_4(thf)_2]$ (**3b**) [5].

Comparing **1a** with **1c** and **1b** with **1d**, it can be seen that the structures are strongly influenced by co-ligands. As far as structures of (phosphino)methyl lithium complexes are concerned, there have been reported only those with chelating N,N donors as co-ligands (**2a–d**). Thus, we were interested to synthesize the (*P*,*P*-diphenylphosphino)methyl lithium tetrahydrofuran adduct and to determine its structure. Of special interest is a comparison of the title compound with the special features observed in the structure of the corresponding amino derivative **3a** having a three



A



B

---

* Author to whom correspondence should be addressed.

coordinated lithium and an approximately planar environment of nitrogen [5].

RESULTS AND DISCUSSION

$Bu_3SnCH_2PPh_2$(Bu = *n*Bu) was prepared (i) by reaction of Bu_3SnCH_2I with $NaPPh_2$ in liquid ammonia and (ii) by reaction of Bu_3SnCl with $LiCH_2PPh_2$/tmeda, *cf.* Scheme 1.

The identity of $Bu_3SnCH_2PPh_2$ was established by microanalysis, NMR (^1H, ^{13}C, ^{31}P, ^{119}Sn) and mass spectroscopy. $Bu_3SnCH_2PPh_2$ react with BuLi in hexane as solvent in the presence of a small amount (*ca* 4 vol-%) of THF to give $[\{Li(CH_2PPh_2)(thf)\}_\infty]$ (**4**) as pale yellow precipitate [eq. (2)]. Without being added THF, the transmetallation reaction proceeds, too, but $LiCH_2PPh_2$ remains in solution.

Complex **4** is very sensitive to air and moisture. It is highly soluble in THF, sparingly soluble in ether and benzene and unsoluble in aliphatic hydrocarbons. **4** starts to decompose at 150°C and its identity was established by NMR spectroscopy. The methylene carbon and hydrogen atoms resonate at relatively high field [$\delta(^{13}C) = 2.0$ ppm, $\delta(^1H) = -0.39$ ppm] and exhibit typical coupling to phosphorus [$^1J(^{31}P,^{13}C) = 46.2$ Hz, $^2J(^{31}P,^1H) = 3.5$ Hz]. These values are the same as those of the TMEDA adduct **2d** [$\delta(^{13}C) = 2.2$ ppm, $\delta(^1H) = -0.37$ ppm, $^1J(^{31}P,^{13}C) = 46.2$ Hz, $^2J(^{31}P,^1H) = 3.4$ Hz] [3b]. The ^{31}P chemical shift amounts to 8.1 ppm. The corresponding value for **2d** is -1.9 ppm [3b].

The recrystallization of **4** from pentane/THF affords crystals suitable for X-ray investigations. A drawing of the solid state structure of complex **4** giving the atom numbering scheme is shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 1. Compound **4** exhibits a polymeric structure in which six-membered $Li_2C_2P_2$ rings and planar four-membered Li_2C_2 rings are arranged alternately. Thus, the coordination of the organo ligands has to be designated as μ_3-(*P,P*-diphenylphosphino)methyl-1:2κ^2*C*:3κ*P*. The midpoints of the four- and six-membered rings are crystallographically imposed inversion centers. $[\{Li(CH_2SMe)(thf)\}_\infty]$ (**1d**) exhibits an analogous structure [4].

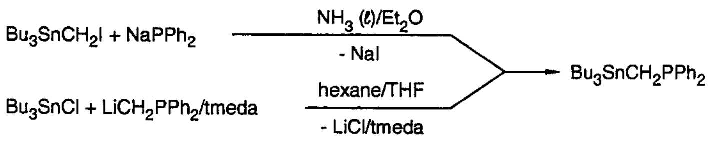
The Li—C distances in the six-membered $Li_2C_2P_2$ rings [Li(1)—C(1) 2.21(1) Å] are a little bit longer than those in the dimeric TMEDA complexes **2** [2.12(1)–2.174(4) Å], see Table 2. The distances between neighbored lithium and phosphorus [Li(1)—P(1′) 2.70(1) Å] correspond to those in the TMEDA adduct **2d** [2.686(5) Å] and in the other complexes **2a**–**2c** (*cf.* Table 2). In $[\{Li[o,o'\text{-}(Me_2PCH_2)_2C_6H_3]\}_2]$, a *P*-functionalized phenyllithium complex with a five membered Li—C—C—C—P ring, the Li—P distances range from 2.513(4) to 2.668(3)° [6].

