Synthesis of α-, γ-Phosphorus Functionalized Alkyl Lithium Species; *X*-Ray Structures of $[\{Li(L)(CH_2PMeR)\}_2]$ [L = *NNN'N'*-tetramethylethylenediamine (tmen), R = Me or Ph; L = (−)sparteine, R = Ph] and $[Li(tmen)\{CH(SiMe_3)C_6H_4PPh_2\text{-}o\}]$ ‡

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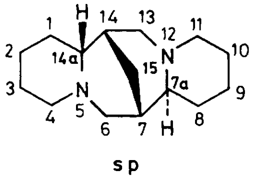
$[\{Li(L)(CH_2PMeR)\}_2]$ [L = tetramethylethylenediamine (tmen), R = Me (**1**) or Ph (**2**); L = (−)-sparteine (sp), R = Ph (**3**)], prepared by treating the appropriate phosphine with $LiBu^n(L)$ in hexane or diethyl ether, are dimeric in the solid. The phosphinomethyl ligands bridge the two lithium atoms as part of six-atom heterocycles; Li–C,P 2.14_5, 2.60_4; 2.1_4, 2.6_4; 2.2_0, 2.7_2 Å, respectively; (**2**) and (**3**) are homochiral and thus have a *meso* configuration. In benzene (**1**), (**2**), and $[Li(tmen)(CH_2PPh_2)]$ (**5**), are monomeric (cryoscopy), and ^7Li–^{31}P coupling only below *ca.* −70 °C for (**1**)—(**3**) and (**5**) in toluene (1 : 1 doublet, ^7Li; 1 : 1 : 1 : 1 quartet, ^{31}P, J_{LiP} 44.0—53.4 Hz) is consistent with the presence of symmetrical dimers of the type found in the solid for (**1**)—(**3**). $[Li(tmen)\{CH(SiMe_3)C_6H_4PPh_2\text{-}o\}]$, (**4**), similarly prepared, has the lithium as part of a chelate ring in the solid, binding through the *ipso* carbon and P^{III} centre; Li–C,P 2.25(1), 2.65(1) Å. Trilithio species based on $P(C_6H_4CHR^-)_3$ (R = H or $SiMe_3$) are generated *via* metallation using $LiBu^n(tmen)$. Treating the monolithio species derived from $P(O)Me_2Ph$ and $LiBu^n(sp)$ with EtI yields $P(O)MePhPr^n$ of 14% estimated optical purity.

Phosphorus(III) functionalized alkyl ligands form a diverse range of metal complexes possessing unusual properties. Our interests centre on zirconium(III,IV) chemistry,[1,2] and complexes of lithium[2] which is the theme of this paper. Lithium to phosphorus(III) bonding forms only when the P centre is part of an anionic group as in phosphides and related species,[3,4] P^{III} functionalized alkoxides[5] and alkyls,[2,4,6,7] and anionic phosphines, *e.g.* $PPh_2CHPPh_2^-$ (ref. 8) and $(PMe_2CH_2)_2AlMe_2^-$ and $PMe_2CH_2AlMe_3^-$ (ref. 9).

While the metallation of PMeRR′[10] (R = R′ = H, R = R′ = Ph, and R = H, R′ = Ph) using various lithium reagents is well documented[11,12] little is known about the nature of the products. Herein we report the structural characterization (*X*-ray) of $[\{Li(tmen)(CH_2PMe_2)\}_2]$ (**1**) (tmen = *NNN′N′*-tetramethylethylenediamine), previously reported briefly,[2] and $[\{Li(L)(CH_2PMePh)\}_2]$ [L = tmen (**2**) or (−)sparteine (sp) (**3**)], and molecular weight determination and variable-temperature ^7Li and ^{31}P n.m.r. on (**1**), (**2**), and the related compound $[\{Li(tmen)(CH_2PPh_2)\}_2]$ (**5**). Sparteine and its I.U.P.A.C. numbering scheme (as a dodecahydromethanodipyridodiazocine) is shown below.



sp

As part of a general study on phosphorus functionalized alkyls we also include (*i*) the synthesis, *via* metallation, and structure of $[Li(tmen)\{CH(SiMe_3)C_6H_4PPh_2\text{-}o\}]$ (**4**), undertaken to determine the effect of positioning phosphorus γ rather than α to the *ipso* carbon, and because of the general interest in the structures of organolithium species[13,14]; (*ii*) the trimetallation of $P(C_6H_4CH_2R\text{-}o)_3$ (R = H or $SiMe_3$); and (*iii*) an investigation of asymmetric monometallation of $P(O)Me_2Ph$ using $LiBu^n(sp)$. To our knowledge lithiation using this reagent is restricted to dilithiation of an amino-substituted ferrocene (3% optical yield)[15] and 2,2′,6,6′-tetramethylbiphenyl (40% optical yield),[16] although there are several complexation studies of sp with organolithium reagents.[17]

Carbanions can be useful synthetically in a variety of ways. Notable examples akin to the present study include: reagents (**1**) and (**5**) with $O{=}CBu^t_2$ yield directly the hindered alkoxide lithium complexes $[\{Li(\mu\text{-}OCBu^t_2CH_2PRR')\}_2]$;[5] and (**1**)—(**4**) and related complexes, *e.g.* $[\{Li(tmen)\}\{CH_2C_6H_4PPh_2\text{-}o\}]$,[18] are useful alkyl transfer reagents for the synthesis of Main Group derivatives[9,10,19] and transition-metal complexes.[1,2,20]

Results and Discussion

Syntheses.—Monolithiations of PMeRR′ (R = R′ = Ph; R = Me, R′ = Ph) in high yield using $LiBu^n(tmen)$ are documented but not data on the derived products [equation (1)];[12] these are included herein. The corresponding metallation of PMe_3 using the same reagent is new; the product, (**1**), was isolated in 89% yield as a colourless crystalline solid which has high hydrocarbon solubility. Other methods of lithiation of PMe_3 include the use of $LiBu^t$, and $LiBu^n$ in diethyl ether where the phosphine is bound to nickel.[21] Treatment of PMe_2Ph with $LiBu^n(sp)$ in diethyl ether, rather than hexane because of solubility problems, yielded (**3**), as a colourless solid although in modest yield, *ca.* 40%.

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‡ (Dimethyl- or methylphenyl-phosphinomethyl)(*NNN′N′*-tetramethylethylenediamine)lithium, (methylphenylphosphinomethyl)[(−)-sparteine]lithium, and [*o*-diphenylphosphinophenyl(trimethylsilyl)-methyl](*NNN′N′*-tetramethylethylenediamine)lithium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii–xx.

$$\mathrm{PMeRR' + LiBu^n(L) \xrightarrow{-\text{butane}} \tfrac{1}{2}[\{Li(L)(CH_2PRR')\}_2]} \quad (1)$$

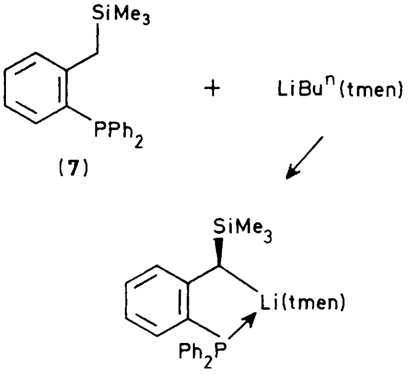
$$\mathrm{L = tmen}$$

$$\mathrm{R = R' = Me\ (1),\ R = Me,\ R' = Ph\ (2),\ R = R' = Ph\ (5)}$$

$$\mathrm{L = sp}$$

$$\mathrm{R = Me,\ R' = Ph\ (3)}$$

Metallation of $MeC_6H_4PPh_2$-*o* using $LiBu^n(tmen)$ has also been reported but the product $[Li(tmen)(CH_2C_6H_4PPh_2$-*o*$)]$, (**6**), was not characterized.[18] Quenching with $SiMe_3Cl$ gave $CH_2(SiMe_3)C_6H_4PPh_2$-*o*, (**7**), which rapidly deprotonated with the same metallating reagent yielding (**4**), equation (2).



