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FULL PAPER

Reaction of tris[(diphenylphosphino)dimethylsilyl]methane with molybdenum hexacarbonyl and deprotonation to give a salt with a planar carbanion. Crystal structures of $(Ph_2PMe_2Si)_3CH$ and $[Li(tmen)_2][C(SiMe_2PPh_2)_3]$, tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine

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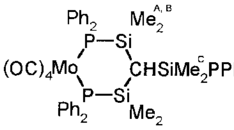
The compound $(Ph_2PMe_2Si)_3CH$ **I** reacted (i) with $[Mo(CO)_6]$ to give *cis*-$[Mo(CO)_4\{(Ph_2PMe_2Si)_3CH\}]$ **1** in which two phosphine groups are co-ordinated to molybdenum and one is free, and (ii) with LiBu in the presence of *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (tmen) to give $[Li(tmen)_2][C(SiMe_2PPh_2)_3]$ **2**, which contains discrete planar carbanions and no Li–P co-ordination. The crystal structures of compounds **I** and **2** have been determined and **1** has been characterised spectroscopically.

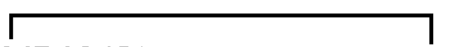
We have been able to isolate a wide range of novel types of organometallic compounds by attaching the bulky ligands $C(SiMe_3)_3$ or $C(SiMe_2Ph)_3$ to metal centres.[1] Recently the emphasis in our research has moved towards use of ligands of the type $C(SiMe_3)_2(SiMe_2X)$ and $C(SiMe_2X)_3$ that have similar bulk around the metal centre to which they are attached but also contain groups X bearing lone pairs capable of co-ordinating intra- or inter-molecularly to the metal. Those used previously include $C(SiMe_3)_2(SiMe_2X)$ with X = OMe[2] or SMe[3] and $C(SiMe_2X)_3$ with X = OMe[4] or NMe_2.[5,6] In particular, the lithium derivative $LiC(SiMe_2NMe_2)_3$, made by metallation of the ligand precursor $(Me_2NMe_2Si)_3CH$, adopts a linear polymeric structure in which the planar lithium ion, co-ordinated by three NMe_2 groups, is well separated from the planar carbanionic centre. Moreover, the highly unusual Grignard reagent $(Me_2NMe_2Si)_3CMgI$ has a planar carbanionic centre without specific interaction with the magnesium atom. We now describe the synthesis of the analogous phosphorus-containing ligand precursor **I**, the molybdenum complex **1**, and the lithium derivative **2** obtained from the reaction between **I** and LiBu/tmen (tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine).

$(Ph_2PMe_2Si)_3CH$ I



1

$[Li(tmen)_2][C(SiMe_2PPh_2)_3]$ 2



$LiP\{C(SiMe_3)_2\}(C_6H_4CH_2NMe_2)_2$ 3

Results and discussion

The precursor **I** was obtained in good yield from the reaction between $(BrMe_2Si)_3CH$[7] and $KPPh_2$ in tetrahydrofuran (thf) and characterised by multinuclear NMR spectroscopy. The ^1H NMR spectrum showed the expected signals assigned to $SiMe_2$, CH and Ph protons. The ^{13}C and ^{29}Si spectra showed complex multiplets which were simulated by the PANIC program. The signal from the *ipso*-carbon of the phenyl group was analysed as the A part of an AXY_2 system, with the $^{12}C/^{13}C$ isotope shift at phosphorus $|\delta_X - \delta_Y| = 0.028$. The signal from the *ortho* carbon was also analysed as the A part of an AXY_2 spin system but with $|\delta_X - \delta_Y| = 0.009$; that from the *meta*-carbon was analysed as the A part of an AXX'_2 spin system, as the isotope shift is attenuated over three bonds. The presence of a ^{13}C nucleus in a methyl site makes the two remote ^{31}P nuclei magnetically inequivalent so that the CH_3 signal appears as the A part of an $AXYY'$ system with $|\delta_X - \delta_Y| = 0.006$. The ^{29}Si signal was analysed as the A part of an AXY_2 system with $|\delta_X - \delta_Y|$ (arising from the $^{29}Si/^{28}Si$ isotope shift at P) = 0.011. The ^{29}Si satellites from the quartet assigned to the tertiary carbon showed that the coupling constant $^1J_{SiC}$ is 33.2 Hz [*cf.* 38.7 Hz for $(Me_3Si)_3CH$[8] and 42 Hz for $(Me_2NSiMe_2)_3CH$[5]]. The phosphorus chemical shift, δ −51, is close to that, δ −56.8, for diphenyl(trimethylsilyl)phosphine.[9] Crystals of compound **I** suitable for an X-ray study were obtained from heptane–thf.