As in the complexes **2a**–**2d**, the P—CH_2 distance [P(1)—C(1) 1.774(7) Å] is substantially shorter than the P—C_{Ph} distances [P(1)—C(2) 1.856(6) Å, P(1)—C(8) 1.861(6) Å] in spite of the smaller covalent radii of sp^2 hybridized carbons in comparison with sp^3 hybridized ones [7]. It seems likely that this in part arises from a stabilizing influence of phosphorus by polarization.

The torsion angles (absolute values) of the six-membered ring [P(1)—C(1)—Li(1)—P(1′) 54.58(5)°, C(1)—Li(1)—P(1′)—C(1′) 63.34(6)°, Li(1)—C(1)—P(1)—Li(1′) 57.63(5)°] indicate some deviations from the 'ideal' chair conformation (60°). A chair conformation was found in the dimeric TMEDA adducts **2a** and **2d**, whereas the phenylmethyl derivatives **2b** and **2c** exhibit six-membered rings with a boat conformation. The 'through space' Li(1)···P(1) distance within the six-membered rings of **4** amounts to 3.10(1) Å indicating a more compact ring structure than those of all other derivatives **2a**–**d** (3.16–3.45 Å), see Table 2.

The six-membered rings $Li_2C_2P_2$ are connected *via* Li—C bonds that form four-membered rings Li_2C_2. These Li—C bonds [Li(1)—C(1′) 2.39(1) Å] are much longer than those within the $Li_2C_2P_2$ rings [Li(1)—C(1) 2.21(1) Å]. They are also longer than those in other organo lithium compounds with Li_2C_2 rings (average: 2.29 Å for sp^3-hybridized carbon atoms [8]). The torsion angles P(1)—C(1)—Li(1)—C(1′) 177.6(5)° and P(1′)—Li(1)—C(1)—Li(1′) 123.0(6)° reveal that two of the four phosphorus atoms which are neighbored to the four-membered Li_2C_2 rings are lying in the planes of these rings.

The interplanar angle between the planar Li_2C_2 rings and the planar Li_2C_2 units that are parts of the neighboring six-membered rings amounts to 145.0(4)°. Thus, a ladder-like structure is obtained. The comparison with the corresponding angle in **1c** (114.7°) [4] reveals that the 'ladder' of structure **4** is more flat than those of **1c**.



(1)

$$Bu_3SnCH_2PPh_2 + BuLi \xrightarrow[-\,Bu_4Sn]{\text{hexane (THF)}} \underset{(\mathbf{4})}{[\{Li(CH_2PPh_2)(thf)\}_\infty]} \qquad (2)$$

