BIS(TRIMETHYLSILYL)PHOSPHIDOMETAL COMPLEXES

I. ISOLATION AND NMR SPECTRA OF $Li_4(\mu_2\text{-}PR_2)_2(\mu_3\text{-}PR_2)_2(THF)_2$ (I), $Li(PR_2)(PMDETA)$ (II), AND X-RAY STRUCTURES OF COMPOUND I AND $[Li(\mu\text{-}PR_2)(THF)_2]_2$ (III) (R = $SiMe_3$) *

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Summary

As shown by Fritz and Hölderich, treatment of tris(trimethylsilyl)phosphine (PR_3) with n-butyllithium in THF affords $[Li(\mu\text{-}PR_2)(THF)_2]_2$ (III), which slowly loses THF in vacuo to yield $Li_4(\mu_2\text{-}PR_2)_2(\mu_3\text{-}PR_2)_2(THF)_2$ (I). The reaction of the bis(trimethylsilyl)phosphidolithium complex III with N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA) in toluene gives $Li(PR_2)(PMDETA)$ (II). Multinuclear NMR data (^1H, ^{13}C, ^7Li, and ^{31}P) on complexes I–III were recorded; under ambient conditions there was no evidence for $^7Li\text{-}^{31}P$ coupling. The bis(trimethylsilyl)phosphide (I) has a fused tricyclic $(LiP)_4$ ladder skeleton. The Li atoms are three-coordinate, with each of the two terminal lithiums (Li_t) bound to two P's and one O (of THF), while the two internal lithiums (Li_i) have 3 P's as nearest neighbours; the internal phosphorus atoms (P_i) are five-coordinate (bonded to 2 Si's and 3 Li's), while each of the terminal phosphorus atoms (P_t) has the coordination number of four (bound to 2 Si's and 2 Li's). The Li–P bond lengths vary from 2.44(2) ($Li_i\text{-}P_t$) to 2.64(2) ($Li_i\text{-}P_i$) Å. The THF-rich complex III is centrosymmetric, with a $(LiP)_2$ rhomboid core, Li–P 2.62(2) Å, Li–P–Li' 80.0(7)° and P–Li–P' 100.0(8)°, each of the Li's and P's being four-coordinate, with ⟨Li–O⟩ 1.98(3) Å.

Introduction

Organic lithium compounds $(LiX)_x$ are of considerable importance as X^--transfer agents, for example to transition metal (M) sites to yield complexes $[MX_mL_n]$ (L_n represents the sum of all ligands, apart from mX^-s, within the inner coordination sphere of M). They are also often of structural and theoretical interest [1].

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* Dedicated to Professor G.E. Coates, with respect and affection, on the occasion of his 70th birthday.

Frequently there appears to be a correlation between structure and reactivity, with the smallest oligomers being the most reactive. The degree of molecular aggregation x is dependent on the nature of the ligating atom of X^-, the bulk of the ligand X^-, and the absence or presence of additional neutral ligands (L) such as tetrahydrofuran (THF), dimethoxyethane (DME), N,N,N',N'-tetramethylethylenediamine (TMEDA), or N,N,N',N',N''-pentamethyltriethylenediamine (PMDETA) (e.g. see ref. [2] for $X = N[SiMe_3]_2$).

We have previously drawn attention to some of the advantages that may accrue when using isolated crystalline lithium reagents, e.g., $LiR'(TMEDA)$ ($R' = CH(SiMe_3)_2$) [3], $[Li(\mu\text{-}OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)(OEt_2)]_2$ [4], $Li\{\eta\text{-}C_5H_4(SiMe_3)\}$-(TMEDA) [5], or $[Li(\mu\text{-}PR'_2)]_2$ [6], rather than solutions of such reagents prepared in situ. Of greatest significance is that such materials are readily purified by recrystallisation, and hence there is precise control of reagent purity and of the stoichiometry for a subsequent reaction.

Crystalline diorganophosphidolithium compounds have received relatively little attention, but X-ray structures have recently been reported on $Li_4(\mu_2\text{-}PBu^t_2)_2(\mu_3\text{-}PBu^t_2)_2(THF)_2$ (IV) [7], $[Li(12\text{-crown-}4)_2][PPh_2]$ (the anion is shown in V) [8], $[Li(\mu\text{-}PR'_2)]_2$ ($R' = CH(SiMe_3)_2$) (VI) [6], and $[Li(\mu\text{-}PR'_2)L]_\infty$ ($R' = Ph$, $L = OEt_2$ or THF; or $R' = c\text{-}C_6H_{11}$, $L = THF$) (VII–IX) [9]. In this paper we describe a new type of structure for the phosphide $LiPR_2$ ($R = SiMe_3$), which has not previously been observed. This consists of a dimeric arrangement with bridging $\overline{P}R_2$ ligands and four-coordinate lithium atoms, i.e. $[Li(\mu\text{-}PR_2)(THF)_2]_2$ (III) (Fig. 2). Moreover, we show that the same combination of lithium with $\overline{P}R_2$ and THF ligands

