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Synthesis and crystal structures of organometallic compounds containing the ligands $C(SiMe_3)_2(SiMe_2H)$ and $C(SiMe_2Ph)_2(SiMe_2H)$

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Abstract

Metallation of $(HMe_2Si)(Me_3Si)_2CH$ (**1**) by LiMe gave the organolithium compound $Li(THF)_2C(SiMe_3)_2(SiMe_2H)$ (**2a**), which exists in toluene solution as a mixture of covalent species and ion pairs $[Li(THF)_4][Li\{C(SiMe_3)_2(SiMe_2H)\}_2]$ (**2b**). Treatment of a mixture of **1** and LiMe with $KOBu^t$ gave $KC(SiMe_3)_2(SiMe_2H)$ (**3**). This reacted with $AlMe_2Cl$ in hexane/THF to give $Al(THF)Me_2\{C(SiMe_3)_2(SiMe_2H)\}$ (**4**). Treatment of $(HMe_2Si)(PhMe_2Si)_2CH$ (**5**) with LiMe in Et_2O/THF gave the THF adduct $[Li(THF)_2C(SiMe_2Ph)_2(SiMe_2H)]$ (**6**); in the presence of $KOBu^t$ the solvent-free $[K][C(SiMe_2Ph)_2(SiMe_2H)]$ (**7**) was obtained. Crystal structure determinations showed that **6** crystallizes in a molecular lattice and **7** in an ionic lattice in which the coordination sphere of the potassium comprises phenyl groups and hydrogen atoms attached to silicon, as well as the central carbon of the bulky carbanion. Compound **7** reacted with an excess of $AlMe_2Cl$ to give $[AlClMe\{C(SiMe_2Ph)_2(SiMe_2H)\}]_2$ (**8**) and $AlMe_3$. A small amount of the methoxo derivative $[Al(OMe)Me\{C(SiMe_2Ph)_2(SiMe_2H)\}]_2$ (**9**) was obtained as a byproduct, presumably after the accidental admission of traces of air. X-ray structural determinations showed that **8** forms halogen-bridged dimers, with the bulky ligands in the *anti*-configuration, and **9** forms methoxo-bridged species in which the bulky ligands are *syn*.

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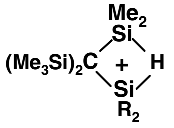
Keywords: Lithium; Potassium; Aluminium; Organosilicon

1. Introduction

There have been reports of Si–H···M interactions both when M is a main group element [1,2] and when it is a transition metal [3–8]. Evidence from X-ray diffraction studies indicates that in some cases the hydrogen atoms are strongly attached to silicon [1,2,6,7,9], and in others strongly attached to the metal [5,10–12]. In a few compounds, the hydrogen appears to be bound to the two centres to a similar degree [13]. The range of possibilities is taken to reflect a likely reaction pathway for industrially important hydrogen transfer processes such as hydrosilylation [14].

In view of the recent confirmation of hydrogen bridges between silicon centres in compounds containing cations **I** [15], we considered it of interest to investigate the extent to which hydrogen attached to silicon could interact with a metal centre in derivatives containing the ligands **II** and **III**.



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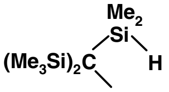

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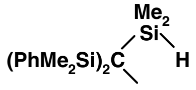

III

These are related to a general class of potentially bidentate ligands of the type $–C(SiMe_3)_2(SiMe_2Z)$, in which the group Z is capable of donating lone pairs or π-electrons to an appropriate electron-deficient metal

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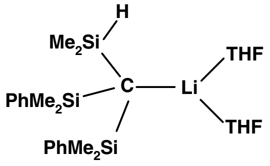
centre M [16]. The structures of such compounds depend on the balance between M···C and M···Z interactions; M···Z interactions predominate when the Lewis acidity of the metal is high, and M···C interactions predominate when the Lewis acidity of M is low. In the latter case Z may interact only weakly or not at all [17]. We describe here some compounds of main group elements containing ligands **II** and **III**; these are potential precursors for the syntheses of transition metal compounds by ligand transfer reactions [18,19].

$(HMe_2Si)(Me_3Si)_2CH$ (1) **$Li(THF)_2C(SiMe_3)_2(SiMe_2H)$ (2a)**

$KC(SiMe_3)_2(SiMe_2H)$ (3) **$Al(THF)Me_2\{C(SiMe_3)_2(SiMe_2H)\}$ (4)**

$(HMe_2Si)(PhMe_2Si)_2CH$ (5)

$[K][C(SiMe_2Ph)_2(SiMe_2H)]$ (7)



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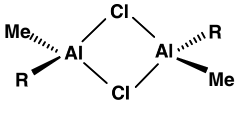

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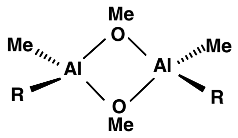

9

$R = C(SiMe_2Ph)_2(SiMe_2H)$

Compounds **2a** and **3–4** were made from the known compound **1** but, on encountering problems arising from disorder in their crystal structures, we switched attention to compounds derived from the new precursor **5**. As we expected from our past experience, these gave better-defined structures and we were able to characterize the organometallic compounds **6–9**.

2. Results and discussion

2.1. The ligand precursors $(HMe_2Si)(Me_3Si)_2CH$ (*1*) and $(HMe_2Si)(PhMe_2Si)_2CH$ (*5*)

Compound **1** was made previously by the reaction between $(Me_3Si)_2CHM$ (M = Li or K) with Me_2SiHCl [20]. Our synthesis from $(Me_3Si)_2CHBr$, Me_2SiHCl and metallic magnesium (Eq. (1)) gave an identical product. The new compound **5** was made similarly in 90% yield.

$$(XMe_2Si)_2CHBr + Me_2SiHCl + Mg/THF \rightarrow (HMe_2Si)(XMe_2Si)_2CH \quad \mathbf{1}\,X = Me \text{ or } \mathbf{5}\,X = Ph \qquad (1)$$

The withdrawal of electron density from the C–H into the Si–C bonds is shown by the low value of $^1J_{CH}$ for the bond to the central carbon (98 Hz in **1**, and 101 Hz in $(Me_3Si)_3CH$ [21]) compared with 118–119 Hz in methyl groups attached to silicon. The value for **5** could not be found because of overlapping peaks. The low values of $^1J_{SiC}$ (38 Hz in **1** and **5**, cf. 39 Hz in $(Me_3Si)_3CH$ and 42 Hz in $(Me_2NSiMe_2)_3CH$ [22]) are found in other compounds in which three silicon atoms are attached to the same carbon centre. In contrast, the values of $^1J_{SiC}$ when only one silicon is attached to carbon, e.g. within $SiMe_3$ groups, are 51–52 Hz. The ^1H and ^{13}C NMR spectra of **5** confirm that the methyl groups within each $SiMe_2Ph$ fragment are inequivalent and that the adjacent carbon atom is prochiral.

2.2. The lithium derivatives *2a* and *6*

Compound **2a** was made more than 10 years ago by the reaction between the chloride $(HMe_2Si)(Me_3Si)_2CCl$ and butyl-lithium at −110 °C. It was not isolated but treated at once with zinc or cadmium halides to give the dialkyl compounds $M\{C(SiMe_3)_2(SiMe_2H)\}_2$ (M = Zn or Cd) [23]. We considered that a more convenient synthesis would be from **1** and lithium diisopropylamide, since the compound $Li(THF)_2\{C(SiMe_2H)_3\}$ (**10a**) can be readily obtained in this way [24].

$Li(THF)_2C(SiMe_2H)_3$ **$[Li(THF)_4][Li\{C(SiMe_2H)_3\}_2]$**

10a **10b**

$Li(THF)_2C(SiMe_3)_3$ **$[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$**

11a **11b**

In our hands, however, **1** did not react with $LiNPr^i_2$ in heptane/THF, either under the conditions employed previously in the metallation of $(HMe_2Si)_3CH$ [24], or under reflux. It did however react with methyllithium in THF to give a good yield of the THF adduct **2a**. The compound **6** was made similarly, but we observed no reaction between **5** and methyllithium when toluene or Et_2O was used as solvent. Both **2a** and **6** were obtained as colourless air- and moisture-sensitive crystals. They were characterized by elemental analysis and NMR spectroscopy but the signals from quaternary carbon atoms could not be detected.