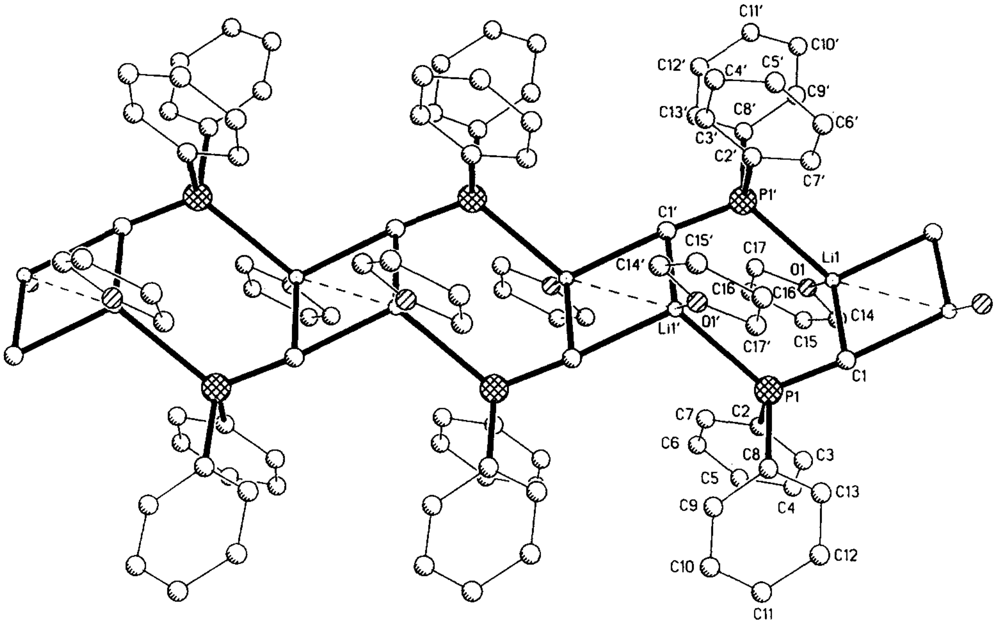


Fig. 1. Drawing of the structure of $[\{Li(CH_2PPh_2)(thf)\}_\infty]$ (**4**). Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for **4**

P(1)—C(1)	1.774(7)	P(1)—C(2)	1.856(6)
P(1)—C(8)	1.861(6)	Li(1)—C(1)	2.21(1)
Li(1)—C(1′)(#2)[a]	2.39(1)	O(1)—Li(1)	2.01(1)
P(1)—Li(1′)(#1)	2.70(1)	P(1)—Li(1)[b]	3.10(1)
Li(1)—Li(1)(#2)	2.80(2)		
C(1)—P(1)—C(2)	104.5(3)	C(1)—P(1)—C(8)	109.9(3)
C(2)—P(1)—C(8)	95.5(3)	C(1)—P(1)—Li(1′)(#1)	116.7(3)
C(2)—P(1)—Li(1′)(#1)	116.4(3)	C(8)—P(1)—Li(1′)(#1)	111.7(3)
C(1)—P(1)—Li(1)	44.3(3)	O(1)—Li(1)—P(1′)(#1)	97.4(5)
C(1)—Li(1)—P(1′)(#1)	112.2(5)	C(1′)(#2)—Li(1)—P(1′)(#1)	112.8(5)
C(1)—Li(1)—C(1′)(#2)	105.2(5)	O(1)—Li(1)—C(1)	126.2(6)
O(1)—Li(1)—C(1′)(#2)	102.8(5)	C(1)—Li(1)—P(1)	34.1(2)
O(1)—Li(1)—P(1)	106.7(5)	P(1′)(#1)—Li(1)—P(1)	90.7(3)
P(1)—C(1)—Li(1)	101.6(4)	P(1)—C(1)—Li(1′)(#2)	175.7(5)
Li(1)—C(1)—Li(1′)(#2)	74.8(5)	C(17)—O(1)—Li(1)	125.3(6)
C(14)—O(1)—Li(1)	127.2(6)		

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x, -y+2, -z+1$; #2: $-x+1, -y+2, -z+1$.
[b] 'Through space' distance.

The coordination sphere of lithium is completed by tetrahydrofuran. Thus, the coordination of Li is distorted tetrahedrally provided the Li(1) ··· P(1) contacts are not considered.

In a marked contrast to **4**, the benzyl substituted complex $[Li(CHPhPPh_2 \times (OEt_2)_2]$ adopts a monomeric solid state structure [9] demonstrating the great variability of structures of $LiCH_2PPh_2$ in dependence not only on co-ligands but also on substituents of the methylene carbon.