The reaction between compound **I** and molybdenum hexacarbonyl gave a white solid which was judged to be the complex *cis*-$[Mo(CO)_4\{(Ph_2PMe_2Si)_3CH\}]$ **1** from (i) the mass spectrum, which showed the successive loss of four carbonyl groups from the molecular ion, (ii) the presence of four bands in the carbonyl stretching region of the infrared spectrum as required for C_{2v} symmetry, and (iii) the presence in the ^{29}Si and ^{31}P NMR spectra of two signals with intensities in the ratio 2 : 1. These are attributed respectively to complexed $Si^{A,B}Me_2PPh_2$ fragments (with δ_P −21, about 30 ppm to higher frequency than the signal for **I**), and uncomplexed $Si^CMe_2PPh_2$ fragments (with δ_P close to that for **I**). The bidentate co-ordination of the ligand in **1** gives a six-membered $\overline{\mathrm{MoPSiCSiP}}$ metallacycle and leaves one free $SiMe_2PPh_2$ fragment. The presence of three signals in each region of the ^1H and ^{13}C spectra, corresponding to the methyl and phenyl substituents in uncomplexed $Si^CMe_2PPh_2$ groups and $Si^{A,B}Me_2PPh_2$ groups on either side of the ring, shows that the chelate structure is preserved in solution and is not fluxional on the NMR timescale. In several other complexes $MoL(CO)_4$ the ligand L containing three phosphorus centres, *e.g.* $(Ph_2P)_3CH$[10] or $(Ph_2PCH_2)_3CCH_3$,[11,12] is bidentate.

Compound **I** was readily metallated by LiBu in the presence of tmen. The product **2** was obtained as pale yellow

Table 1 Bond lengths (Å) and angles (°) in $(Ph_2PSiMe_2)_3CH$ **I** and $[(Ph_2PSiMe_2)_3C]^-$

	$(Ph_2PSiMe_2)_3CH$ **I**			$[(Ph_2PSiMe_2)_3C]^-$		
Si–C	1.898(5)[a]			1.809(7)[a]		
Si–Me	1.871(6)[a]			1.879(8)[a]		
P–Si	2.275(2)[a]			2.323(3)[a]		
P–Ph	1.837(5)[a]			1.837(8)[a]		
	Si1	Si2	Si3	Si1	Si2	Si3
Si–C–Si	114.7(3)	112.1(3)	114.5(3)	120.7(4)	120.2(4)	118.6(4)
Ph–P–Ph	101.9(2)	101.9(2)	103.0(2)	102.4(3)	105.2(4)	102.2(4)
Si–P–Ph	101.1(2)	107.9(2)	97.7(2)	106.0(3)	106.3(3)	104.2(3)
	106.5(3)	98.7(2)	106.8(2)	101.4(3)	102.2(3)	106.8(3)
Me–Si–Me	107.1(3)	106.3(3)	104.6(3)	104.0(4)	105.9(4)	103.4(4)
C–Si–Me	116.1(2)	116.1(2)	118.1(2)	114.9(4)	114.6(3)	116.6(3)
	111.5(3)	110.8(3)	110.6(3)	116.6(3)	117.2(3)	114.7(3)
C–Si–P	107.9(2)	108.0(2)	107.3(2)	112.7(2)	114.1(3)	110.8(3)
Me–Si–P	103.4(2)	111.5(2)	109.4(2)	105.3(3)	103.3(2)	102.3(3)
	110.1(2)	103.4(2)	106.3(2)	101.8(3)	99.8(3)	107.8(3)

[a] Mean value. Numbers in parentheses indicate the precision of individual measurements, none of which differed significantly from the mean.