(7)

(4)

(2)

The above organolithium compounds were isolated as crystalline solids and characterized using ^1H, ^{13}C, ^7Li, and ^{31}P n.m.r. spectroscopy, cryoscopy, *X*-ray structure determinations for (**1**)—(**4**) (see below), and for (**4**) and (**6**) by the formation of $SiMe_3Cl$ derivatives, *viz.* $CH(SiMe_3)_2C_6H_4PPh_2$-*o* (**8**) and $CH_2(SiMe_3)C_6H_4PPh_2$-*o* (**7**), respectively [equation (2)].

Treatment of $P(C_6H_4Me$-*o*$)_3$ with *ca.* 3.3 mol equivalents of $LiBu^n(tmen)$ gave a red viscous oil which failed to crystallize and accordingly was treated with $SiMe_3Cl$ yielding $P(C_6H_4CH_2SiMe_3$-*o*$)_3$ (**9**), isolated in 76% yield thus demonstrating the formation of tricarbanions [equation (3)]. Compound (**9**) also gave tricarbanions under the same conditions, which is not surprising given the expected increase in thermodynamic acidity of the methyl group on attaching polarizing silicon centres. Again a red oil was obtained. This yielded the corresponding hexakis(trimethylsilyl) compound, $P[C_6H_4CH(SiMe_3)_2$-*o*$]_3$, (**10**), on treatment with $SiMe_3Cl$ in *ca.* 62% yield [equation (3)]. The facile generation of tricarbanions is noteworthy; there are only a few of them (or higher charged carbanions) in the literature and reagents more reactive than $LiBu^n(tmen)$ are usually required, *e.g.* $LiBu^n$–$KOBu^t$ (ref. 22). Compounds (**7**)—(**10**) have potential as highly hindered phosphines. They were characterized using n.m.r. spectroscopy; for (**8**) and (**10**) the unique methine proton resonance appears as a doublet (J_{PH} 7 Hz), probably *via* coupling to phosphorus. The steric crowding forces this proton into close proximity to the P^{III} centre.

$$\mathrm{P(C_6H_4CH_2R\text{-}\mathit{o})_3 + 3.3LiBu^n(tmen) \longrightarrow P(C_6H_4CHRLi\text{-}\mathit{o})_3} \quad (3)$$

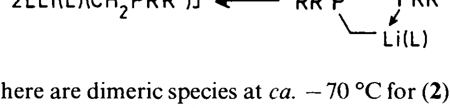
$$\mathrm{R = H\ or\ SiMe_3}$$

Selective asymmetric $-CH_3$ metallation of PMe_2Ph using $LiBu^n(sp)$ is possible, especially noting that the product, (**3**), in the solid is comprised of homochiral dimers. We sought unsuccessfully to explore this by treating (**3**) with various electrophiles. However, the corresponding phosphine oxide, (**11**), prepared in the same way met with some success; treatment of (**11**) with EtI yielded $P(O)MePhPr^i$ [equation (4)] in good yield, optical purity *ca.* 14% based on an optical rotatory power of $-2.9°$, *cf.* -21.2 for 100% optical purity.[23]

$$\mathrm{P(O)Me_2Ph \xrightarrow{LiBu^n(sp)} \underset{(\mathbf{11})}{[Li(sp)\{CH_2P(O)MePh\}]} \xrightarrow{EtI} P(O)MePhPr^i} \quad (4)$$

Solution Structures.—In the solid (**1**) and (**2**) [and (**3**)] are dimeric and adopt either chair or boat conformations (see below), but in benzene at *ca.* 5 °C and *ca.* 0.5 mol dm^{-3} they and (**5**) are monomeric (cryoscopy). At this temperature no ^7Li–^{31}P coupling was evident which suggests that the monomeric species present possess lithium bound to only the *ipso* carbon of the hydrocarbyl group and they are co-ordinatively unsaturated. It is noteworthy that the *ipso*-carbon protons in (**1**)—(**3**) and (**5**) couple to phosphorus, but not to Li as in (**4**) and (**11**) which is typical of organolithium species,[24] and the ^7Li chemical shifts[25] and associated relaxation times, T_1[24,26] (measured by the inversion–recovery pulse method),[27] are in the range established for a variety of organolithium reagents.

^7Li–^{31}P coupling in (**1**)—(**3**) and (**5**) was only present below *ca.* -70 °C, with each lithium coupled to one phosphorus centre (1:1 doublet) and *vice versa* (1:1:1:1 quartet), the J_{LiP} values being 53.4, 49.3, 44.0, and 47.3 Hz respectively which are within the limits found for a variety of compounds.[3a,28] The coupling supports the presence of dimers with Li–P bonding, presumably *via* association as in the solid state. A feature of the ^7Li n.m.r. spectra is that there is no simple coalescence pattern; lowering the temperature results in reduction in peak height as the doublet starts to appear. This is consistent with a temperature-dependent equilibrium between monomeric and dimeric species, equation (5), with lower temperatures favouring dimer formation.



(5)

If there are dimeric species at *ca.* -70 °C for (**2**), and (**3**), then only one of two possible isomers are present, most likely the same as in the solid, *viz.* where the two P^{III} centres in each molecule have the same chirality. The relative order of J_{LiP} and ^{31}P chemical shifts reflect the Lewis basicity of the P^{III} centres, (**1**) > (**2**) > (**5**), as do the Li–P distances in (**1**) and (**2**), see below.

X-*Ray Structures.*—Results of the structure determinations of (**1**)—(**4**) are given in Tables 1—7 and Figures 1—4. Complexes (**1**) and (**3**) are dimeric with the $-CH_2PRR'$ moieties bridging successive lithium centres through the *ipso* carbon and P^{III} atoms as part of six-atom heterocycles [equation (5)]. The asymmetric units comprise two halves of two independent molecules in (**1**) and (**3**), the other halves being generated by inversion centres and two-fold axes respectively, or a complete dimer in (**2**) of approximate C_2 symmetry. Compound (**4**) crystallizes as discrete molecules in which the carbanion group acts as a chelate through the *ipso* carbon and the P^{III} centres, the asymmetric unit being one molecule. One OEt_2 molecule of crystallization per dimer is found in (**3**) and is rapidly lost *in vacuo*.

The lithium environments in all four compounds are tetrahedral as is common for a variety of organolithium reagents. While (**1**)—(**3**) are similarly dimeric the geometries around the lithium centres differ significantly in several respects. The Li–P distances of 2.60_4, (**1**), 2.6_4, (**2**), and 2.7_2 Å, (**3**) (mean) reflect the

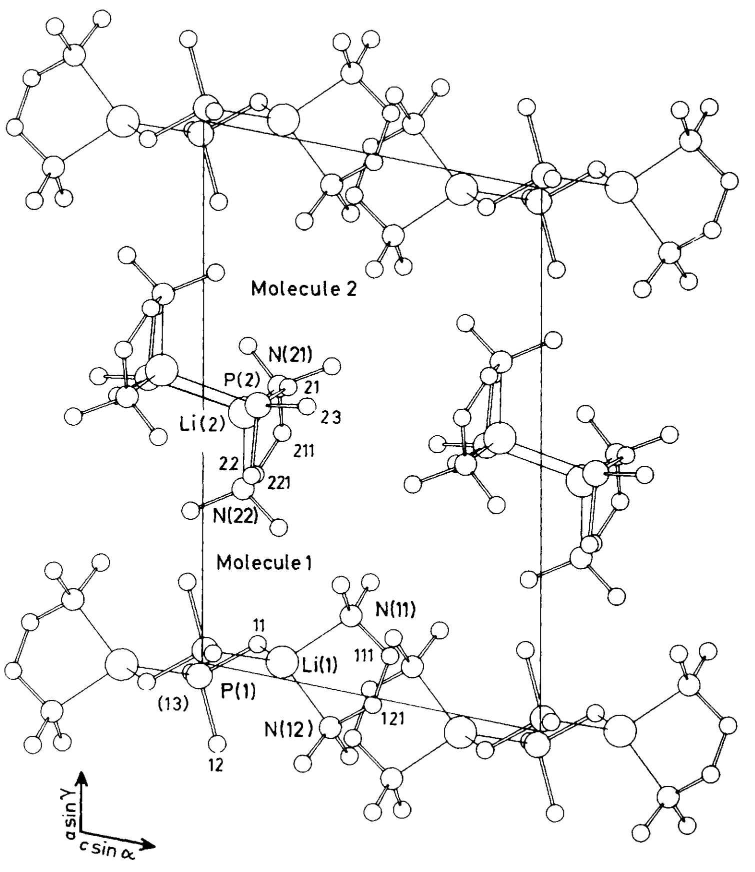


Figure 1. Unit-cell contents of (**1**) projected down *b*; atoms have arbitrary radii