In the same way as for **4**, (*P*,*P*-phenylmethylphosphino)methyl lithium, $LiCH_2PPhMe$, could be prepared in 50% yield from the reaction of Bu_3SnCH_2PPhMe with BuLi in *n*-hexane as solvent. To date such transmetallation reactions have been used to prepare other compounds $LiCH_2YR_n$ with nitrogen ($YR_n = NR_2$) [5,10,11,12] oxygen ($YR_n = OR$) [10,13] and sulfur ($YR_n = SR$) [4,10] as Lewis-basic heteroatoms Y but not with phosphorus. The phosphinomethyl lithium compounds are obtained with a high purity free of N,N chelating ligands *via* this transmetallation reaction that seems to be superior to the metallation of methylphosphines with BuLi/tmeda [2,3,14,15] or ^{t}BuLi [16,17,18,19]

Table 2. Selected bond lengths (Å) and angles (°) in complexes $[\mathrm{Li_2(CH_2PRR')_2(L)_2}]$ with six-membered rings $[\mathrm{Li_2C_2P_2}]$

R/R′	Ph/Ph	Ph/Ph	Me/Me	Ph/Me	Ph/Me
L	thf	tmeda	tmeda	tmeda	sparteine
	(**4**)[a]	(**2d**) [3]	(**2a**) [2]	(**2b**) [2]	(**2c**) [2]
Ring conformation	chair	chair	chair	boat	boat
Li—$\mathrm{CH_2}$	2.21(1)	2.174(6)	2.150(8)/2.141(6)	2.15(1)/2.12(1)	2.21(3)/2.18(3)
P—$\mathrm{CH_2}$	1.774(7)	1.752(3)	1.751(3)/1.754(5)	1.730(8)/1.755(7)	1.77(1)/1.78(1)
P—CRR′	1.856(6)/1.861(6)	1.836(3)/1.872(3)	1.825(5)–1.853(5)	1.836(8)–1.857(9)	1.83(1)–1.87(2)
Li—P	2.70(1)	2.686(5)	2.593(7)/2.615(6)	2.67(1)/2.61(1)	2.74(2)/2.70(2)
Li···P[b]	3.10(1)	3.28[c]	3.23/3.26	3.16/3.17	3.32/3.45

[a] This work.

[b] 'Through space' distance.

[c] Calculated with data given in lit. [3c].

where dimetallation might occur [14,18] and the separation from the starting phosphine might be difficult [17].

EXPERIMENTAL

General comments

All reactions and manipulations were carried out under purified argon using standard Schlenk techniques. *n*-Hexane, *n*-pentane and THF-d_8 were dried with $\mathrm{LiAlH_4}$. THF and diethyl ether were distilled from sodium benzophenone ketyl. NMR spectra were recorded on Varian Gemini 300 or Varian Unity 500 NMR spectrometers using the protio impurities and the ^{13}C resonances of the deuterated solvents as references for ^{1}H and ^{13}C NMR spectroscopy, respectively. The chemical shift $\delta(^7\mathrm{Li})$ is reported relative to a solution of LiCl in THF-d_8 (external). Microanalyses (C, H) were obtained from the microanalytical laboratory of the Department of Chemistry.

Synthesis of $\mathrm{Bu_3SnCH_2PPh_2}$

(*i*). To $\mathrm{NaPPh_2}$ (0.1 mol) in liquid ammonia (300 $\mathrm{cm^3}$) and diethyl ether (50 $\mathrm{cm^3}$) [prepared from $\mathrm{PPh_3}$ (26.2 g, 0.1 mol) and Na (4.6 g, 0.2 mol) [20]], $\mathrm{Bu_3SnCH_2I}$ [21] (43.1 g, 0.1 mol) in diethyl ether (50 $\mathrm{cm^3}$) was added dropwise at −50°C. After evaporating ammonia and removing the solvents *in vacuo* 300–400 $\mathrm{cm^3}$ diethyl ether were added. The precipitate (NaI) was filtered off, the solvents were distilled off *in vacuo* and the residue was fractionated (b.p. 165–174°C at 0.01 torr). Yield 21.3 g (45%).