Crystals obtained from solutions of **2** were disordered, with the $SiMe_3$ and $SiMe_2H$ fragments distributed randomly over the three sites adjacent to the central carbon. Although details of the structure are not publishable, it is clear that an ate complex $[Li(THF)_4][Li\{C(SiMe_3)_2(SiMe_2H)\}_2]$ (**2b**) is formed in the solid state, analogous to that found previously for $[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$ (**11b**) [25]. The structure of compound **6** was determined without difficulty and found to comprise molecular species like those in the compounds $[Li(THF)C(SiMe_2Ph)_3]$ (**12**) [26] and $[Li(OEt_2)\{C(SiMe_3)_2(SiMe_2Ph)\}]$ (**13**) [27], in which there are significant Li···Ph interactions, and [Li(THF){C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2 (**14**) [18] or [Li(THF)$_2${C(SiMe$_3$)$_2$(SiMe$_2$Z)}] with Z = NMe$_2$ (**15**) or OMe (**16**) [28]. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. Compound **6** is the first in this series in which there is no chelation, i.e. interaction between lithium and substituents attached to silicon. The Li···H1 distance, 3.27 Å, is much greater than the sum of the van der Waals radii, and the shortest distances from lithium to the carbon atoms of the phenyl groups (Li···C6 or C7 = 2.8 Å) are much greater that those in **12** [2.40(2) Å] or **13** [2.487(11) Å]. Two moles of coordinated solvent are bound to lithium, rather than one as in **12–14**. The Li–O distance (1.958(5) Å) is significantly longer than those in **12–14** (1.85(2)–1.885(10) Å), but similar to those in **15–16** (1.949(11)–1.980(8) Å), in which the coordination number of lithium is four rather than three. The Li–C distance in **6** (2.226(5) Å) is a little shorter than those (2.287(9)–2.304(11) Å) in **15–16**, but not as short as those in **12–14** (Li–C1 2.096(10)–2.144(8) Å), in which there is only one coordinated solvent molecule. The other intraligand bond lengths and angles in **6** are very similar to those in **13**.

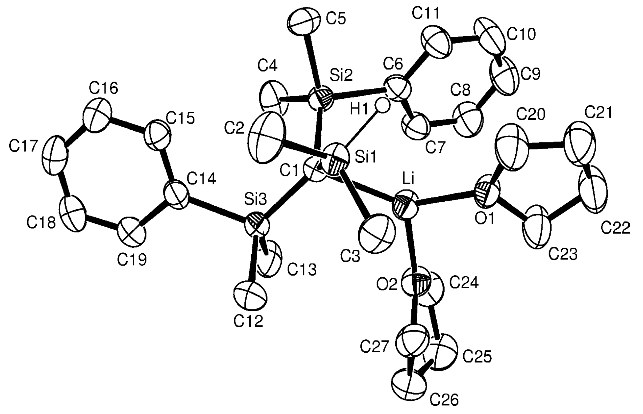

Fig. 1. Molecular structure of **6**.

Table 1
Bond lengths (Å) and angles (°) in Li(THF)$_2$C(SiMe$_2$Ph)$_2$(SiMe$_2$H) (**6**)

Bond lengths			
Li–O[a]	1.958(5)	Si–Me[a]	1.882(3)
Li–C	2.226(5)	Si–Ph[a]	1.913(3)
Si–C[a]	1.821(2)		
Bond angles			
O–Li–O	101.6(2)	Si2–C–Si3	118.66(13)
O1–Li–C1	130.7(2)	Si1–C–Li	94.15(15)
O2–Li–C1	123.5(2)	Si2–C–Li	95.99(16)
Si1–C–Si2	114.43(13)	Si3–C–Li	111.53(16)
Si1–C–Si3	116.68(13)	Me–Si–Me[a]	104.96(17)

[a] Average value with e.s.d's of individual measurements in parentheses. None differs significantly from the mean.

$$\underset{\mathbf{2a}}{2\mathrm{Li(THF)_2\{C(SiMe_3)_2(SiMe_2H)\}}} \leftrightharpoons \underset{\mathbf{2b}}{[\mathrm{Li(THF)_4}][\mathrm{Li\{C(SiMe_3)_2(SiMe_2H)\}_2}]}$$

The ^{1}H, ^{13}C, ^{7}Li and ^{29}Si spectra of **2a** at 298 K show sharp peaks in toluene-d$_8$ solution, as expected if the species in solution has a molecular structure like that found for crystalline **6**. As the solution of **2a** is cooled below 258 K, however, new signals, ascribed to the ionic form **2b**, appear. The peaks remain sharp, indicating that chemical exchange is slow on the NMR time scale and that the two species coexist (Eq. (2)). The proportion of **2b** increases as the temperature is lowered, and more concentrated solutions require less cooling before peaks for **2b** are observed. The predominance of molecular species at higher temperature and lower concentrations suggest that the ion-pairs **2b** are (at least in toluene) held together in a solvent cage, rather than dissociated. The ionic species must be the less soluble since it crystallizes from solution preferentially. A similar equilibrium between **10a** and **10b** was proposed to account for the discrepancy between the ^{7}Li NMR spectra of a solid sample and a solution in C$_6$D$_6$ [24]. The compound **11b** also dissolves in toluene to give a solution containing covalent species and ion-pairs [29] but, because the spectra vary in a complex way with the concentration, temperature and solvent, a quantitative comparison between thermodynamic data for compounds **2**, **10** and **11** is not yet possible.

2.3. The potassium compounds 3 and 7

Treatment of the precursors **1** and **5** with methyllithium in the presence of potassium *t*-butoxide gave the organopotassium compounds **3** and **7** (Eq. (3)).

$$\begin{aligned}&(\mathrm{HMe_2Si})(\mathrm{XMe_2Si})_2\mathrm{CH} + \mathrm{LiMe} + \mathrm{KOBu^t}\\ &\qquad \mathrm{X} = \mathrm{Me}\ \mathbf{1}\ \mathrm{or\ Ph}\ \mathbf{5}\\ &\rightarrow [\mathrm{K}][\mathrm{C(SiMe_2X)_2(SiMe_2H)}] + \mathrm{LiOBu^t} + \mathrm{CH_4} \qquad (3)\\ &\qquad \mathrm{X} = \mathrm{Me}\ \mathbf{3}\ \mathrm{or\ Ph}\ \mathbf{7}\end{aligned}$$

It is likely that the metallating agent was methylpotassium, generated in situ at room temperature from the reaction between methyllithium and potassium *t*-butoxide. The alternative reaction sequence, viz. metallation of **1** or **5** by methyllithium, followed by reaction of **2a** or **6** with KOBu^t, is unlikely since the metallation step requires forcing conditions, e.g. reaction in THF under reflux (see Section 3). Compounds **3** or **7** could be washed free from LiOBu^t with heptane and obtained, after crystallization from benzene, as yellow crystals. Elemental analysis of **3** showed that the crystals did not contain coordinated solvent but a satisfactory X-ray structure determination was precluded by crystallographic disorder. The NMR spectrum revealed that the compound contained about 20% of [K][C(SiMe$_3$)$_3$] [30], showing that some of the methylpotassium formed from the reaction between LiMe and $KOBu^t$ had reacted at the Si–H rather than the C–H bond. Compound **7** was made similarly but in this case there was no evidence from the NMR spectra that there was any $KC(SiMe_3)(SiMe_2Ph)_2$ impurity [27], indicating that there had been clean reaction at the C–H bond.

An X-ray study confirmed that **7** crystallized as the ionic solid $[K][C(SiMe_2Ph)_2(SiMe_2H)]$. The asymmetric unit comprises three independent ion-pairs, two of them disordered with lower occupancy Si sites sharing the unresolved methyl and phenyl groups. The disordered ion-pairs are repeated by unit cell translations to form zig-zag chains along the *a* axis (Fig. 2); the undisordered ion-pair, shown in Fig. 3, is repeated by the *a* glide plane. The bond lengths and angles in Table 2 are for this undisordered species; those for the other ion-pairs are identical within experimental uncertainty. There are significant differences between bond distances from the central carbon atoms (e.g. C39) to silicon within each of the three independent species. These differences must be treated with caution because of the uncertainties resulting from disorder, but the short average Si–C distance [1.817(8) Å] and wide average Si–C–Si angle [118.8(5)°] strongly indicate that electronic charge is transferred from potassium to the adjacent carbon and delocalized into the Si–C bonds.

Each potassium atom interacts with (a) the adjacent carbanionic centre (C39 in Fig. 3), (b) two phenyl groups from the next ion-pair in the chain, (c) a methyl group in a neighbouring chain (C2″, C21 and C40″ in Fig. 2) and (d) the hydrogen atoms attached to silicon (H7s in Fig. 3). The coordination sphere can be considered as a distorted trigonal bipyramid with (a) and (b) occupying the three equatorial and (c) and (d) the two axial positions [the sum of angles subtended by C39, C47″ and C53″ is 358° and H21a–K3–H7s 153°]. The interaction (a) gives a K–C distance of 3.167(8) Å, slightly longer than that in $[K][C(SiMe_3)_3]$ [Av. 3.097(11) Å] but similar to the shortest distances in $[K][C(SiMe_2Ph)_3]$ [3.26(2) Å] [30], $[K][C(SiMe_3)_2(SiMe_2NMe_2)]$ [3.1870(12) Å] [31] or $[K][C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)]$ [3.207(3) Å] [18]. If it is assumed (somewhat arbitrarily) that K···C distances <3.5 Å (Table 2) indicate significant interactions (b) between potassium and the two adjacent phenyl groups, one phenyl group, C52–C57, can be designated as η^6 and the other, C44–C49, from which only *meta*- or *para*-C atoms are involved, can be considered to be η^2. The K···C(aryl) distances are typical of those found in a range of organopotassium derivatives [32]. The interactions (c) link the chains into layers perpendicular to the *c* axis (Fig. 2). The interchain K···Me distances [3.461(10) to 3.484(7) Å] are only slightly longer than the intrachain K···Me distances in $[K][C(SiMe_3)_3]$ [3.16(2)–3.311(11) Å] [30] or $[K][C(SiMe_3)_2(SiMe_2NMe_2)]$ [3.113(2)–3.49 Å] [31].