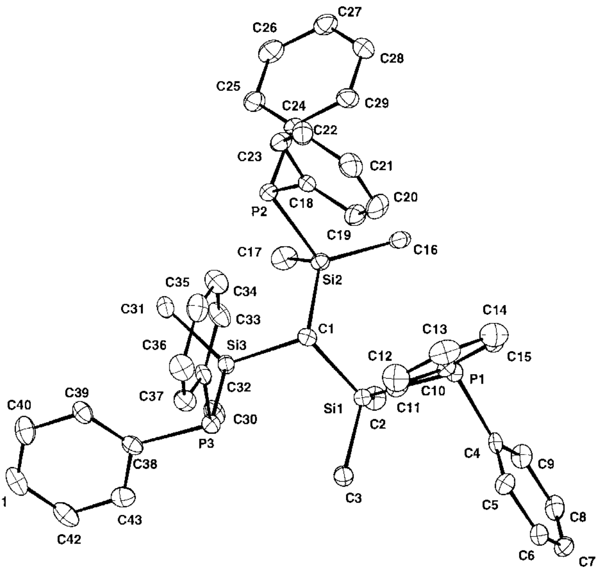


Fig. 1 Molecular structure of $(Ph_2PMe_2Si)_3CH$ **I**.

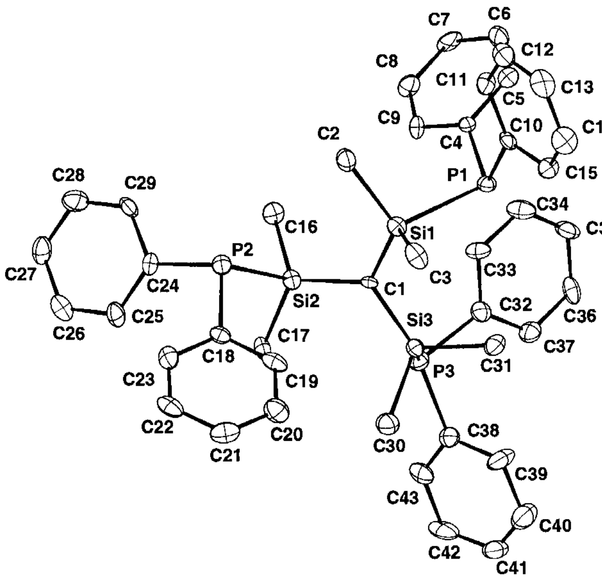


Fig. 2 Structure of the anion of $[Li(tmen)_2][C(SiMe_2PPh_2)_3]$ **2**.

crystals from warm toluene and shown by an X-ray study to be ionic, with a lattice consisting of discrete $[Li(tmen)_2]^+$ cations and $[C(SiMe_2PPh_2)_3]^-$ anions. The CSi_3 core of the carbanion is planar, like those in $[Li(thf)_4][C(SiMe_2C_6H_4Me\text{-}o)_3]$[13] and $[Li(12\text{-crown-}4)_2][C(SiMe_3)(SiMeBu^t_2)(SiMe_2F)]$.[14] The ionic structure of **2** contrasts with the polymeric structure of the amino derivative $LiC(SiMe_2NMe_2)_3$,[5] and the molecular structure of the recently described compound $[LiP\{C(SiMe_3)_2\}(C_6H_4CH_2NMe_2)_2]$ **3**,[15] which has a planar carbanionic centre and lithium co-ordinated both by the lone pair on phosphorus and by those on the two nitrogen atoms.

The ^{31}P NMR spectrum of a thf solution of compound **2** consisted of a singlet at δ −39.4. The absence of Li–P coupling and the small difference between the chemical shifts of **2** and of the precursor **I** indicate that in solution, as in the solid, the phosphorus atoms in **2** are not co-ordinated to lithium.