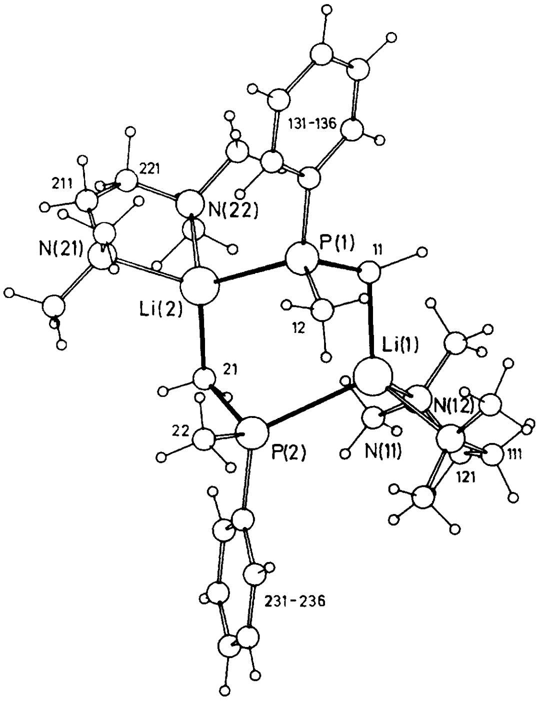


Figure 2. Projection of the dimer of (**2**) showing 20% thermal envelopes for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å

expected greater donor property of the P^{III} centre in $-CH_2PMe_2$ relative to $-CH_2PPhMe$. Compensating seemingly tighter Li–P bonding in (**1**) is weaker Li–N bonding, 2.2_0 *cf.* 2.1_6 in (**2**) and 2.1_4 Å in (**3**). There are no meaningful variations in Li,P to *ipso*-carbon distances. Angular variations are more pronounced and presumably are in consequence of different ring conformations, most likely arising from different steric constraints of the anions and/or tertiary amines. All molecules in (**1**) are in a chair conformation whereas in (**2**) and (**3**) they are nearer the boat conformation with phenyl groups in equatorial positions and the methyls axial, but splayed apart, most likely because of non-bonding interactions. In (**3**), the 'prows' of the boat are phosphorus atoms in molecule 1 but carbon atoms in molecule 2. [The chirality of the P^{III} centres present in dimers of (**2**) and (**3**) are the same, *viz.* the molecules are *meso* isomers.] The conformation in the related compound $[Li(tmen)\{(PMe_2CH_2)_2AlMe_2\}]$ (**12**) is of the pseudo-envelope type.[9] Interestingly the dimeric molecules $[\{Li(tmen)(CH_2SR)\}_2]$ (R = Me or Ph) have different structures.[14] For R = Ph there are six-atom rings with the lithium bridging the carbanion centres and the functional group, as in (**1**)—(**3**), whereas for R = Me dimers with classical electron-deficient bonding prevail, (**13**).

The bridging mode of the α-P^{III} functionalized alkyls found in (**1**)—(**3**) appears to be the preferred bonding mode for lithium, at least in the solid, and other Main Group metals,[9,19b] and also the preferred mode for heavier Group 5 (≡15) analogues of $-CH_2PRR'$ with lithium.[29] Transition-metal complexes on the other hand can display bidentate bonding or the bridging mode, *e.g.* in $[\{Ni(\eta\text{-}C_5H_5)(CH_2PPh_2)\}_2]$.[30] Substitution at the *ipso* carbon appears to yield complicated structures with lithium, *e.g.* (**14**) for alkyl groups,[7] and (**15**) (thf = tetrahy-

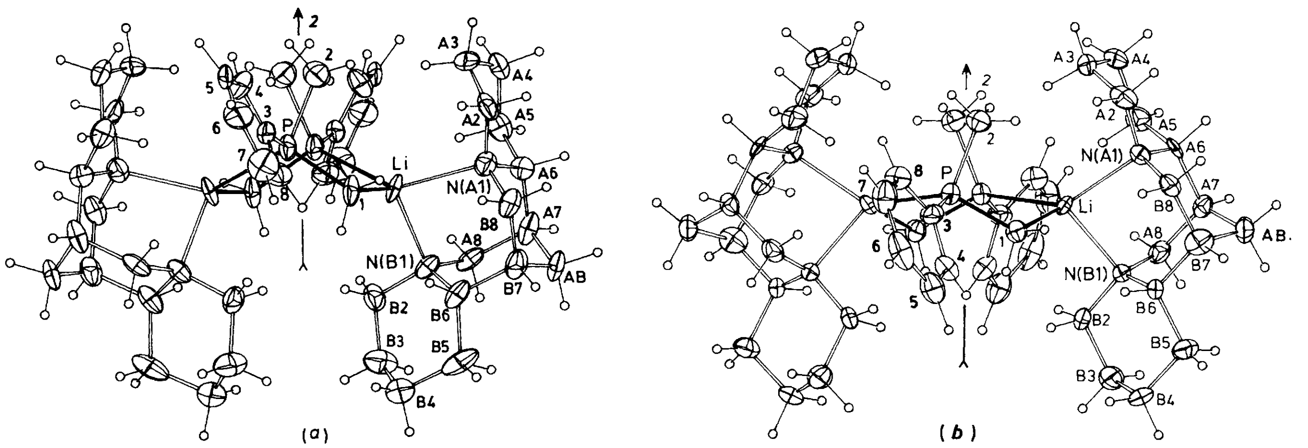


Figure 3. Projections of (**3**), molecules 1 (*a*) and 2 (*b*); details as for Figure 2

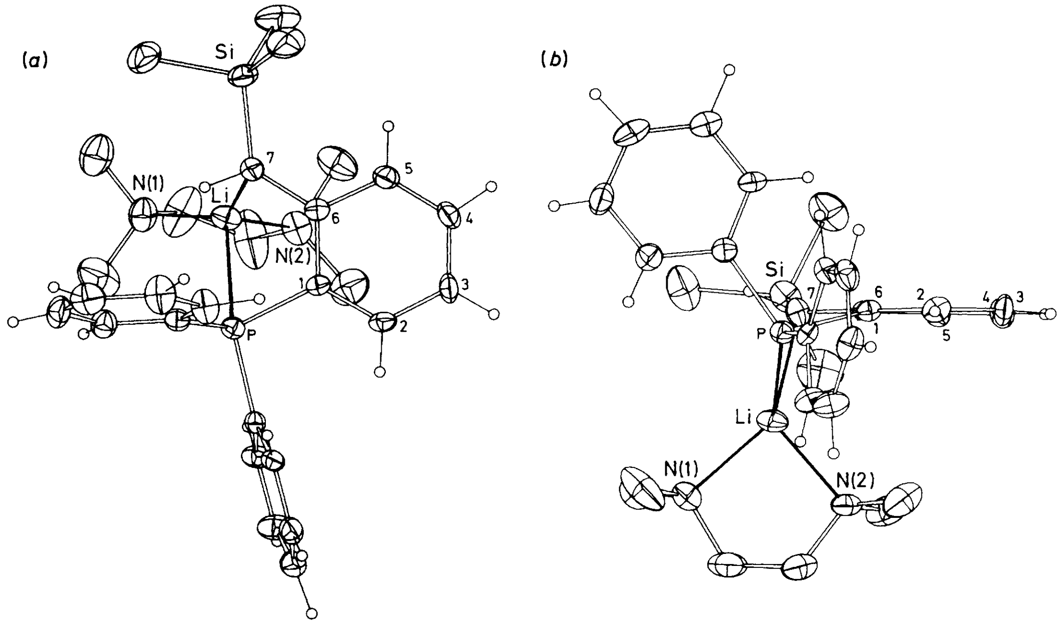
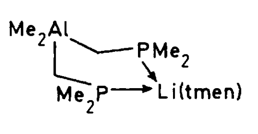
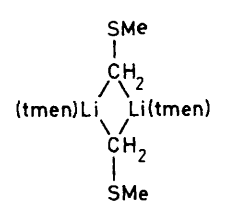


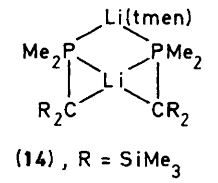
Figure 4. Projections of the molecules of (**4**) (*a*) normal to the ligand aromatic planes and (*b*) through C(1)—C(6); details as for Figure 2



