ELSEVIER

Journal of Organometallic Chemistry 631 (2001) 76–86

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Crystal structures of organometallic compounds of lithium and magnesium containing the bulky ligands $C(SiMe_3)_2(SiMe_2X)$ $X = Me, Ph, NMe_2$, or C_5H_4N-2

Salih S. Al-Juaid, Anthony G. Avent, Colin Eaborn *, Salima M. El-Hamruni, Simon A. Hawkes, Michael S. Hill, Martijn Hopman, Peter B. Hitchcock, J. David Smith *

School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton BN1 9QJ, UK

Received 13 March 2001; received in revised form 4 April 2001; accepted 4 April 2001

Abstract

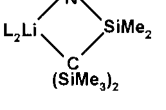
The complex $[Li(TMEDA)\{C(SiMe_3)_2SiMe_2NMe_2\}]$ (**1**) (TMEDA = *N*,*N*,*N′*,*N′*-tetramethylethane-1,2,-diamine) was found to crystallise with an internally coordinated structure like that of $[Li(THF)_2\{C(SiMe_3)_2SiMe_2NMe_2\}]$ (THF = tetrahydrfuran). In contrast, the compound with Ph in place of NMe_2 crystallised as a dialkyllithate $[Li(TMEDA)_2][Li\{C(SiMe_3)_2(SiMe_2Ph)\}_2]$ (**4**). The reaction of **4** with $MgBr_2$ gave the doubly bromide-bridged lithium–magnesium complex $[Li(TMEDA)(\mu\text{-}Br)_2Mg\{C(SiMe_3)_2(SiMe_2Ph)\}(THF)]$ (**6**), and that of $[Li(THF)\{C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)\}]$ gave the singly bridged compound $[Li(THF)_3(\mu\text{-}Br)MgBr\{C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)]$ (**8**). The Grignard reagents $[Mg\{C(SiMe_3)_3\}I(OEt_2)]_2$ (**10**) and $[Mg\{C(SiMe_3)_2(SiMe_2Ph)\}I(OEt_2)]_2$ (**11**) were obtained from the reactions between $(Me_3Si)_3CI$ and $(Me_2Ph)(Me_3Si)CI$, respectively, with magnesium metal and shown to have halide-bridged structures. The unsymmetrical dialkylmagnesium $[MgBu\{C(SiMe_3)_2(SiMe_2NMe_2)\}(THF)]$ (**13**), was prepared from a mixture of LiBu, **1** and $[MgBr_2(OEt_2)_2]$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium; Magnesium; Bulky ligands

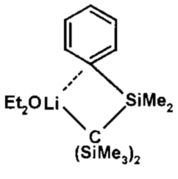
---

1. Introduction

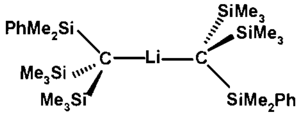
Organolithium and to a lesser extent organomagnesium compounds containing bulky tris(triorganosilyl)methyl groups are starting materials for the preparation of organometallic compounds of a wide range of elements [1]. In many cases they are made in ether solution and used without isolation, but the lithium and magnesium compounds themselves show a variety of structural types. In this paper we describe the X-ray structures of seven such compounds and compare them with those of previously described related species.



1 L_2 = TMEDA
2 $L_2 = (THF)_2$



3



anion of **4**

---

* Corresponding authors. Tel.: +44-1273-678-124; fax: +44-1273-677-196 (J.D.S.).
E-mail address: j.d.smith@sussex.ac.uk (J.D. Smith).

PII: S0022-328X(01)01032-4

2. Results and discussion

2.1. The dimethylamino compound **1**

The TMEDA derivative of $LiC(SiMe_3)_2(SiMe_2NMe_2)$ was prepared in order to compare the complexing power of TMEDA with that of: (a) THF as shown in the previously reported complex **2** [2]; and (b) the NMe_2 substituent in the ligand. A 1:1 mixture of TMEDA and **2** in hexane gave a high yield of **1**, the THF having been displaced by TMEDA. The crystals of the product **1** contained two independent molecular species with barely significant differences in bond lengths and angles. One of these is shown in Fig. 1 and molecular parameters are given in Table 1. The molecular structures of **1** and **2** are similar. The N–Li–N bite angle of the TMEDA in **1** (83.0(3)°) is narrower than the O–Li–O angle (95.7(3)°) in **2** and there are minor differences in bond angles at Li, but the other bond lengths and angles in **1** are not significantly different from the corresponding parameters in **2**. The differences between the Li–N bond lengths in **1** are not significant, indicating that the bonds to the NMe_2 groups of the TMEDA and the ligand are of similar strength. Steric effects associated with the LiNSiC ring have been discussed elsewhere [2].