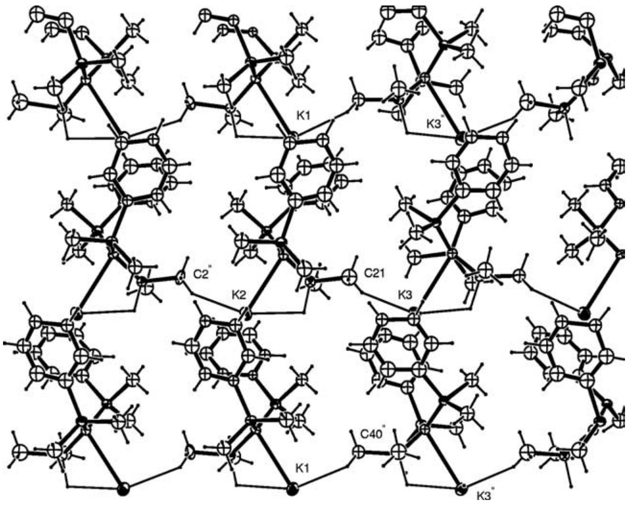

Fig. 2. Lattice of **7** showing interactions between ion-pairs.

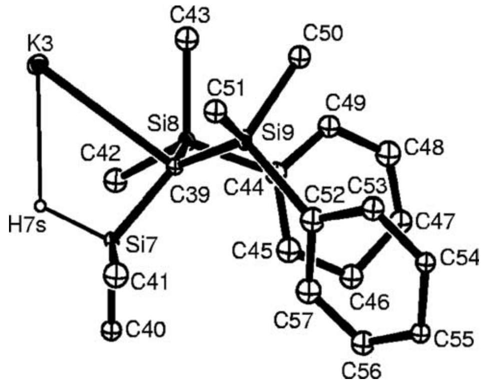

Fig. 3. Structure of the undisordered ion-pair of **7**.

Table 2
Bond lengths (Å) and angles (°) in the undisordered molecule in the structure of $KC(SiMe_2Ph)_2(SiMe_2H)$ (**7**)

Bond lengths			
K–C39[a]	3.167(8)	C39–Si(Ph)	1.869(8) 1.770(8)
K–C(Ph)[a] η^6	3.248(8)–3.395(7)	Si–Me[c]	1.896(8)
K–C(Ph)[a] η^2	3.293(8)–3.326(10)	Si–Ph[c]	1.925(8)
K–C(Me)[a,b]	3.461(10)	K···Si	3.457
C39–Si(H)	1.817(8)	K···H	2.57(9)
Bond angles			
Si–C–Si	116.8(4) 116.9(4) 122.8(4)	K–C–Si8	94.5(3)
K–C–Si7	83.1(3)	K–C–Si9	110.7(3)

[a] K···C distances >3.5 Å are not shown.

[b] To C21 in adjacent ion-pair.

[c] Average value; with e.s.d. of individual measurements in parentheses. None differs significantly from the mean.

The hydrogen atoms attached to silicon were located and their positions refined. Those shown as H7s in Fig. 3 appear to be attracted towards the adjacent potassium centres, as shown by the narrow K–C–Si(H) angles [81.8(3) to 83.1(3)° c.f. K–C–Si(Ph) 94.5(3) to 110.7(3)°] and the K···H distances 2.57(9)–2.77(9) Å. These are similar to those observed in [K(18-crown-6)][H_2SiPh_3] (2.69 and 3.21 Å) [2], and [$KOsH_3(PMe_2Ph)_3]_2$ (2.52–3.02 Å) [11] by X-ray diffraction and in [K(18-crown-6)][$W(PMe_3)_3H_5$] by neutron diffraction (2.684(6) to 2.750(6) Å) [12]. All are less than the sum of the van der Waals radii (≈3.95 Å [33]) or the distance [2.854(1) Å] between the six-coordinate ions in KH [34]. However, a search of the Cambridge Crystallographic Data Centre data base gives a number of K···HC distances of ≈2.6 Å in organopotassium compounds [18,35] and crown ether complexes [36]. In **7** itself, the K3–H21 distance between potassium and the hydrogen in a methyl group in an adjacent ion-pair-chain is 2.69(9) Å and the K2–H2″ and K1–H40″ distances are 2.85 and 2.87 Å, respectively. In compounds in which the lattices are held together by predominantly electrostatic attraction the coordination number of potassium is large and not very well defined, and hydrogen atoms at the periphery of the anions are brought into the 'coordination sphere.' Where, as in **7**, the anions contain local centres of partial negative charge (e.g. hydridic hydrogen) it is not surprising that they adopt configurations in which these centres point towards the cation to give the interactions discussed here. It is not clear, however, that these should be described as 'K···H bonds'.

The average Si–Me distance [1.894(8) Å] may be compared with those in [K][$C(SiMe_3)_3$] [1.873(13) Å], [K][$C(SiMe_2Ph)_3$] [1.89(2) Å], [K][$C(SiMe_3)_2(SiMe_2NMe_2)$] [1.8920(14) Å], [K][$C(SiMe_3)_2(SiMe_2C_5H_4N$-2)] [1.890(4) Å] and the mean Si–Ph distance [1.925(8) Å] with that in [K][$C(SiMe_2Ph)_3$] [1.92(2) Å].

Compounds **3** and **7** are poorly soluble in aliphatic hydrocarbons, as is consistent with the adoption of structures in which there are significant interactions between ion-pairs. They are more soluble in benzene and toluene, which are presumably able to break potassium–phenyl interactions by solvation. The solubility of **7** is, however, still quite low and samples for NMR spectra were warmed to 50 °C to reveal the weaker signals. The peak assigned to the methyl protons of the $SiMe_2Ph$ group appears as a sharp singlet (contrast **5** above), which does not significantly broaden when a sample in toluene-d_8 is cooled to 198 K. This shows that in solution there is ready inversion at the centre of the $[C(SiMe_2Ph)_2(SiMe_2H)]^-$ carbanion. In the slightly more crowded compound [K][$C(SiMe_2Ph)_2(SiMe_3)$], inversion became sufficiently slow below 189 K for two signals to be observed in the $SiMe_2Ph$ region of the ^1H NMR spectrum [27].

It has been shown that Si–H···M interactions may be detected by low coupling constants $^1J_{SiH}$ [4,6]. Our compounds **1**–**4** and **5**–**8** all give values (155–184 Hz) in the usual range [8]; the weak interaction detected by crystallography in **7** appears to be broken in toluene solution.

2.4. The aluminium compounds 4, 8 and 9

The reaction of the lithium compound **2** with aluminium chloride gave an intractable oil. With $AlMe_2Cl$ in THF a crystalline product was obtained and this was shown by chemical analysis and NMR spectroscopy to be the compound [Al(THF)Me_2{$C(SiMe_3)_2(SiMe_2H)$}] (**4**). The structure was shown by an X-ray study to be like that of [Al(THF)Me_2{$C(SiMe_3)_3$}] [37] but crystallographic disorder, again arising from different orientations of the $C(SiMe_3)_2(SiMe_2H)$ group, made the data too imprecise for publication. The NMR spectra indicated that there was a small amount of Al(THF)MeCl{$C(SiMe_3)_2(SiMe_2H)$} (**17**) present as an impurity. Like the previously described related compound Al(THF)MeCl{$C(SiMe_3)_3$} [38], this gave two signals in the ^1H NMR spectrum at 298 K for the α-CH_2 protons of the coordinated THF, showing that the species in solution contained the chiral AlCMeClO fragment in which the THF was firmly bound to aluminium. At higher temperatures the THF (but not the Si–H) signals broadened and at 338 K irradiation at the THF signals of the minor species resulted in saturation transfer at the signal of the major species. This chemical exchange probably proceeds by the dissociation of a small fraction of the THF complexes **4** and **17**.

We argued that we were unlikely to obtain species containing Si–H–Al bridges in the presence of solvents, such as THF, that can coordinate to aluminium more strongly than hydride, so we turned to [K][$C(SiMe_2Ph)_2(SiMe_2H)$] (**7**) as an alkylating agent. The reaction between **7** and one equivalent of $AlMe_2Cl$ in hexane gave a white air- and moisture-sensitive solid that was almost insoluble in hydrocarbons, strongly suggesting that the structure was ionic or polymeric. The experiment was repeated several times with the same result. In one instance, however, the mass spectrum of the solid showed peaks ascribed to the compound $AlMe_2${$C(SiMe_2Ph)_2(SiMe_2H)$}. A small amount of soluble material was extracted into heptane and shown by an X-ray structure determination to be the methoxo-derivative [Al(OMe)Me{$C(SiMe_2Ph)_2(SiMe_2H)$}]$_2$ (**9**), presumably formed by the admission of traces of air. Because very little material was available, further characterisation was not possible, but it was clear that oxygen had reacted preferentially at the more electron-rich unsubstituted methyl groups, rather than at the relatively electron-poor, more hindered, silyl-substituted methyl group.