(*ii*). To $\mathrm{LiCH_2PPh_2}$/tmeda (0.25 mol) in hexane (250 $\mathrm{cm^3}$) [prepared by metallation of $\mathrm{PPh_2Me}$ (50.0 g, 0.25 mol) with BuLi/tmeda (0.25 mol, 1.6 M in hexane) [14, 22]] $\mathrm{Bu_3SnCl}$ (80.6 g, 0.25 mol) in THF (200 $\mathrm{cm^3}$) was added dropwise at 0°C. After stirring for 2 h at room temperature, water (250 $\mathrm{cm^3}$) was added at 0°C. The reaction mixture was neutralized with an aqueous solution of $\mathrm{NH_4Cl}$. The separated aqueous layer was washed twice with ether and the combined organic layers were dried ($\mathrm{Na_2SO_4}$). The solvents were distilled off and the residue was fractionated (b.p. 170–180°C at 0.01 torr). Yield 71.0 g (60%). Anal. Calcd: C, 61.42; H, 8.03. Found: C, 62.08; H, 7.90. ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 0.8 (t, 6H, $\mathrm{CH_3CH_2CH_2C}H_2$), 1.40–1.46 (m, 6H, $\mathrm{CH_3CH_2C}H_2\mathrm{CH_2}$), 1.31 (se, 6H, $\mathrm{CH_3C}H_2\mathrm{CH_2CH_2}$), 0.93 (t, 9H, $\mathrm{C}H_3\mathrm{CH_2CH_2CH_2}$), 1.49 (s, 2H, $\mathrm{C}H_2\mathrm{P}$), 7.52 (m, 4H, *o*-H), 7.28–7.38 (m, 6H, *m*, *p*-H). ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$): δ 9.91 [dd, $^1J(^{119}\mathrm{Sn,C}) = 325.1$ Hz, $^3J(\mathrm{P,C}) = 4.0$ Hz, $\mathrm{CH_3CH_2CH_2}C\mathrm{H_2}$], 28.9 [d, $^2J(^{119}\mathrm{Sn,C}) = 20.0$ Hz, $\mathrm{CH_3CH_2}C\mathrm{H_2CH_2}$], 27.2 [d, $^3J(^{119}\mathrm{Sn,C}) = 58.8$ Hz, $\mathrm{CH_3}C\mathrm{H_2CH_2CH_2}$], 13.6 (s, $C\mathrm{H_3CH_2CH_2CH_2}$), 5.2 [dd, $^1J(^{119}\mathrm{Sn,C}) = 209.4$ Hz, $^1J(\mathrm{P,C}) = 33.8$ Hz, $C\mathrm{H_2P}$], 142.5 [dd, $^3J(^{119}\mathrm{Sn,C}) = 23.8$ Hz, $^1J(\mathrm{P,C}) = 14.9$ Hz, *i*-C], 132.2 [d, $^2J(\mathrm{P,C}) = 19.0$ Hz, *o*-C], 128.08 (s, *m*-C), 128.13 (s, *p*-C). ^{31}P NMR (32 MHz, $\mathrm{CDCl_3}$): δ −17.6 [s+d, $^2J(^{119}\mathrm{Sn,P}) = 76.0$ Hz]. ^{119}Sn NMR (30 MHz, $\mathrm{CDCl_3}$): δ −10.2 [d, $^2J(^{119}\mathrm{Sn, P}) = 77.2$ Hz]. MS (70 eV, EI): *m*/*e* 434 (12%, $\mathrm{Bu_2SnCH_2PPh_2+H}$), 377 (4%, $\mathrm{BuSnCH_2PPh_2+H}$), 321 (75%, $\mathrm{SnCH_2PPh_2+2H}$), 255 (11%, BuSnPh + H), 197 (49%, SnPh), 177 (20%, BuSn), 121 (100%, $\mathrm{CH_2PPh-H}$), 120 (17%, Sn), 77 (13%, Ph).

