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Invited review

Synthesis, structure and reactions of organometallic compounds of Groups 1–3 containing bulky silicon-substituted alkyl groups

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Abstract

A review is presented of the chemistry of organometallic compounds containing very bulky ligands of the types $C(SiMe_2X)_3$ (X = Me, Ph or OMe) and $C(SiMe_3)_2(SiMe_2X)$ (X = Ph or OMe) attached to metals of Groups 1–3. The structures and reactions of these compounds show novel features not observed for analogues containing less bulky alkyl groups.

Keywords: Silicon, Groups 1–3; Tris(trimethylsilyl)methyl

1. Introduction

This review describes the chemistry of organometallic compounds containing ligands of the type $C(SiMe_2X)_3$ (X = Me, Ph, OMe) and $C(SiMe_3)_2(SiMe_2X)$ (X = Ph, OMe) attached to metals of Groups 1–3. The structures of these compounds show many novel features not observed in analogues with less bulky alkyl groups. These features provide valuable insight into properties and reactions that often differ markedly from those of compounds containing smaller alkyl groups. The emphasis is on recent results; earlier work has been summarised elsewhere [1–3].

2. Derivatives of the alkali metals

2.1. *Tris(trimethylsilyl)methyl derivatives*

The lithium compound LiR (R = $C(SiMe_3)_3$) is usually obtained (Eq. (1)) by metallation of RH with methyllithium [4–6] in tetrahydrofuran (THF) or butyllithium–tetramethylethylenediamine (TMEN) in hexane [7,8], and used in situ. It can also be made from the reactons of RCl or RBr with lithium metal [4,9] or with methyllithium in THF/Et_2O [4] or butyllithium in Et_2O [10] or Et_2O/TMEN [4]. More recently, solvent-free LiR has been obtained from the reaction between RHgBr and 2 equivalents of butyllithium in hexane (Eq. (2)) [11].

$$RH + MMe \longrightarrow RM + MeH \quad (1)$$

$$RHgBr + 2BuLi \longrightarrow RLi + LiBr + HgBu_2 \quad (2)$$

The compounds of the heavier alkali metals MR (R = Na [12], K [13], Rb or Cs [14]), are also obtained by metallation of RH (Eq. (1)) with the methyl derivatives MMe, now readily available through the work of Weiss and co-workers [15]. Good yields of MR are obtained provided that the temperature is carefully controlled to suppress the reaction between MeM and the ether solvent. When M = Na, the metallation in Et_2O is so slow compared with the reaction with the solvent that satisfactory yields of RNa cannot be obtained unless a stronger donor such as TMEN is added. This accelerates the metallation but TMEN is incorporated into the product [12].

The alkali metal derivatives adopt an astonishing range of structures. The solvent-free Li compound **1a** (R = $C(SiMe_3)_3$) is dimeric, with additional interactions between lithium atoms and C–H bonds ($Li \cdots C$ 254.1(7) and 246.6 (6) pm) in methyl groups attached to one silicon atom from each of the two $C(SiMe_3)_3$ groups, making the coordination round the lithium quasi-tetrahedral as in **2** [11]. Within the central planar

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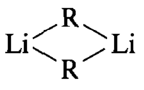
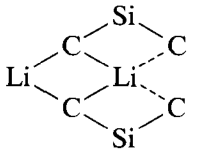


1a



2

$M'^{+}[R\text{-}Li\text{-}R]^{-}$

3a $M' = [Li(THF)_4]$

3b $M' = [Li(TMEN)_2]$

3c $M' = [(PMDETA)Li(\mu\text{-}Cl)Li(PMDETA)]$

four-membered ring the Li–C–Li angles are narrow (61.6°), as expected for three-centre bonding. The crystals obtained from solvents containing ether or amine donors consist of the ate complexes **3a–c** (PMDETA = pentamethyldiethylenetriamine), the only known examples of diorganolithates [8,16,17]. It has been shown by multinuclear magnetic resonance studies that ion pairs containing the diorganolithate anions persist in solution and predominate above room temperature. They exchange rapidly on the NMR time-scale with further species which can be detected in spectra recorded at low temperatures. These species are tentatively identified [8] as solvated monomers **1b** in THF (like those found in the solid-state structure of compound **10** below) and as dimers or aggregates $(LiR)_n$ in toluene (**1a** or **1c**). (Scheme 1).

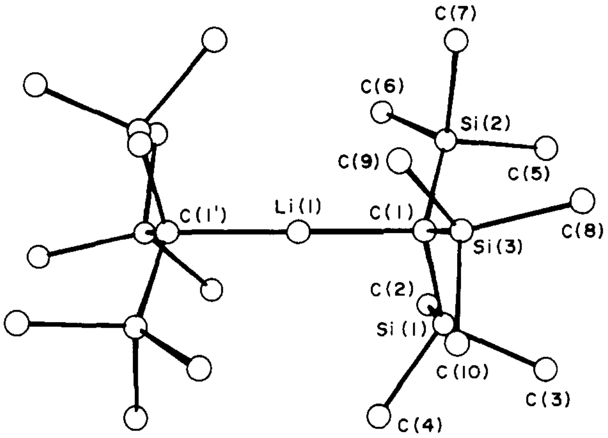


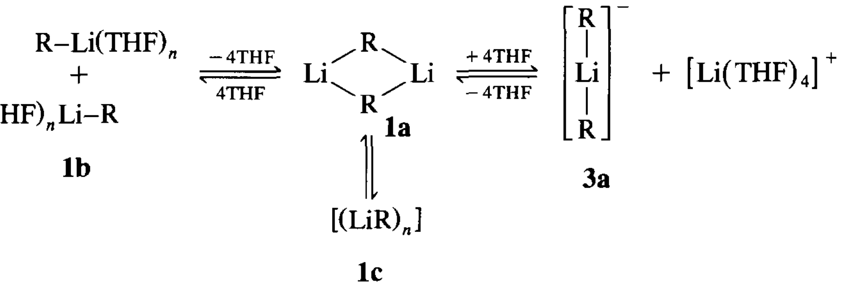
Fig. 1. Structure of the anion $[LiR_2]^-$ in $[(THF)_4Li][LiR_2]$ (**3a**).

