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CRYSTAL STRUCTURE OF BIS(DIPHENYLPHOSPHINO)-METHYLLITHIUM(*N*,*N*,*N′*,*N′*-TETRAMETHYLETHYLENEDIAMINE): AN ORGANOLITHIUM COMPOUND WITHOUT LITHIUM–CARBON BONDING

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Summary

The single crystal X-ray structure and ^{13}C NMR data are reported for $(Ph_2P)_2CHLi \cdot TMEDA$. The crystals belong to the triclinic space group $P\bar{1}$ with a 9.3665(8), b 9.9952(9), c 18.326(2) Å, α 93.827(8), β 85.687(8), γ 117.968(6)°, $Z = 2$ and d_{calc} 1.118 g cm^{-3}. Refinement converged with a conventional R value of 0.046 for 4012 observed reflections. The monomeric molecules contain slightly puckered CP_2Li four-membered rings with mean Li–P and C–P distances of 2.582(2) and 1.722(2) Å, respectively.

Introduction

Several complexes containing the $(Ph_2P)_2CH^-$ ligand have been reported [1,2]. Not only the phosphorus atoms but occasionally also the central carbon atom have been shown to participate in metal ligand bonding; for example, both bidentate and tridentate ligands are present in $[(Ph_2P)_2CHCu]_3$ [2]. Recently the possibility of $(Ph_2P)_2CHLi$ containing a $\overline{P{-}C{-}P{-}Li}$ four-membered ring devoid of Li–C bonding interactions was suggested in order to explain the $^7Li{-}^{31}P$ coupling found at low temperatures in ether [3]. Such a stereochemistry would contrast with that found for $[(Me_2P)_3CLi \cdot THF]_2$ *, which shows both Li–C and Li–P bonding interactions [4]. Furthermore, an intimate contact between the metal cation and the carbanionic center is a characteristic of organolithium compounds [5]. In order to elucidate the mode of the metal carbanion interaction, we have determined the structure of $(Ph_2P)_2CHLi \cdot TMEDA$ (I).

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* Abbreviations are: THF = tetrahydrofuran, TMEDA = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine.

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Results and Discussion

Bis(diphenylphosphino)methyllithium(*N,N,N',N'*-tetramethylethylenediamine) (I) was obtained by lithiation of bis(diphenylphosphino)methane [1] with methyllithium in the presence of tetramethylethylenediamine in ether.

$$(\mathrm{Ph_2P})_2\mathrm{CH_2} \xrightarrow[-\mathrm{CH_4}]{\mathrm{MeLi,\ TMEDA}} \underset{(\mathrm{I})}{(\mathrm{Ph_2P})_2\mathrm{CHLi}\cdot\mathrm{TMEDA}} \qquad (1)$$

The crystal structure of I (Tab 1, 2; Fig. 1) shows no bonding interaction between the Li atom and the bridging carbon atom C(1), but instead contains a CP_2Li four-membered ring system with two Li–P bonds. These Li–P bond lengths are identical, 2.582(5) Å, and compare well with the corresponding bond distances in $Me_2Al(CH_2PMe_2)_2Li \cdot TMEDA$ (2.606(5) Å) [6], $(Me_2PCH_2Li \cdot TMEDA)_2$ (2.593(7) and 2.615(6) Å) [7], and $[(Me_2P)_3CLi \cdot THF]_2$ (2.588(3) and 2.684(3) Å) [4]. The last compound displays Li–P distances of 2.945(3) and 2.998(3) Å which have

TABLE 1

SELECTED BOND DISTANCES (Å) IN $(Ph_2P)_2CHLi \cdot TMEDA$ (I)

P(1)–C(1)	1.722(3)	P(1)–Li	2.582(4)	N–C	1.46(2) [a]
P(2)–C(1)	1.722(2)	P(2)–Li	2.582(6)	C(*i*)–C(*o*)	1.386(6) [a]
P(1)–C(2)	1.838(2)	Li–N(1)	2.033(5)	C(*o*)–C(*m*)	1.381(6) [a]
P(1)–C(8)	1.846(2)	Li–N(2)	2.072(6)	C(*m*)–C(*p*)	1.37(1) [a]
P(2)–C(14)	1.845(2)	C(28)–C(29)	1.482(7)	C(1)–H(1)	0.84(3)
P(2)–C(20)	1.839(3)				

[a] Average values with $\sigma = [\Sigma(l - \bar{l})^2/(n-1)]^{1/2}$.