Synthesis of $[\{\mathrm{Li(CH_2PPh_2)(thf)}\}_\infty]$ (**4**)

To $\mathrm{Bu_3SnCH_2PPh_2}$ (20.0 g, 42 mmol) in hexane (100 $\mathrm{cm^3}$) and THF (4 $\mathrm{cm^3}$) a solution of BuLi in hexane (50 mmol, 1.5 M) was added dropwise at 0°C. After stirring for 30 min at room temperature the precipitate was filtered off, washed with hexane (2 × 30 $\mathrm{cm^3}$) and dried *in vacuo*. Yield 10.8 g (92%). ^{1}H NMR (200 MHz, THF-d_8): δ −0.39 [d, 2H, $\mathrm{CH_2}$; $^2J(\mathrm{P,H}) = 3.5$ Hz], 6.83–6.95 (m, 2H, *p*-H), 6.96–7.04 (m, 4H, *m*-H), 7.41–7.49 (m, 4H, *o*-H). ^{13}C NMR (50 MHz, THF-d_8): δ 2.0 [d, $\mathrm{CH_2}$; $^1J(\mathrm{P,C}) = 46.2$ Hz], 125.0 (s, *p*-C), 127.1 [d, *m*-C, $^3J(\mathrm{P,C}) = 4.6$ Hz], 132.3

[d, *o*-C, $^2J(P,C) = 17.0$ Hz], 155.3 [d, *i*-C, $^1J(P,C) = 23.9$ Hz]. ^{31}P NMR (81 MHz, THF-d_8): δ 8.13 (s). ^7Li NMR (194 MHz, THF-d_8): δ 0.52 (s). (Due to partial hydrolysis a small amount of PPh_2Me was detected in the spectra.)

X-ray structure determination of **4**

A suitable single crystal ($0.24 \times 0.16 \times 0.08$ mm^3) was obtained from pentane/THF solution at -35°C. X-ray measurement was performed on a Stoe STADI 4 diffractometer with Mo-K_α radiation ($\lambda = 0.71073$ Å, graphite monochromator) at 210(2) K. Due to the very weak diffracting power of the small crystal used data were collected only up to $2\theta = 40.0°$. The structure was solved by direct methods with SHELXS86 [23] and refined using full-matrix least-squares procedures on F^2 (SHELXL93) [24]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were geometrically positioned with fixed isotropic displacement parameters being 1.2 times the values of the equivalent isotropic displacement parameters of the carrying carbon atoms. Crystal data, details of data collection, structure solution and refinement are summarized in Table 3. Complete tables of the atomic coordinates, H atom parameters, bond distances, bond angles and anisotropic thermal parameters have been deposited with the Editor as supplementary material.

Table 3. Crystal data and structure refinement for **4**

Empirical formula	$C_{17}H_{20}LiOP$
Fw	278.24
Crystal system	monoclinic
Space group	$P2_1/n$
a, *b*, *c* (Å)	5.824(1), 17.001(3), 15.736(3)
α, β, γ (°)	90, 95.71(3), 90
V (Å^3)	1550.4(5)
Z	4
D_{calcd} (g cm^{-3})	1.192
μ(Mo-K_α) (mm^{-1})	0.168
F(000)	592
Scan range (°)	$1.77 < \theta < 20.00$
Index ranges	$-5 \leqslant h \leqslant 5$, $-16 \leqslant k \leqslant 16$, $-15 \leqslant l \leqslant 15$
Reflections collected	2901
Independent reflections	1460 ($R_{int} = 0.1118$)
Observed reflections [$I > 2\sigma(I)$]	716
Parameters refined	187
Goodness-of-fit on F^2	1.004
Weighting scheme	$w = 1/[\sigma^2(F_o^2)+(0.0343P)^2]$ $P = (F_o^2+2F_c^2)/3$
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0565$, $wR2 = 0.0857$
R indices (all data)	$R1 = 0.1675$, $wR2 = 0.1148$
Largest diff. peak and hole (e Å^{-3})	0.213 and -0.212

Acknowledgment—We are grateful to Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for financial support.