The structures of some similar ate complexes of sodium (**4**) [12], copper (**5**) [18] and silver (**6**) [19], have been determined.

$[Na(TMEN)_2(OEt_2)][NaR_2]$ **4** $[Li(THF)_4][CuR_2]$ **5**

$[Li(THF)_4][AgR_2]$ **6**

The low quality of the X-ray diffraction data for these ate complexes means that it is not possible to discern the more subtle variations from structure to structure. However, some general features are clear. In all compounds the inner Si–C bonds (182–184 pm) are shorter than the outer Si–Me bonds (190–195 pm) (the apparently short Si–Me bond in **4** is considered to be an artefact arising from libration of methyl groups). The Si–C–Si angles (114°–116°) are larger and the Me–Si–Me angles (103°–104°) are smaller than the tetrahedral value. The M–C bond lengths, viz. Cu–C 205(1), Li–C 218(1), Ag–C 218(1) and Na–C 247.9(6) pm, show that, in these isostructural ions, lithium and silver are about the same size, with copper apparently smaller and sodium larger. In all cases one methyl group of each $SiMe_3$ points directly away from the metal and the other two point only slightly inwards (Fig. 1), leaving the metal exposed. It is instructive to compare the molecular parameters of the sodium species $[NaR_2]^-$ with those of the isoelectronic MgR_2 [20,21]. As the charge on the nucleus of the metal is increased from 11 to 12, electron density is drawn into the M–C bonds from the inner Si–C bonds but the outer Si–Me bonds are similar in the two species. The M–C bond is strengthened and shortened to 211.6(2) pm and the Si–C bond is weakened and lengthened (from 181.7(8) to 187.7(3) pm). At the same time, the CSi_3 system becomes more pyramidal, and the $SiMe_3$ groups are forced to rotate so that three methyl groups on one side of the molecule point inwards towards the metal to interlock with three from the other side (Fig. 2). This protects the metal from attack by nucleophiles and is



Scheme 1.

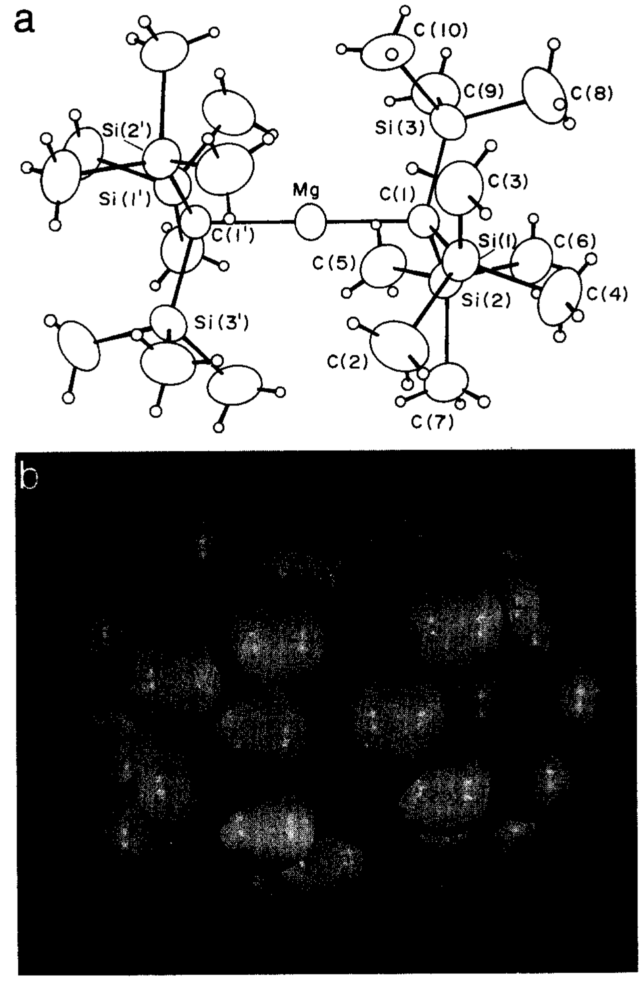


Fig. 2. Structure of the dialkyl MgR_2: (a) line drawing and (b) space filling model.

probably the main cause of the low reactivity of the dialkylmagnesium (see below).

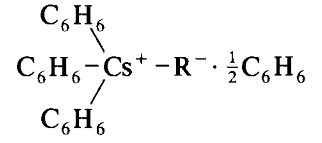
To our surprise, the derivatives MR of potassium (**7**) [13] and rubidium (**8**) [14] crystallized without lattice solvent, even from solutions containing diethyl ether. Their crystal structures are similar but not identical. Both contain infinite chains of M^+ and planar $[C(SiMe_3)_3]^-$ ions, with only weak interactions between the chains (Fig. 3).

$\cdots R^-M^+R^-M^+ \cdots$

$R = C(SiMe_3)_3$
M = K, **7**
M = Rb, **8**

$\cdots R'^-M^+R'^-M^+ \cdots$

$R' = C(SiMe_2Ph)_3$
M = Na, **11**
M = K, **12**
M = Cs, **13**



$\underset{C_6H_6}{\overset{C_6H_6}{C_6H_6\text{-}Cs^+}}-R^-\cdot\tfrac{1}{2}C_6H_6$