(IV , R' = Bu^t) (V) (VI , R' = CH(SiMe$_3$)$_2$)

(VII , R' = Ph , L = OEt$_2$;

VIII , R' = Ph , L = THF ;

IX , R' = c-C$_6$H$_{11}$, L = THF)

$$PR_3 \xrightarrow[\substack{X = Me, Bu^n, PHMe, \\ or\ PEt_2}]{LiX, L(-SiMe_3X)} Li(PR_2)(L)_n \xleftarrow[X = Me, Bu^n, or\ PHMe]{LiX, L(-XH)} PHR_2$$
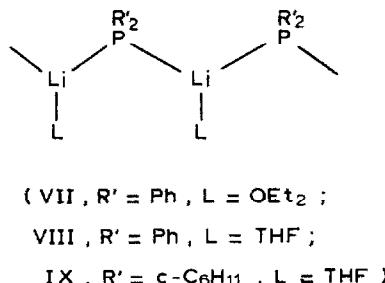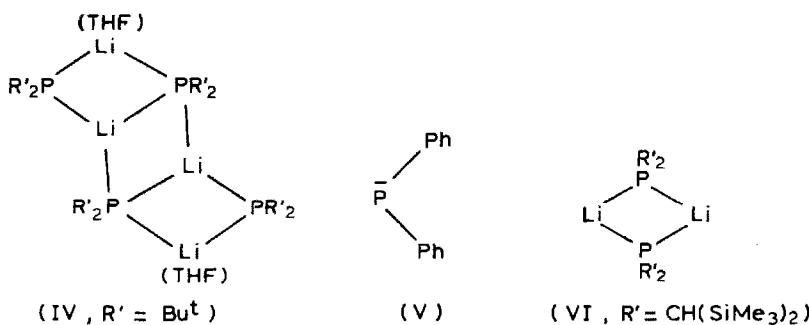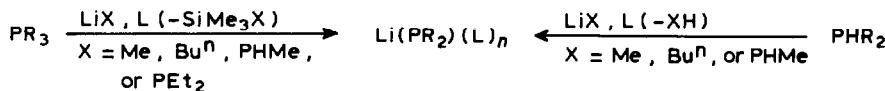
SCHEME 1. Routes to bis(trimethylsilyl)phosphidolithium complexes $Li(PR_2)(L)_n$ [11].

gives rise to a further X-ray-characterised complex $Li_4(\mu_2\text{-}PR_2)_2(\mu_3\text{-}PR_2)_2(THF)_2$ (I) (Fig. 1), which is structurally similar to the di-t-butylphosphidolithium compound IV. Compounds I and III appear to be the first example of a pair of crystalline X-ray-characterised compounds of type $[LiX(L)_n]_x$ [1]. The new complex $Li(PR_2)(PMDETA)$ (II) is believed to be a monomer, but X-ray data are not to hand (although single crystals were obtained). NMR data are available for $Li(PR'_2)(TMEDA)$ ($R' = CH(SiMe_3)_2$) and are consistent with a monomeric structure ($^7Li^{31}P$ coupling) [6].

The first bis(trimethylsilyl)phosphidolithium complex, $Li(PR_2)(DME)$, was prepared in 1974 from PH_2R, $Li(PHMe)$, and DME [10], but a more convenient general route, due to Fritz and Hölderich, depends on the cleavage of a P–Si bond of $P(SiMe_3)_3$ ($\equiv PR_3$), using a lithium-alkyl or -methylphosphide [11]. In this fashion, several bis(trimethylsilyl)phosphidolithium complexes $Li(PR_2)(L)_n$ have been obtained, while others were prepared from PHR_2, Scheme 1: $(L)_n \equiv (DME)$, $(diglyme)_{1.2-1.4}$, (triglyme), $(THF)_{0.5, 1.8, or\ 2.0}$, or $(OEt_2)_{0.5}$. Five of these compounds were isolated as crystals: $Li(PR_2)(L)_n$ (L_n = DME, triglyme, $(THF)_{1.8}$, $(THF)_2$, or $(OEt_2)_{0.5}$), while amorphous $Li(PR_2)$ was prepared from $PHR_2 + LiBu^n$ in $c\text{-}C_5H_{10}$ or C_5H_{12}. The value of n was determined by NMR measurements.

