Synthesis and Structures of Dilithium (1,2-Diphosphido)benzenes§

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Treatment of the appropriate (1,2-diphosphino)benzenes $C_6H_3(PHR)_2$-1,2-R′-4 (R′ = Me or H; R = H, Ph or $SiMe_3$) with $LiBu^n$ and tmen [tmen = $Me_2N(CH_2)_2NMe_2$] in hexane afforded the dilithium diphosphides $[Li(tmen)]_2[C_6H_3(PR)_2$-1,2-R′-4] (R′ = H, R = Ph **1**; R′ = H, R = $SiMe_3$ **2**; R′ = Me, R = Ph **3**; R′ = H = R **4**). Crystal structures of **1** and **2** show that each phosphorus atom is bonded equivalently to the two lithium atoms (and conversely each Li to the two P atoms), the two lithium atoms being on opposite sides of the $C_6H_4P_2$ plane. Solution multinuclear NMR spectral studies of the parent diphosphines, their dilithio-derivatives **1**–**3** and the phosphole **10** [of which $C_6H_4(PHSiMe_3)_2$-1,2 **6** and $C_6H_3(PHPh)_2$-1,2-Me-4 **7**, and the phosphole $C_6H_3[\{(PPh)_2\text{-}1,2\}PPh]$-Me-4 **10** and **1**–**3** are new compounds] have been carried out. The diphosphine $C_6H_4(PHPh)_2$ **5**, like **6** and **7**, was a *ca.* 1 : 1 mixture of diastereoisomers, **6** having a much larger (9.2 ppm) chemical shift difference between P and P′ than **5** (0.66 ppm). Virtual coupling from both phosphorus atoms was observed for the $SiMe_3$ ^1H, ^{13}C and ^{29}Si NMR signals of **6**. Variable-temperature ^{31}P-{^1H} and ^7Li-{^1H} NMR spectra for **1** and **2** revealed dynamic behaviour; the low-temperature limiting spectra for each of **1** and **2** showed septets [^{31}P-{^1H}] and triplets [^7Li-{^1H}], consistent with the structures of the crystalline molecules.

We have a long-standing interest in the synthesis, structure and reactivity of metal complexes of formally monoanionic ligands L^- which are bulky, free from β-hydrogen atoms, and are C-, N-, P-, As-, O- or S-centred.[1]

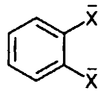
The conjugate acids HL of these ligands have been the starting point for much of their chemistry, and have been converted into crystalline lithium,[2] sodium,[3] rubidium,[3] magnesium,[4] calcium,[5] strontium[6] or thallium[7] derivatives. The latter, with or without a neutral co-ligand [*e.g.*, OEt_2, tetrahydrofuran (thf), $Me_2NCH_2CH_2NMe_2$ (tmen) or $NMe(CH_2CH_2NMe_2)_2$ (pmdeta)] have been characterized structurally and used as L^- ligand-transfer reagents to a wide range of metals and metalloids. The role of the co-ligand has been to increase the reactivity of the reagent, a consequence of lowering its state of molecular aggregation; for example, crystalline lithium bis(trimethylsilyl)amide is a cyclotrimer $[\{Li(\mu\text{-}NR_2)\}_3]$ (R = $SiMe_3$),[8] while dimeric or monomeric analogues are $[\{Li(\mu\text{-}NR_2)(OEt_2)\}_2]$[9] or $[Li(NR_2)(tmen)]$.[10]

Organolithium compounds are important as reagents;[11] their structures have also attracted much attention.[11,12] Lithium organophosphides are used in the preparation of organophosphines and of organophosphidometal complexes. Several crystalline lithium monoanionic phosphides have been structurally X-ray-characterized, including $[Li(12\text{-crown-}4)_2][PPh_2]$ (12-crown-4 = 1,4,7,10-tetraoxacyclododecane),[13] $[Li(PPh_2)L]$ (L = tmen or pmdeta),[14] $[Li\{P(PPh)_2C_6H_4\text{-}1,2\}(thf)_3]$ (thf = tetrahydrofuran),[15] $[\{Li(\mu\text{-}PR'_2)\}_2]$ [R′ = $CH(SiMe_3)_2$],[16] $[\{Li(\mu\text{-}PR_2)(thf)_2\}_2]$ (R = $SiMe_3$),[17] $[Li_4(\mu\text{-}PR'_2)_2(\mu^3\text{-}PR'_2)_2(thf)_2]$ (R′ = Bu^t[18] or $SiMe_3$[17]), $[\{Li(\mu\text{-}PR_2)(dme)\}_2]$ (dme = 1,2-dimethoxyethane)[19] $[\{Li(\mu\text{-}PR_2)\}_6]$,[20] $[\{Li(\mu\text{-}PR'_2)L\}_\infty]$ (R′ = Ph, L = OEt_2 or thf; or R′ = C_6H_{11}, L = thf),[21] $[Li(PHR)(tmen)(thf)]$ (R = $C_6H_2Me_3$-2,4,6),[22] $[Li(PHR)(thf)_3]$[23] $[\{Li(\mu\text{-}PR_2)(OEt_2)\}_2]$[23] and $[\{(LiR')[Li(PHR')]\}_2]$ (R′ = $C_6H_2Bu^t_3$-2,4,6).[24] The compound $[Li(tmen)_2][P(SiH_3)_2]$ has recently been described and characterized by X-ray crystallography.[25]

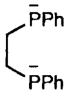
An extension has involved studies of metal complexes derived from the dianionic ligands $[L–L]^{2-}$ = **I**,[26,27] **II**,[27,28] **III**,[29] **IV**,[30,31] **V**[32] or **VI**.[33]

The objectives of this series are to explore the chemistry of metal and metalloid complexes derived from dianionic diphosphido ligands such as **IV**, **V** and **VI**. In the present paper the synthesis, NMR spectra and structures of (*a*) the dilithio complexes of **IV** and **VI** and of two derivatives: $[Li(tmen)]_2[C_6H_3(PR)_2$-1,2-R′-4] (R′ = H, R = Ph **1**; R′ = H, R = $SiMe_3$ **2**; R′ = Me, R = Ph **3**; R′ = H = R **4**], and (*b*) their diphosphine conjugate acids are described. In due course we shall report on (*i*) the use of **1** or **2** and their diphosphine conjugate acids, and (*ii*) the role of **1** or **2** as precursors to the chelate metal or metalloid complexes $[M\{(PR)_2C_6H_3\text{-}1,2\text{-}R'\text{-}4\}L]$ in which ML = $Zr(\eta\text{-}C_5H_5)_2$, BR′, SiR'_2, $SnMe_2$ or SnR'_2 [R′ = $CH(SiMe_3)_2$].