9

$(THF)LiC(SiMe_2Ph)_3$

10

The planarity of the anions is of interest, since the anion in KCD_3 has been shown by neutron diffraction to be pyramidal (D–C–D = 106°) [15]. Planar anions are also found in solvent-free $NaCH(SiMe_3)_2$ [22], in the solvent-separated ion pair $[Li(12\text{-crown-}4)_2][CPh_3]$-THF [23] and in $[M(PMDETA)][CPh_3]$ (M = K(THF), Rb or Cs) [24]. There is a subtle but interesting difference between the potassium and rubidium compounds which appears to result from the difference in cation size. In KR the average distance from potassium to the two central carbon atoms is 309.7(11) pm, but there are six other $K \cdots C$ distances in the range 318.7–331.1 pm, to three methyl groups on one side and three on the other, making the metal effectively eight-coordinate (cf. Li_2R_2 above) and at the same time preserving the threefold symmetry along the chain axis. In RbR, however, the cation is large enough to interact with eight methyl groups from the adjacent anions, four from one side and four from the other. Only one methyl group from each anion has no close interaction with the cation. The symmetrical disposition of the two rubidium atoms on either side of the anion maintains the planar CSi_3 framework but two methyl groups, one, C(9), involved in interaction with the cation and one, C(4),

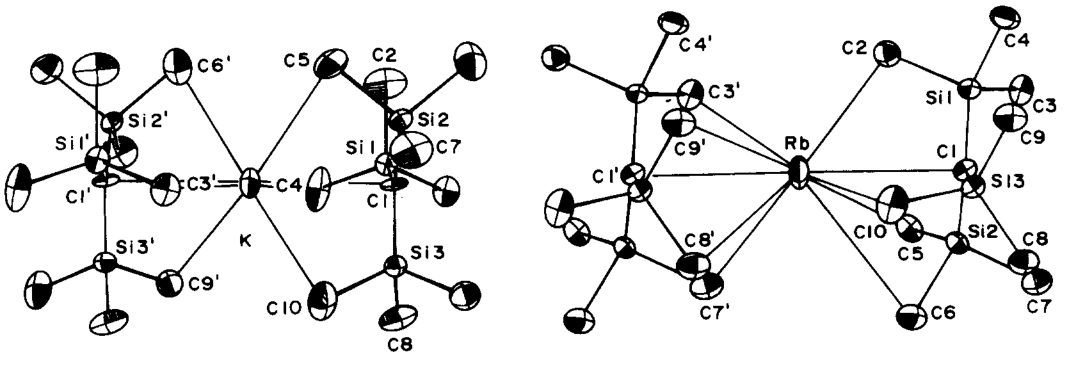


Fig. 3. View across the chains in the one-dimensional ionic solids (a) K^+R^-(**7**) and (b) Rb^+R^-(**8**).

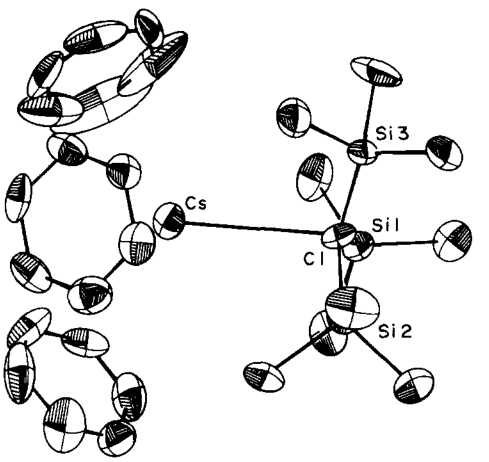


Fig. 4. Structure of the benzene solvate $[Cs(C_6H_6)_3][R^-](9)$. There is a further 0.5 C_6H_6 per formula unit loosely bound in the lattice.

which is not, are forced into the space between Si(1) and Si(3) so that one Si–C–Si angle (126.6(4)°) is significantly wider than the other two (116.5(4)) and 116.8(4)°). The coordination number of rubidium is effectively 10 (Rb–C 328–377 pm) [14].

Like KR (**7**) and RbR (**8**) the caesium analogue CsR was recrystallised from benzene. In this case, the solid was found to be a solvate $CsR \cdot 3.5C_6H_6$ (**9**) [14], with three η^6-benzene molecules coordinated to each caesium and further benzene in lattice interstices (Fig. 4). No diethyl ether was coordinated to caesium even though it was present in the solvent from which the compound was initially isolated. When M = Cs, the $M^+ \cdots (C_6H_6)$ interactions must be strong enough to prevent the formation of ionic chains of the type found when M = K or Rb, so that individual ion pairs are separated by benzene solvent molecules and the packing diagram looks like that of an organic compound in which interactions between molecules are weak. The coordination around caesium can be described as tetrahedral, with the distance to the central carbon of the anion 332.5(12) pm and distances of 343.3, 350.7 and 379.0 pm to the centroids of the benzene rings. It is reasonable to suggest that in benzene solution the potassium and rubidium derivatives may exist as species similar to those in the solid caesium analogue.

For the compounds $X–C(SiMe_3)_3$, there is a good correlation between the lengths of the inner Si–C bonds and the ionicity of the X–C bonds [25]. The short Si–C bonds (185.5(3) pm in **1a**, 182.2(10) in **7**, 181.5(7) in **8** and 181.7(11) in **9**), indicating delocalization of electron density into the CSi_3 skeleton, are associated with highly ionic X–C bonds in all the solvent-free alkyls.

The compounds MR ($R = C(SiMe_3)_3$) are starting materials for the synthesis of organometallic compounds of a wide range of metals and metalloids [1–3]. Most of the work so far with M = Li has been with solutions in THF (complex **3a**); under these circumstances, the products are often lithium-containing ate complexes [26,27]. Reactions involving the TMEN complex **3b** have also been studied [7,28,29]. Factors contributing to the reactivity of **3a** and **3b** include the highly carbanionic nature of their $C(SiMe_3)_3$ groups (as shown by the wide Si–C–Si angles), the accessibility of the metal and the solubility of the ion pairs in organic solvents.

The reactions of LiR with organic substrates are limited by proton abstraction to give RH, but non-enosilable aldehydes, ketones, acid chlorides, alkyl halides and CO_2 give products with new carbon–carbon bonds. Alkoxide products usually rearrange with transfer of an Me_3Si group from carbon to oxygen [5,30]. The potassium compound **7** reacts readily with toluene to give benzylpotassium, which separates out [31], but solutions in benzene and to a lesser extent diethyl ether are reasonably stable. These solutions are excellent reagents for the generation of organometallic compounds of Groups 2 and 3. It is likely that they will find use in other areas of the Periodic Table since (a) the presence of diethyl ether is not essential, so that organometallic compounds which are unstable in diethyl ether can be made in benzene [31,32], and (b) the potassium reagent **7** is much less prone than the lithium compound **3a** to give ate complexes.