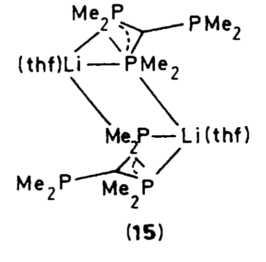
(**12**)



(**13**)



(**14**), R = SiMe$_3$



(**15**)

drofuran) for $-PR_2$ groups.[6] For the latter Li···P interactions can be at the expense of Li···C interactions, *e.g.* in $[(Li(tmen)\{(PPh_2)_2CH\}]$.[7] A similar parallel has recently been shown for lanthanum complexes of $C(PPh_2)_3^-$.[31]

The Li···P distances in (**1**)—(**4**) lie within the values established for tertiary phosphines, *viz.* 2.50—2.68 Å.[5–8] The lowest distance being in the P^{III} functionalized alkoxide complex $[\{Li(\mu\text{-}OCBu^t_2CH_2PMe_2)\}_2]$.[5] Li···P distances in phosphido[3] and related anionic ligand complexes, *e.g.* $[\{Li(tmen)\}_3P_7]$[32] can be slightly shorter, presumably because of Coulombic attraction; the lowest value is 2.44(2) Å.[3e] The Li–N distances in the four compounds are unexceptional as are the geometries of the Li(tmen)$^+$ sections.

The P–CH$_2$ distances in (**1**)—(**3**) are much shorter than the P–CH$_3$ or P–C(Ph), 1.75_3 (**1**), 1.74_3 (**2**), and 1.7_8 Å (**3**) *cf. ca.* 1.85 Å. This can be viewed as arising from in part the stabilizing influence of phosphorus by polarization.[13c] Alternatively, each phosphorus can be considered as a four-co-ordinate phosphonium centre and the P–CH$_2$ distance diminished by its ylide character. The computed Li···P in LiCH$_2$PH$_2$, 1.944 Å, is

Table 1. Non-hydrogen atom co-ordinates for (**1**)

	Molecule l = 1			Molecule l = 2		
Atom	x	y	z	x	y	z
Li(l)	0.031 3(4)	0.127 7(6)	0.236 0(6)	0.476 0(4)	0.882 7(6)	0.121 9(7)
N(l1)	0.142 0(2)	0.300 9(3)	0.439 0(4)	0.537 6(2)	0.782 7(3)	0.223 1(3)
C(l11)	0.082 5(5)	0.336 9(7)	0.554 5(6)	0.452 4(5)	0.678 9(6)	0.233 5(8)
C(l12)	0.211 1(4)	0.259 5(5)	0.495 0(7)	0.600 5(4)	0.725 9(6)	0.131 5(6)
C(l13)	0.195 3(5)	0.414 5(6)	0.408 1(7)	0.593 8(4)	0.881 5(5)	0.379 4(5)
N(l2)	−0.071 2(2)	0.184 2(3)	0.378 6(4)	0.335 0(2)	0.732 9(3)	0.118 4(4)
C(l21)	−0.013 6(5)	0.311 2(6)	0.503 9(7)	0.365 6(5)	0.645 3(7)	0.154 3(12)
C(l22)	−0.116 8(4)	0.082 1(5)	0.435 5(6)	0.277 0(4)	0.785 5(5)	0.224 3(7)
C(l23)	−0.148 3(4)	0.198 5(7)	0.298 1(7)	0.275 6(4)	0.655 7(7)	−0.035 3(6)
P(l)	−0.024 98(7)	−0.192 48(9)	−0.008 55(10)	0.494 74(7)	1.181 70(9)	0.161 66(10)
C(l1)	0.054 8(3)	−0.060 0(3)	0.162 8(4)	0.539 5(3)	1.101 3(4)	0.250 9(4)
C(l2)	−0.144 2(3)	−0.220 9(5)	0.044 6(6)	0.362 2(3)	1.101 8(5)	0.142 9(6)
C(l3)	−0.021 6(3)	−0.357 9(4)	−0.031 8(5)	0.510 6(4)	1.354 6(4)	0.306 4(5)

Table 2. Non-hydrogen atom co-ordinates for (**2**)

	Section l = 1			Section l = 2		
Atom	x	y	z	x	y	z
Li(l)	0.222 7(8)	0.174 2(10)	0.255 5(13)	0.292 1(8)	0.461 3(9)	0.108 1(12)
N(l1)	0.139 7(5)	0.007 6(5)	0.257 7(8)	0.286 6(7)	0.588 7(7)	−0.032 7(10)
C(l11)	0.194 2(8)	−0.047 7(8)	0.349 0(12)	0.347 4(11)	0.689 9(12)	0.052 3(19)
C(l12)	0.063 8(7)	0.019 6(8)	0.321 4(12)	0.314 2(8)	0.554 1(9)	−0.168 2(12)
C(l13)	0.113 3(7)	−0.060 9(8)	0.114 0(10)	0.202 5(9)	0.613 0(10)	−0.057 2(14)
N(l2)	0.320 8(4)	0.110 3(6)	0.372 8(7)	0.382 5(5)	0.601 3(7)	0.259 1(9)
C(l21)	0.284 2(8)	−0.010 2(10)	0.355 0(12)	0.392 2(11)	0.690 9(12)	0.181 5(17)
C(l22)	0.334 0(6)	0.165 0(8)	0.522 9(9)	0.357 7(8)	0.639 2(9)	0.395 8(12)
C(l23)	0.403 0(6)	0.126 1(10)	0.324 9(10)	0.462 6(8)	0.566 5(10)	0.286 7(16)
P(l)	0.159 7(1)	0.406 8(2)	0.238 3(2)	0.267 7(1)	0.191 8(2)	−0.005 7(2)
C(l1)	0.199 0(5)	0.333 3(6)	0.367 3(7)	0.347 4(5)	0.321 2(6)	0.033 3(8)
C(l2)	0.060 6(5)	0.303 3(6)	0.139 9(8)	0.190 7(5)	0.216 0(7)	−0.153 7(8)
C(l31)	0.106 1(5)	0.518 3(6)	0.318 4(8)	0.303 4(6)	0.070 6(6)	−0.111 2(7)
C(l32)	0.120 3(5)	0.556 8(7)	0.468 0(9)	0.391 0(6)	0.077 0(6)	−0.099 6(8)
C(l33)	0.081 6(5)	0.640 4(8)	0.530 9(9)	0.423 6(6)	−0.010 7(9)	−0.169 9(10)
C(l34)	0.027 8(7)	0.689 6(7)	0.448 4(13)	0.370 0(9)	−0.105 9(9)	−0.254 8(11)
C(l35)	0.012 3(6)	0.654 1(8)	0.301 5(13)	0.281 7(8)	−0.114 8(8)	−0.270 2(9)
C(l36)	0.051 3(6)	0.569 6(7)	0.236 0(8)	0.249 1(5)	−0.027 5(8)	−0.197 8(9)

much longer than in (**1**)—(**3**), as is the distance for the bidentate structure, $\overline{LiCH_2P}H_2$;[13c] the large stabilising effect of $-PH_2$ is thought to be nearly eliminated by the electrostatic stabilization of the anion lone pair by the lithium. The P–C distance in (**4**) for the *o*-substituted ring, 1.820(7) Å, is slightly less than for the phenyl groups, 1.83_6 Å, in accordance with some delocalization of charge onto the ring; the arguments for the shortening then follow as for (**1**)—(**3**).