The reaction of **7** with an excess of $AlMe_2Cl$ gave a well-defined crystalline solid, shown by elemental analysis, NMR spectroscopy and an X-ray structure determination to be the dialkylaluminium chloride **8** (Eq. (4)).

$$\underset{\mathbf{7}}{[\mathrm{K}][\mathrm{C}(\mathrm{SiMe_2Ph})_2(\mathrm{SiMe_2H})]} + \mathrm{AlMe_2Cl} \rightarrow \mathrm{KCl} + \mathrm{AlMe_3} + 0.5\underset{\mathbf{8}}{[\mathrm{AlClMe}\{\mathrm{C}(\mathrm{SiMe_2Ph})_2(\mathrm{SiMe_2H})\}]_2} \quad (4)$$

Compound **8** could be formed either by rapid reaction of $AlMe_2Cl$ with a (non-polymeric) $AlMe_2\{C(SiMe_2Ph)_2(SiMe_2H)\}$ intermediate or by reaction of **7** with $AlMeCl_2$ initially present in the $AlMe_2Cl$.

In one experiment compound **7** was made from **5**, LiMe and $KOBu^t$ (by a procedure like that described in Section 3.3), and without purification treated with $AlMe_2Cl$ to give colourless crystals. These were not suitable for an X-ray structure determination and an attempt to obtain larger crystals by sublimation at 0.001 mm Hg gave only oily decomposition products. The crystals were dissolved in toluene-d_8 to give NMR spectra that showed the presence of Bu^tO groups. In this sample, therefore, *t*-butoxide was incompletely removed from the crude **7** and a molecular, rather than a polymeric, species was apparently obtained. Although it was not possible to determine the structure of the initially formed crystals from NMR spectra alone, the data are consistent with the presence of alkoxide–alkyl complexes like those postulated to explain the reactivity of 'super-bases' [39]. What little information is available on these species indicates that their structures can be quite complex [40]. The spectra underwent a complex series of changes when they were rerecorded as the sample was heated to 348 K then allowed to stand for 22 h at 298 K. In the final product *t*-butoxide appeared to be attached to aluminium and the bulky anion to potassium. The ^1H, ^{13}C and ^{29}Si spectra are quite similar to those of **7**, but the broadening and splitting of the $SiMe_2Ph$ peak on cooling below 294 K shows that free **7** is not present. The central carbon of the anion appeared to be four- rather than three-coordinate.

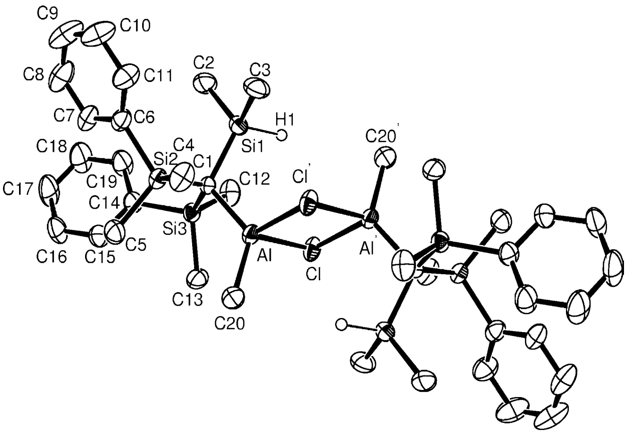

Fig. 4. Molecular structure of **8**.

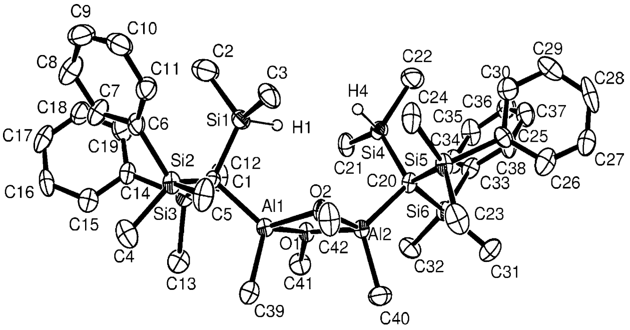

Fig. 5. Molecular structure of **9**.

Table 3
Bond lengths (Å) and angles (°) in $[AlCXMe\{C(SiMe_2Ph\}_2(SiMe_2H)\}]_2$ X = Cl (**8**) or OMe (**9**)

	8 X = Cl	**9** X = OMe[d]
Bond lengths		
Al–C[a]	1.972(3)	2.023(7)[b]
Al–Me	1.938(4)	1.951(9)[b]
Al–X	2.3216(12)[b]	1.869(5)[b]
C–Si[a]	1.902(3)[b]	1.896(8)[b]
Si(H)–Me[c]	1.874(4)[b]	1.871(9)[b]
Si(Ph)–Me[c]	1.877(4)[b]	1.874(9)[b]
Si–Ph	1.892(3)[b]	1.890(8)[b]
Bond angles		
Al–X–Al	93.47(4)	99.6(2)[b]
X–Al–X′	86.53(4)	79.0(2)[b]
X–Al–Me	107.66(13) 102.82(12)	106.0(3)–109.2(3)
C–Al–X[a]	114.33(9) 111.55(10)	117.9(3)–121.0(3)
Me–Al–C[a]	126.50(14)	117.6(3)
Si–C–Si[a]	111.13(15) 116.77(14) 109.48(15)	111.7(4)[b]
Me–Si–Me	105.28(18)[b]	105.5(4)[b]
Me–Si–Ph	105.74(16)[b]	105.1(4)[b]
C–Si(H)–Me[a,c]	114.56(15)–116.00(16)	113.2(4)–118.8(4)
C–Si(Ph)–Me[a,c]	110.79(15)–112.83(15)	110.7(3)–114.3(4)
C–Si–Ph[a]	113.42(14) 118.21(14)	113.0(3)–117.8(3)
Al–C–Si[a]	104.12(14) 111.60(13) 103.34(14)	104.8(3)–109.4(4)

[a] C1 or C20.

[b] Average value with e.s.d.'s of individual measurements in parentheses. None differs significantly from the mean.

[c] Si(H): Si1 or Si4; Si(Ph): Si2,3,5,6.

[d] C–O 1.451(8) Å[b]; C–O–Al 122.2(4)°.[b]

The structures of the derivatives $AlXMe\{C(SiMe_2Ph)_2(SiMe_2H)\}$ X = Cl (**8**) or OMe (**9**) are shown in Figs. 4 and 5 and selected bond lengths and angles are given in Table 3. Both compounds form dimers. Those of **8** have a centre of symmetry and adopt an *anti* configuration about the strictly planar Al_2Cl_2 ring with the bulky groups pointing away from each other. Those of **9** have no crystallographically imposed symmetry; the central Al_2O_2 ring is slightly folded (dihedral angle 15.7°), and the conformation about the mean plane of the ring is *syn*, i.e. the two bulky groups are on the same side. There is no significant difference in the bond lengths from the central carbon atom to the silicon atoms that bear the hydrogen substituent and those that do not, and no significant difference between Si-alkyl and Si-aryl bonds. In both **8** and **9** the bonds from aluminium to the central carbon of the $C(SiMe_2Ph)_2(SiMe_2H)$ group are significantly longer than the Al–Me bonds, as is commonly found in compounds that contain bulky groups. The Al–C, Al–Cl and Al–O bond lengths are all in the usual range [41–43].

The corresponding intraligand dimensions in the two compounds are identical within experimental error. The smaller size of oxygen than of chlorine results in weaker cross-ring inner shell repulsions and thus wider Al–X–Al and narrower X–Al–X angles in the methoxo derivative than in the chloride. Angles at aluminium involving the carbon atoms C1 or C20 are wider, and angles involving only X and Me are narrower than the tetrahedral value. This may partly be explained on steric grounds but C–Al–C angles of 120–125° are commonly found in compounds $AlMe_2X$ [42,43]. The distances between the hydrogen atoms attached to Si1 or Si4 and aluminium (3.409 Å in **8** and 3.204, 3.395 Å in **9**) are greater than the sum of the van der Waals radii so there in no evidence of engagement of the Si–H bond with the metal centre.