The structures of the anion of compound **2** and the corresponding protonated species **I** are shown in Figs. 1 and 2. (The cation in **2** is similar to that described in several other compounds and is not discussed further here.) Bond lengths and angles are given in Table 1. For each species the individual Si–C, Si–Me, P–Si and P–C bond lengths differ insignificantly from the corresponding mean values, but there is considerably more variation in the bond angles, which means that neither the anion in **2** nor the corresponding protonated species **I** has any crystallographic symmetry. The anion has one $SiMe_2PPh_2$ group on one side of the CSi_3 plane and two on the other. {There is a similar configuration of $SiMe_2C_6H_4Me\text{-}o$ groups in the anion $[C(SiMe_2C_6H_4Me\text{-}o)_3]^-$.[13]} In contrast, the molecule **I** is propeller-shaped, with approximate C_3 symmetry and all the $SiMe_2PPh_2$ groups lying on the side opposite the C–H bond. The Si–C1 distances are much shorter in the anion (mean 1.809 Å) than in the protonated species **I** (mean 1.898 Å) showing that the anionic charge is delocalised into C1–Si bonds, probably by negative hyperconjugation.[16] Data for a number of related species are given in Table 2. The Si–C1 distances in the silyl-stabilised carbanions are all short compared with those in the corresponding silyl-substituted methanes. The bond lengths show little systematic variation with the nature of the substituent X. The Si–P bonds are longer in the anion than in **I**, and in other organosilylphosphines or organosilylphosphine complexes.[20] The P–C bond lengths are in the normal range, 2.20–2.29 Å, and all the Si–Me bond lengths are, within experimental error, the same as those in $SiMe_4$ [1.875(2) Å].[21] The Si–C–Si angles are larger in the anion than in the protonated species, as expected if the ionic charge is delocalised over the CSi_3 system [*cf.* $C(SiMe_3)_3$[17] and $C(SiMe_2Ph)_3$[16] derivatives]. The other mean bond angles in **I** are similar (within 4°) to those in the anion of **2** but there is more scatter in the protonated than

Table 2 Si–C1 Distances (Å) in compounds $HC(SiMe_2X)_3$ and anions $[C(SiMeX)_3]^-$

X	$HC(SiMe_2X)_3$	Ref.	$[C(SiMeX)_3]^-$	Ref.
Me	1.887(6)	17	1.818(10)–1.822(10)	17
Ph	1.895(1)	19(*a*)	1.800(3)–1.812(3)	13[a]
PPh_2	1.898(5)	This work	1.809(7)	This work
NMe_2			1.793(6)	5
OMe			1.805(4)	4
Br	1.884(5)	19(*b*)		

[a] For $C(SiMe_2C_6H_4Me\text{-}o)_3$.

in the unprotonated species. The geometry at phosphorus is pyramidal with C–P–C and C–P–Si angles less than the tetrahedral value, as found in other silylphosphine complexes.[20]

The chemistry of the compounds described here shows several novel features. (a) Although the organolithium compound **2** reacted in the normal way with a stoichiometric amount of MeOH-d_4 to give the expected $(Ph_2PMe_2Si)_3CD$ in high yield, reactions with other electrophiles *e.g.* MeI or I_2 resulted in cleavage of Si–P bonds. Similar cleavages have been observed for Ph_2PSiMe_3[20] but it is remarkable that attack at the Si–P bond in **2** appears to occur more readily rather than that at the carbanionic centre.

(b) There is a considerable difference in reactivity between Si–N or Si–S bonds on the one hand and Si–P bonds on the other. Whereas the compounds $LiC(SiMe_2NMe_2)_3$[4,5] and $LiC(SiMe_3)_2(SiMe_2SMe)$[3] could each be used as a reagent for the transfer of the C-centred ligands to other metals, reactions of compound **2** with $HgBr_2$ and $PtCl_2$ did not proceed cleanly. Tetraphenyldiphosphine P_2Ph_2 was always obtained as the principal product but the additional presence of PPh_2H in some cases may indicate that PPh_2Li and PPh_2Br are intermediates in the ligand degradation. It has not been possible to isolate the silicon-containing products in a pure state.

(c) The isolation of complex **1** suggests that in the absence of electrophiles the compound **I** has some potential as a mono-, di- or tri-dentate ligand towards transition metals. This area of chemistry is however likely to be restricted by ligand degradation and by slow attack of **I** on the thf commonly used as a solvent.

(d) The stability of compound **I** in the absence of electrophiles is also shown by the fact that it reacts in the normal way with metal methyl derivatives, *e.g.* with LiBu to give the compound **2**.