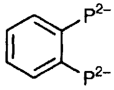
In preliminary communications we reported in outline on (*i*) the synthesis of compound **1** from $C_6H_4(PHR)_2$-1,2 + $2LiBu^n$ + 2tmen, (*ii*) selected NMR spectroscopic and



	X
I	CH_2
II	$CH(SiMe_3)$
III	$NSiMe_3$
IV	PPh
VI	$PSiMe_3$



V



VII

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Non-SI unit employed: mmHg ≈ 133 Pa.

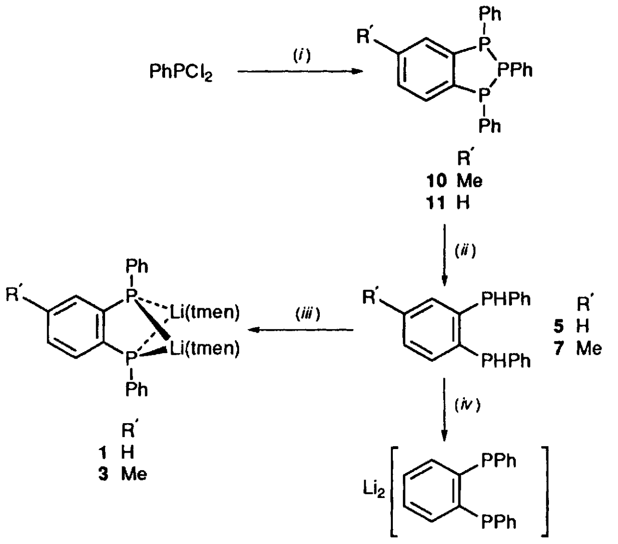
X-ray data for **1** and (*iii*) its reactions with 2SiClMe$_3$ or SnCl$_2$R''$_2$ [R'' = Me or CH(SiMe$_3$)$_2$].[30] Item (*iii*) was further elaborated to include the X-ray structure of $[\overline{\mathrm{Sn(L{-}L)}}\{\mathrm{CH(SiMe_3)_2}\}_2]$, $[\overline{\mathrm{Zr(L{-}L)}}\{\eta\text{-}\mathrm{C_5H_3(SiMe_3)_2\text{-}1,3}\}_2]$ and $[\overline{\mathrm{B(L{-}L)}}(\mathrm{C_6H_2Bu^t_3\text{-}2,4,6})]$ $\{[\mathrm{L{-}L}]^{2-} = \mathbf{IV}\}$.[31] Finally, we have recently briefly reported on the synthesis and reactions of [Li(tmen)]$_2$[C$_6$H$_4$(PR)$_2$-1,2] (R = SiMe$_3$) **2**, with (*a*) [Zr{η-C$_5$H$_3$(SiMe$_3$)$_2$-1,3}$_2$Cl$_2$] and (*b*) (–)-(*R*,*R*)-MeC(OCHCH$_2$OSO$_2$C$_6$H$_4$Me-*p*)$_2$ or SiBu^{t}Cl$_3$, showing that **2** was capable of behaving either as (*a*) a C$_6$H$_4$(PR)$_2$-1,2 (*cf.* **VI**) or (*b*) a C$_6$H$_4$(P^{2-})$_2$-1,2 (*cf.* **VII**) synthon.[33]

Results and Discussion

*Synthesis of the Dilithium (*1,2-*Diphosphido)benzene Compounds* **1**–**4**.—The preparation of the (1,2-diphosphido)benzenes C$_6$H$_3$(PHR)$_2$-1,2-R'-4 (R' = H, R = Ph **5**; R' = H, R = SiMe$_3$ **6**; R' = Me, R = Ph **7**; R' = R = H **8**) and C$_6$H$_4$[P(SiMe$_3$)$_2$]$_2$-1,2 **9** and the dilithium compounds **1**, **2**, **3** and **4** are summarized in Schemes 1 and 2. An alternative route (Scheme 3) for preparing **5** has been developed, although the yield was only moderate. Using a similar method to prepare **7** has not been successful. Of the diphosphines, only **6** and **7** are new compounds; **5**,[34,35] **8**,[36] and **9**[37] have previously been described. Metallation of **5**, **8** and **9** using LiBu^n in a polar solvent such as thf to yield the appropriate dilithium reagents for subsequent reactions has been reported;[34,36,37] however, these dilithium complexes were not isolated or fully characterized spectroscopically or structurally.

Metallation of each of the diphosphines **5**–**9** was carried out using LiBu^n in conjunction with *N*,*N*,*N*'*N*'-tetramethylethylenediamine (tmen) in hexane. These reactions afforded the crystalline tmen co-ordinated dilithiated complexes **1**–**4** in high yield.

The reaction of LiBu^n with **5** or **9** in hexane in the absence of tmen gave in each case a yellow, insoluble, pyrophoric solid, possibly of polymeric nature. The use of LiBu^n in conjunction with tmen has widespread application for direct metallation of various organic substrates.[11] As far as isolation of organic lithium compounds is concerned, LiX(tmen) complexes are often low-molecular weight aggregates, have good hydrocarbon solubility and are readily crystallized. The use of such pure, crystalline compounds enables their precise stoichiometry for further reaction to be controlled.



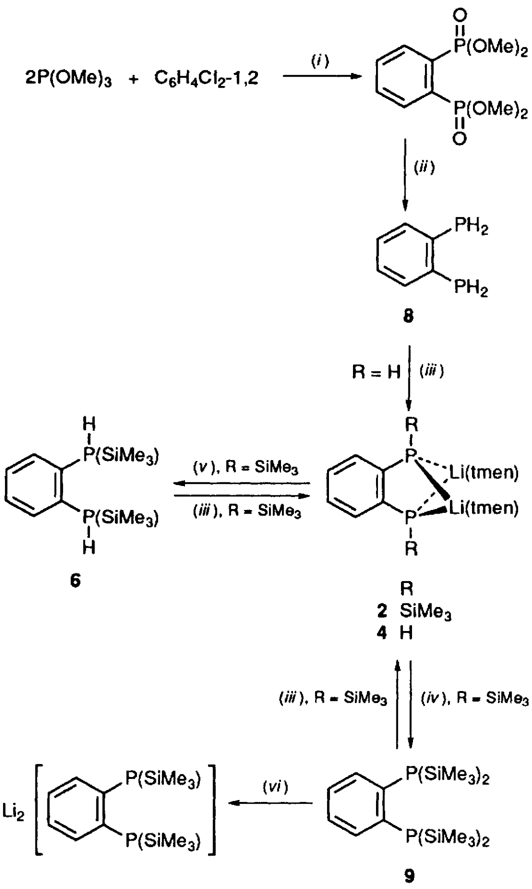
Scheme 1 Preparation and reactions of two diphosphines and a phosphole. *Reagents and conditions:* (*i*) (*a*) Li (excess), thf, –20 °C, (*b*) C$_6$H$_3$Cl$_2$-1,2-Me-4 or C$_6$H$_4$ClBr-1,2, thf; (*ii*) Li[AlH$_4$], thf, 25 °C, reflux for 2 h; (*iii*) 2 LiBu^n, 2 tmen, *n*-hexane, 0 °C; (*iv*) 2 LiBu^n, 2 tmen, *n*-hexane, 25 °C (R' = H)

Metallation of **9**, resulting in the cleavage of a P–Si bond resembles that of the lithiation of P(SiMe$_3$)$_3$.[38] An attempt to prepare **6** by treatment of **2** with HCl in diethyl ether was not successful, a mixture of diphosphines being obtained. The pure diphosphine **6** was prepared by treatment of **2** with an excess of water.