Silylphosphines have an interesting chemistry, and work-up to 1982 is described in a review by Fritz [12]. The compound $Li(PR_2)(THF)_{1.8\ or\ 2}$ has featured widely.
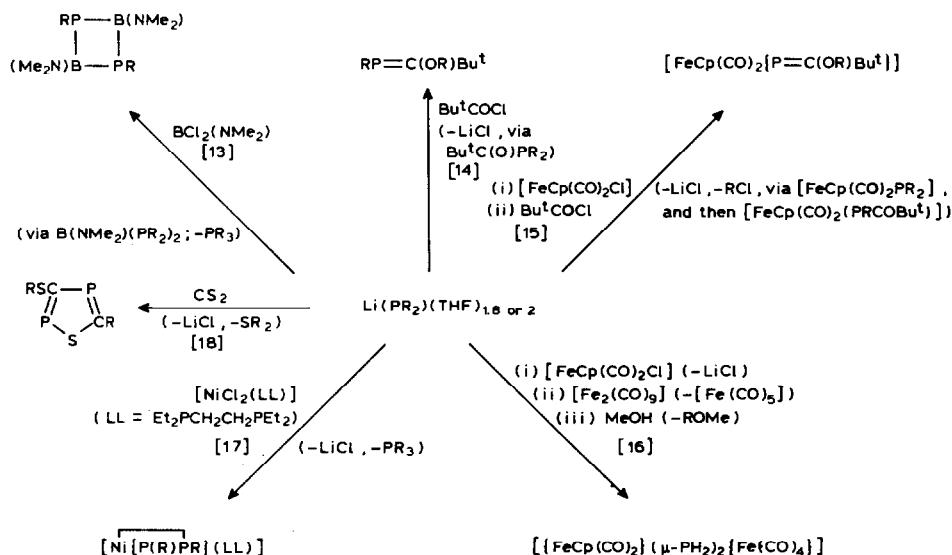
SCHEME 2. Some representative examples of $Li(PR_2)THF_{1.8\ or\ 2}$ reactions with metal or metalloid halides ($R = SiMe_3$).

The bis(trimethylsilyl)phosphido ligand $\bar{P}R_2$ is particularly noteworthy because of the possibility of facile loss of an $SiMe_3$ ($\equiv$ R) group, e.g., as RCl, PR_3, or ROMe. This versatility is illustrated by just a few selected examples in Scheme 2.

The objectives of the present series are further to explore the potential of the $\bar{P}(SiMe_3)_2$ ligand in both main group element and transition metal chemistry. In the present paper we consider principally the structures of some of the lithium bis(trimethylsilyl)phosphides. Thereafter, we shall describe inter alia their use in the synthesis of zirconocene(IV) complexes, such as $[ZrCp_2(PR_2)X]$ (X = Cl, Me, or PR_2), the structures of such Zr compounds, and a variety of their chemical reactions.

Results and discussion

1. Synthesis and characterisation of bis(trimethylsilyl)phosphidolithium complexes I–III

These compounds were made as shown in Scheme 3. The starting material was $P(SiMe_3)_3$, prepared according to the procedure of Becker and Hölderich [19]. The THF adducts I and III were obtained from PR_3 by minor modifications of recipes of Fritz and Hölderich [11]. Single crystals of X-ray quality were grown from n-pentane solutions for each of I–III. The PMDETA adduct II had m.p. 157–159°C.

NMR data for complexes I–III are listed in Table 1. For none was $^7Li-^{31}P$ coupling observed at ambient temperature, cf., ref. [6].

2. X-Ray structures of $Li_4(\mu_2-PR_2)_2(\mu_3-PR_2)_2(THF)_2$ (I) and $[Li(\mu-PR_2)(THF)_2]_2$ (III)

The molecular structures of complexes I and III and atom numbering schemes are illustrated in Figs. 1 and 2, respectively. Bond lengths and angles are in Tables 2 and 3. Some of the important structural parameters are placed in the context of other diorganophosphidolithium structures in Table 4. Atomic coordinates are in Tables 5 and 6. For each of I and III, the molecule lies on a crystallographic inversion centre. In I, the atoms of the $Li_4P_4O_2$ framework are coplanar to within 0.05 Å.
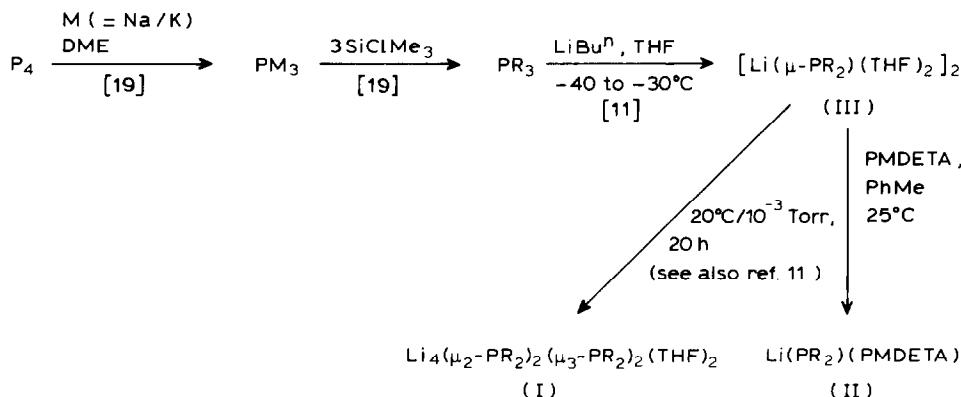
SCHEME 3. Synthesis of the bis(trimethylsilyl)phosphidolithium complexes I–III (R = $SiMe_3$).