TABLE 2

SELECTED BOND ANGLES (°) IN $(Ph_2P)_2CHLi \cdot TMEDA$ (I)

C(1)–P(1)–Li	88.0(1)	P(1)–Li–P(2)	68.4(1)
C(1)–P(1)–C(2)	109.9(1)	P(1)–Li–N(1)	118.5(2)
C(1)–P(1)–C(8)	107.7(1)	P(1)–Li–N(2)	124.5(2)
Li–P(1)–C(2)	121.9(1)	P(2)–Li–N(1)	111.4(2)
Li–P(1)–C(8)	128.2(1)	P(2)–Li–N(2)	147.2(2)
C(2)–P(1)–C(8)	99.1(1)	N(1)–Li–N(2)	89.4(2)
C(1)–P(2)–Li	88.0(1)	Li–N(1)–C(28)	100.3(3)
C(1)–P(2)–C(14)	108.0(1)	Li–N(2)–C(29)	102.8(3)
C(1)–P(2)–C(20)	108.5(1)	N(1)–C(28)–C(29)	113.3(5)
Li–P(2)–C(14)	121.0(1)	N(2)–C(29)–C(28)	112.5(4)
Li–P(2)–C(20)	127.6(1)	C(Me)–N–C(Me)	108.9(4) [a]
C(14)–P(2)–C(20)	101.0(1)	C(*o*)–C(*i*)–C(*o'*)	117.4(5) [a]
P(1)–C(1)–P(2)	114.8(2)	C(*i*)–C(*o*)–C(*m*)	121.2(4) [a]
H(1)–C(1)–P(1)	122(2)	C(*o*)–C(*m*)–C(*p*)	120.3(4) [a]
H(1)–C(1)–P(2)	123(2)	C(*m*)–C(*p*)–C(*m'*)	119.7(4) [a]

[a] Average values as in Table 1.

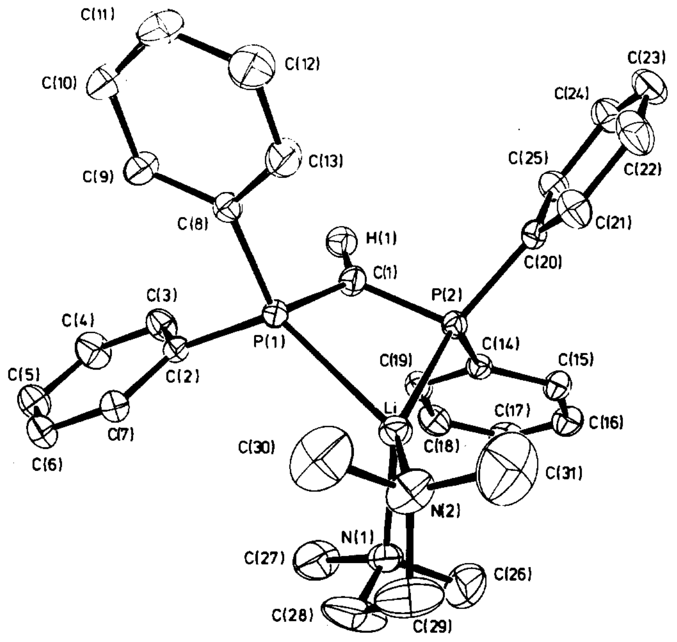

Fig. 1. A perspective drawing of $(Ph_2P)_2CHLi \cdot TMEDA$ (I) with 20% probability thermal ellipsoids.

also been regarded as bonding [4]. The lithium coordination in I resembles that in $(TMEDA \cdot Li)_3P_7$, in which each lithium atom bonds to two of the three equatorial phosphorus atoms (average 2.555 Å) [8]. The Li–P bond lengths found in diorganophosphide compounds average 2.47(1) Å in $\{[(Me_3Si)_2CH]_2PLi\}_2$ [9] and vary from 2.48(1) to 2.669(9) Å in $[Li_2(\mu_3\text{-tBuP})(\mu_2\text{-tBuP}) \cdot THF]_2$ [10].