2.2. *Tris(dimethylphenylsilyl)methyl derivatives*

The white crystals obtained from solutions of the lithium compound LiR′ ($R' = C(SiMe_2Ph)_3$) are made up of the discrete solvated monomers **10** [33]. An X-ray diffraction study shows that the O–Li–C angle is 144(1)° and the distance between Li and the *ipso* carbon of a phenyl group is 240(6) pm, not very different from the average Li–C distance (229.7(6) pm) in the four-membered ring of **1a**, or from that (236(1) pm) in $LiBMe_4$ [34] and between tetramers in solid $(LiMe)_4$ [35].

The tris(dimethylphenylsilyl)methyl derivatives of the heavier alkali metals crystallize as yellow solids that are poorly soluble in organic solvents, though sufficiently so for recording of NMR spectra. Their structures are similar but with subtle differences. In each case anions with almost planar CSi_3 frameworks alternate with cations to make chains. In the sodium compound **11** [12] (Fig. 5) and the potassium derivative **12** [13], the asymmetric unit consists of two ion pairs linked by strong interactions between a cation and two phenyl groups from the same ion pair and one from the adjacent ion pair. In **11**, these asymmetric units are related by a glide plane parallel to the long (33.2 Å) *c* axis. In **12** the asymmetric units are related by the threefold axis so that the *c* axis is extended to 50.2 Å; as a result, the X-ray reflections overlap and the quality of the X-ray data is considerably lowered. In the caesium compound **13** [31], each cation interacts with one phenyl group from the same ion pair and two from the adjacent pair.

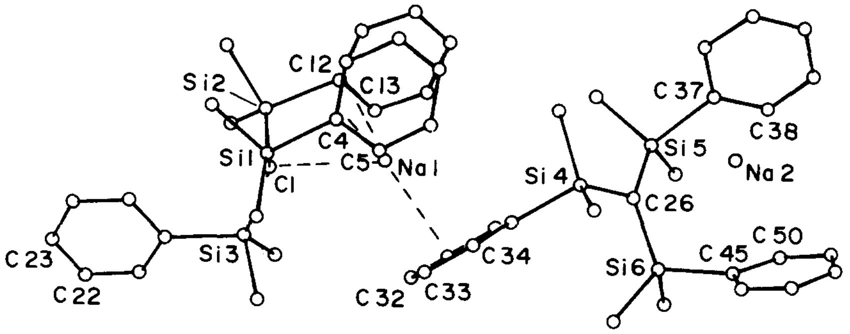


Fig. 5. Structure of $NaC(SiMe_2Ph)_3$(**11**).

The chains pack more compactly with a smaller repeat distance. For all the compounds **11–13** it is possible to describe the coordination of the alkali metal as quasi-tetrahedral, with each cation coordinated to the central carbon of its counterion and to three phenyl groups. As the size of the cation increases more carbon atoms can be accommodated near to it, and the hapticity of the phenyl-coordination increases from η^1 in **10** to η^2 or η^4 in **11** and η^6 in **12** and **13**. The strong interaction between Cs and Ph groups in **13** is similar to that between Cs and benzene in **9**. The distances between Cs and the centroids of the aromatic rings in **13** are shorter than those in **9**; indeed, the mean Cs · · · C(Ph) distance is shorter than that between Cs and the central carbon of the anion, suggesting that the principal cation–anion interaction is between the metal and the aromatic ring. It is of interest that η^6-coordination to phenyl is more important than that from the central carbon atom of the anion in $[M(PMDETA)CPh_3]$ (M = K(THF) or Rb), but the structure of the caesium analogue is more complicated, with both metal–phenyl coordination and interaction between the metal and the central carbon [24]. Similar potassium–arene interactions have been found in the chain structures of tetrakis(aryloxy)lanthanates [36].

Molecular parameters for some [tris(dimethylphenylsilyl)methyl]metal compounds $X{-}C(SiMe_2Ph)_3$ are given in Table 1. Fig. 6 shows the relations between the

Table 1
Geometric parameters of some tris(trimethylsilyl)methyl derivatives $L_nXC(SiMe_2Ph)_3$