TABLE 1

SOME NMR CHEMICAL SHIFTS (δ, ppm) AND COUPLING CONSTANTS (J, Hz) FOR THE BIS(TRIMETHYLSILYL)PHOSPHIDOLITHIUM COMPOUNDS I–III IN $C_6D_5CD_3$ AT ca. 30°C

Compound	^{1}H	^{13}C{^{1}H}	^{7}Li [b]	^{31}P{^{1}H} [a]
Li(PR$_2$)(THF)$_{1/2}$ (I)	0.62s (SiMe$_3$) 1.46 to 1.62, m ⎫ ⎬ (THF) 3.77 to 3.93, m ⎭	6.37 (SiMe$_3$) 24.22s and 68.22s (THF)	ca. 2.4br	−297.7s
Li(PR$_2$)(PMDETA) (II)	0.58d (SiMe$_3$) [c] 1.89s (CH$_2$) 2.11s (Me$_2$) and 2.17s (Me)	8.67d (SiMe$_3$) [d] 45.40 (Me) 57.21 (Me$_2$) 46.31 and 53.55 (CH$_2$)	0.80br [e]	−294.5s
Li(PR$_2$)(THF)$_2$ [f] (III)	0.54 and 0.58, d [g] (SiMe$_3$) 1.30 to 1.51, m ⎫ ⎬ (THF) 3.60 to 3.80, m ⎭	7.74 [h] 25.51s and 68.66s (THF)	1.14s	−297.6s

[a] Relative to 85% H_3PO_4. [b] Relative to aq. LiNO$_3$. [c] $^4J(^{31}P^1H)$ 3.42 Hz. [d] $^2J(^{31}P^{13}C)$ 10.4 Hz. [e] ^{6}Li 1.51 ppm. [f] NMR data for Li(PR$_2$)(THF)$_{1.8}$ from ref. 11 in PhMe: $\delta(^1H)$ 0.5 (SiMe$_3$) [$^3J(^{31}P^1H)$ 3.85 Hz]; $\delta(^{31}P)$ −297. [g] $^3J(^{31}P^1H)$ 5.91 Hz; [h] $^3J(^{31}P^1H)$ 10.4 Hz.

It is also of interest to consider the structure of the bis(trimethylsilyl)phosphido-lithium compounds I and III relative to those of the related picnogenides. Thus Li[N(SiMe$_3$)$_2$] exists as a cyclic trimer in the crystal, having a planar (LiN)$_3$ ring [20], whereas from diethyl ether the solvate is a dimer having three-coordinate
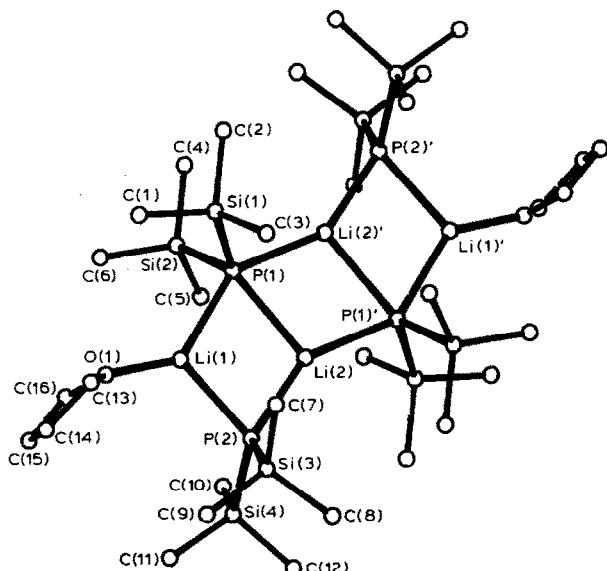

Fig. 1. The molecular structure and atom numbering scheme for Li$_4$(μ_2-PR$_2$)$_2$(μ_3-PR$_2$)$_2$(THF)$_2$ (I) (R = SiMe$_3$).

lithium, i.e., [Li{μ-N(SiMe$_3$)$_2$}(OEt$_2$)]$_2$ [2,21]. The X-ray structure of the compound [Li{μ-As(SiMe$_3$)$_2$}(DME)]$_2$ [22] is very similar to that of III, as is [Li{μ-SCH(SiMe$_3$)$_2$}(THF)$_2$]$_2$ [23]. The corresponding antimony [24] and bismuth [25] compounds, however, are chain polymers with alternate four-coordinate Li and Sb or Bi atoms. Attention has recently been drawn to "the laddering principle" in lithium amide chemistry, as in X where Y$^-$ is a cyclic amido ligand, illustrated by