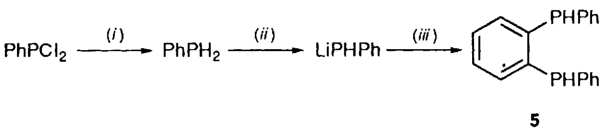
Yields and some physical properties of $\mathrm{C_6H_3\text{-}[\overline{\{(PPh)_2\text{-}1,2\}}PPh]\text{-}Me\text{-}4}$ **10**, the diphosphines **5**–**9** and the dilithium compounds **1**–**4** are shown in Tables 1 and 2, respectively.

Spectroscopic Characterisation of Compounds **1**–**10**.—The ^{1}H and ^{1}H-{^{31}P} NMR spectroscopic data for the diphosphines **5**–**9** and the phosphole **10** are summarised in Table 3; ^{31}P-{^{1}H} data are in Table 4.

The ^{31}P-{^{1}H} spectrum of the new phosphole **10** showed signals at δ 30.8 (d), 29.5 (d) and –40.3 (t), assigned to P$_A$ (or P$_B$), P$_B$ (or P$_A$) and P$_C$, respectively, with ^1J(P$_A$–P$_C$) = 259.4 Hz and ^1J(P$_B$–P$_C$) = 267.0 Hz. Coupling between P$_A$ and P$_B$ was not observed. The precise conformation of **10** is unknown, but in



Scheme 2 Preparation and reactions of dilithium diphosphides. *Reagents and conditions:* (*i*) *hv*, 60 °C; (*ii*) Li[AlH$_4$], SiMe$_3$Cl, thf, 20 °C; (*iii*) 2 LiBu^n, 2 tmen, *n*-hexane, 0 °C; (*iv*) SiMe$_3$Cl, *n*-hexane, 0 °C; (*v*) water, 20 °C; (*vi*) 2 LiBu^n, *n*-hexane, 20 °C



Scheme 3 An alternative route for the preparation of the diphosphinobenzene **5**. *Reagents and conditions:* (*i*) (*a*) Li (excess), thf, –20 °C, followed by (*b*) water, thf, –20 °C; (*ii*) LiBu^n, *n*-hexane, –20 °C; (*iii*) C$_6$H$_4$Cl$_2$-1,2, thf, 0 °C, then reflux for 2.5 h

Table 1 Yields, colours[a] and b.p.s for diphosphines **5**–**9** and the phosphole **10**

Compound	Yield (%)	B.p./°C (mmHg)
5 $C_6H_4(PHPh)_2\text{-}1,2$	40	170–174 (10^{-3})
6 $C_6H_4(PHSiMe_3)_2\text{-}1,2$	93	120–124 (10^{-2})
7 $C_6H_3(PHPh)_2\text{-}1,2\text{-Me-}4$	81	160–165 (10^{-2})
8 $C_6H_4(PH_2)_2\text{-}1,2$	79 (83)[b]	94–98 (7–10)
9 $C_6H_4[P(SiMe_3)_2]_2\text{-}1,2$	90 (94.5)[c]	132–136 (10^{-3})
10 $C_6H_3[\{(PPh)_2\text{-}1,2\}PPh]\text{-Me-}4$	9	*d*

[a] Compounds are colourless except for **9** which is pale yellow. [b] Ref 36. [c] Ref. 37. [d] M.p. 149–151 °C.

Table 2 Yields and colours for dilithium diphosphides and some reference compounds

Compound	Yield[a] (%)	Colour
1 $[Li(tmen)]_2[C_6H_4(PPh)_2\text{-}1,2]$	94[b]	Orange-yellow
2 $[Li(tmen)]_2[C_6H_4(PSiMe_3)_2\text{-}1,2]$	82–89	Orange-yellow
3 $[Li(tmen)]_2[MeC_6H_3(PPh)_2\text{-}1,2\text{-Me-}4]$	96	Orange-yellow
4 $[Li(tmen)_{1.5}]_2[C_6H_4(PH)_2\text{-}1,2]$	71	Yellow
$Li_2[C_6H_4(PSiMe_3)_2\text{-}1,2]$	94[c]	Yellow
$Li[PHPh]$	96[c]	Yellow

[a] Not optimised. [b] Not reported in ref. 30. [c] Insoluble in non-co-ordinating organic solvents; not characterised.

view of the similar values for $^1J(P_A\text{–}P_C)$ and $^1J(P_B\text{–}P_C)$, we assign it the structure **10a**.

The $^{31}P\text{-}\{^1H\}$ and $^1H\text{-}\{^{31}P\}$ NMR spectra of $C_6H_3(PHPh)_2\text{-}1,2\text{-Me-}4$ **7** showed it to be a mixture of *rac* diastereoisomers **7a** and **7b**. The $^{31}P\text{-}\{^1H\}$ NMR spectrum displayed two sets of AB quartets, Fig. 1, because for each of **7a** and **7b** the two phosphorus centres were chemically inequivalent. The ^1H NMR spectrum showed a complicated pattern in the PH region, coupling from two inequivalent phosphorus nuclei in the ABXY systems resulting in a second-order spectrum. The $^1H\text{-}\{^{31}P\}$ NMR spectrum showed four distinct PH protons: H_a, H_b, H_c and H_d.

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of the diphosphine $C_6H_4(PHSiMe_3)_2\text{-}1,2$ **6** gave two singlets of similar intensity, separated by 9.2 ppm, consistent with this being a 1 : 1 mixture of *meso*-(**6a**) and *rac*-(**6b**) isomers, Fig. 2(*a*) In contrast, for the phenyl analogue $C_6H_4(PHPh)_2\text{-}1,2$ **5**, the chemical shift difference was only 0.66 ppm. The ^{31}P NMR spectrum of **6** showed AA′XX′ patterns for each of **6a** and **6b**, the observed spectrum [Fig. 2(*b*)] being simulated using the PANIC program, Fig. 2(*c*). This revealed a major difference between **6a** and **6b**, the former having $^3J(PP') = 140.8$ Hz and the latter the much smaller value of *ca.* 20 Hz. The lone pairs on each phosphorus atom of **6a** are in close proximity, which we propose is the cause of the large $^3J(PP')$ value; whereas in **6b**, the lone pairs are in an *anti* relationship and hence the result is a smaller value for $^3J(PP')$.