L_nX	r(X–C) (pm)	r(Si–C) (pm)	r(SiMe) [a] (pm)	r(Si–Ph) [b] (pm)	SiCX (°)	SiCSi (°)	CSiC (°)	E [c]	Ref.
Cs	365.5(7) [d]	181.2(3)	189.7(6)	191.5(6)	93.4(3)	119.6(4)	103.0(2)	0.8	[31]
K	326(2) [d]	184(2)	189(2)	192(2)		118(2)	103(1)	0.8	[13]
Na	275.4(4) [d]	181.2(12)	187.2(12)	191.4(14)		118.8(7)	103.4(6)	0.9	[12]
Li	212(2) [d]	185.3(12)	186.9(13)	190.0(12)	98.1 [e]	118.0(6)	103.8(7)	1.0	[33]
LiH_3Al	204.5(3)	188.7(4)	186.7(4)	190.5(4)	108.0(2)	110.9(2)	104.8(2)	1.6	[69]
HOZn	195.3(7)	188.4(8)	190(1)	189(1)	105(1)	114(1)1	106(1)	1.65	[70]
ClZn	197.7(8)	189.6(8)	186.8(9)	188.9(9)	105.5 [f]	113.1 [f]	105.7(6)		[38a]
ClCd	219.6(6)	188.1(5)	186.6(8)	189.4(6)	104.6 [f]	113.8(3)	106.1 [f]	1.7	[38a]
BrCd	219(1)	188.6(7)	187(1)	189(1)	104.7 [f]	113.8(4)	106.1 [f]		[38b]
H_2OBrCd	222(2)	188(2)	190(1)	188(2)	101.5(9)	116(1)	106(1)		[38b]
$LiCl_3Ga$	200(1)	192(1)	190(1)	188(1)	105.3 [f]	113.3(5)	105.0(6)	1.8	[27]
FMe_2Sn	218.5(2)	192.0(2)	187.4(3)	189.0(3)	107.0 [f]	111.8 [f]	105.7 8uf	1.9	[46]
NO_3Me_2Sn	217.8	192.7(7)	187.8(9)	188.6(6)	107.9 [f]	111.0 [f]	105.5 [f]		[41]
$SNCMe_2Sn$	223(3)	191(3)	188(4)	190(4)	104 [f]	115	105(2)		[41]
Cl_3Si	186(2)	196.3(6)	185(2)	188(2)	106.4(5)	112.3(7)	104.6(8)	1.9	[45]
ClHg	209.8(9)	190.8(10)	187.0(12)	187.9(10)	104.8 [f]	113.7(5)	106.8 [f]	2.0	[38]
LiH_3B	175(2)	188(2)	190(2)	191(2)	106(1)	113(1)	105(1)	2.0	[44]
F(HO)B	154.9(8)	191.6(5)	185.5(6)	188.9(6)	106.8(4)	112.0(4)	106.2(3)		[39]
H		189.5(1)	185.0(2)	188.7(2)		114.0(1)	106.7(a)	2.2	[40]
Cl_2P	182.0(3)	196.4(3)	186.5(4)	189.5(4)	108.9 [f]	109.9(2)	105.8(2)	2.2	[42]

[a] Mean 187.6 pm. The value in $SiMe_4$ is 187.5(2) pm [37a].
[b] Mean 189.5 pm. The value in $SiPh_4$ is 187.2(7) pm [37b].
[c] Electronegativity of atom X.
[d] X–C distances to nearest phenyl groups: Li 240, Na 298.3(14), K 346(3), Cs 355.4(6) pm.
[e] Mean of 99.8, 89.7 and 105°.
[f] Estimated standard deviations not given because angles vary by 7–10°.

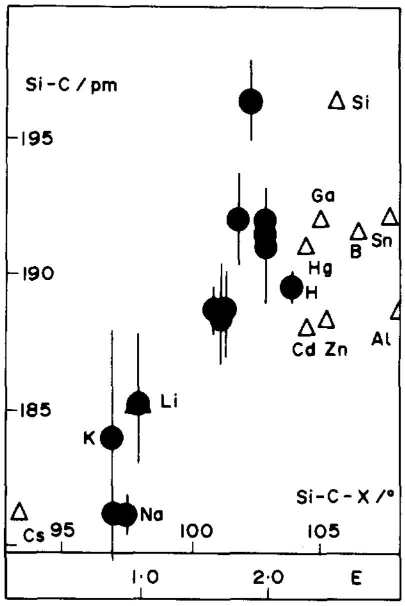


Fig. 6. Variation of the Si–C (inner) distance in tris(dimethylphenylsilyl)methyl derivatives $L_nXC(SiMe_2Ph)_3$ with the electronegativity of X (circles) and with Si–C–X angles (triangles).

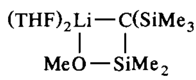
inner Si–C bond lengths and (a) the electronegativity of the atom X attached to carbon and (b) the associated Si–C–Si angles. The data are similar to those for $C(SiMe_3)_3$ derivatives [25], but at present span a more limited electronegativity range. The short inner Si–C bonds in the alkali metal derivatives and the near planarity of their CSi_3 skeletons (sum of angles 355° and 358° in **11**, 352° and 358° in **12** and 359° in **13**) show that negative charge is extensively delocalized from carbon to silicon. However, the averages of the outer Si–Me and Si–Ph bond lengths in Table 1 are close to the values for $SiMe_4$ and $SiPh_4$, respectively [37]. This suggests that the electronegativity of X has a marked effect on the geometry of the the CSi_3 skeleton but little influence on the peripheral Si–C bonds. However, the $C(SiMe_2Ph)_3$ group as a whole can adopt a series of configurations by rotations about Si–C bonds [38]. In some cases the overall symmetry is C_3 [39,40] and in others the phenyl groups are splayed out irregularly [38a,41,42]. In some cases the phenyl groups are almost parallel to the X–C bond [43] and in others they are spread like the blades of a propeller [40,44]. These variations in configuration have been attributed to steric effects, and for some compounds there is evidence from NMR spectra that they persist in solution [45]. The configurations observed in the solid-state structures of **11–13** (see Fig. 5 for the structure of **11**), in which the three phenyl groups are parallel to the X–C bond but one points in one direction and two in the other, have not been observed elsewhere. They illustrate the considerable scope available within the $C(SiMe_2Ph)_3$ group for accommodation of both electronic and steric constraints.

The lithium compound **10** is an excellent reagent for the preparation of derivatives of a wide range of metals and metalloids, although ate complexes are often obtained. The products usually give much better X-ray data than tris(trimethylsilyl)methyl analogues, in which problems with disorder are rife [26,46]. Compound **10** is less reactive than **3a** as a ligand transfer reagent. This has been tentatively attributed to the different structures of the species present in solution [47], but more work is required to quantify the effect. Only a few reactions of the potassium compound **12** have been examined [31], but preliminary results suggest that it is less reactive than the tris(trimethylsilyl)methyl derivative **7**.

2.3. *Derivatives containing other silicon-substituted methyl groups*

The work described in the two previous sections has led to a study of the chemistry of the alkali metal compounds $M[C(SiMe_3)_2(SiMe_2Y)]$ and $M[C(SiMe_2Y)_3]$ (Y = H, Ph, CH=CH$_2$ or OMe) [48,49].