We now turn to a discussion of the Li ··· C interactions. In (**1**)—(**3**) the associated distances are rather short and comparable to those in $[\{Li(tmen)(CH_2SPh)\}_2]$,[14] 2.131(4) Å, and other four-co-ordinate (or lower) structures devoid of electron-deficient bonding and where a polarizing group is attached to the *ipso* carbon, *e.g.* 2.12(2) Å in $[Li(thf)\{C(SiMe_2Ph)_3\}]$[33] and 2.13(5) Å in $[Li(pmdien)\{CH(SiMe_3)_2\}]$ (pmdien = *NNN′N″N″*-pentamethyldiethylenetriamine);[34] the Li ··· C distances in (**15**) are much longer than in (**1**)—(**3**), 2.290(4) Å, presumably due to the greater number of Li–ligand interactions. (In general lithium prefers to interact simultaneously with as many atoms as possible.[13]) In compound (**14**) the Li–C distances associated with electron-deficient bonding are also longer (2.24_0 Å).[10]

The *ipso* carbon in (**4**) is almost trigonal planar (Figure 4) [*cf.* pyramidal in (**1**)—(**3**)] as is typical of benzyl-lithium compounds where the *ipso* carbon bears a silyl group. The Li–C distance [2.25(1) Å] compares with 2.26(1) Å in $[Li(pmdien)\{CH(SiMe_3)C_6H_4Me\text{-}o\}]$,[35] a structure which relates to (**4**) in having three neutral donor groups on lithium. Structures with two such groups possess shorter Li–C distances, *e.g.* 2.2_1 Å in $[\{Li(tmen)\}_2\{(2\text{-}CHSiMe_3C_6H_4)_2\}]$,[36] and 2.10(1) and 2.14(1) Å for the *para*- and *meta*-isomers of $[\{Li(tmen)\}_2\{(CHSiMe_3)_2C_6H_4\}]$[37] but these have additional Li to carbanion contacts to the adjacent ring carbon and in some cases its nearest neighbour at *ca.* 2.3–2.7 Å. Both the *ipso* carbon–ring carbon distance of 1.43(1) Å and the apparent sp^2 hybridization of *ipso* carbon are suggestive of delocalization of charge onto the ring. The Si–*ipso*-carbon distance is contracted relative to the $Si–CH_3$ distances by *ca.* 0.05 Å which can be attributed to the high polarizability of silicon.[13c]

Experimental

Materials and Methods.—All the lithium compounds are extremely air- and moisture-sensitive and were handled under an argon atmosphere or *in vacuo* using standard Schlenk techniques. Solvents were dried over and distilled from sodium–benzophenone (diethyl ether), Na (benzene and toluene), $LiAlH_4$ (pentane and thf), or CaH_2 (hexane) under a dinitrogen atmosphere prior to use.

Table 3. Non-hydrogen atom co-ordinates for (**3**)

	Molecule 1			Molecule 2		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Li	0.923 0(8)	0.358(2)	0.880 2(10)	0.537 9(8)	0.343 1(17)	0.632 5(10)
Phosphine ligand						
P	1.067 6(2)	0.441 1(−) *	0.982 5(2)	0.578 9(1)	0.320 8(3)	0.491 6(2)
C(1)	1.014 9(5)	0.351 9(13)	0.901 0(6)	0.588 8(5)	0.395 1(11)	0.578 1(7)
C(2)	1.034 0(6)	0.588 5(13)	0.948 1(8)	0.606 6(5)	0.174 7(11)	0.531 4(8)
C(3)	1.136 1(5)	0.472 2(11)	0.978 0(6)	0.640 8(5)	0.361 5(10)	0.476 3(7)
C(4)	1.168 2(6)	0.568 5(14)	1.003 9(7)	0.665 7(5)	0.469 1(12)	0.499 4(7)
C(5)	1.218 5(5)	0.586 5(13)	0.999 2(7)	0.712 1(6)	0.508 9(13)	0.487 8(8)
C(6)	1.237 5(6)	0.507 7(13)	0.965 1(9)	0.730 2(5)	0.434 8(16)	0.449 1(7)
C(7)	1.206 1(6)	0.406 8(16)	0.940 5(10)	0.702 7(6)	0.327 1(16)	0.423 9(8)
C(8)	1.153 3(6)	0.387 5(12)	0.946 8(8)	0.658 9(5)	0.289 2(11)	0.434 7(8)
Sparteine ligand						
N(A1)	0.855 7(4)	0.401 4(9)	0.754 9(5)	0.586 9(4)	0.240 5(8)	0.737 9(5)
C(A2)	0.869 1(5)	0.517 1(12)	0.740 3(7)	0.598 9(6)	0.127 0(11)	0.718 1(8)
C(A3)	0.855 2(7)	0.610 2(11)	0.786 0(8)	0.542 5(6)	0.062 5(12)	0.661 6(7)
C(A4)	0.791 5(6)	0.598 7(13)	0.767 5(7)	0.500 3(7)	0.050 3(12)	0.693 4(8)
C(A5)	0.779 1(6)	0.476 1(13)	0.776 3(8)	0.491 0(6)	0.169 9(12)	0.721 7(8)
C(A6)	0.790 7(5)	0.391 2(11)	0.728 8(7)	0.553 2(5)	0.226 8(10)	0.778 0(6)
C(A7)	0.773 8(5)	0.268 7(13)	0.730 1(7)	0.546 3(5)	0.343 5(11)	0.813 6(6)
C(A8)	0.809 3(5)	0.208 9(11)	0.815 0(7)	0.510 5(5)	0.435 4(11)	0.752 2(7)
N(B1)	0.875 8(4)	0.195 0(9)	0.851 5(5)	0.538 0(4)	0.477 4(8)	0.707 5(5)
C(B2)	0.907 0(6)	0.134 7(12)	0.929 7(7)	0.502 4(5)	0.569 4(11)	0.651 2(6)
C(B3)	0.898 1(7)	0.004 5(13)	0.926 5(9)	0.507 4(6)	0.687 0(12)	0.690 1(8)
C(B4)	0.917 9(7)	−0.055 0(13)	0.879 6(9)	0.572 9(7)	0.723 6(11)	0.737 5(8)
C(B5)	0.881 1(6)	0.001 5(12)	0.791 8(10)	0.611 9(7)	0.629 5(11)	0.800 7(8)
C(B6)	0.886 8(5)	0.138 2(12)	0.790 9(7)	0.602 1(5)	0.509 5(10)	0.760 2(6)
C(B7)	0.850 4(6)	0.197 1(13)	0.705 6(7)	0.638 7(5)	0.415 8(12)	0.822 1(8)
C(B8)	0.868 5(5)	0.320 7(14)	0.704 0(7)	0.643 3(5)	0.302 0(11)	0.784 9(7)
C(AB)	0.783 8(5)	0.192 0(13)	0.674 9(7)	0.612 2(5)	0.390 6(12)	0.876 9(7)
Solvent						
C(1)	0.786(1)	0.381(3)	0.266(2)			
C(2)	0.823(2)	0.368(6)	0.350(3)			
C(3)	0.883(1)	0.295(4)	0.446(2)			
C(4)	0.951(2)	0.313(4)	0.482(3)			
O	0.840(1)	0.338(3)	0.362(2)			

* Defines origin.

Hydrogen-1 n.m.r., carbon-13 n.m.r., and mass spectra were recorded on Hitachi–Perkin-Elmer R-24B (60 MHz), Bruker WP-80, and Hewlett Packard-4986 spectrometers. Phosphorus-31 and lithium-7 n.m.r. were obtained on a Bruker WP-80 or AM 300 spectrometer. Chemical shifts (δ) are reported relative to $SiMe_4$ (^1H, external), [$^2H_6$]benzene (^{13}C), 85% H_3PO_4 (^{31}P, external), and aqueous $LiNO_3$ (^7Li, external). Elemental analyses were performed by the Canadian Microanalytical Laboratory and the Australian Mineral Development Laboratories.

The ligands tmen and (−)sparteine sulphate were purchased from Aldrich and anhydrous (−)sparteine prepared by treatment of the sulphate with NaOH, followed by filtration and distillation *in vacuo*. $LiBu^n$ was purchased from Metallgesellschaft, and PMe_3, PMe_2Ph, $PMePh_2$, and $P(C_6H_4Me\text{-}o)_3$ from Strem. $MeC_6H_4PPh_2\text{-}o$[37] was prepared according to the literature procedure, and $P(O)Me_2Ph$ by treating PMe_2Ph in hexane with excess 70% H_2O_2 then sublimation *in vacuo*, m.p. 139—140 °C (lit. 140 °C[38]).