There is no simple explanation for the difference in the conformations adopted by **8** and **9**. Most compounds containing four-membered Al_2O_2 rings crystallize with the *anti* configuration [37,44], presumably because it is the less crowded. However, there are reports in the literature that indicate that the difference in energy between the *syn* and *anti* forms may be small [41]. In some cases both isomers are present in the equilibrium mixture in solution and either may constitute the least soluble species and thus crystallize preferentially. Compounds that crystallize with the *syn* configuration, i.e. with bulky groups on the same side of the Al_2O_2 ring, are $[\overline{\mathrm{Al}\{C(SiMe_3)_2(SiMe_2R)\}(CH_2)_4\mathrm{O}}]_2$ (R = Me or Cy) [45] and the mentholato compound $[R_2AlOC_{10}H_{19}]_2$ (R = Me, but when R = Bu^i the configuration is *anti*) [43]. For **9** it is possible that the energy of the *anti* configuration is raised by repulsive interactions between the methyl groups C41 and C42 and those of the bulky ligand. (The distances from C42 to C5, C23, and C24 are all less than 3.65 Å.) The energy of the *syn* configuration is lowered by the presence of hydrogen substituents on Si1 and Si4, so that the bulky ligands may lie on the same side of the ring without being pushed too close together. (The H1–H4 distance (2.48 Å) is close to the sum of the van der Waals radii.) Both *syn*- and *anti*-configurations are found also in compounds containing Al_2N_2 rings [46]. For example, NMR spectroscopic studies showed that a solution of $[AlBrEtNHBu^t]_2$ in benzene contained a mixture of species that included the all-*cis* isomer in which the two Bu^t groups and the two Br atoms are all on the same side of the Al_2N_2 ring.

2.5. Conclusion

We have synthesized a number of main group organometallic compounds that contain the ligand $C(SiMe_3)_2(SiMe_2H)$ **II** and the new ligand $C(SiMe_2Ph)_2(SiMe_2H)$ **III**. Both have the potential to give compounds in which the Si–H group might bind to the metal centre, but only weak interactions in the crystalline potassium compound **7** have so far been detected. The H···K distances are similar to those recently reported in [K(18-crown-6)][H_2SiPh_3] [2], but also similar to those in organopotassium compounds that are usually described as showing K···Me or K···Ph interactions. Further examples of Si–H···M interactions are likely to be found in compounds that do not contain ligands having lone pairs that can preferentially coordinate to metal centres. Compounds containing the ligand **III** are less likely to suffer from crystallographic disorder than those containing ligand **II**.

3. Experimental

Air and moisture were excluded as far as possible by use of flame-dried glassware, Schlenk techniques with argon as blanket gas, and a nitrogen-filled drybox. NMR spectra were recorded at 500.1 (^1H), 125.8 (^{13}C), 194.5 (^7Li), 130.4 (^{27}Al) or 99.4 Hz (^{29}Si); chemical shifts are relative to $SiMe_4$, aqueous LiCl or aqueous $Al(NO_3)_3$. EI mass spectra were obtained at 70 eV; m/z values are given for ^{28}Si and ^{35}Cl.

3.1. Synthesis of $(HMe_2Si)(Me_3Si)_2CH$ (**1**)

A solution of $(Me_3Si)_2CHBr$ (15.0 g, 62.8 mmol) in THF (50 ml) was added dropwise to a mixture of Me_2SiHCl (15 ml, 138 mmol) and magnesium metal (1.50 g) in THF (50 ml). The mixture was then heated under reflux for 2 h, stirred as it was allowed to cool overnight, and filtered. The filtrate was washed with water, the product extracted with hexane and the extract dried over Na_2SO_4. The solvent was removed from the extract under reduced pressure and the residue, distilled at 97 °C/28 mmHg (10.9 g, 80%), was shown to be identical with that obtained previously [20]: ^1H NMR (C_6D_6) δ−0.89 (1H, d, $^3J_{HH} = 0.8$ Hz, $^2J_{SiH} = 9.7$ Hz, CH), 0.11 (18H, s, $SiMe_3$), 0.14 (6H, d, $^3J_{HH} = 3.8$ Hz, $SiMe_2$), 4.25 (1H, dsept, $^3J_{HH}$ (sept) = 3.8 Hz, $^3J_{HH}$ (d) = 1 Hz, $^1J_{SiH} = 183.5$ Hz, SiH). ^{13}C NMR: δ−0.4 (qm, $^1J_{CH} = 119$ Hz, $^1J_{SiC} = 50.7$ Hz, $SiMe_2$), 2.1 (d, $^1J_{CH} = 98$ Hz, $^1J_{SiC} = 38$ Hz, CH), 2.7 (qm, $^1J_{CH} = 118.4$ Hz, $^1J_{SiC} = 51.2$ Hz, $SiMe_3$). ^{29}Si NMR: δ−15.7 ($^1J_{SiH} = 183.8$ Hz, $^2J_{SiH} = 10$ Hz, $SiMe_2H$), 0.1 ($SiMe_3$). MS: m/z 217 (90, M–H), 203 (100, M–Me), 129 (50, $Me_2Si{=}CHSiMe_2$), 73 (50, $SiMe_3$).

3.2. $Li(THF)_2C(SiMe_3)_2(SiMe_2H)$ (**2a**)

There was no reaction between $(HMe_2Si)(Me_3Si)_2CH$ and $LiNPr^i_2$ in heptane/THF (1:10) during 16 h either at room temperature or under reflux.

A solution of LiMe (7.84 mmol) in Et_2O (4.9 ml) was added to a solution of **1** (1.50 g. 6.88 mmol) in THF (50 ml). The mixture was heated under reflux for 2 h, then the solvents were removed under vacuum to leave a white solid that was crystallised from toluene to give colourless crystals (2.13 g, 84%), mp 123 °C. Anal. Calc. for $C_{17}H_{41}LiO_2Si_3$: C, 55.38; H, 11.21. Found: C, 55.0; 11.35. ^1H NMR (toluene-d_8, 298 K): δ 0.33 (18H, s, $SiMe_3$); 0.39 (6H, d, $^3J_{CH} = 3.6$ Hz, $SiMe_2$), 1.26 (8H, m, THF), 3.33 (8H, m, THF), 4.73 (1H, hept, $^1J_{SiH} = 161$ Hz, $^3J_{CH} = 3.6$ Hz). ^{13}C NMR: δ 4.8 ($SiMe_2$), 7.0 ($SiMe_3$), 25.1 and 68.3 (THF). ^7Li NMR: δ 0.8. ^{29}Si NMR: δ −23.7 ($SiMe_2$), −9.8 ($SiMe_3$).

As the toluene solution was cooled below 258 K, new signals, ascribed to the ionic form $[Li(THF)_4][Li\{C(SiMe_3)_2(SiMe_2H)\}_2]$ (**2b**), appeared. ^1H NMR (208 K) **2a**: δ 0.59 ($SiMe_3$), 0.66 ($SiMe_2$), 1.68 and 3.28 (THF), 4.98 (SiH); **2b**: 0.70 ($SiMe_2/SiMe_3$), 1.05 and 3.12 (THF), 5.12 (SiH). ^{13}C NMR (220 K) **2a**: δ 3.0 ($SiMe_2$), 6.9 ($SiMe_3$), 25.6 and 68.1 (THF); **2b**: 4.8 ($SiMe_2$), 7.2 ($SiMe_3$), 24.8 and 67.9 (THF). ^7Li NMR (208 K) **2a**: δ 0.8; **2b**: −0.9 and 3.5. The ratio **2b/2a** was concentration dependent but in a typical experiment the ^1H spectra showed that it was 0.20 at 248 and 1.5 at 208 K.

3.3. $KC(SiMe_3)_2(SiMe_2H)$ (**3**)

A solution of **1** (2.00 g, 9.17 mmol) and LiMe (9.17 mmol) in Et_2O (25 ml) was added to a slurry of $KOBu^t$ (1.03 g, 9.20 mmol) in Et_2O (20 ml). The mixture was stirred overnight and the slightly cloudy solution was filtered. Volatile material was removed from the filtrate under vacuum and the white residue was washed with heptane then crystallized from benzene to give **3** (2.10 g, 89%) as colourless needles, mp 230–235 °C (decomp). Anal. Calc. for $C_9H_{25}KSi_3$: C, 42.12; H, 9.82. Found: 41.82; H, 10.04. ^1H NMR: δ 0.31 (s, 18H, $^2J_{SiH} = 5.8$ Hz, $SiMe_3$); 0.40 (6H, d, $^3J_{HH} = 3.5$ Hz, $SiMe_2$); 4.67 (1H, sept, $^1J_{SiH} = 155$ Hz, $^3J_{HH} = 3.5$ Hz, SiH). ^{13}C NMR: δ 5.0 ($^1J_{CSiMe} = 53.4$, $^1J_{CSiH} = 51.3$ Hz, CSi_3), 5.7 ($^1J_{SiC} = 46.2$ Hz, $SiMe_2$), 7.7 ($^1J_{SiC} = 46.8$ Hz, $SiMe_3$). ^{29}Si NMR: δ−25.3 ($SiMe_2$), 12.1 ($SiMe_3$). Minor peaks (≈20%) at δ_H 0.31, δ_C 8.4 ($^1J_{SiC} = 46.5$ Hz) and δ_{Si} −12.7, were assigned to $KC(SiMe_3)_3$ [30].