$Li[C(SiMe_3)_2(SiMe_2CH{=}CH_2)]$
14
$Li[C(SiMe_3)_2(SiMe_2H)]$
15
$Li[C(SiMe_3)_2(SiMe_2Ph)]$
16


$(THF)_2Li-C(SiMe_3)_2$, $MeO-SiMe_2$
17

$[\{LiC(SiMe_2OMe)_3\}_2]$
18
$BrC(SiMe_2OMe)_3$
19
$KC(SiMe_3)_2(SiMe_2Ph)\cdot\frac{1}{2}(C_6H_6)$
20

The compounds **14** [49], **15** [50], **16** [50] and **17** [50–53] have all been made by metallation of the corresponding chlorides by butyllithium, usually in THF–Et_2O–hexane at −110°C [54]:

$$RCl + BuLi \rightarrow RLi + BuCl \qquad (3)$$

Careful control of temperature is essential. The lithium compounds have been used in situ for the synthesis of organometallic compounds of other elements, particularly those of Groups 12 and 14, but compounds **14–16** have not so far been isolated in the crystalline state. The nature of the species in solution is unknown.

Compound **18**, obtained from the reaction (Eq. (4)) between butyllithium and $(MeOSiMe_2)_3CCl$ at −78°C, has, however, been isolated as a solid and its structure determined by X-ray diffraction [48,55]. Dimers are formed both in the

$$(MeOSiMe_2)_3CCl + BuLi \longrightarrow \tfrac{1}{2}\underbrace{[(MeOSiMe_2)_3CLi]_2}_{\mathbf{18}} + BuCl \qquad (4)$$

solid state and in solution [56] (Fig. 7). The principal interaction between lithium and the rest of the molecule is via the lone pairs of the methoxy groups. The long

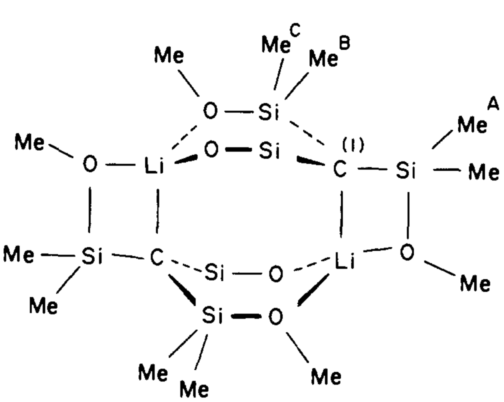
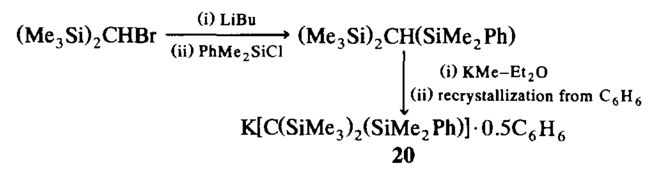


Fig. 7. Structure of [{LiC(SiMe$_2$OMe)$_3$}$_2$](**18**), with some methyl groups omitted for clarity.

Li–C bonds (240.1(9) pm; cf. **1** and **10**, Section 2.2), the short Si–C(1) bonds (180.5(4) pm; cf. 190.6(10) pm in BrC(SiMe$_2$OMe)$_3$ (**19**) [57]) and the wide Si–C–Si angle (117.2°; cf. 112.5° in **19**) all suggest that the dimers consist of two ion pairs. The methyl groups attached to silicon, designated A, B and C in Fig. 7, are inequivalent in the solid-state NMR spectrum, but a solution in toluene gives only one signal, suggesting that exchange is fast on the NMR time-scale. Only a few reactions of **18** have been studied; it reacts in the usual way with chlorosilanes to give the products SiPh$_2$HR″, SiMe$_2$HR″ and SiMe$_2$ClR″ (R″ = C(SiMe$_2$OMe)$_3$) [48].

The potassium compound **20** is obtained without difficulty by metallation of (Me$_3$Si)$_2$CH(SiMe$_2$Ph) with methylpotassium [31] (Scheme 2). The structure consists of chains of alternate K$^+$ cations and anions R‴$^-$ (R‴ = [C(SiMe$_3$)$_2$(SiMe$_2$Ph)]), but as there are two distinct coordination environments for potassium it is best described as a potassium dialkylpotassate [K(C$_6$H$_6$)][KR‴$_2$] (Fig. 8). The potassium atom in the anion has an environment which resembles that in **7** (Fig. 3), with close interactions to two central carbons C(1) and C(1′) and six other methyl groups, three on either side, but the K–C(1) distance, 291.4(5) pm, is significantly shorter than that (309.7(11) pm) in **7**. The other potassium is coordinated to phenyl groups from the adjacent potassate anions and to an extra benzene from the solvent of recrystallisation. This benzene is tenaciously held; it shows up in NMR spectra in THF-d_8 of the residue left after by prolonged pumping at room temperature. In contrast, the benzene of the solvate **9** is readily lost in vacuum. A polymeric potassium potassate [K(THF)]$_n^+$-{K[C$_3$N$_3$Ph$_2$Bu^{t}Bu]$_2$}$_n$ containing substituted triazine residues has recently been described [58], but **20** is thought to be the first dialkylpotassate to be isolated.



$$(\mathrm{Me_3Si})_2\mathrm{CHBr} \xrightarrow[\text{(ii) PhMe}_2\text{SiCl}]{\text{(i) LiBu}} (\mathrm{Me_3Si})_2\mathrm{CH(SiMe_2Ph)} \xrightarrow[\text{(ii) recrystallization from C}_6\text{H}_6]{\text{(i) KMe–Et}_2\text{O}} \underset{\mathbf{20}}{\mathrm{K[C(SiMe_3)_2(SiMe_2Ph)]\cdot 0.5C_6H_6}}$$

Scheme 2.