Synthesis of [{Li(tmen)(CH_2PMe_2)}$_2$], (**1**).—To a mixture of $LiBu^n$ (5.53 cm^3, 1.70 mol dm^{-3} in hexane, 9.4 mmol) and tmen (1.03 cm^3, 8.85 mmol) at 0 °C was added PMe_3 (1.0 cm^3, 9.83 mmol). After 1 d at room temperature volatiles were removed *in vacuo* yielding a white crystalline solid of the *title compound*, 1.56 g, 89% yield, m.p. >310 °C. Crystals for the *X*-ray experiment were obtained by recrystallization from hexane. ^1H N.m.r. (80 MHz, [$^2H_6$]benzene) δ 2.23 (12 H, s, NMe), 2.03 (4 H, s, NCH_2), 1.29 (6 H, s, PMe), −0.35 (2 H, s, $LiCH_2$); ^{13}C n.m.r. (20.1 MHz, ^1H decoupled, [$^2H_6$]benzene) δ 57.3 (s, NCH_2), 46.4 (s, NMe), 24.5 (d, PMe, J_{CP} 9 Hz), 10.3 (d, PCH_2, J_{CP} 27.5 Hz); ^{31}P n.m.r. (32.44 MHz, [$^2H_8$]toluene) δ −43.8 (s); ^7Li n.m.r. (116.3 MHz, [$^2H_8$]toluene, ^1H decoupled) δ 1.98 (s, 20 °C), −0.18 (d, J_{LiP} 53.4 Hz; s, −80 °C). Molecular weight (benzene): 197(5), calc. 198.1.

Synthesis of [{Li(tmen)(CH_2PMePh)}$_2$], (**2**).—This was prepared according to the literature procedure.[12] Crystals suitable for the *X*-ray experiment were grown from hexane at −30 °C. ^{31}P N.m.r. (121.5 MHz, [$^2H_8$]toluene, ^1H decoupled) δ −23.6 (s, 20 °C; q, −70 °C, J_{LiP} 49.3 Hz); ^7Li n.m.r. (116.3 MHz, [$^2H_8$]toluene) δ 2.07 (s, 20 °C; d, −70 °C, J_{LiP} 49.3 Hz). Molecular weight (benzene); 234(35), calc. 260.3.

Synthesis of [{Li(sp)(CH_2PMePh)}$_2$], (**3**).—(−)Sparteine (4.8 cm^3, 21.0 mmol) was added to a solution of $LiBu^n$ (13.1 cm^3, 1.7 mol dm^{-3} in hexane, 21.0 mmol) and PMe_2Ph (3.0 cm^3, 21.0 mmol) in diethyl ether (20 cm^3). After 5 h at room temperature the mixture was cooled to −30 °C and after 3 d the resulting yellow solid of the *title compound* was collected, washed with pentane (3 × 5 cm^3), and then dried *in vacuo*, 3.2 g, 40%, m.p. 79 °C (decomp.). ^1H N.m.r. (80 MHz, [$^2H_6$]benzene) δ −0.12 (2 H, d, CH_2, J_{PH} 2.8 Hz), 0.8—3.1 (29 H, m, sp and PMe), 7.2 (3 H, m, Ph), 7.95 (2 H, m, Ph); ^{13}C n.m.r. (20.1 MHz, [$^2H_6$]-benzene, ^1H decoupled) δ 19.4 (d, Ph, J_{CP} 3.4 Hz), 35.6 (d, CH_2, J_{CP} 3.4 Hz), 124.7 (Ph), 127.2 (d, Ph, $^3J_{CP}$ 3.4 Hz), 130.4 (d, Ph, $^2J_{CP}$ 11.4 Hz), 158.1 (d, Ph, J_{CP} 29.8 Hz); 6.4, 8.1, 14.2, 25.2, 25.7, 28.8, 29.8, 47.5, 54.1, 57.3, 61.4 ($C^{2,3,15,9,10,1,8,4,6,11,13}$, sp), 59.9 ($C^{7,14}$, sp), 67.5 ($C^{7a,14a}$, sp); ^{31}P n.m.r. (121.5 MHz, [$^2H_8$]toluene, ^1H decoupled) δ −22.3 (s, 20 °C; q, −53 °C, J_{LiP} 44.0 Hz); ^7Li n.m.r. (116.63 MHz, [$^2H_8$]toluene) δ −1.3 (s, 20 °C; d, −53 °C, J_{LiP} 44.0 Hz).

Synthesis of [Li(tmen){CH(SiMe$_3$)$C_6H_4PPh_2$-*o*}], (**4**).—To a solution of LiBu^n (1.7 cm^3, 1.7 mol dm^{-3} in hexane, 2.7 mmol) and tmen (0.38 cm^3, 2.5 mmol) was slowly added $CH_2(SiMe_3)C_6H_4PPh_2$-*o* (1.0 g, 2.9 mmol). After 12 h the resulting

Table 4. Non-hydrogen atom co-ordinates for (**4**)

Atom	*x*	*y*	*z*
Li	0.283 5(6)	0.310 1(8)	0.774 9(12)
P	0.335 67(8)	0.138 74(11)	0.834 50(−)*
C(1)	0.405 8(3)	0.177 5(4)	0.735 1(6)
C(2)	0.430 2(4)	0.119 2(5)	0.647 1(7)
C(3)	0.470 3(4)	0.154 1(7)	0.556 9(6)
C(4)	0.485 1(4)	0.252 2(7)	0.554 8(7)
C(5)	0.463 2(4)	0.312 0(5)	0.641 6(8)
C(6)	0.422 8(4)	0.278 2(5)	0.737 8(7)
C(7)	0.398 9(3)	0.342 2(5)	0.825 7(8)
Si	0.429 4(1)	0.465 2(1)	0.851 9(3)
C(8)	0.398 7(6)	0.556 9(6)	0.746 6(12)
C(9)	0.529 5(4)	0.480 5(6)	0.860 8(10)
C(10)	0.391 5(5)	0.501 9(7)	0.994 8(10)
C(11)	0.323 0(4)	0.009 8(4)	0.801 5(5)
C(12)	0.375 3(4)	−0.060 3(4)	0.826 8(7)
C(13)	0.364 1(5)	−0.155 1(6)	0.797 4(7)
C(14)	0.300 5(6)	−0.181 9(7)	0.740 5(8)
C(15)	0.249 0(5)	−0.113 9(6)	0.717 1(8)
C(16)	0.260 1(4)	−0.018 5(5)	0.747 0(6)
C(21)	0.378 1(4)	0.135 7(5)	0.975 8(6)
C(22)	0.334 8(5)	0.142 7(6)	1.071 0(7)
C(23)	0.363 6(6)	0.149 7(7)	1.180 3(8)
C(24)	0.437 3(7)	0.145 1(7)	1.192 7(9)
C(25)	0.481 5(6)	0.138 1(8)	1.099 8(9)
C(26)	0.452 3(4)	0.131 3(7)	0.992 1(8)
N(1)	0.179 9(3)	0.346 3(5)	0.829 7(8)
C(101)	0.142 7(6)	0.362 4(10)	0.721 4(12)
C(102)	0.149 0(5)	0.267 5(8)	0.895 4(13)
C(103)	0.174 1(6)	0.431 9(8)	0.897 8(10)
N(2)	0.246 3(4)	0.308 0(5)	0.611 6(6)
C(201)	0.169 1(6)	0.316 4(12)	0.624 9(10)
C(202)	0.277 2(6)	0.390 1(7)	0.552 2(9)
C(203)	0.262 8(6)	0.220 6(8)	0.542 3(8)

* Defines origin.

Table 6. $Li_2P_2C_2$ ring torsion angles (°) for (**1**)—(**3**)

Bond	Li–P	Li–C	P–C
(**1**)			
Molecule 1	50.8*	−50.1	52.0
Molecule 2	−55.8*	55.2	−57.8
(**2**)			
Section 1	48.0*	31.1	−66.5
Section 2	51.7*	28.1	−63.2
(**3**)			
Molecule 1	−54.9*	−19.2	62.4
Molecule 2	−17.7*	47.7	61.2

* The second atom is in the other section or symmetry-related segment.