3.4. $Al(THF)Me_2\{(C(SiMe_3)_2(SiMe_2H)\}$ (**4**)

A solution of $AlMe_2Cl$ (2.8 ml, 1 M) in hexane was added to a solution of **2a** (0.60 g, 1.63 mmol) in THF (25 ml) and the mixture was stirred overnight. The volatile components were removed under vacuum to leave a white solid that was crystallized from heptane at −20 °C to give colourless crystals of **4**, mp 198–202 °C (0.47 g, 84%). Anal. Calc. for $C_{15}H_{39}AlSi_3O$: C, 52.0; H, 11.34. Found: C, 51.60; H, 11.58. ^1H NMR (298 K): δ−0.51 (6H, s, $AlMe_2$), 0.28 (18H, s, $^2J_{SiH} = 6.1$ Hz, $SiMe_3$), 0.33 (6H, d, $^3J_{HH} = 3.6$ Hz, $SiMe_2$), 1.02–1.05 (4H, m, THF), 3.54 (4H, t, THF), 4.41 (1H, hept, $^1J_{SiH}$ 177 Hz, $^3J_{HH} = 3.6$ Hz, SiH). ^{13}C NMR: δ−4.1 (b, $AlMe_2$), 5.3 ($SiMe_3$), 6.2 ($SiMe_2$), 24.4 (THF), 72.4 (THF). ^{29}Si NMR: δ−18.1 ($SiMe_2H$), −4.2 ($SiMe_3$). ^{27}Al NMR: δ (353 K) 174, $\Delta\nu_{1/2} = 1.9$ kHz. MS: m/z 331 (30, M–Me), 317 (70, M–Me–CH_2), 260 (100, RAlO [R = $C(SiMe_3)_2$-$(SiMe_2H)$]). The sample appeared to contain about 20% of $Al(THF)ClMe\{(C(SiMe_3)_2(SiMe_2H)\}$ as a byproduct. ^1H NMR: δ−0.50 (3H, s, AlMe), 0.30 (18H, s, $SiMe_3$), 0 33 (6H, d, $^3J_{HH} = 3.8$ Hz, $SiMe_2$), 1.00–1.02 (4H, m, THF), 3.59 and 3.82 (2H, m, THF), 4.38 (1H, hept, SiH). ^{13}C NMR: δ 2.1 ($SiMe_2$), 6.2 ($SiMe_3$), 24.3 (THF), 73.6 (THF). ^{29}Si NMR: δ−18.3 ($SiMe_2H$), −4.7 ($SiMe_3$). ^{27}Al NMR: δ (353 K) 151, $\Delta\nu_{1/2} = 1.6$ kHz. Selective decoupling at δ 1.1 gave doublets at δ 3.59 and 3.82 with $^2J_{HH} = 8.1$ Hz. MS: m/z 279 (55, RAlCl), 264 (50, RAlCl−Me) [R = $C(SiMe_3)_2(SiMe_2H)$].

3.5. $HMe_2Si(PhMe_2Si)_2CH$ (**5**)

A solution of $(PhMe_2Si)_2CHBr$ [27] (10.5 g, 28.9 mmol) in THF (50 ml) was added slowly to a mixture of $SiMe_2HCl$ (15 ml, 135 mmol) and Mg (0.69 g, 28.9 mmol) in THF (100 ml) at room temperature. The mixture was heated under reflux for 4 h then treated with water, and the product was extracted with hexanes. The extract was dried over Na_2SO_4 and solvent was removed under vacuum to leave an oil that was distilled at 120 °C/0.001 mm to give **5** as a colourless liquid (9.1 g, 92%). Anal. Calc. for $C_{19}H_{30}Si_3$: C, 66.59; H, 8.82. Found: C, 66.73; H, 9.12. ^1H NMR (CD_2Cl_2): δ−0.06 (1H, d, $^3J_{HH} = 1$ Hz, CH), −0.03 (12H, d, $^3J_{HH} = 3.8$ Hz, $SiMe_2H$), 0.24 and 0.35 (12H, s, $SiMe_2Ph$), 4.04 (1H, heptd, $^1J_{SiH} = 183.5$ Hz, $^3J_{HH} = 3.8$ and 1.2 Hz), 7.30–7.33 (6H, m, *m*-and *p*–H), 7.47–7.49 (4H, m, *o*–H). ^{13}C NMR: δ−0.8 ($^1J_{SiC} = 51$ Hz, $SiMe_2H$), 0.2 ($^1J_{SiC} = 38$ Hz, CH), 0.5 and 1.1 ($^1J_{SiC} = 53$ Hz, $SiMe_2Ph$), 127.9, (*m*-C), 128.9 (*p*-C), 133.8 (*o*-C), 141.6 (*i*-C). ^{29}Si NMR: δ−15.2 ($SiMe_2H$) and −4.0 ($SiMe_2Ph$). MS: m/z 327 (10, M−Me), 269 (20, M−$SiMe_3$), 249 (80, $Me_2Si{=}C(SiMe_2Ph)(SiMeH)$), 191 (30, $Me_2Si{=}CHSiMePh$), 135 (100, $SiMe_2Ph$).

3.6. $Li(THF)_2C(SiMe_2Ph)_2(SiMe_2H)$ (**6**)

Methyllithium (1.8 ml 1.6 M solution in Et_2O) was added to a solution of **5** (1.00 g, 2.92 mmol) in THF (30 ml). The mixture was heated under reflux for 2 h then stirred at room temperature overnight. The solvents were removed and the white solid residue was dissolved in heptane (5 ml). The solution was kept at −30 °C to give colourless crystals of **6** (0.75 g, 52%), mp 65 °C. Anal. Calc. for $C_{27}H_{45}Si_3O_2Li$: C, 65.80; H, 9.20. Found: C, 65.85; H, 9.27. ^{1}H NMR: δ 0.33 (6H, d, $^3J_{HH} = 3.6$ Hz, $SiMe_2H$), 0.56 (12H, s, $SiMe_2Ph$), 1.21 and 3.18 (8H, m, THF), 4.80 (1H, hept, $^1J_{SiH} = 165.5$, $^3J_{HH} = 3.6$ Hz, SiH), 7.02 (2H, tt, *p*-H), 7.10 (4H, m, *m*-H), 7.59 (4H, dd, $^3J_{HH} = 7.9$ Hz, $^4J_{HH} = 1.4$ Hz, *o*-H). ^{13}C NMR: δ 4.8 ($SiMe_2H$), 5.1 ($SiMe_2Ph$), 25.2 and 68.0 (THF), 127.4 (*p*-C), 128.2 (*m*-C), 133.4 (*o*-C), 149.3 (*i*-C). The signal from the quaternary carbon was not found. ^{7}Li NMR: δ 0.39. ^{29}Si NMR: δ−24.5 ($SiMe_2H$), −11.7 ($SiMe_2Ph$). Compound **5** did not react with LiMe in toluene or Et_2O.

3.7. $KC(SiMe_2Ph)_2(SiMe_2H)$ (7)

The procedure was the same as that used for **3**. The product from **5** (1.00 g, 2.92 mmol), LiMe (2.88 mmol) and $KOBu^t$ (2.92 mmol) was obtained from hot benzene as yellow crystals (Yield 1.05 g, 95%), mp 173–175 °C. Anal. Calc. for $C_{19}H_{29}KSi_3$: C, 59.93; H, 7.68. Found: C, 59.77; H, 7.47. ^{1}H NMR (toluene-d_8, 323 K): δ 0.18 (6H, d, $^3J_{HH} = 3.6$ Hz, $SiMe_2H$), 0.52 (18H, s, $SiMe_2Ph$), 4.50 (1H, hept, $^1J_{SiH} = 156$ Hz, $^3J_{HH} = 3.6$ Hz, SiH), 6.88 (4H, tt, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.5$ Hz, *p*–H), 6.97 (8H, m, *m*-H), 7.49 (4H, dd, $^3J_{HH} = 7.9$ Hz, $^4J_{HH} = 1.4$ Hz, *o*-H). ^{13}C NMR: δ 3.8 (CSi_3), 5.2 ($SiMe_2Ph$), 5.6 ($SiMe_2H$), 126.6 (*p*-H), 128.0 (*m*-H), 133.1 (*o*-H), 152.9 (*i*-C). ^{29}Si NMR: δ−26.7 ($SiMe_2H$), −13.8 ($SiMe_2Ph$).

3.8. Reaction between $KC(SiMe_2Ph)_2(SiMe_2H)$ (7) and $AlMe_2Cl$

A solution of $AlMe_2Cl$ (0.79 ml, 1.0 M) in hexane was added to a solution of **7** (0.39 g, 0.80 mmol) in toluene (20 ml) and the mixture was stirred overnight. Solvent was removed from the clear solution under vacuum to give a white solid that was almost insoluble in heptane. Some of the solid did dissolve, however, and cooling the heptane solution (5 ml) to −20 °C gave a small crop of white crystals, which were shown by an X-ray structure determination to be **9**. The low yield (precise value not recorded) suggested that traces of air had been admitted inadvertently during Schlenk-tube manipulation. Attempts to crystallize the major product were unsuccessful but the compound $AlClMe_2\{C(SiMe_2Ph)_2(SiMe_2H)\}$ was detected by mass spectrometry: *m*/*z* 398 (60, M), 383 (95, M−Me), 325 (100, $(PhMe_2Si)_2CHAlMe$), 309 (40), 247 (35), 175 (60), 135 (60), 73 (40).