TABLE 2

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES FOR Li$_4$(μ_2-PR$_2$)$_2$(μ_3-PR$_2$)$_2$(THF)$_2$ (I) (R = SiMe$_3$) [a]

Li(1)–P(1)	2.55(3)	Li(1)–P(2)	2.48(3)
Li(1)–O(1)	1.89(3)	Li(2)–P(1)	2.64(2)
Li(2)–P(1)′	2.54(2)	Li(2)–P(2)	2.44(2)
P(1)–Si(1)	2.203(6)	P(1)–Si(2)	2.222(6)
P(2)–Si(3)	2.206(6)	P(2)–Si(4)	2.216(6)
Si(1)–C(1)	1.91(2)	Si(1)–C(2)	1.87(3)
Si(1)–C(3)	1.85(2)	Si(2)–C(4)	1.91(2)
Si(2)–C(5)	1.96(3)	Si(2)–C(6)	1.87(2)
Si(3)–C(7)	1.81(2)	Si(3)–C(8)	1.92(2)
Si(3)–C(9)	1.94(2)	Si(4)–C(10)	1.83(2)
Si(4)–C(11)	1.89(3)	Si(4)–C(12)	1.90(3)
O(1)–C(13)	1.37(2)	O(1)–C(16)	1.33(2)
C(13)–C(14)	1.53(3)	C(14)–C(15)	1.46(3)
C(15)–C(16)	1.48(3)		
P(1)–Li(1)–P(2)	105.4(9)	P(1)–Li(1)–O(1)	135(2)
P(2)–Li(1)–O(1)	119(2)	P(1)–Li(2)–P(1)′	106.9(9)
P(1)–Li(2)–P(2)	104.0(7)	P(1)′–Li(2)–P(2)	149(1)
Li(1)–P(1)–Li(2)	72.9(8)	Li(1)–P(1)–Li(2)′	145.9(9)
Li(1)–P(1)–Si(1)	97.4(6)	Li(1)–P(1)–Si(2)	100.3(6)
Li(2)–P(1)–Li(2)′	73.1(8)	Li(2)–P(1)–Si(1)	124.5(5)
Li(2)–P(1)–Si(2)	128.9(5)	Li(2)′–P(1)–Si(1)	103.4(5)
Li(2)′–P(1)–Si(2)	99.2(6)	Si(1)–P(1)–Si(2)	106.5(3)
Li(1)–P(2)–Li(2)	77.6(8)	Li(1)–P(2)–Si(3)	113.7(6)
Li(1)–P(2)–Si(4)	114.8(6)	Li(2)–P(2)–Si(3)	120.6(5)
Li(2)–P(2)–Si(4)	119.1(5)	Si(3)–P(2)–Si(4)	108.2(3)
P(1)–Si(1)–C(1)	113.0(6)	P(1)–Si(1)–C(2)	117.8(7)
P(1)–Si(1)–C(3)	103.3(9)	C(1)–Si(1)–C(2)	101(1)
C(1)–Si(1)–C(3)	114(1)	C(2)–Si(1)–C(3)	108(1)
P(1)–Si(2)–C(4)	113.1(6)	P(1)–Si(2)–C(5)	102.1(9)
P(1)–Si(2)–C(6)	115.0(6)	C(4)–Si(2)–C(5)	111(1)
C(4)–Si(2)–C(6)	107(1)	C(5)–Si(2)–C(6)	109(1)
P(2)–Si(3)–C(7)	105.8(8)	P(2)–Si(3)–C(8)	112.9(5)
P(2)–Si(3)–C(9)	114.9(6)	C(7)–Si(3)–C(8)	109(1)
C(7)–Si(3)–C(9)	108(1)	C(8)–Si(3)–C(9)	105.5(9)
P(2)–Si(4)–C(10)	105.8(8)	P(2)–Si(4)–C(11)	114.1(7)
P(2)–Si(4)–C(12)	112.7(6)	C(10)–Si(4)–C(11)	110(1)
C(10)–Si(4)–C(12)	108(1)	C(11)–Si(4)–C(12)	106(1)
Li(1)–O(1)–C(13)	123(1)	Li(1)–O(1)–C(16)	125(1)
C(13)–O(1)–C(16)	109(1)	O(1)–C(13)–C(14)	104(2)
C(13)–C(14)–C(15)	111(2)	C(14)–C(15)–C(16)	97(2)
O(1)–C(16)–C(15)	116(2)		