The ^1H NMR spectrum of **6** also showed it to be a *ca.* 1 : 1 mixture of *meso* and *rac* diastereoisomers. Thus, the PH protons gave two doublets at δ 3.06 and 3.62, $^1J(^{31}P\text{–}^1H) = 220.7$ Hz, $^3J(^{31}P\text{–}^1H) = 140.8$ Hz, $^3J(P\text{–}P')$ (see above) being much smaller. Virtual coupling of proton to phosphorus was observed for the $SiMe_3$ signals, with an apparent triplet at δ 0.96 for **6a** [$^3J(P\text{–}P')$ (140.8 Hz) $\gg$ $\{^3J(PH) + {}^6J(P\text{–}H)\}$ (4.8 Hz)] and a multiplet at δ 0.05 for **6b** [$^3J(P\text{–}P') = 20$ Hz] of similar magnitude (4.8 Hz). Virtual coupling from both phosphorus atoms was also found in the ^{13}C and ^{29}Si NMR spectra of **6**, as summarized in Table 5.

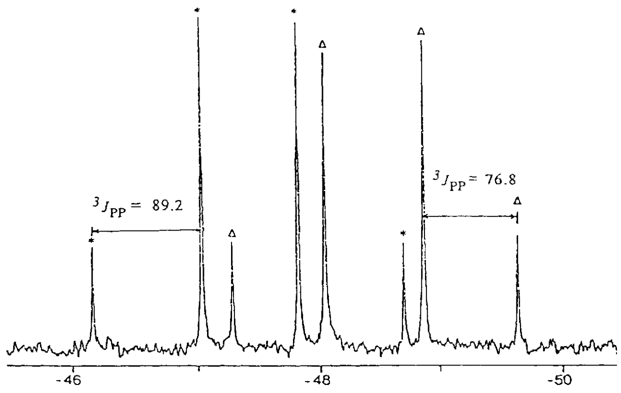
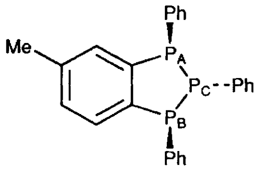
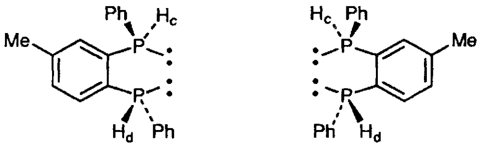


Fig. 1 The $^{31}P\text{-}\{^1H\}$ NMR spectrum of $C_6H_3(PHPh)_2\text{-}1,2\text{-Me-}4$ **7** (*) *rac*- and (Δ) *meso*-diastereoisomers



10a

7a



7b

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of $C_6H_4[P(SiMe_3)_2]_2\text{-}1,2$ **9** was previously reported as a broad singlet at δ −139.4.[37] However, we find a more complicated situation, observing ^{13}C and ^{29}Si satellites: $^1J(P\text{–}Si) = 25$ Hz, $^1J(P\text{–}C) = 14$ Hz and $^3J(P\text{–}P') = 65$ Hz. There was good agreement between the observed and computer simulated (PANIC program) spectra, Fig. 3.

Variable-temperature $^{31}P\text{-}\{^1H\}$ and ^7Li NMR spectroscopic data for $[Li(tmen)]_2[C_6H_4(PPh)_2\text{-}1,2]$ **1** and $[Li(tmen)]_2[C_6H_4(PSiMe_3)_2\text{-}1,2]$ **2**, together with ambient-temperature data for $[Li(tmen)]_2[C_6H_3(PPh)_2\text{-}1,2\text{-Me-}4]$ **3** and $[Li(tmen)]_2[C_6H_4(PH)_2\text{-}1,2]$,[39] are summarized in Table 6.

The $^{31}P\text{-}\{^1H\}$ spectrum of **2** showed a broad singlet at 303 K, which at 263 K was resolved into a 1 : 2 : 3 : 4 : 3 : 2 : 1 septet, due to coupling with two equivalent ^7Li ($I = \frac{3}{2}$) nuclei. The ^7Li NMR spectrum showed in its low-temperature limiting spectrum a 1 : 2 : 1 triplet, which coalesced at *ca.* 285 K to a broad singlet, Fig. 4. It is clear, therefore, that the low-temperature limiting structure of a toluene solution of **2** is identical to that found in the crystal, with each lithium atom bonded equivalently to each of the two phosphorus atoms, and conversely each phosphorus atom bonded symmetrically with respect to each of the two lithium atoms. At higher temperatures, fluxionality evidently sets in, presumably due to

Table 3 Proton and $^1H\text{-}\{^{31}P\}$ NMR spectroscopic data for some 1,2-diphosphinobenzenes and the benzotriphosphole **10**

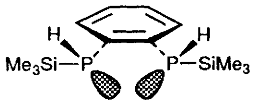
	δ^a			δ^a		
Compound	$SiMe_3/CH_3$	PH (^1H)	$^1J_{PH}$/Hz	PH ($^1H\text{-}\{^{31}P\}$)	Aromatics	Solvent
8 $C_6H_4(PH_2)_2$-1,2		3.84 (m, 4 H)		3.84 (s, 4 H)	6.88 (m, 2 H)	C_6D_6
					7.20 (m, 2 H)	
5 $C_6H_4(PHPh)$-1,2		5.15 (d, 1 H)	210			C_6D_6
		5.36 (d, 1 H)	210			
10 $C_6H_3[\{(PPh)_2\text{-}1,2\}PPh]$-Me-4	1.75 (s, 3 H)				6.8–7.7 (m, 19 H)	$(CD_3)_2CO$
7 $C_6H_3(PHPh)$-1,2-Me-4	1.74 (s, 3 H)	5.19 (m, 1 H)[b]		5.12 (s, 1 H)	6.60 (d, 1 H)	$C_6D_5CD_3$
				5.12 (s, 1 H)	6.78–7.82 (m, 12 H)	
		5.31 (m, 1 H)[c]		5.31 (s, 1 H)		
				5.32 (s, 1 H)		
6 $C_6H_4(PHSiMe_3)_2$-1,2	0.05 (m, 18 H)	3.06 (d, 2 H)[b]	220.7		6.79 (m, 2 H)	$C_6D_5CD_3$
					7.11 (m, 2 H)	
	0.96 (m, 18 H)	3.62 (d, 2 H)[c]	220.7		6.79 (m, 2 H)	
					7.17 (m, 2 H)	
9 $C_6H_4[P(SiMe_3)_2]_2$-1,2	0.31 (m, 36 H)				7.40–7.56 (m, 2 H)	C_6D_6
					7.80–7.98 (m, 2 H)	

[a] Referred to residual protonated solvent relative to $SiMe_4$, T = 298 K; frequency = 80 (for **10**) or 250 MHz. [b] (*RS*/*SR*) isomers. [c] (*RR*/*SS*) isomers.