When an excess of $AlMe_2Cl$ was added to a solution of **7** in toluene (30 ml) at room temperature and the mixture stirred overnight, a white precipitate was formed. The solvent was removed and the residue extracted with heptane (10 ml). The extract was kept at 5 °C to give colourless crystals of $[AlClMe\{C(SiMe_2Ph\}_2(SiMe_2H)\}]_2$ (**8**), mp 150–152 °C. Anal. Calc. for $C_{20}H_{32}AlClSi_3$: C, 57.31; H, 7.69. Found: C, 57.07; H, 7.81. ^{1}H NMR (toluene-d_8): δ−0.68 (6H, s, AlMe), 0.06 (6H, d, $^3J_{HH} = 3.6$ Hz, $SiMe_2H$), 0.51 and 0.58 (6H, s, $SiMe_2Ph$), 4.55 (1H, hept, $^3J_{HH} = 3.7$, $^1J_{SiH} = 184$ Hz, SiH), 7.03–7.12 (6H, m, *m*-and *p*-H), 7.54 (4H, dd, *o*-H). ^{13}C NMR: δ−2.3 (b, AlMe), 1.7, 2.9 and 4.0 ($SiMe_2$), 128.1 (*m*-C), 129.1 (*p*-C), 135.4 (*o*-C), 140.0 (*i*-C). ^{27}Al NMR: δ 183, $\Delta\nu_{1/2} = 5$ kHz. ^{29}Si NMR: δ−19.0 ($SiMe_2H$), −8.5 ($SiMe_2Ph$). MS: *m*/*z* 418 (5, monomer (M)), 403 (70, M–Me), 383 (10, M–Cl), 367 (10, M–Me–HCl), 340 (50, $(PhMe_2Si)_2C{=}SiMe_2$), 325 (70, $(PhMe_2Si)_2CHAlMe$), 309 (70, $PhMeSi{=}C(SiMe_2Ph)AlMe$), 264 (30, $(PhMe_2Si)(HMe_2Si)C{=}SiMe_2$), 249 (70, $PhMeSi{=}C(SiMe_2H)SiMe_2$), 175 (100, $Me_2Si{=}CHAlPh$), 135 (80, $PhMe_2Si$), 73 (80).

In another experiment, $AlMe_2Cl$ (4.7 ml, 1.0 M solution in hexane) was added to **7** (1.8 g, 4.7 mmol), prepared from **5**, $KOBu^t$, and LiMe in toluene (30 ml) as described for **3** above, and the mixture was stirred overnight. The solvents were removed, the residue was extracted with hexane, and the extract was kept at 5 °C to give colourless crystals: ^{1}H NMR: δ−0.22 (AlMe), 0.52 (d, $SiMe_2H$), 0.65 ($SiMe_2Ph$), 0.81 (Bu^t), 6.9 and 7.6 (b, Ph). The spectra were rerecorded as the sample was heated to 348 K then allowed to stand for 22 h at 298 K. ^{1}H NMR: δ−0.51 (AlMe), 0.26 ($SiMe_2H$), 0.38 ($SiMe_2Ph$), 1.1 (Bu^t), 4.5 (heptet, Si–H), 6.9, 7.0 and 7.4 (Ph). ^{13}C NMR: δ−1.0 (AlMe), 4.9 ($SiMe_2Ph$) and 5.0 ($SiMe_2H$), 31.2 and 74.3 (Bu^t), 128.2, 129.0, 133.7, and 148.2 (Ph). ^{29}Si NMR: δ−24.5 ($SiMe_2H$), −12.0 ($SiMe_2Ph$). ^{27}Al NMR: δ 153.3, $\Delta\nu_{1/2}$ 1.5 kHz. The Si–H peak, not observed initially (presumably because it was too broad), now appeared as a heptet, and the peaks in the aromatic region gave multiplets like those in **7**. NOE experiments indicated that the Si–Me protons giving signals at δ0.33 were close to the Si–Ph protons but not to the Bu^t or Al–Me protons, suggesting that the ligand $\{C(SiMe_2Ph\}_2(SiMe_2H)\}$was not attached to aluminium. On cooling, the $SiMe_2Ph$ signals in the ^{1}H spectrum broadened and split into two with a coalescence temperature of 294 K.

3.9. Crystallography

Data were collected on a Kappa CCD diffractometer and processed without correction for absorption. Details are given in Table 4. The structures were determined by direct methods and full-matrix least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms attached to silicon were refined and the others were placed in calculated positions in riding mode. In the structure of **7**, there is disorder, with resolved Si atom sites and unresolved overlapping C atom sites, so all carbon atoms were left as isotropic in the final cycles of least-squares refinement. The crystal of

Table 4
Summary of crystallographic data for **6**, **7**, **8** and **9**

	6	**7**	**8**	**9**
Chemical formula	$C_{27}H_{45}LiO_2Si_3$	$C_{19}H_{30}KSi_3$	$C_{40}H_{64}Al_2Cl_2Si_6$	$C_{42}H_{70}Al_2O_2Si_6$
Formula weight	492.8	381.8	838.3	829.5
T (K)	173(2)	173(2)	223(2)	223(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$C2/c$ (No 15)	$Pna2_1$ (No 33)	$P2_1/n$ (No 14)	$P2_1/c$ (No 14)
a (Å)	36.6018(8)	15.649(2)	13.2226(2)	17.4792(11)
b (Å)	10.1624(2)	23.540(9)	11.1732(3)	16.2942(10)
c (Å)	16.1529(4)	17.411(3)	16.5654(3)	18.2873(13)
β (°)	100.047(1)	90	107.822(1)	113.309(3)
U (Å^3)	5916.1(2)	6414(3)	2329.9(1)	4783.3(5)
Z	8	12	2	4
μ (mm^{-1})	0.18	0.42	0.36	0.24
R_1 wR_2 $I > 2\sigma(I)$	0.052, 0.124	0.065, 0.152	0.057, 0.148	0.093, 0.193
All data	0.077, 0.137	0.092, 0.171	0.073, 0.155	0.170, 0.233
Measured/independent reflections (R_{int})	17570/5134/0.074	61023/10684/0.069	18078/5506/0.046	23605/6578/0.155
Reflections with $I > 2\sigma(I)$	3889	7994	4447	3678

9 diffracted only weakly. In Figs. 1–5 thermal ellipsoids are for 50% probability.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre CCDC nos. 224314-224317 for compounds **6**, **7**, **8**, and **9**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: www.ccdc.cam.ac.uk).

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References

[1] A. Sekiguchi, M. Ichinohe, M. Takahashi, C. Kabuto, H. Sakurai, Angew. Chem. Int. Ed. Engl. 36 (1997) 1533;
H. Pritzkow, T. Lobreyer, W. Sundermeyer, N.J.R. van Eikema Hommes, P.v.R. Schleyer, Angew. Chem. Int. Ed. Engl. 33 (1994) 216;
B. Goldfuss, P.v.R. Schleyer, S. Handschuh, F. Hampel, W. Bauer, Organometallics 16 (1997) 5999.

[2] M.J. Bearpark, G.S. McGrady, P.D. Prince, J.W. Steed, J. Am. Chem. Soc. 123 (2001) 7736.

[3] J.Y. Corey, J. Braddock-Wilking, Chem. Rev. 99 (1999) 175;
Z. Lin, Chem. Soc. Rev. 31 (2002) 239;
F. Carré, E. Colomer, R.J.P. Corriu, A. Vioux, Organometallics 3 (1984) 1272.

[4] G.J. Kubas, J. Organomet. Chem. 635 (2001) 37.

[5] F. Delpech, S. Sabo-Etienne, B. Chaudret, J.-C. Daran, J. Am. Chem. Soc. 119 (1997) 3167.

[6] (2) A. Ohff, P. Kosse, W. Baumann, A. Tillack, R. Kempe, H. Görls, V.V. Burlakov, U. Rosenthal, J. Am. Chem. Soc. 117 (1995) 10399;
E. Spaltenstein, P. Palma, K.A. Kreutzer, C.A. Willoughby, W.M. Davis, S.L. Buchwald, J. Am. Chem. Soc. 116 (1994) 10308.

[7] L.J. Procopio, P.J. Carroll, D.H. Berry, J. Am. Chem. Soc. 116 (1994) 177;
W.A. Herrmann, N.W. Huber, J. Behm, Chem. Ber. 125 (1992) 1405.

[8] U. Schubert, Adv. Oragnomet. Chem. 30 (1990) 151.