In I and in $[(Me_2P)_3CLi \cdot THF]_2$ the Li–P bonds are found in CP_2Li four-membered rings with respective P–Li–P bond angles of 68.4(1) and 65.3(1)°, the latter value applying to the ring with the shorter Li–P distances. This ring in I is somewhat puckered, the dihedral angle formed by the normals to the P(1),C(1),P(2) and P(1),Li,P(2) planes being 9.4(1)°. The deviation of H(1) from the first of these planes, 0.12(3) Å, suggests that the central carbon atom C(1) is essentially sp^2 hybridized. Thus the lone pair of electrons which is formally localized on C(1) must occupy the $2p\pi$ orbital. No interaction between this $2p\pi$ orbital and the lithium atom appears to be possible, since the only symmetry-allowed overlap is with the lithium $2p$ orbital lying perpendicular to the P(1)–Li–P(2) plane, an orbital which is involved in Li–N bonding. The non-bonding nature of the Li–C(1) interaction is further emphasized by the transannular Li–C(1) distance, 3.054(6) Å, which is considerably longer than any known Li–C bond [5].

The stereochemical activity of electrons in the $2p\pi$ orbital of C(1) is revealed by comparison of the P–C bond lengths; thus those formed by C(1) are on the average 0.120(5) Å shorter than those formed by the *ipso* phenyl carbon atom (C(*i*)), although all of these carbon atoms are similarly hybridized. If this electron pair was involved in a C–Li bond then longer C(1)–P distances would have been expected. For example, the central carbon atom of $[(Me_2P)_3CLi \cdot THF]_2$ is four-coordinate, and the P–C bonds in the CP_2Li rings (average 1.796(2) Å) are distinctly longer

TABLE 3

COMPARISON OF ^{13}C NMR DATA [a] FOR $(Ph_2P)_2CHLi \cdot TMEDA$ (I) AND $(Ph_2P)_2CH_2$

	$CH_2/CHLi$	C(*i*)	C(*o*)	C(*m*)	C(*p*)
$(Ph_2P)_2CH_2$ [b]	28.0 (24)	138.9 (7.8) [d]	132.7 (20.5) [d]	128.2 (6.8) [d]	128.5
I [c]	20.7 (21.5)	150.0 (19.1) [d]	132.8 (15.2) [d]	128.7 (7.2) [d]	127.3

[a] Chemical shifts (rel. to tetramethylsilane) are given in ppm; $^{31}P-^{13}C$ coupling constants (Hz) are given in parentheses. [b] In $CDCl_3$. [c] In C_7D_8. [d] $J(P(A)-C+P(B)-C)$.

(0.074(3) Å) than those in I, a difference which can hardly be explained by the presence of a third phosphino substituent in the former compound. Similarly, the P–C bonds to the central carbon atoms in $[(Ph_2P)_2CHCu]_3$ were found to be 1.84(2) Å for the two tridentate ligands but 1.74(2) Å for the bidentate ligand [2].

Compared to the ^{13}C resonances of the corresponding atoms in $(Ph_2P)_2CH_2$ (Tab. 3), those of C(1) and C(*i*) in the anion are shifted 7.3 ppm upfield and 11.1 ppm downfield, respectively. The former shift is comparable to the ~ 10 ppm upfield shift of methyllithium compared to methane while the latter may indicate a flow of negative charge to the phenyl groups upon metallation [11]. Such an electron transfer is not inconsistent [12] with the fact that the average C(*o*)–C(*i*)–C(*o*) angle in I, 117.4(5)°, is significantly smaller than that in Ph_3P, 119.8(7)° [13].