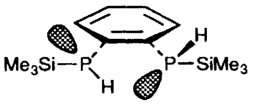
Table 4 $^{31}P\text{-}\{^1H\}$ NMR spectroscopic data for some diphosphines and benzotriphospholes

Compound	$\delta(RS/SR)^a$	$\delta(RR/SS)^a$	$^3J_{PP}$/Hz	Solvent	Ref.
8 $C_6H_4(PH_2)_2$-1,2	−120.1 (s)			C_6D_6	36
5 $C_6H_4(PHPh)_2$-1,2	−41.8 (s)	−42.4 (s)		C_6D_6	34, 35
11 $C_6H_4[\{(PPh)_2\text{-}1,2\}PPh]$	39.4 (t)		265 (^1J)		34
	−32.5 (d)		265 (^1J)		
10 $C_6H_3[\{(PPh)_2\text{-}1,2\}PPh]$-Me-4	30.8 (d)		259 (^1J)	$(CD_3)_2CO$	*b*
	29.5 (d)		267 (^1J)		
	−40.3 (t)		259, 267 (^1J)		
7 $C_6H_3(PHPh)_2$-1,2-Me-4	−46.9		89.2	$C_6D_5CD_3$	*b*
	−48.0				
		−47.8	76.8		
		−49.1			
6 $C_6H_4(PHSiMe_3)_2$-1,2	−115.1 (s/m[c])		140.8[c]	$C_6D_5CD_3$	*b*
		−124.3 (s/d[c])	20[c]		
9 $C_6H_4[P(SiMe_3)_2]_2$-1,2	−138.7[d]			C_6D_6	*b*

[a] Relative to external H_3PO_4, T = 298 K, frequency = 32.4 MHz (for **10**) or 101.256 MHz, and (*RS*/*SR*) and (*RR*/*SS*) only applies to those with $R \neq R'$. [b] This work. [c] Observed in the ^{31}P NMR spectrum; values obtained from computer simulation using the PANIC simulation program. [d] Ref. 37 δ −139.4.



6a



6b

site exchange of the two lithium centres. Variable-temperature data on **1** are broadly similar, the septet and triplet signals for $^{31}P\text{-}\{^1H\}$ and $^7Li\text{-}\{^1H\}$ being observed at the lower temperature of 203 K. In $[Li(tmen)]_2[C_6H_4(PH)_2\text{-}1,2]$ **4**, the corresponding spectra were not resolved, possibly because the site-exchange processes are faster (assuming that its solution structure is similar to that of **1** and **2**).[39]

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **3** in $[^2H_8]$toluene at ambient temperature showed a broad singlet at δ −49.2 (*cf.* δ −45.2 for **1**). It is likely, therefore, that **3** is structurally related to **1**.

The ^1H, ^{13}C and ^{29}Si NMR spectra of **2** showed virtual coupling of both phosphorus atoms to protons, carbons and silicon of the $SiMe_3$ groups, in each case as a pseudo-triplet, because $^3J(P\text{-}P') \gg {^3J}(P\text{-}H)$ (for ^1H NMR), $^3J(P\text{-}P') \gg {^2J}(P\text{-}C)$ (for ^{13}C NMR) and $^3J(P\text{-}P) \gg {^1J}(P\text{-}Si)$ (for ^{29}Si NMR). The data are summarized in Table 7.

X-Ray Molecular Structures of $[Li(tmen)]_2[C_6H_4(PR)_2\text{-}1,2]$ (R = Ph **1** *or* $SiMe_3$ **2**).—The molecular structure of crystalline **2**, with atom numbering scheme, is shown in Fig. 5. Selected intramolecular bond lengths and angles are shown in Table 8 and atomic coordinates in Table 9. X-Ray data for **1** have been published,[30] but the quality of the crystals was such that the state of refinement was low (see Experimental section); however, it is clear that the skeletal molecular structure of **1** is very similar to that of **2**.

The molecular structure of compound **2** shows that each lithium atom is bound almost equivalently to the two phosphorus atoms at 2.508(7) and 2.544(8) Å. The two lithium atoms are on opposite sides of the planar $C_6H_4P_2$-1,2 moiety. Thus, the overall configuration of crystalline **2** is similar to that in the quasi-isoelectronic compound $[Li(tmen)]_2[C_6H_4(CHSiMe_3)_2\text{-}1,2]$.[40] The Li–P distances are unexceptional, *cf.*, the average Li–P bond length of 2.56 Å in $[Li(thf)_2]_2[PPh(CH_2)_2PPh]$.[32] The Li–P–Li′ angles of 88.4(3) and 90.0(2)° in **2** are significantly narrower than those in **1**,[30] 103.4(9) and 102.0(9)°. As a consequence the dihedral angle between the PLiP planes is smaller in **2**, the four-co-ordination around each phosphorus being akin to a trigonal-bipyramidal fragment with a vacant axial site. The P–Li–P′ angles of 72(1)° in **1** are significantly narrower than the 76.9(2)° in **2**.

Table 5 Carbon-13 and ^{29}Si NMR spectroscopic data in [^{2}H$_8$]toluene and assignments for $C_6H_4(PHSiMe_3)_2$-1,2 **6**

	^{13}C[a]		^{29}Si[b]	
Assignment	δ	$^2J_{PC} + {}^5J_{PC}$ (Hz)	δ	$^1J_{PSi} + {}^4J_{PSi}$ (Hz)
SiMe$_3$	0.10 (t)	12.0	4.37 (t)	20.6
	0.47 (t)	12.4	4.65 (t)	20.6
Aromatics	124–138 (m)			

[a] Referred to solvent relative to SiMe$_4$, T = 298 K, frequency = 62.896 MHz. [b] Relative to external SiMe$_4$, T = 298 K, frequency = 49.697 MHz.