[a] Symmetry element ′ is $-x$, $-y$, $-z$.
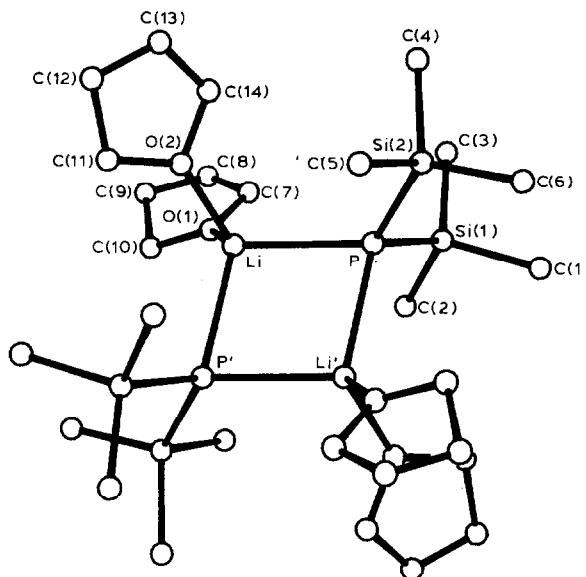
Fig. 2. The molecular structure and atom numbering scheme for [Li(μ-PR$_2$)(THF)$_2$]$_2$ (III) (R = SiMe$_3$).

the X-ray structure of [{H$_2$$\overline{\text{C(CH}_2)_3\text{N}}$Li}$_3$(PMDETA)]$_2$ [26]; compounds I and IV clearly have a similar skeletal structure. The dotted lines in X are reproduced from

(X)
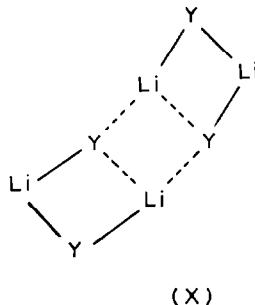
ref. [26], but in none of I, IV, or X are the Li $\cdots$ Y contacts significantly shorter than Li–Y.

The bis(trimethylsilyl)phosphides I and III represent rare examples of crystallographically characterised alkali metal phosphides in which the phosphorus atom does not possess directly P-bonded hydrocarbonyl substituents (cf., IV–IX). Another is [K(18-crown-6)][P(CN)$_2$] [27].

Experimental

Preparation of compounds I–III (see Scheme 3)

Tris(trimethylsilyl)phosphine was prepared as described in ref. 19. Compound III, [Li(μ-PR$_2$)(THF)$_2$], was obtained therefrom using the procedure of ref. 11. The conversion of III to Li$_4$(μ_2-PR$_2$)$_2$(μ_3-PR$_2$)$_2$(THF)$_2$ (I) was achieved by removal of

TABLE 3

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES FOR $[Li(\mu\text{-}PR_2)(THF)_2]_2$ (III) (R = SiMe$_3$) [a]

P–Si(1)	2.196(5)	P–Si(2)	2.194(6)
P–Li	2.62(2)	P–Li′	2.62(2)
Si(1)–C(1)	1.95(2)	Si(1)–C(2)	1.94(2)
Si(1)–C(3)	1.90(2)	Si(2)–C(4)	1.97(2)
Si(2)–C(5)	1.927(14)	Si(2)–C(6)	1.88(2)
O(1)–C(7)	1.40(2)	O(1)–C(10)	1.40(2)
O(1)–Li	2.03(3)	O(2)–C(11)	1.37(2)
O(2)–C(14)	1.42(2)	O(2)–Li	1.92(2)
C(7)–C(8)	1.31(3)	C(8)–C(9)	1.33(3)
C(9)–C(10)	1.51(3)	C(11)–C(12)	1.53(2)
C(12)–C(13)	1.39(3)	C(13)–C(14)	1.37(2)
Si(1)–P–Si(2)	104.7(2)	Si(1)–P–Li	120.3(5)
Si(1)–P–Li′	114.6(4)	Si(2)–P–Li	118.8(4)
Si(2)–P–Li′	117.8(5)	Li–P–Li′	80.0(7)
P–Si(1)–C(1)	112.4(6)	P–Si(1)–C(2)	107.3(5)
P–Si(1)–C(3)	114.3(5)	C(1)–Si(1)–C(2)	107.7(7)
C(1)–Si(1)–C(3)	106.5(8)	C(2)–Si(1)–C(3)	108.4(7)
P–Si(2)–C(4)	112.9(5)	P–Si(2)–C(5)	105.8(6)
P–Si(2)–C(6)	115.5(5)	C(4)–Si(2)–C(5)	107.0(7)
C(4)–Si(2)–C(6)	107.6(8)	C(5)–Si(2)–C(6)	107.7(8)
C(7)–O(1)–C(10)	106(1)	C(7)–O(1)–Li	127(1)
C(10)–O(1)–Li	127(1)	C(11)–O(2)–C(14)	108(1)
C(11)–O(2)–Li	128(1)	C(14)–O(2)–Li	123(1)
O(1)–C(7)–C(8)	107(2)	C(7)–C(8)–C(9)	115(2)
C(8)–C(9)–C(10)	101(2)	O(1)–C(10)–C(9)	103(2)
O(2)–C(11)–C(12)	107(1)	C(11)–C(12)–C(13)	105(1)
C(12)–C(13)–C(14)	110(2)	O(2)–C(14)–C(13)	109(2)
P–Li–P′	100.0(8)	P–Li–O(1)	112.5(9)
P–Li–O(2)	114(1)	P′–Li–O(1)	113.6(9)
P′–Li–O(2)	118.2(9)	O(1)–Li–O(2)	99(1)

[a] Symmetry element ′ is $1.5 - x, 0.5 - y, 1 - z$.

volatile tetrahydrofuran at reduced pressure (25°C at 10^{-1} mmHg) to constant weight (ca. 20 h).