Table 7. The lithium environment for (**4**); *r* are the Li–N, C, P distances (Å). Other entries in the matrix are the angles (°) subtended at the lithium by the atoms at the head of the relevant row and column

Atom	*r*	C(7)	N(1)	N(2)
P	2.65(1)	76.4(4)	117.9(6)	111.0(5)
C(7)	2.25(1)		137.6(7)	124.7(7)
N(1)	2.07(1)			89.2(6)
N(2)	2.04(2)			

Table 5. Molecular (non-hydrogen) core geometries for (**1**)—(**3**); distances in Å, angles in °; the second entry is for the other section of independent molecule

	(**1**)	(**2**)	(**3**)
Li–P	2.593(7), 2.615(6)	2.67(1), 2.61(1)	2.74(2), 2.70(2)
Li–C(1)	2.150(8), 2.141(6)	2.15(1), 2.12(1)	2.21(3), 2.18(3)
Li–N(*l*1, A1)	2.218(5), 2.169(8)	2.17(1), 2.17(2)	2.16(2), 2.10(2)
Li–N(*l*2, B1)	2.177(8), 2.216(7)	2.14(2), 2.17(1)	2.15(1), 2.13(2)
P–C(1)	1.751(3), 1.754(5)	1.730(8), 1.755(7)	1.77(1), 1.78(1)
P–C(2)	1.825(5), 1.844(5)	1.845(7), 1.836(8)	1.86(2), 1.83(1)
P–C(3)	1.853(5), 1.842(4)	1.845(8), 1.857(9)	1.87(2), 1.85(2)
P–Li–C(1)	110.7(2), 108.2(3)	112.9(5), 115.2(5)	108.3(6), 106.2(7)
P–Li–N(*l*1, A1)	110.0(3), 109.7(3)	113.1(5), 116.6(6)	128.3(8), 128.5(10)
P–Li–N(*l*2, B1)	109.7(3), 109.5(2)	106.3(6), 106.1(5)	107.3(10), 105.6(8)
C(1)–Li–N(*l*1, A1)	113.0(4), 112.1(3)	120.9(7), 116.3(7)	111.0(11), 114.9(10)
C(1)–Li–N(*l*2, B1)	126.4(3), 130.2(3)	114.6(5), 113.1(6)	115.6(12), 111.0(10)
N(*l*1, A1)–Li–N(*l*2, B1)	83.7(2), 84.1(3)	85.2(5), 85.1(5)	84.5(6), 87.8(8)
Li–P–C(1)	114.4(2), 112.7(2)	101.8(4), 102.6(3)	107.3(5), 108.8(6)
Li–P–C(2)	106.4(3), 105.6(2)	120.9(3), 120.3(4)	116.7(7), 117.7(6)
Li–P–C(3)	123.5(2), 125.3(2)	121.4(3), 120.0(4)	121.9(5), 119.6(6)
C(1)–P–C(2)	103.4(2), 102.7(3)	103.3(3), 103.2(4)	102.6(6), 102.5(6)
C(1)–P–C(3)	109.3(2), 109.8(2)	112.2(4), 111.9(4)	111.8(7), 109.5(6)
C(2)–P–C(3)	96.3(3), 96.6(2)	96.3(3), 97.9(4)	94.9(7), 97.0(6)
P–C(1)–Li	113.2(3), 111.8(3)	108.6(5), 109.1(5)	113.10(9), 120.8(8)

orange prisms of the *title compound* (suitable for the *X*-ray experiment) were collected and washed with pentane (2 × 5 cm^3) then dried *in vacuo*, 1.1 g, 91%, m.p. 148 °C. ^{1}H N.m.r. (60 MHz, [^{2}H$_6$]benzene) δ 0.31 (9 H, s, SiMe), 1.70 (1 H, s, SiCH), 1.80 (4 H, s, CH$_2$N), 1.90 (12 H, s, MeN), 7.3 (14 H, m, Ph and C$_6$H$_4$); ^{13}C n.m.r. (20.1 MHz, [^{2}H$_6$]benzene, ^{1}H decoupled) δ 2.9 (SiMe), 45.9 (MeN), 57.1 (CH$_2$N) 110.3—159.1 (Ph and C$_6$H$_4$); ^{31}P n.m.r. (121.5 MHz, [^{2}H$_6$](benzene, ^{1}H decoupled) δ −14.7.

Synthesis of [{Li(tmen)(CH$_2$PPh$_2$)}$_2$], (**5**).—This was prepared according to the literature procedure.[12] ^{31}P N.m.r. (121.5 MHz, [^{2}H$_8$]toluene, ^{1}H decoupled) δ 2.29 (s, 20 °C); ^{7}Li n.m.r. (116.3 MHz, [^{2}H$_8$]toluene) δ 2.05 (s, 20 °C; d, −70 °C, J_{LiP} 47.3 Hz). Molecular weight (benzene); 341(50), calc. 395.4.

Synthesis of [Li(tmen)(CH$_2$C$_6$H$_4$PPh$_2$-*o*)], (**6**).—MeC$_6$H$_4$PPh$_2$-*o* (1.03 g, 3.7 mmol) was treated with LiBu^n (2 cm^3, 1.7 mol dm^{-3} in hexane, 3.4 mmol) then tmen (0.5 cm^3, 3.3 mmol) at 0 °C. The resulting orange crystals of the *title compound* were collected and washed with hexane (3 × 5 cm^3) then dried *in vacuo*, 1 g, 72%, m.p. 146—148 °C. ^{1}H N.m.r. (60 MHz, [^{2}H$_6$]benzene) δ 1.95 (16 H, s, C*H$_2$Me*N), 2.42 (2 H, s, CH$_2$Li), 2.7 (14 H, m, Ph and C$_6$H$_4$); ^{13}C n.m.r. (20.1 MHz, [^{2}H$_6$]benzene, ^{1}H decoupled) δ 3.35 (CH$_2$Li), 46.0 (MeN), 57.9 (CH$_2$N), 127.3—135.5 (Ph and C$_6$H$_4$); ^{31}P n.m.r. (121.5 MHz, [^{2}H$_6$]benzene, ^{1}H decoupled) −15.8.

Synthesis of CH$_2$(SiMe$_3$)C$_6$H$_4$PPh$_2$-*o*, (**7**).—LiBu^n (4 cm^3, 1.7 mol dm^{-3} in hexane, 6.4 mmol), tmen (0.94 cm^3, 6.2 mmol), and MeC$_6$H$_4$PPh$_2$-*o* (1.76 g, 6.4 mmol) were mixed at 0 °C. The resulting orange solid was dissolved in hexane (50 cm^3) and SiMe$_3$Cl (1 cm^3, 8 mmol) added. After 12 h at room temperature the solution was filtered and volatiles removed *in vacuo*. The *title compound* was distilled as a colourless liquid, 1.76 g, 79%, b.p. 158—160 °C at 10^{-2} mmHg (Found: C, 75.85; H, 7.20. C$_{22}$H$_{25}$PSi requires C, 75.80; H, 7.35%). ^{1}H N.m.r. (60 MHz, [^{2}H$_1$]chloroform) δ 0.1 (9 H, s, SiMe), 2.4 (2 H, s, CH$_2$), 7.2 (14 H, m, Ph and C$_6$H$_4$); ^{13}C n.m.r. (20.1 MHz, [^{2}H$_1$] chloroform, ^{1}H decoupled) δ 3.0 (SiMe), 26.3 (d, CH$_2$, J_{CP} 21.7 Hz), 125.6—146.7 (Ph and C$_6$H$_4$); ^{31}P n.m.r. (121.5 MHz, [^{2}H$_1$]chloroform, ^{1}H decoupled) δ −14.3.

Synthesis of CH(SiMe$_3$)$_2$C$_6$H$_4$PPh$_2$-*o*, (**8**).—To an ice-cooled mixture of (**4**) (4 g, 8.2 mmol) in hexane (20 cm^3) was added SiMe$_3$Cl (1.3 cm^3, 9.8 mmol). After 12 h at room temperature volatiles were removed *in vacuo* and the *title compound* crystallized as colourless crystals from ethanol, 1.95 g, 56.4%, m.p. 105—107 °C (Found: C, 71.4; H, 7.85. C$_{25}$H$_{33}$PSi$_2$ requires C, 71.40; H, 8.00%). ^{1}H N.m.r. (60 MHz, [^{2}H$_1$]chloroform) δ 0.27 (18 H, s, SiMe), 2.70 (1 H, d, Si$_2$CH, J_{HP} 7 Hz), 6.9 (14 H, m, Ph and C$_6$H$_4$); ^{13}C n.m.r. (20.1 MHz, [^{2}H$_1$]chloroform, ^{1}H decoupled) δ 1.1 (SiMe), 26.9 (d, J_{CP} 22 Hz), 124.7—150.6 (s, Ph and C$_6$H$_4$); ^{31}P n.m.r. (32.44 MHz, [^{2}H$_6$]benzene, ^{1}H decoupled) δ −17.8 (s).