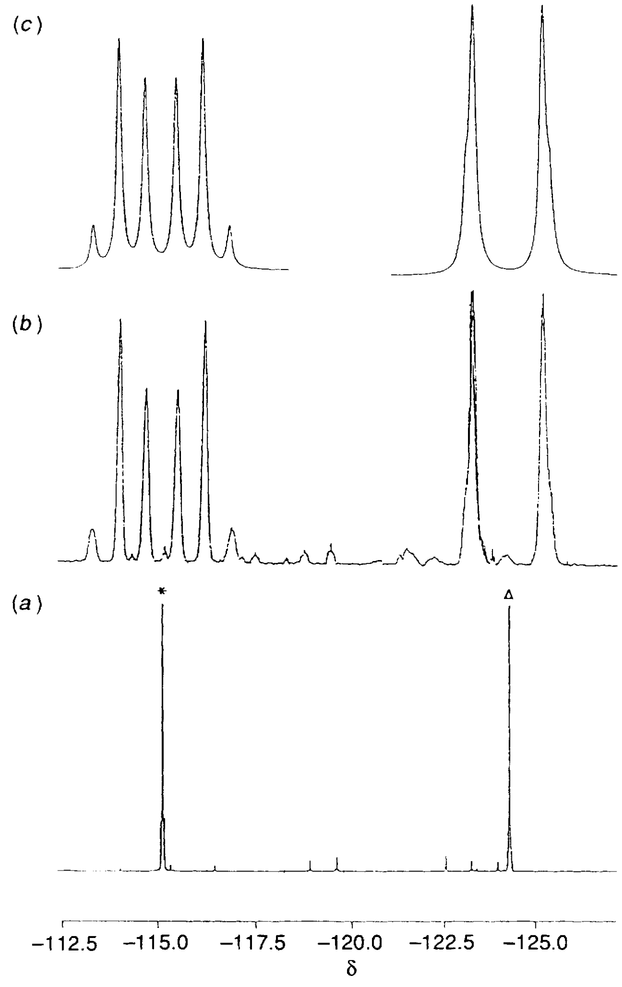


Fig. 2 The ^{31}P-{^{1}H} (*a*), ^{31}P (*b*) and computer simulated (*c*) ^{31}P NMR spectra of $C_6H_4(PHSiMe_3)_2$-1,2 **6** (*) *meso*- and (Δ) *rac*-diastereoisomers

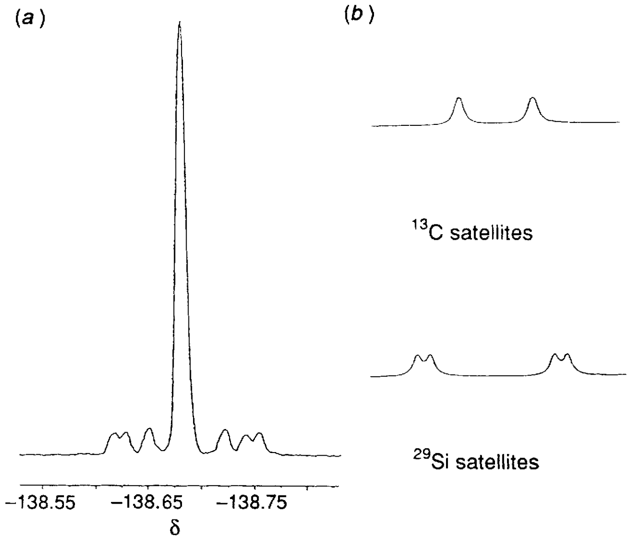


Fig. 3 The ^{31}P-{^{1}H} (*a*) and computer simulated (*b*) NMR spectra of $C_6H_4[P(SiMe_3)_2]_2$-1,2 **9**

Experimental

Manipulations, including rigorous drying of solvents, were carried out in an atmosphere of argon or dinitrogen, using standard Schlenk-tube and vacuum-line techniques. The NMR spectra were recorded on Bruker WP80, AC250 or WC360 instruments. The diphosphine preparations and reactions were carried out in well ventilated fumecupboards.

An Alternative Synthesis of $C_6H_4(PHPh)_2$-1,2 **5**.—A solution of LiBu^n in *n*-hexane (1.6 mol dm^{-3}, 58.0 cm^3, 92 mmol) was added dropwise to a solution of phenylphosphine (10.10 g, 92 mmol) in *n*-hexane (30 cm^3) at −20 °C. The yellow mixture was allowed to warm to 25 °C and was left stirring for 16 h. Solvent was removed *in vacuo* to yield a yellow solid, which was washed with *n*-hexane (2 × 20 cm^3), dried *in vacuo*, and dissolved in thf (80 cm^3). To this solution, $C_6H_4Cl_2$-1,2 (6.8 g, 46 mmol) in thf (20 cm^3) was added dropwise at 0 °C. The resulting mixture was allowed to warm to 25 °C and was refluxed for 2.5 h. Upon removing solvent *in vacuo*, a pale yellow, oily residue was obtained, which was extracted into *n*-hexane (3 × 50 cm^3). The extracts were filtered, combined, concentrated, and distilled to yield **5** (5.36 g, 37 mmol, 40%), as a colourless, viscous oil, b.p. 170–174 °C at 10^{-3} mmHg (lit.,[34] 175–176 °C at 10^{-2} mmHg).

Synthesis of $[Li(tmen)]_2[C_6H_4(PPh)_2$-1,2] **1**.—A solution of LiBu^n in *n*-hexane (1.6 mol dm^{-3}, 7.40 cm^3, 11.8 mmol) was added dropwise to a solution of **5** (1.58 g, 5.37 mmol) and tmen (1.37 g, 11.8 mmol) in *n*-hexane (100 cm^3) at 0 °C. An orange-yellow precipitate and a red oil were formed. The mixture was stirred at 25 °C until the red oil disappeared and was then kept at −30 °C for 16 h. The orange-yellow solid **1** (2.72 g, 5.05 mmol, 94%) was collected by filtration and dried *in vacuo*, m.p. 88–90 °C.

Synthesis of $C_6H_3(PHPh)_2$-1,2-Me-4 **7**.—Lithium aluminium hydride (0.86 g, 25.3 mmol) was added in portions to a suspension of $C_6H_3[\{(PPh)_2$-1,2$\}PPh]$-Me-4 **10** (3.10 g, 7.49 mmol) in dry thf (50 cm^3) in an ultrasound bath. A change from colourless to red was observed. The reaction mixture was refluxed for 2 h and then set aside for 16 h. Volatiles were removed to leave a paste to which diethyl ether (250 cm^3) and then deoxygenated dilute HCl (3 mol dm^{-3}, *ca.* 30 cm^3) were slowly added. The separated organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated. Distillation of the filtrate gave the clear, colourless oil **7** (1.77 g, 6.07 mmol, 81%), b.p. 160–165 °C (10^{-2} mmHg).

Synthesis of $[Li(tmen)]_2[C_6H_3(PPh)_2$-1,2-Me-4] **3**.—A solution of LiBu^n (1.6 mol dm^{-3}, 7.78 cm^3, 12.45 mmol) in *n*-

Table 6 The $^{31}P-\{^{1}H\}$ and ^{7}Li NMR spectroscopic data for some dilithium diphosphides in $[^{2}H_8]$toluene

	Compound	$\delta(^{31}P)^a$	$^{1}J_{PLi}$/Hz	$\delta(^{7}Li)^b$
	$[Li(tmen)_{1.5}]_2[C_6H_4(PH)_2$-1,2]^c	−126.5 (s) −127.3 (s) −127.5 (s) −128.4 (s)		1.09 (s)
1	$[Li(tmen)]_2[C_6H_4(PPh)_2$-1,2]^d	−45.2 (spt)^e	35/37	0.7 (t)^f
2	$[Li(tmen)]_2[C_6H_4(PSiMe_3)_2$-1,2]	−149.6 (spt)^g	38.3	6.7 (t)^f
3	$[Li(tmen)]_2[C_6H_3(PPh)_2$-1,2-Me-4]	−49.2 (s)		

^{a} Relative to external H_3PO_4, $T = 298$ K, unless otherwise stated; frequency = 101.256 MHz. ^{b} Relative to external LiBr, $T = 298$ K, unless otherwise stated; frequency = 97.206 MHz. ^{c} Ref. 39. ^{d} Ref. 30. ^{e} $T = 203$ K (this work). ^{f} $T = 298$ K (this work). ^{g} $T = 263$ K (this work).