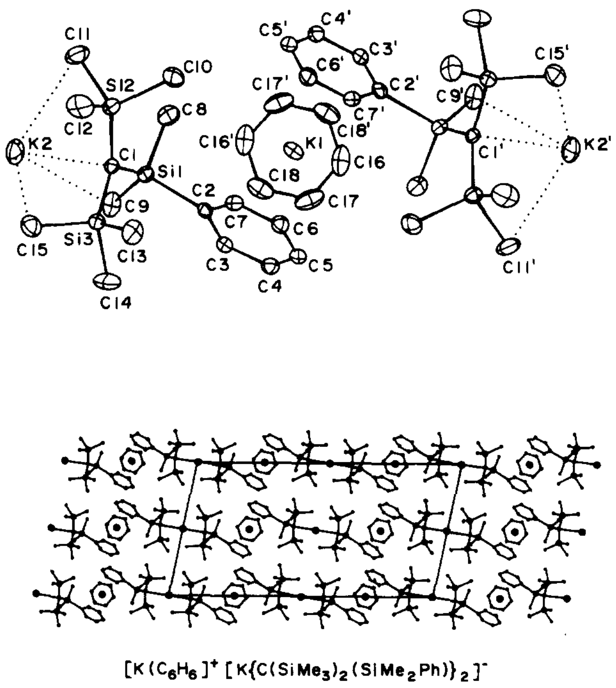


Fig. 8. Structure of the potassium potassate [K(C$_6$H$_6$)][K{C(SiMe$_3$)$_2$-(SiMe$_2$Ph)}$_2$] (**20**).

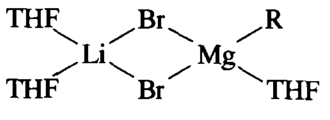
3. Derivatives of beryllium, magnesium and the alkaline earth metals

3.1. *Compounds of beryllium*

As far as we are aware, there have been no reports of relevant compounds of beryllium.

3.2. *Tris(trimethylsilyl)methyl derivatives of magnesium*

The reaction between the lithium compound **3a** and a one molar equivalent of magnesium bromide–diethyl ether in THF yields the ate complex **21** (R = C(SiMe$_3$)$_3$), which can be obtained pure by recrystallisation from hot heptane. It does not react with an excess of **3a** to give the dialkylmagnesium **22** [26], but when it is heated in vacuum **22** sublimes as a white solid.



21

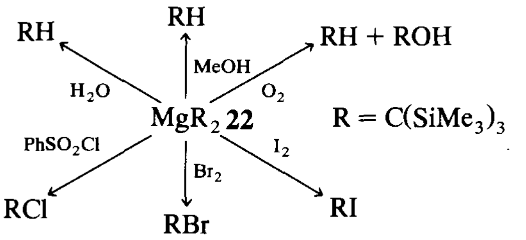
R-Mg-R

22

RMg(μ-Br)$_3$Mg(THF)$_3$

23

It was initially thought that **22** might be a useful selective reagent for the synthesis of organic or organo-



Scheme 3.

metallic compounds, but this proved not to be the case because it was so unreactive, not reacting with BCl_3 or even with boiling neat acetyl chloride. Although **22** reacts with some very reactive electrophiles (Scheme 3), the products do not contain magnesium–carbon bonds even when a deficiency of reagent is used, indicating that the intermediates RMgX (X = OH, OMe or halogen) are more reactive than the starting material MgR_2.

The low reactivity of **22** is attributable to the way in which the methyl groups, C(2) C(5) and C(10) in Fig. 2, interlock with the symmetry-related groups to protect the central metal atom (the related compound ZnR_2, with an shorter metal–carbon distance (198.2(2) pm), is stable in air and can even be distilled unchanged in steam [59,60]). Put another way, the group R subtends a cone angle of greater than 180°; values of 190(8)–216(12)° have been suggested by calculations based on molecular mechanics [61]. However, the work described in this review shows that the tris(trimethylsilyl)methyl group R is able to undergo significant changes in configuration, driven mainly by electronic factors. This means that the concept of a transferable cone angle must be limited to series of very similar compounds.

In compounds XR ($R = C(SiMe_3)_3$), steric strain within the group R is usually relieved by rotation of Me_3Si groups by about 20° away from the fully staggered positions. This imparts chirality to the R fragment, and in centrosymmetric molecules such as **22** the two R groups have opposite hands; for further discussion, see Refs. [8] and [26].

The Grignard reagent RMgBr ($R = C(SiMe_3)_3$) appears to be obtained in the usual way from the reaction between magnesium turnings (activated with 1,2-dibromoethane) and the bromide RBr in diethyl ether. Its formation is confirmed by reactions with iodine, benzyl chloride and $HgCl_2$ to give good yields (65–82%) of RI, RCH_2Ph and HgR_2, respectively [9]. It seems, however, that the synthesis of RMgBr is successful only in the presence of an excess of magnesium bromide, e.g. from the 1,2-dibromoethane used to activate the magnesium. Thus reaction between RBr and magnesium is not detectable if the activated magnesium is thoroughly washed with THF and diethyl ether before use [62]. When the Grignard reagent is made in THF instead of diethyl ether, a crystalline product **23** may be isolated. This contains both four- and six-coordinate magnesium and it is likely that a similar complex is obtained in diethyl ether. The high Br/R ratio in the product may be associated with formation of radicals $R^{\cdot}$ in the reaction between RBr and magnesium; these would go on to give RH, reducing the proportion of R in the organometallic product **23**.

3.3. *Tris(trimethylsilyl)methyl compounds of calcium*

Attempts to make organometallic compounds of calcium by the reaction of the bromide $BrC(SiMe_3)_3$ with calcium metal under a variety of conditions have not so far been successful. The reaction between KR (**7**) and anhydrous calcium iodide in benzene yields a white crystalline solid, which appears to be the dialkyl CaR_2 (**24**), analogous to **22**. Work on this and the corresponding strontium and barium compounds is in progress [63].

4. Derivatives of the lanthanides

As shown below, the lanthanide(II) dialkyls react with diethyl ether and so can be isolated only from starting materials that are ether–free. The potassium compound **7** reacts with YbI_2 in benzene to yield a solution from which a highly air- and moisture-sensitive orange solid YbR_2 (**25**) ($R = C(SiMe_3)_3$) can be obtained [32]. Similar reactions give EuR_2 (**26**) [31]. These compounds are the first solvent-free σ-bonded diorganolanthanides to be characterized, although various substituted cyclopentadienyl compounds have been known for some time [64].