Experimental

Air and moisture were excluded as far as possible from all reactions by the use of standard Schlenk techniques and Ar as blanket gas. Solvents were dried by normal procedures and distilled immediately before use. The NMR spectra were recorded at 300.13 (^1H), 125.8 (^{13}C), 99.4 (^{29}Si), 121.4 (^{31}P) and 32.53 MHz (^{95}Mo) and chemical shifts are relative to $SiMe_4$ for H, C and Si, H_3PO_4 for P, and Ξ 6.515 for Mo. The ^{29}Si spectra were obtained by inverse gated decoupling and signals from ternary carbon were detected by the DEPT procedure. Coupling constants derived from PANIC simulation are accurate to ±0.2 Hz. The EI mass spectra were recorded at 70 eV: m/z values are given for ^1H, ^{12}C, ^{28}Si and ^{98}Mo.

Syntheses

$(Ph_2PMe_2Si)_3CH$ I. A solution of $KPPh_2$ (130 cm^3, 0.5 M in thf) was added dropwise to $(BrMe_2Si)_3CH$ (9.08 g, 21.3 mmol) in thf (100 cm^3) at room temperature and the mixture stirred for 4 h. The solvent was removed under vacuum, the residue extracted with benzene (3 × 20 cm^3), the extract filtered, the solvent removed, and the residue recrystallised from thf–heptane (10 : 1) to give colourless needles of compound **I** (14.2 g, 89%), mp 192 °C (Found: C, 68.1; H, 6.4; P, 13.8. $C_{43}H_{49}P_3Si_3$ requires C, 69.5; H, 6.4; P, 12.5%). No carbon- or phosphorus-containing impurity was detected by NMR spectroscopy. δ_H (C_6D_6) 0.51 (18 H, s, $SiMe_2$), 1.20 (1 H, q, $^3J_{PH}$ 3.5 Hz, CH), 6.98 (18 H, m, *m*- and *p*-H) and 7.52 (12 H, m, *o*-H). δ_C 1.9 (DEPT q, $^1J_{SiC}$ 33.2, $^2J_{CP}$ 11.1, CH), 2.0 (m, $^2J_{CP}$ 8.1, $^4J_{CP}$ 9.4, 0.4, $^4J_{PP}$ 9.4, $SiMe_2$), 127.7 (*p*-C), 128.8 (m, $^3J_{CP}$ 6.5, $^4J_{PP}$ 9.4, *m*-C), 134.6 (m, $^2J_{CP}$ 18.4, $^4J_{PP}$ 9.4, *o*-C) and 136.5 (m, *ipso*-C, $^1J_{CP}$ 18.6, $^5J_{CP}$ −0.5, $^4J_{PP}$ 9.4 Hz). δ_{Si} 2.8 ($^1J_{SiP}$ 27.2, $^3J_{SiP}$ −3.9 Hz). δ_P −50.6. m/z 557 (5, $M - PPh_2$), 370 (75, P_2Ph_4), 185 (80, PPh_2) and 183 (100%, $PPh_2 - H_2$).

Compound **I** reacted slowly (during 1 week) with thf at room temperature with formation of some P_2Ph_4, the presence of which was deduced from the ^{31}P NMR spectrum.