While the Li–N(1) and Li–N(2) bond lengths (2.033(5) and 2.072(6) Å, respectively) should obviously be compared to those in $Me_2Al(CH_2PMe)_2Li \cdot TMEDA$, the relevant dimensions were not reported in the short communication about the latter [6]. The average Li–N bond length in $(TMEDA \cdot Li)_3P_7$, 2.071 Å [8], differs little from that in I. Interestingly, these bonds in I are shorter than those found in the cations of $[Li(TMEDA)_2][MeNi(C_2H_4)_2]$, 2.10–2.16 Å [14] and $[Li(TMEDA)_2][(TMEDA)Li(CH_2Ph)_2Mg(CH_2Ph)_2]$, 2.08–2.21 Å [15], which may imply that TMEDA competes more successfully than $(Ph_2P)_2CH$ for free lithium valencies. This view is supported by the fact that the mean Li–N bond length in I is 0.53(3) Å less than the Li–P bond lengths, although the difference in the tetrahedral covalent radii of nitrogen and phosphorus is only 0.40 Å [16]. The apparent discrepancy is less if the negative charge is formally localized on the lithium-bonded phosphorus atoms, as in $(TMEDA \cdot Li)_3P_7$ where the observed difference is only 0.484 Å [9].

If the coordination sphere of the lithium atom were undistorted then the dihedral angle between the P(1), Li, P(2) and N(1), Li, N(2) planes would be 90°, and the angle between the bisector of the P(1)–Li–P(2) and N(1)–Li–N(2) angles would be 180°. The observed values are 77.9 and 163.0°, with N(2) lying closer to the P(1),Li,P(2) plane than N(1). There is no obvious reason for the distortions, and the intermolecular contacts (the shortest being H(1)· · H(28B) ($x-1$, y, z) (2.36(3) Å)) are normal.

Experimental

The ^{13}C NMR spectra were measured on a Varian FT 80 NMR apparatus at room temperature.

Preparation

Compound I was prepared by a published method [1] involving deprotonation of $(Ph_2P)_2CH_2$ with MeLi/TMEDA. It slowly crystallized from diethyl ether at room temperature.

X-Ray data collection and reduction

A crystal of I having dimensions of ca. 0.23 × 0.28 × 0.58 mm was sealed in a thin-walled glass capillary under argon. Only triclinic symmetry was found by Weissenberg photographs, diffractometer searches, and reduced cell calculations. The lattice constants derived from the Bragg angles of 48 reflections measured at 25°C with a Siemens AED 1 diffractometer employing Zr-filtered Mo-K_α radiation, λ(Mo-$K_{\bar{\alpha}}$) 0.71073 Å, are a 9.3665(8), b 9.9952(9), c 18.326(2) Å, α 93.827(8), β 85.687(8), γ 117.968(6)°. The density calculated for two molecules in this primitive unit cell is 1.118 g cm^{-3}.

Intensity data (hkl, $\bar{h}kl$, $h\bar{k}l$, $\bar{h}\bar{k}l$, $4 \leqslant 2\theta \leqslant 50^0$) were collected by the ω–2θ step scan technique. The number of steps (49–56, $\Delta\omega$ 0.02^0, 0.61 s/step) was so chosen that the peak was enclosed in the middle two-thirds of the scan range. If the first scan yielded an intensity between 2 and 25σ (I), then the measurement was repeated and the data were accumulated. The data were corrected for a slight drift (±1%) of three monitor reflections and converted to structure factor amplitudes. Of the 5285 unique reflections measured, only 4012 with $|F_0| \geqslant 4\sigma(|F_0|)$ were deemed observed and used in the refinement of the structure.