The starting material for the synthesis of Li(PR$_2$)(PMDETA) (II) was compound III. Thus, N,N,N',N',N''-pentamethyldiethylenetriamine (2 ml) was added to III (0.9 g) in toluene (20 ml) at 25°C. The mixture was stirred for 10 min, whereafter volatiles were removed in vacuo. White crystals of II (0.70 g, 70%) were obtained by recrystallisation from toluene/pentane at −30°C. Found: C, 49.8; H, 11.7; N, 11.2. $C_{15}H_{41}N_3LiPSi_2$ calc: C, 50.4; H, 11.6; N, 11.7%.

X-Ray structure determinations

$Li_4(\mu_2\text{-}PR_2)_2(\mu_3\text{-}PR_2)_2(THF)_2$ *(I)*. Crystal data: $C_{32}H_{88}Li_4O_2P_4Si_8 \cdot C_4H_8O$, $M = 953.5$, monoclinic, space group $P2_1/n$, a 12.845(2), b 19.456(3), c 14.346(7) Å, β 108.00(3)°, U 3413.2 Å^3, $Z = 2$, D_c 0.93 g cm^{-3}. Monochromated Mo-K_α radiation, λ 0.71069 Å, μ 2.7 cm^{-1}.

Crystal size ca. $0.8 \times 0.6 \times 0.4$ mm, CAD4 diffractometer, θ–2θ mode. $\Delta\theta = (0.80 + 0.35 \tan \theta)°$, maximum scan time 1 min. 5329 total reflections measured for

TABLE 4

SELECTED BOND DISTANCES (Å) AND ANGLES (°) IN LITHIUM DIORGANOPHOSPHIDES [Li(PR′$_2$)(L)$_n$]$_x$

Compound	Li–P	Li–O	Li–P–Li	P–Li–P	Ref.
I	2.44(2)–2.64(2) [a]	1.89(3)	72.9(8), 73.1(8), 77.6(8), 145.9(9) [b]	104.0(7), 105.4(9), 106.9(9), 149(1) [b]	This work
III	2.62(2)	1.92(2), 2.03(3)	80.0(7)	100.0(8)	This work
IV	2.476(10)–2.669(9) [a]	1.923(10)			7
V	–	2.308(7)–2.487(6)	–	–	8
VI	2.456(9)–2.481(10)	–	72.0(3), 72.4(3)	107.5(3), 108.1(3)	6
VII	2.483(10)–2.496(10)	1.925(10), 1.966(1)	126.0(3), 136.9(4)	129.6(4), 139.6(4)	9
VIII	2.629(22), 2.634(21)	1.937(22), 1.988(22)	135.0(5)	123.1(8)	9
IX	2.455(9), 2.543(9)	1.936(8)	119.7(2)	145.6(3)	9

[a] Using the numbering scheme of Fig. 1, comparative bond lengths (Å) for the isostructural compounds I and IV (in parentheses) are Li(1)–P(1) 2.55(3) [2.595(10)], Li(1)–P(2) 2.48(3) [2.476(10)], Li(2)–P(1) 2.64(2) [2.669(9)], Li(2)–P(1)′ 2.54(2) [2.586(9)], and Li(2)–P(2) 2.44(2) [2.498(9)]. [b] Using the numbering scheme of Fig. 1 comparative bond angles (°) for compounds I and IV (in parentheses, where available) are Li(1)–P(1)–Li(2) 72.9(8), Li(2)–P(1)–Li(2)′ 73.1(8), Li(1)–P(2)–Li(2) 77.6(8), Li(1)–P(1)–Li(2)′ 145.9(9), P(1)–Li(1)–P(2) 105.4(9) [107.3(3)], P(1)–Li(2)–P(2) 104.0(7) [104.9(3)], P(1)–Li(2)–P(1)′ 106.9(9) [109.71(33)], P(1)′–Li(2)–P(2) 149(1) [145.46(39)].