Synthesis of P(C$_6$H$_4$CH$_2$SiMe$_3$-*o*)$_3$, (**9**).—To a solution of P(C$_6$H$_4$Me-*o*)$_3$ (2.0 g, 6.6 mmol) and tmen (3.3 cm^3, 22 mmol) in hexane (200 cm^3) was added LiBu^n (14 cm^3, 1.6 mol dm^{-3} in hexane, 22 mmol). After 15 h SiMe$_3$Cl (4.2 cm^3, 33 mmol) in hexane (20 cm^3) was added to the resulting deep red solution at 0 °C. The mixture was stirred for 2 h, filtered then the volatiles removed *in vacuo*. The *title compound* was crystallized as colourless crystals from methanol, 2.6 g, 76%, m.p. 156 °C (Found: C, 69.55; H, 8.90. C$_{30}$H$_{45}$PSi$_3$ requires C, 69.15; H, 8.70%). ^{1}H N.m.r. (60 MHz, [^{2}H$_1$]chloroform) δ 0.01 (27 H, s, SiMe), 2.2 (6 H, s, CH$_2$Si), 6.7—7.0 (12 H, m, C$_6$H$_4$); ^{13}C n.m.r. (20.1 MHz, [^{2}H$_1$]chloroform, ^{1}H decoupled) δ −0.6 (SiMe), 25.8 (d, CH$_2$Si, J_{CP} 17.2 Hz), 125.0—145.8 (C$_6$H$_4$); ^{31}P n.m.r. (121.5 MHz, [^{2}H$_1$]chloroform, ^{1}H decoupled) δ −23.1.

Synthesis of P[C$_6$H$_4$CH(SiMe$_3$)$_2$-*o*]$_3$, (**10**).—The procedure was as described for the synthesis of (**9**). Yield 62%, m.p. 255 °C (Found: C, 63.60; H, 9.15; P, 4.60. C$_{39}$H$_{69}$PSi$_6$ requires C, 63.60; H, 9.45; P, 4.20%). ^{1}H N.m.r. (60 MHz, [^{2}H$_1$]chloroform) δ −0.11 (27 H, s, SiMe), 0.26 (27 H, s, SiMe), 2.26 (3 H, d, CHSi$_2$, J_{HP} 7 Hz), 7.0 (12 H, m, C$_6$H$_4$); ^{13}C n.m.r. (20.1 MHz, [^{2}H$_1$]chloroform, ^{1}H decoupled) δ 0.8, 1.6 (SiMe), 25.7 (d, CHSi$_2$, J_{CP} 13.7 Hz), 124.1—149.3 (C$_6$H$_4$); ^{31}P n.m.r. (121.5 MHz, [^{2}H$_1$]chloroform, ^{1}H decoupled) δ −22.4.

Synthesis of [Li(sp){CH$_2$P(O)MePh}] (**11**).—P(O)Me$_2$Ph (0.8 g, 5.2 mmol) was added to a solution of LiBu^n (3.1 cm^3, 1.7 mol dm^{-3}, 5.3 mmol) and sparteine (1.2 cm^3, 5.2 mmol). After 18 h at room temperature the solvent was removed *in vacuo*. The resulting pale yellow solid of the *title compound* was washed with pentane (3 × 10 cm^3) and dried *in vacuo*, 1.17 g, 57%, m.p. 74—77 °C (decomp.). ^{1}H N.m.r. (300 MHz, [^{2}H$_6$]benzene) δ 0.5—2.8 (31 H, m, sp and PMe, CH$_2$), 7.0 (3 H, m, Ph), 8.1 (2 H, m, Ph); ^{13}C n.m.r. (75.5 MHz, [^{2}H$_6$]benzene, ^{1}H decoupled) δ 21.0 (d, PMe, J_{CP} 68.1 Hz), 30.8 (d, PCH$_2$, J_{CP} 64.9 Hz), 127.1, 131.4 (Ph) 143.6 (Ph); 23.0 (C^{2,3}, sp), 25.1 (C^{9,10}, sp), 26.2, 28.1 (C^{1,8}, sp), 29.6 (C^{15}, sp), 33.6, 36.9 (C^{7,14}, sp), 54.0, 55.7, 56.5, 62.3 (C^{4,6,11,13}, sp), 64.3, 66.5 (C^{7a,14a}, sp); ^{31}P n.m.r. (121.5 MHz, [^{2}H$_6$]benzene, ^{1}H decoupled) δ 52.8.

Synthesis of P(O)MePhPr^i.—EtI (1.0 cm^3, 12.4 mmol) was added to a stirred hexane (20 cm^3) solution of (**11**) (1.17 g, 5.2 mmol) at −95 °C and the mixture warmed to room temperature over 18 h. The solvent was removed *in vacuo* and the *title compound* distilled as a colourless liquid, b.p. 135 °C, 0.1 mmHg, which solidified, m.p. 58—60 °C, lit.[25] 57—58 °C; α(589.3 nm, 16 g dm^{-3} in MeOH, 20 °C) −2.9°.

Crystallography.—Unique data sets were measured at 295 K within a preset $2\theta_{\text{max.}}$ limit determined from the extent of the data using a Syntex $P\bar{1}$ four-circle diffractometer fitted with a monochromatic Mo-K_α radiation source (λ = 0.710 6$_9$ Å) and operating in conventional $2\theta/\theta$ scan mode. *N* Independent reflections were obtained, N_0 with $I > 3\sigma(I)$ [or $> 2\sigma(I)$ for (**3**)] being considered 'observed' and used in the full-matrix least-squares refinement without absorption correction after solution of the structures by direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{\text{iso}})_{\text{H}}$ were included constrained at idealized values. R, R' on $|F|$ are quoted at convergence; reflection weights were $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral complex scattering factors were used;[39] computation used the XTAL[40] program system implemented on a Perkin-Elmer 3240 computer.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Crystal Data.—For (**1**). (C$_9$H$_{24}$LiN$_2$P)$_2$, M = 396.4, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 14.918(7), b = 11.567(5), c = 9.621(4) Å, α = 113.94(3), β = 91.92(3), γ = 109.79(3)°, U = 1 399 Å^3, $D_c(Z = 2)$ = 0.94 g cm^{-3}, $F(000)$ = 440, μ_{Mo} = 1.7 cm^{-1}, $2\theta_{\text{max.}}$ = 50°, N = 4 501, N_0 = 3 019; R = 0.059, R' = 0.078.

For (**2**). (C$_{14}$H$_{26}$LiN$_2$P)$_2$, M = 520.6, triclinic, space group $P\bar{1}$, a = 16.10(1), b = 11.96(1), c = 9.382(8) Å, α = 98.87(7), β = 97.38(6), γ = 101.57(6)°, U = 1 724(2) Å^3, $D_c(Z = 2)$ = 1.00 g cm^{-3}, $F(000)$ = 568, μ_{Mo} = 1.5 cm^{-1}, $2\theta_{\text{max.}}$ = 45°, N = 4 519, N_0 = 2 240; R = 0.058, R' = 0.056.

For (**3**). (C$_{23}$H$_{36}$LiN$_2$P)$_2$OEt$_2$, M = 831.1, monoclinic, space group C_2(C_2^3, no. 5), a = 26.097(7), b = 11.517(9), c =

19.506(5) Å, $\beta = 122.50(2)°$, $U = 4\,945(6)$ Å^3, D_c $(Z = 4) = 1.32$ g cm^{-3}, $F(000) = 1\,816$, $\mu_{Mo} = 1.5$ cm^{-1}, $2\theta_{max.} = 50°$, $N = 3\,945$, $N_0 = 2\,100$; $R = 0.083$, $R' = 0.072$.

For (**4**). $C_{28}H_{40}LiN_2PSi$, $M = 470.6$, orthorhombic, space group $Pna2_1$ (C^9_{2v}, no. 33), $a = 18.395(8)$, $b = 13.825(5)$, $c = 11.737(5)$ Å, $U = 2\,985(2)$ Å^3, $D_c(Z = 4) = 1.05$ g cm^{-3}, $F(000) = 1\,016$, $\mu_{Mo} = 2.1$ cm^{-1}, $2\theta_{max.} = 45°$, $N = 2\,078$, $N_0 = 1\,222$; $R = 0.039$, $R' = 0.043$. [For this compound, $(x, y, z)_H$ were refined for the non-methyl hydrogen atoms.]

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