Structure solution and refinement

The structure was solved by multisolution direct methods (fourth-best E-map) and standard Fourier techniques. Except for H(1), the hydrogen atoms were placed

TABLE 4

POSITIONAL PARAMETERS FOR THE NONHYDROGEN ATOMS OF $(Ph_2P)_2CHLi \cdot TMEDA$ (I)

Atom	x	y	z	Atom	x	y	z
P(1)	0.48338(7)	0.15462(6)	0.74241(3)	C(14)	0.6984(3)	0.6045(2)	0.6665(1)
P(2)	0.63683(7)	0.48340(6)	0.74648(3)	C(15)	0.8036(3)	0.7599(3)	0.6716(1)
N(1)	0.9569(3)	0.3544(3)	0.6930(1)	C(16)	0.8631(4)	0.8439(3)	0.6093(2)
N(2)	0.9068(3)	0.2777(3)	0.8451(2)	C(17)	0.8181(4)	0.7763(4)	0.5414(2)
C(1)	0.4700(3)	0.3153(3)	0.7246(1)	C(18)	0.7143(4)	0.6237(4)	0.5350(2)
H(1)	0.383(3)	0.311(3)	0.713(1)	C(19)	0.6553(3)	0.5394(3)	0.5973(1)
C(2)	0.4270(3)	0.0237(2)	0.6619(1)	C(20)	0.5716(3)	0.5922(2)	0.8131(1)
C(3)	0.3361(3)	0.0281(3)	0.6072(1)	C(21)	0.5983(4)	0.5910(3)	0.8861(1)
C(4)	0.2954(4)	−0.0751(4)	0.5490(2)	C(22)	0.5424(5)	0.6616(4)	0.9397(2)
C(5)	0.3468(4)	−0.1841(3)	0.5443(2)	C(23)	0.4584(4)	0.7340(3)	0.9208(2)
C(6)	0.4391(4)	−0.1889(3)	0.5971(2)	C(24)	0.4316(4)	0.7376(3)	0.8500(2)
C(7)	0.4798(3)	−0.0858(3)	0.6553(1)	C(25)	0.4868(3)	0.6674(3)	0.7956(2)
C(8)	0.3119(3)	0.0418(2)	0.8060(1)	C(26)	1.0694(5)	0.5092(5)	0.6816(3)
C(9)	0.1750(3)	−0.0902(3)	0.7879(1)	C(27)	0.8896(5)	0.2812(5)	0.6237(2)
C(10)	0.0528(3)	−0.1673(3)	0.8401(2)	C(28)	1.0247(6)	0.2660(7)	0.7224(3)
C(11)	0.0652(4)	−0.1160(4)	0.9106(2)	C(29)	1.0526(6)	0.2965(7)	0.8016(3)
C(12)	0.1997(5)	0.0143(4)	0.9299(2)	C(30)	0.8045(6)	0.1220(5)	0.8672(3)
C(13)	0.3208(4)	0.0915(3)	0.8786(1)	C(31)	0.9596(7)	0.3764(6)	0.9116(3)
				Li	0.7819(5)	0.3276(5)	0.7719(2)

in ideal positions (C–H 0.95 Å, phenyl H's on external C–C–C bisectors and methyl groups tetrahedral and staggered), and were constrained to ride on the bonded carbon atoms and assigned group isotropic thermal parameters. Nonhydrogen atoms were refined anisotropically. Dispersion-corrected relativistic Hartree-Fock scattering factors were used for all atoms except H, SDS [17].

The structure was refined by large-block, least-squares methods with the program SHELX-76 [18]. Refinement of the 339 parameters converged, $|\zeta/\sigma|_{max} = 0.08$, with $R = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.046$ and $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2} = 0.060$ where the summations are taken over the observed reflections and $w^{-1} = \sigma^2(F_0) + 0.0004|F_0|^2$. These residuals are 0.065 and 0.063, respectively, for all reflections [19]. The final difference Fourier map, 0.36 to -0.21 e Å^{-3}, confirms the completeness of the structure. Corrections for absorption (μ(Mo-K_α) 1.6 cm^{-1}) and extinction were judged to be unnecessary. Positional parameters are listed in Tab. 4, and the numbering scheme is defined in Fig. 1 [20].

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