TABLE 5

FINAL ATOM COORDINATES ($\times 10^4$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES FOR $Li_4(\mu_2\text{-}PR_2)_2(\mu_3\text{-}PR_2)_2(THF)_2$ (I) (R = SiMe$_3$) [a]

Atom	x	y	z
Li(1)	610(21)	1775(12)	-745(20)
Li(2)	636(18)	192(10)	-715(16)
P(1)	-224(3)	1026(2)	297(3)
P(2)	1449(3)	963(2)	-1637(3)
Si(1)	679(5)	1468(3)	1733(4)
Si(2)	-1905(4)	1459(3)	-109(4)
Si(3)	3243(4)	1064(3)	-1254(4)
Si(4)	750(5)	1000(3)	-3255(4)
O(1)	722(8)	2732(4)	-931(7)
C(1)	754(24)	2445(8)	1712(15)
C(2)	119(21)	1320(12)	2777(13)
C(3)	2029(17)	1040(17)	2038(19)
C(4)	-2626(13)	1289(11)	850(14)
C(5)	-2640(21)	972(17)	-1333(17)
C(6)	-1995(15)	2403(8)	-353(16)
C(7)	3748(17)	1092(13)	67(13)
C(8)	3909(13)	310(9)	-1714(14)
C(9)	3743(15)	1881(10)	-1758(17)
C(10)	-725(15)	883(14)	-3520(16)
C(11)	1040(24)	1826(13)	-3823(15)
C(12)	1283(17)	286(13)	-3886(13)
C(13)	1683(18)	3088(9)	-574(17)
C(14)	1632(19)	3615(11)	-1382(18)
C(15)	543(20)	3624(11)	-2104(17)
C(16)	37(18)	3100(10)	-1636(16)
C(17)	-1142(29)	5120(20)	-875(26)
C(18)	-1182(27)	4544(18)	-13(24)
C(19)	380(23)	4654(16)	794(21)
C(20)	666(22)	5134(17)	207(22)
C(21)	361(26)	5624(17)	-785(24)

[a] Atoms C(17) to C(21) have scattering factors of 0.8 C + 0.2 O and occupancies of 0.5.

$2 < \theta < 23°$, $+h + k \pm l$, 1771 unique reflections with $|F^2| > \sigma(F^2)$ used in the refinement, $\sigma(F^2) = (\sigma^2(I) + (0.04I)^2)^{1/2}/Lp$. No crystal decay. No absorption correction.

Structure solution and refinement involved routine direct methods. Full matrix least squares refinement was carried out, with all atoms anisotropic. A set of ten small peaks close to an inversion centre were assumed to be a distorted molecule of THF solvent and were included with half occupancy and averaged scattering factors. Hydrogen atoms could not be located and were not included. The weighting scheme was $w = 1/\sigma^2(F)$, with final residuals $R = 0.094$, $R' = 0.099$. A final difference map was everywhere < 0.5 eÅ^{-3}. Programs from the Enraf–Nonius SDP-Plus package were run on a PDP11/34 computer.

[Li(μ-PR$_2$)(THF)$_2$]$_2$ (III). Crystal data: $C_{28}H_{68}Li_2O_4P_2Si_4$, $M = 657.2$, monoclinic, space group $C2/c$, a 17.838(2), b 13.979(6), c 18.765(6) Å, β 109.53(3)°, U 4410.0 Å^3, $Z = 4$, D_c 0.99 g cm^{-3}. Monochromated Mo-K_α radiation, λ 0.71069 Å, μ 2.3 cm^{-1}.

TABLE 6

FINAL ATOM COORDINATES ($\times 10^4$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES FOR [Li(μ-PR$_2$)(THF)$_2$]$_2$ (III) (R = SiMe$_3$)

Atom	x	y	z
P	7713(2)	1090(3)	5119(2)
Si(1)	8383(2)	330(3)	6161(2)
Si(2)	7426(3)	−11(3)	4235(2)
O(1)	6384(5)	2335(7)	6106(4)
O(2)	5572(4)	2028(7)	4444(6)
C(1)	9362(8)	−242(12)	6107(10)
C(2)	8677(8)	1265(13)	6972(7)
C(3)	7809(10)	−670(12)	6431(8)
C(4)	6703(10)	−999(11)	4376(8)
C(5)	6870(10)	641(14)	3304(7)
C(6)	8304(9)	−638(12)	4107(8)
C(7)	6454(10)	1557(16)	6596(8)
C(8)	6002(11)	1737(15)	7004(9)
C(9)	5577(9)	2533(18)	6820(9)
C(10)	6027(10)	3067(13)	6388(10)
C(11)	4947(9)	2641(14)	4129(14)
C(12)	4241(10)	2023(14)	3676(12)
C(13)	4525(10)	1092(15)	3796(12)
C(14)	5262(11)	1080(15)	4340(15)
Li	6616(12)	2333(16)	5120(11)

Details of the structure analysis are the same as for I except for the following: crystal size $0.3 \times 0.3 \times 0.4$ mm, 4174 total reflections measured for $2 < \theta < 25°$, 1043 unique reflections with $|F^2| > \sigma(F^2)$. Final residuals were $R = 0.113$, $R' = 0.099$.

Lists of thermal parameters and structure factors are available from the authors.

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