***cis*-[Mo(CO)$_4${(Ph$_2$PMe$_2$Si)$_3$CH}] 1.** A suspension of $[Mo(CO)_6]$ (0.712 g, 2.69 mmol) and **I** (2.00 g, 2.69 mmol) in toluene (150 cm^3) was slowly heated to reflux, then maintained at reflux for 3 h to give a red solution. The solution was allowed to cool to room temperature and the solvent removed to leave a yellow solid which was judged to be complex **1** (2.34 g, 90%), mp 101 °C (Found: C, 52.9; H, 5.4; Mo, 9.9; P, 9.4. $C_{47}H_{49}MoO_4P_3Si_3$ requires C, 59.3; H, 5.2; Mo, 10.1; P, 9.7%). The low value for the carbon analysis is puzzling since the NMR data were fully consistent with the proposed structure. $\tilde{\nu}_{max}$/cm^{-1} 2018s, 1950 (sh), 1925s and 1880s. δ_H (C_6D_6) 0.15 (6 H, d, $^3J_{PH}$ 3.5, SiMe), 0.31 (6 H, d, $^3J_{PH}$ 6.6, SiMe), 0.36 (6 H, d, $^3J_{PH}$ 2.3, SiMe), 0.93 (1 H, d, $^3J_{PH}$ 5.3 Hz, CH), 6.8–7.2 (18 H, m, *m*- and *p*-H), 7.26 (4 H, m, *o*-H), 7.50 (4 H, m, *o*-H) and 7.76 (4 H, m, *o*-H). δ_C 0.64 (d, $^2J_{CP}$ 14.4, $SiMe_2$), 2.16 (dd, $^2J_{CP}$ 9.6, $^4J_{CP}$ 1.2, $SiMe_2$), 3.25 (d, $^2J_{CP}$ 9.3, $SiMe_2$), 3.45 (q, $^2J_{CP}$ 7.2, CH), 128.06 (A of AXX′, $^3J_{CP}$ 9.6, $^2J_{PP}$ *ca.* 2, *m*-C^{A,B}), 128.42 (s, *p*-C), 128.46 (A of AXX′, $^3J_{CP}$ 9.4, $^2J_{PP}$ *ca.* 2, *m*-C^{A,B}), 128.57 (s, *p*-C), 129.05 (s, *p*-C), 129.14 (d, $^3J_{CP}$ 7.0, *m*-C^C), 133.61 (A of AXX′, $^2J_{CP}$ 10.3, $^2J_{PP}$ *ca.* 2, *o*-C^{A,B}), 134.69 (d, $^2J_{CP}$ 18.5, *o*-C^C), 134.84 (d, $^1J_{CP}$ 17.5, *ipso*-C), 135.24 (d, $^1J_{CP}$ 24.0, *ipso*-C), 135.36 (A of AXX′, $^2J_{CP}$ 12.3, $^2J_{PP}$ *ca.* 2, *o*-C^{A,B}), 137.56 (d, $^1J_{CP}$ 25.6, *ipso*-C), 206.4 (t, $^2J_{CP}$ 7.6, *cis*-CO), 215.9 (dd, $^2J_{CP\text{-}trans}$ 22.2, $^2J_{CP\text{-}cis}$ 9.4, *trans*-CO) and 216.3 (t, $^2J_{CP}$ 7.6 Hz, *cis*-CO). δ_{Si} −2.2 (2 Si, d, $^1J_{SiP}$ 18.7, Si^{A,B}) and 0.1 (1 Si, dt, $^1J_{SiP}$ 30.9, $^3J_{SiP}$ 7.2 Hz, Si^C). δ_P −48.7 (1 P, t, $^4J_{PP}$ 2.0, P^C) and −17.7 (2 P, d, $^4J_{PP}$ 2.0 Hz, P^C). δ_{Mo} −1290 ($\Delta\nu_{\frac{1}{2}}$ 500 Hz). m/z 924 (8, M − CO), 896 (30 M − 2CO), 868 (100, M − 3CO), 840 (55, M − 4CO) and 682 (50, M − 3CO − $PHPh_2$) and 654 (80%, M − 4CO − $PHPh_2$).

[Li(tmen)$_2$][C(SiMe$_2$PPh$_2$)$_3$] 2. A solution of LiBu (3.23 mmol) in hexane (1.3 cm^3) was added to a mixture of **I** (2.0 g, 2.7 mmol) and tmen (4.5 cm^3, 30 mmol) in toluene (30 cm^3) at room temperature. After about 30 min an orange solid separated. This was filtered off, washed first with light petroleum (bp 40–60 °C, 2 × 10 cm^3) then with benzene (3 × 10 cm^3), and recrystallised from warm toluene to give pale yellow air- and moisture-sensitive plates of compound **2** (1.73 g, 65%), mp 187 °C (decomp.) (Found: C, 66.1; H, 8.2; N, 5.7. $C_{55}H_{80}LiN_4P_3Si_3$ requires C, 67.3; H, 8.2; N, 5.7%). δ_H (thf-d$_8$) 0.16 (18 H, s, $SiMe_2$), 2.15 (24 H, s, NMe_2), 2.31 (8 H, s, CH_2), 6.91–7.37 (20 H, m, Ph) and 7.66–7.73 (10 H, m, Ph). δ_C 4.75 (m, $SiMe_2$), 4.8 (DEPT, q, $^1J_{SiC}$ 59.7, $^2J_{CP}$ 20.3 Hz, CSi_3), 46.1 and 58.8 (free tmen, displaced by solvent), 125.3 (s), 127.8 (m) and 134.8 (m). δ_{Si} −0.9. δ_P −39.4.