Table 7 Proton, ^{13}C and ^{29}Si NMR spectroscopic data in $[^{2}H_8]$-toluene and assignments for $[Li(tmen)]_2[C_6H_4(PSiMe_3)_2$-1,2] **2**

Assignment	$\delta(^{1}H)^a$	$\delta(^{13}C)^b$	$\delta(^{29}Si)^c$
$SiMe_3$	0.69 (t, 18 H)^d	3.56 (t)^e	−5.62 (t)^f
NCH_2	1.84 (s, 8 H)	45.8 (s)	
NCH_3	2.04 (s, 24 H)	56.5 (s)	
Aromatics	6.9 (m, 2 H)	120 (s)	
	7.7 (m, 2 H)	130 (s)	
		151.2 (dd)^g	

^{a} Referred to residual protonated solvent relative to $SiMe_4$, $T = 298$ K; frequency = 250 MHz. ^{b} Referred to solvent relative to $SiMe_4$, $T = 298$ K; frequency = 62.896 MHz. ^{c} Relative to external $SiMe_4$, $T = 298$ K; frequency = 49.697 MHz. ^{d} $^{3}J_{PH} + {}^{6}J_{PH} = 4.8$ Hz. ^{e} $^{2}J_{PC} + {}^{5}J_{PC} = 14.5$ Hz. ^{f} $^{1}J_{PSi} + {}^{4}J_{PSi} = 7.1$ Hz. ^{g} $^{1}J_{PC} = 3.2$, $^{2}J_{PC} = 5.2$ Hz (assignments tentative).

Table 8 Selected intramolecular bond distances (Å) and angles (°) for $[Li(tmen)]_2[C_6H_4(PSiMe_3)_2$-1,2] **2** with estimated standard deviations (e.s.d.s) in parentheses*

Li–P(1)	2.508(7)	Li–P(2)	2.544(8)
Li–N(1)	2.100(9)	Li–N(2)	2.048(9)
P(1)–Si(1)	2.196(2)	P(1)–C(1)	1.837(6)
P(2)–Si(2)	2.199(2)	P(2)–C(2)	1.838(5)
P(1)–Li–P(2)	76.9(2)	P(1)–Li–N(1)	125.8(4)
P(1)–Li–N(2)	120.8(3)	P(2)–Li–N(1)	128.9(3)
P(2)–Li–N(2)	121.3(4)	N(1)–Li–N(2)	88.0(3)
Li–P(1)–Li′	90.0(2)	Li–P(1)–Si(1)	131.8(2)
Li–P(1)–C(1)	91.6(2)	Si(1)–P(1)–C(1)	107.2(2)
Li–P(2)–Li′	88.4(3)	Li–P(2)–Si(2)	133.1(2)
Li–P(2)–C(2)	90.5(2)	Si(2)–P(2)–C(2)	106.8(2)

* Primed atoms related to unprimed equivalents by *x*, 0.5 − *y*, *z*.

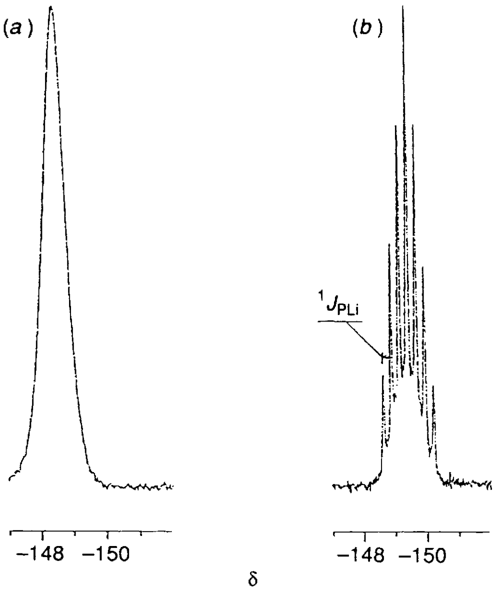


Fig. 4 The $^{31}P-\{^{1}H\}$ NMR spectra of $[Li(tmen)]_2[C_6H_4\{P(SiMe_3)_2$-1,2$\}]$ **2** at 303 (*a*) and 263 K (*b*)

hexane was added dropwise to a solution of **7** (1.76 g, 5.66 mmol) and tmen (1.45 g, 12.5 mmol) in *n*-hexane (150 cm^3) at −5 °C and an orange-yellow precipitate was formed. The reaction mixture was warmed to 25 °C and was stirred for a further 15 min. The orange solid was collected by filtration and dried *in vacuo* to give **3** (3.01 g, 5.43 mmol, 96%).

Synthesis of $C_6H_4[P(SiMe_3)_2]_2$-1,2 **9**.—A solution of LiBu^n in *n*-hexane (1.74 mol dm^{-3}, 96.3 cm^3, 167 mmol) was added to a solution of $C_6H_4(PH_2)_2$-1,2 (11.87 g, 83.5 mmol) in diethyl ether (250 cm^3) at −30 to −40 °C. The yellow reaction mixture was stirred for a further 0.5 h at −35 °C, to which $SiMe_3Cl$ (18.15 g, 167 mmol) was added at −40 °C. The white suspension was warmed to 25 °C and stirred for 1 h. A further portion of a solution of LiBu^n in *n*-hexane (1.735 mol dm^{-3}, 96.30 cm^3, 167 mmol) was added at −30 to − 40 °C and stirring was continued at −35 °C for 0.5 h and then $SiMe_3Cl$ (18.15 g, 167 mmol) was added at −40 °C. The resulting mixture was warmed to 25 °C and stirred for 1 h. Filtration through Celite gave a colourless filtrate from which volatiles were removed *in vacuo* to give a pale yellow oily residue. Distillation gave **9** (35.99 g, 75.2 mmol, 90%) (lit.,[37] 94%), a pale yellow oil, b.p. 132–136 °C (10^{-3} mmHg), which crystallized after 16 h at 25 °C.