The most interesting feature of the solid-state structures is the C–M–C angle: 137° in **25** (Fig. 9) and 136° in **26**. All other neutral species MR_2, such as **22**, are linear [21]. It seems, however, that the lanthanide–carbon bonds (249.5(9) pm in **25** and 260.8(6) in **26**)

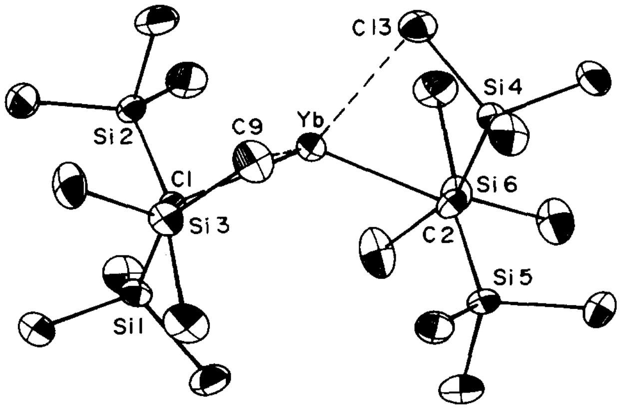
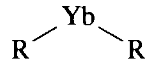


Fig. 9. Structure of the ytterbium(II) dialkyl $Yb[C(SiMe_3)_3]_2$(**25**).

are sufficiently longer than the Group 12 metal–carbon bonds (ca. 200 pm),



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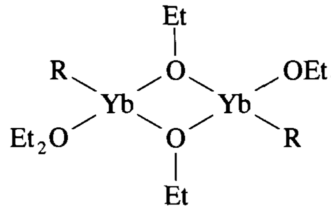

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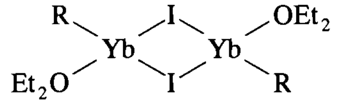

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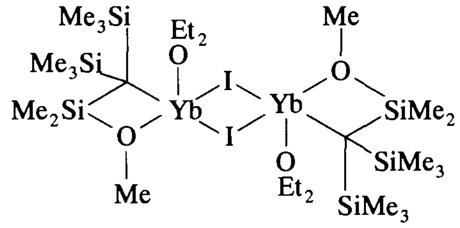

29

and the CSi_3 skeleton in the lanthanide compounds is sufficiently more planar than that in the Group 12 derivatives, for bending to be possible. In YbR_2 (**25**) (see Fig. 9), the metal interacts with two methyl groups, C(9) and C(13), which are only slightly further away (290(1) and 285(1) pm, respectively) than the atoms C(1) and C(2). In EuR_2 (**26**), there are similar interactions between the metal and three methyl groups. Various explanations have been given for the non-linearity of molecules MX_2, where M is a heavier Group 2 or a divalent Group 3 element and X is halogen or cyclopentadienyl. It appears that in some cases the energy differences between linear and bent systems are small, and that in **25** the extra metal–methyl interactions may be enough to stabilise the bent form. Our work suggests that dialkyls, like bis(cyclopentadienyls), of heavier elements may in general be bent, and it will be interesting to see whether this is so as more compounds are isolated.

The chemistry of **25** and **26** is being studied. Compound **25** reacts with diethyl ether in C_6D_6 at 20°C according to Eq. (6).

$$\underset{\mathbf{25}}{YbR_2} + 2Et_2O \longrightarrow \underset{\mathbf{27}}{0.5[RYb(OEt)(OEt_2)]_2} + RH + CH_2{=}CH_2 \qquad (6)$$

A similar reaction occurs with ethyl butyl ether but not with dibutyl ether. The compound **27** was obtained from the reaction between **3a**, KO^tBu and YbI_2 in Et_2O, and its crystal structure was determined by others [65]. Bis(cyclopentadienyl)ytterbium(II) compounds are usually oxidized by alkyl halides to give bis(cyclopentadienyl)ytterbium(III) derivatives, but the reaction between **25** and iodomethane results instead in substitution, to give a new Yb(II) compound **28**. Grignard analogues like **28** have been used in organic synthesis [66] but have not previously been isolated, and the structures of the species in solution are not known. A simpler route to **28**, isolated as exceedingly air- and moisture-sensitive yellow–green plates, involves the reaction between $IC(SiMe_3)_3$ and Yb metal in diethyl ether. This type of reaction can be used to make other organoytterbium compounds. For example, the iodide $(Me_3Si)_2(MeOMe_2Si)CI$ [67] reacts readily with ytterbium metal in diethyl ether to give **29**. This has been isolated as bright yellow plates and its structure has been determined by X-ray diffraction [31]. There is evidently room for the ytterbium to expand its coordination number from 4 in **28** to 5 in **29**, with formation of a tight chelate ring.

6. Conclusions

This review has covered the tris(trimethylsilyl)methyl and related derivatives of the more electropositive elements. Compounds of less electropositive metals and metalloids will be reviewed elsewhere [68]. There is clearly much further chemistry to be developed but the following conclusions can be drawn from the results so far.

(1) The use of very bulky silicon-containing ligands allows the isolation of a wide range of previously inaccessible types of compound.

(2) The silicon-substituted methyl groups are capable of making considerable adjustments, especially in the inner CSi_3 skeleton, in response to the electronic demands of the adjacent element. These adjustments can have significant effects on chemical reactivity.

(3) A common feature of the compounds of the most electropositive metals is that there appear to be significant interactions between metal ions and methyl groups on the periphery of the anions. The anion conformation adjusts to maximise these interactions. It would be of considerable interest to know whether the M · · · Me interactions are between metal and carbon, metal and hydrogen, or both, but the X-ray evidence so far is not clear on this point.

(4) Interactions between the heavier metal ions and aromatic rings are especially strong and appear to play a dominant role in determining the structures of the solids that are obtained by crystallisation from aromatic solvents.

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