Reactions of complex 2

With CD$_3$OD. The compound CD_3OD (0.4 cm^3) in benzene (5 cm^3) was added to a suspension of **2** (0.94 g, 0.95 mmol) in benzene (10 cm^3) to give a clear solution immediately. The solvent was removed to leave the deuteriated species $(Ph_2PMe_2Si)_3CD$ as a white solid (0.54 g, 76%). m/z 558.188 ($M - PPh_2$); $C_{31}H_{38}DP_2Si_3$ requires m/z 558.190. The ^{13}C and ^{31}P NMR spectra were identical with those for **I**; the proportion of **I**

Table 3 Crystallographic data and details of structure refinement for compounds **I** and **2**

	I	**2**
Empirical formula	$C_{43}H_{49}P_3Si_3$	$C_{55}H_{80}LiN_4P_3Si_3$
Formula weight	743.0	981.4
T/K	173(2)	173(2)
λ/Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	18.314(4)	15.023(4)
b/Å	10.398(3)	16.592(4)
c/Å	21.859(7)	23.174(11)
β/°	100.61(2)	90.78(3)
U/Å^3	4091(2)	5776(3)
Z	4	4
μ/mm^{-1}	0.26	0.20
θ Range/°	2–22	2–23
Reflections collected	5170	8371
Unique reflections	4993	8027
	(R_{int} = 0.0357)	(R_{int} = 0.0698)
Reflections with $I > 2\sigma(I)$	3229	4106
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.053, 0.107	0.090, 0.145
(all data)	0.105, 0.136	0.189, 0.179
Data/restraints/parameters	4992/0/446	8026/0/595

estimated from the signal at δ 1.2 in the ^{1}H NMR spectrum was less than 10%.

With MeI. A solution of MeI (0.36 mmol) in thf (0.72 cm^3) was added to compound **2** (0.32 mmol) in thf (10 cm^3) at −70 °C. The mixture was allowed to warm to room temperature and stirred for 2 h. After removal of the solvent the residue was extracted with light petroleum to give, according to the ^{31}P NMR spectrum and integration of the ^{1}H spectrum, a mixture of PPh_2Me (51%), and PPh_2H/P_2Ph_4 (49%), identified by comparison of the ^{31}P chemical shifts with those of commercially available samples and with values in the literature.[23] With an eight-fold excess of MeI, **2** gave a white solid which was shown by its ^{1}H, ^{13}C and ^{31}P NMR spectra[18] to be $[PMe_2Ph_2]I$, isolated in 87% yield. Positive FAB MS: m/z 557 (2, $[PPh_2Me_2]_2I$) and 215 (90, PPh_2Me_2).

With I_2. A solution of I_2 (0.7 mmol) in thf (0.8 cm^3) was added to compound **2** (0.7 mmol) in thf (10 cm^3) at −78 °C, and the mixture allowed to warm to room temperature. A white solid was filtered off and the ^{31}P NMR spectrum of the filtrate showed the presence of P_2Ph_4 as the only detectable phosphorus-containing thf-soluble product. The solid was not investigated further.

With metal halides. The reaction of compound **2** with $PtCl_2$ gave P_2Ph_4 and that with $HgBr_2$ gave Hg, P_2Ph_4 (75% of thf-soluble products) and PPh_2H (25%). Unidentified white solids were obtained in both reactions and their NMR spectra showed that they contained neither phosphorus nor aromatic protons.

Crystallography

Details are given in Table 3. All non-hydrogen atoms were refined anisotropically. The H atoms were included in riding mode with $U_{iso}(H) = 1.2U_{eq}(C)$ except for Me groups which were fixed at idealised geometry but with the torsion angles defining the H atom position refined and $U_{iso}(H) = 1.5U_{eq}(C)$. The high value of R for complex **2** is a consequence of the weak diffraction from a thin plate.

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See http://www.rsc.org/suppdata/dt/1999/831/ for crystallographic files in .cif format.

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