Synthesis of $[Li(tmen)]_2[C_6H_4(PSiMe_3)_2$-1,2] **2**.—A solution of LiBu^n in *n*-hexane (1.74 mol dm^{-3}, 15.5 cm^3, 27.0 mmol) was added to a solution of **9** (5.53 g, 12.8 mmol) and tmen (3.13 g, 27.0 mmol) in *n*-hexane (150 cm^3) at 0 °C to yield a yellow mixture, which was stirred at 0 °C for a further 0.5 h, and then set aside at −30 °C for 16 h yielding yellow crystals. The mother-liquor was concentrated and collected at −30 °C to give a second fraction of these crystals. The two fractions were combined and dried *in vacuo* to give the yellow, crystalline **2** (5.7 g, 10.8 mmol, 84%).

Synthesis of $C_6H_4(PHSiMe_3)_2$-1,2 **6**.—Water (30 cm^3, an excess) was added to a suspension of **2** (4.25 g, 7.99 mmol) in *n*-hexane (30 cm^3) at 25 °C. The reaction mixture was shaken vigorously and two clear layers were obtained. Volatiles were removed *in vacuo* from the separated organic layer to give the colourless oil **6** (2.13 g, 7.43 mmol, 93%), b.p. 120–124 °C (10^{-2} mmHg) (with decomposition).

Crystallography.—Crystal data. $C_{30}H_{46}Li_2N_4P_2$, $M = 538.6$, monoclinic, space group $P2_1/n$ (non-standard no. 14), $a = 17.246(3)$, $b = 10.835(3)$, $c = 19.399(3)$ Å, $\beta = 109.22(5)°$, $U = 3423$ Å^3, $Z = 4$, $D_c = 1.05$ g cm^{-3}, $F(000) = 1160$. Monochromated Mo-Kα radiation, $\lambda = 0.710\,69$ Å, $\mu = 1.5$

Table 9 Fractional atomic coordinates (× 10^4) for compound **2** with e.s.d.s in parentheses

Atom	x	y	z
Li	2267(7)	3605(5)	3050(7)
P(1)	610(2)	2500	2136(1)
P(2)	2562(2)	2500	4701(1)
Si(1)	−1042(2)	2500	525(2)
Si(2)	3563(2)	2500	6630(2)
N(1)	3735(4)	4147(3)	2227(4)
N(2)	1628(4)	4785(2)	3338(4)
C(1)	−163(5)	2500	3469(4)
C(2)	734(5)	2500	4636(4)
C(3)	155(5)	2500	5647(5)
C(4)	−1219(5)	2500	5581(5)
C(5)	−2070(6)	2500	4458(5)
C(6)	−1533(5)	2500	3427(5)
C(7)	−173(9)	2500	−769(6)
C(8)	−2180(6)	3437(5)	356(5)
C(9)	5413(6)	2500	6618(6)
C(10)	3233(5)	3436(4)	7526(4)
C(11)	3586(6)	5031(4)	2484(7)
C(12)	2356(7)	5314(4)	2686(6)
C(13)	5117(6)	3892(4)	2771(7)
C(14)	3461(9)	3978(6)	957(6)
C(15)	1957(8)	4954(4)	4638(6)
C(16)	189(6)	4902(5)	2922(8)

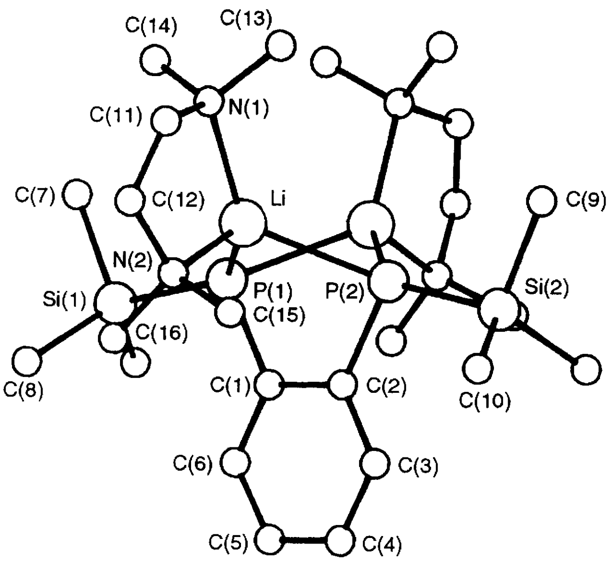


Fig. 5 The X-ray molecular structure of $[Li(tmen)]_2[C_6H_4\{P(SiMe_3)_2\text{-}1,2\}]$ **2** with the atom numbering scheme

cm^{-1}. Crystal size: 0.20 × 0.15 × 0.10 mm, mounted in a sealed capillary under argon.

$C_{24}H_{54}Li_2N_4P_2Si_2$ **2**, $M = 530.7$, monoclinic, space group $P2_1/m$ (no. 11), $a = 10.127(2)$, $b = 16.039(4)$, $c = 11.289(3)$ Å, $\beta = 102.19(2)°$, $U = 1792$ Å^3, $Z = 2$, $D_c = 0.98$ g cm^{-3}, $F(000) = 580$. Monochromated Mo-Kα radiation, $\lambda = 0.710\ 69$ Å, $\mu = 1.5$ cm^{-1}. Crystal size: 0.3 × 0.3 × 0.3 mm, mounted in a sealed capillary under argon.

Structure determination. For **1**. Data were measured on an Enraf-Nonius CAD4 diffractometer. Intensities for $h\ k \pm l$ reflections with $2 < \theta < 22°$ were measured by θ–2θ scans. Data were corrected for L_p effects but not for absorption and after averaging any equivalent reflections, 1362 reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement. The value of $\sigma(F^2)$ was taken as $[\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/L_p$. The structure was solved by direct methods (MULTAN[41]). Refinement of P, Li and N atoms with anisotropic thermal parameters and the carbon atoms with isotropic thermal parameters was by full-matrix least squares. Hydrogen atoms were omitted. Refinement converged at $R = 0.127$, $R' = 0.120$ when the maximum shift/error was 0.003 and the weighting scheme $w = 1/\sigma^2(F)$. A final difference map was everywhere < 0.5 e Å^{-3}.

For **2**. Data were measured on an Enraf-Nonius CAD4 diffractometer. Intensities for $h\ k \pm l$ reflections with $2 < \theta < 25°$ were measured by θ–2θ scans. A total of 1306 unique reflections with $|F^2| > 3\sigma(F^2)$, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/L_p$, was used in the refinement. There was no correction for absorption. The structure was solved by direct methods (SHELXS 86).[42] Non-hydrogen atoms were refined anisotropically by full-matrix least squares using programs from the Enraf-Nonius SDP-Plus package.[43] Hydrogen atoms were held fixed at calculated positions with $U_{iso} = 1.3\ U_{eq}$ for the atom to which they are bonded. With a weighting scheme of $w = 1/\sigma^2(F)$, the refinement converged at $R = 0.044$, $R' = 0.053$, and with $S = 1.4$, $(\Delta/\sigma)_{max} = 0.01$, $\Delta\rho_{max,min} = 0.16, -0.16$ e Å^{-3} in a final difference map.

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