[9] F. Delpech, S. Sabo-Etienne, B. Donnadieu, B. Chaudret, Organometallics 17 (1988) 4926.

[10] U. Schubert, K. Ackermann, B. Wörle, J. Am. Chem. Soc. 104 (1982) 7378.

[11] J.C. Huffman, M.A. Green, S.L. Kaiser, K.G. Caulton, J. Am. Chem. Soc. 107 (1985) 5111.

[12] A. Berry, M.L.H. Green, J.A. Bandy, K. Prout, J. Chem. Soc. Dalton Trans. (1991) 2185.

[13] M. Tanabe, T. Yamada, K. Osakada, Organometallics 22 (2003) 2190;
Y.-J. Kim, S.-C. Lee, J.-I. Park, K. Osakada, J.-C. Choi, T. Yamamoto, Organometallics 17 (1998) 4929;
H. Suzuki, T. Takao, M. Tanaka, Y. Moro-oka, J. Chem. Soc. Chem. Commun. (1992) 476.

[14] B. Marciniec, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, VCH, Weinheim, 1996, p. 487.

[15] C. Eaborn, J. Chem. Soc. Dalton Trans. (2001) 3397, and references therein;
P.D. Lickiss, K. Batz, P.C. Masangane, W. Sohal, G.L. Veneziani, Isolation, structural characterisation, and reactions of bridged silylium ions, in: XIII International Symposium on Organosilicon Chemistry, Guanajuato, Mexico, 2002.

[16] C. Eaborn, J.D. Smith, J. Chem. Soc. Dalton Trans. (2001) 1541.

[17] C. Eaborn, M.S. Hill, P.B. Hitchcock, J.D. Smith, J. Chem. Soc. Dalton Trans. (2002) 2467.

[18] S.S. Al-Juaid, C. Eaborn, P.B. Hitchcock, M.S. Hill, J.D. Smith, Organometallics 19 (2000) 3224.

[19] S.S. Al-Juaid, C. Eaborn, S.M. El-Hamruni, P.B. Hitchcock, J.D. Smith, S.E. Sözerli-Can, J. Organomet. Chem. 649 (2002) 121.

[20] D. Seyferth, H. Lang, Organometallics 10 (1991) 551.

[21] B. Wrackmeyer, W. Biffar, Z. Naturforsch Teil B 34 (1979) 1270.

[22] A.G. Avent, D. Bonafoux, C. Eaborn, S.K. Gupta, P.B. Hitchcock, J.D. Smith, J. Chem. Soc., Dalton Trans. (1999) 831.

[23] S.S. Al-Juaid, C. Eaborn, A. Habtemariam, P.B. Hitchcock, J.D. Smith, J. Organomet. Chem. 437 (1992) 41.

[24] E.J. Hawrelak, F.T. Ladipo, D. Sata, J. Braddock-Wilking, Organometallics 18 (1999) 1804.

[25] C. Eaborn, P.B. Hitchcock, J.D. Smith, A.C. Sullivan, J. Chem. Soc., Chem. Commun. (1983) 827.

[26] C. Eaborn, P.B. Hitchcock, J.D. Smith, A.C. Sullivan, J. Chem. Soc., Chem. Commun. (1983) 1390.

[27] C. Eaborn, W. Clegg, P.B. Hitchcock, M. Hopman, K. Izod, P.N. O'Shaughnessy, J.D. Smith, Organometallics 16 (1997) 4728.

[28] S.S. Al-Juaid, C. Eaborn, S.M. El-Hamruni, P.B. Hitchcock, J.D. Smith, Organometallics 18 (1999) 45;
C. Eaborn, P.B. Hitchcock, J.D. Smith, S.E. Sözerli, Organometallics 17 (1998) 4322.

[29] A.G. Avent, C. Eaborn, P.B. Hitchcock, G.A. Lawless, P.D. Lickiss, M. Mallien, J.D. Smith, A.D. Webb, B. Wrackmeyer, J. Chem. Soc., Dalton Trans. (1993) 3259.

[30] C. Eaborn, P.B. Hitchcock, K. Izod, A.J. Jaggar, J.D. Smith, Organometallics 13 (1994) 753.

[31] S.S. Al-Juaid, C. Eaborn, S. El-Hamruni, A. Farook, P.B. Hitchcock, M. Hopman, J.D. Smith, W. Clegg, K. Izod, P. O'Shaughnessy, J. Chem. Soc., Dalton Trans. (1999) 3267.

[32] J.D. Smith, Adv. Organomet. Chem. 43 (1999) 267.

[33] A. Bondi, J. Phys. Chem. 68 (1964) 441.

[34] S.R. Gunn, L.G. Green, J. Am. Chem. Soc. 80 (1958) 4782.

[35] R.D. Rogers, J.L. Atwood, Organometallics 3 (1984) 271;
A.M. McPherson, G. Stucky, H. Lehmkuhl, J. Organomet. Chem. 152 (1978) 367;
R.B. Hallock, O.T. Beachley, Y.-J. Li, W.M. Sanders, M.R. Churchill, W.E. Hunter, J.L. Atwood, Inorg. Chem. 22 (1983) 3683;
M.M. Olmstead, L. Pu, R.S. Simons, P.P. Power, Chem. Commun. (1997) 1595;
R.M. Fabicon, M. Parvez, H.G. Richey, J. Am. Chem. Soc. 113 (1991) 1412;
A.P. Purdy, C.F. George, Organometallics 11 (1992) 1955;
K. Jonas, G. Burkart, C. Häselhoff, P. Betz, C. Krüger, Angew. Chem. Int. Ed. Engl. 29 (1990) 322;
H. Meyer, G. Schmidt-Lukasch, G. Baum, W. Massa, A. Berndt, Z. Naturforsch. Teil B 43 (1988) 801.

[36] G.B. Deacon, E.E. Delbridge, C.M. Forsyth, Angew. Chem. Int. Ed. Engl. 38 (1999) 1766;
U. Müller, C. Grebe, B. Neumüller, B. Schreiner, K. Dehnicke, Z. Anorg. Allg. Chem. 619 (1993) 500.

[37] C. Schnitter, H.W. Roesky, T. Albers, H.-G. Schmidt, C. Röpken, E. Parisini, G.M. Sheldrick, Chem. Eur. J. 3 (1997) 1783.

[38] C. Schnitter, K. Klimek, H.W. Roesky, T. Albers, H.-G. Schmidt, C. Röpken, E. Parisini, Organometallics 17 (1998) 2249.

[39] M. Schlosser, Pure Appl. Chem. 60 (1988) 1627;
T. Kremer, S. Harder, M. Junge, P.v.R. Schleyer, Organometallics 15 (1996) 585;
W. Bauer, L. Lochmann, J. Am. Chem. Soc. 114 (1992) 7482, and references therein;
D. Hoffmann, W. Bauer, P.v.R. Schleyer, U. Pieper, D. Stalke, Organometallics 12 (1993) 1193, and references therein.

[40] M. Marsch, K. Harms, L. Lochmann, G. Boche, Angew. Chem. Int. Ed. Engl. 29 (1990) 308;
P.G. Willard, G.J. MacKewan, J. Am. Chem. Soc. 111 (1989) 7671;
S. Harder, A. Streitwieser, Angew. Chem. Int. Ed. Engl. 32 (1992) 1066.

[41] J.P. Oliver, R. Kumar, Polyhedron 9 (1990) 409.

[42] C.E. Holloway, M. Melnik, J. Organomet. Chem. 543 (1997) 1.

[43] M.L. Sierra, R. Kumar, V.S.J. de Mel, J.P. Oliver, Organometallics 11 (1992) 206.

[44] J.D. Fisher, J.T. Golden, P.J. Shapiro, G.P.A. Yap, A.L. Rheingold, Main Group Met. Chem. 19 (1996) 521;
A. Kunicki, J. Topczewski, S. Szumacher, A. Cebulski, Main Group Met. Chem. 23 (2000) 773;
R.J. Wehmschulte, W.J. Grigsby, B. Schiemenz, R.A. Bartlett, P.P. Power, Inorg. Chem. 35 (1996) 6694;
C. Boker, M. Noltemeyer, H. Gornitzka, B.O. Kneisel, M. Teichert, R. Herbst-Irmer, A. Meller, Main Group Met. Chem. 211 (1998) 565.

[45] C. Schnitter, H.W. Roesky, C. Röpken, R. Herbst-Irmer, H.-G. Schmidt, M. Noltemeyer, Angew. Chem. Int. Ed. 37 (1998) 1952;
M. Schormann, K.S. Klimek, H. Hatop, S.P. Varkey, H.W. Roesky, C. Lehmann, C. Röpken, R. Herbst-Irmer, M. Noltemeyer, J. Solid State Chem. 162 (2001) 225.

[46] R.E. Bowen, K. Gosling, J. Chem. Soc. Dalton Trans. (1974) 964;
K. Wakatsuki, T. Tanaka, Bull. Chem. Soc. Jpn. 48 (1975) 1475.