REFERENCES

1. Amstutz, R., Laube, T., Schweizer, W. B., Seebach, D. and Dunitz, J. D., *Helv. Chim. Acta*, 1984, **67,** 224.
2. Byrne, L. T., Engelhardt, L. M., Jacobsen, G. E., Leung, W.-P., Papasergio, R. I., Raston, C. L., Skelton, B. W., Twiss, P. and White, A. H., *J. Chem. Soc., Dalton Trans.*, 1989, **105**.
3. (a) Blaurock, S., Kühl, O. and Hey-Hawkins, E., *Organometallics*, 1997, **16,** 807; (b) Fraenkel, G., Winchester, W. R. and Williard, P. G., *Organometallics*, 1989, **8,** 2308; (c) Cambridge Structural Database (CSD), Cambridge Crystallographic Centre, University Chemical Laboratory, Cambridge, England.
4. Becke, F., Heinemann, F. W. and Steinborn, D., *Organometallics*, 1997, **16,** 2736.
5. Becke, F., Steinborn, D., Heinemann, F. W., Rüffer, T., Wiegeleben, P., Boese, R. and Bläser, D., *J. Organomet. Chem.*, submitted.
6. Pape, A., Lutz, M. and Müller, G., *Angew. Chem.*, 1994, **106,** 2375.
7. Huheey, J. E., Keiter, E. A. and Keiter, R. L., *Inorganic Chemistry, Principles of Structure and Reactivity*, 4th ed.; Harper Collins College Publ., New York (1993).
8. Setzer, W. N. and v. Ragué Schleyer, P., *Adv. Organomet. Chem.*, 1985, **24,** 353.
9. Decken, A. and Cowley, A. H., *J. Organomet. Chem.*, 1996, **509,** 135.
10. Peterson, D. J., *Organomet. Chem. Rev. A*, 1972, **7,** 295.
11. Peterson, D. J., *J. Am. Chem. Soc.*, 1971, **93,** 4027.
12. Steinborn, D., Becke, F. and Boese, R., *Inorg. Chem.*, 1995, **34,** 2625.
13. Schöllkopf, U. in E. Müller (ed.), *Methoden der Organischen Chemie* (*Houben-Weyl*), Vol. XIII/1, p. 87. Thieme Verlag, Stuttgart (1970).
14. Peterson, D. J., *J. Organomet. Chem.*, 1967, **8,** 199.
15. Rausch, M. D. and Ciappenelli, D. J., *J. Organomet. Chem.*, 1967, **10,** 127.
16. Peterson, D. J. and Hays, H. R., *Organomet. Chem. Rev. A*, 1965, **30,** 1939.
17. Karsch, H. H. and Schmidbaur, H., *Z. Naturforsch.*, 1977, **32b,** 762.
18. Peterson, D. J. and Collins, J. H., *Organomet. Chem. Rev. A*, 1966, **31,** 2373.
19. Karsch, H. H., *Z. Naturforsch.*, 1979, **34b,** 1178.
20. Gee, W., Shaw, R. A. and Smith, B. C., *Inorg. Synthesis*, 1967, **9,** 19.
21. Seyferth, D. and Andrews, S. B., *J. Organomet. Chem.*, 1971, **30,** 151.
22. Schore, N. E., Benner, L. S. and LaBelle, B. E., *Inorg. Chem.*, 1981, **20,** 3200.
23. Sheldrick, G. M., SHELXS-86, *Program for the Solution of Crystal Structures*, University of Göttingen, Germany, 1986; Sheldrick, G. M., *Acta Cryst. Sect. A*, 1990, **46,** 467.
24. Sheldrick, G. M., *SHELXL*-93, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1993.