The Li–C bond lengths in both **1** (2.315(8) Å) and **2** (2.287(9) Å) are significantly longer than those in other monomeric organolithium compounds (cf. 2.096(10) Å in $Li(OEt_2)C(SiMe_3)_2(SiMe_2Ph)$ **3** [3], 2.13(16) Å in LiPh·PMDTA (PMDTA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine) [4], 2.12 Å in $LiC_6H_2Bu^t_3$-2,4,6·TMPN (TMPN = *N*,*N*,*N*′*N*′-tetramethylpropane-1,2-diamine) [5], and 2.13(5) Å in $Li\{CH(SiMe_3)_2\}$·PMDTA [6]) and the Si–C1 bonds (1.803(4) Å in **1** and 1.806(4) Å in **2**) are significantly shorter (cf. 1.830(5) Å in **3** and av. 1.853(12) Å in $Li(THF)C(SiMe_2Ph)_3$ [7]. A similar effect was noted in the structures of the compounds $Li(THF)_2C(SiMe_3)_2(SiMe_2OMe)$ (Li–C 2.304(11) and Si–C 1.792(6) Å) [8] and $[LiC(SiMe_3)(SiMe_2OMe)_2]_2$ (Li–C 2.256(9) and Si–C 1.808(3) Å) [9]. In all cases, coordination of NMe_2 or OMe results in a significant weakening of the Li–C bond, and the carbanionic charge is more effectively delocalised into the bonds between carbon and the silicon bearing the nitrogen or oxygen substituents than into the other C–Si bonds.

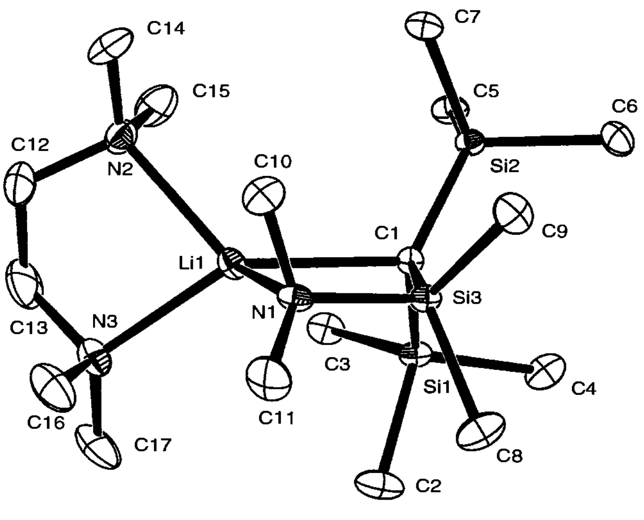


Fig. 1. Molecular structure of one of the independent molecules of $[Li(TMEDA)C\{(SiMe_3)_2(SiMe_2NMe_2)\}]$ (**1**).

2.2. The ate complex **4**

The compound $LiC(SiMe_3)_3$ crystallises from THF as an ate complex $[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$ [10]. If TMEDA is added to the THF solution, the THF is displaced from the coordination sphere of the lithium and the compound $[Li(TMEDA)_2][Li\{C(SiMe_3)_3\}_2]$ (**5**) crystallises out [11,12]. Crystals suitable for a determination of the structure of the species separating from THF solutions of $LiC(SiMe_3)_2(SiMe_2Ph)$ could not be obtained but better crystals formed when the organolithium compound was prepared in Et_2O [3]. These were shown to contain molecular species **3**, in which the lithium is linked by bonds to carbon and oxygen, and interacts weakly with the *ipso*-carbon atom of the phenyl group. There are similar interactions in $[Li(THF)C(SiMe_2Ph)_3]$ [7] and $[\{LiCH(SiMe_2Ph)_2\}_2]$ [3]. Treatment of a THF solution of $LiC(SiMe_3)_2(SiMe_2Ph)$ with one equivalent of TMEDA gave a white solid **4**, and elemental analysis and NMR spectra showed that the crystalline compound contained no THF. Although the initial batch of crystals was not of sufficient quality for an X-ray diffraction study, a second batch, obtained during several months from a concentrated solution in benzene, proved to be satisfactory. The crystals were shown to consist of the ate complex $[Li(TMEDA)_2][Li\{C(SiMe_3)_2(SiMe_2Ph)\}_2]$ (**4**). The cation, which lies on a two-fold rotation axis, is not discussed further; the anion, shown in Fig. 2, lies on an inversion centre, so the C–Li–C skeleton is linear.

Although diorganolithates were postulated by Wittig 50 years ago [13], very few have been isolated in the solid state and structurally characterised [10,12,14–16]. As in the case of previously reported examples, the high angle diffraction from **4** was weak, but the structural data are free from crystallographic disorder and can be compared with those from related compounds. The Li–C bond length (2.191(6) Å) is longer than those in monomeric organolithium compounds, but similar to that (2.213(5) Å) in the dialkyllithate **5**. The mean inner

Table 1
Selected bond lengths (Å) and bond angles (°) for **1**, **4**, **6**, **8**, **10**, **11** and **13**

Bond lengths		Bond angles			
$[Li(TMEDA)C\{(SiMe_3)_2(SiMe_2NMe_2)\}]$ (**1**) [a]					
Li–N (tmen) [b]	2.234(8)	Li–C–Si3	83.9(2)		
Li–C	2.315(8)	C–Si3–N1	107.8(2)		
Li–N	2.195(8)	Si3–N1–Li	87.8(2)		
N–Si	1.790(4)	N1–Li–C1	80.1(3)		
Si–C1	1.803(4)	N2–Li–N3	83.0(3)		
Si–C(*exo*) [b]	1.829(4)	N1–Li–N2	123.7(4)		
N–C [b]	1.463(6)	N1–Li–N3	111.6(3)		
Si–Me [b]	1.885(5)				
$[Li(TMEDA)_2][Li\{C(SiMe_3)_2(SiMe_2Ph)\}_2]$ (**4**)					
Li–C	2.191(6)	C–Li–C	180		
Si–C1 [b]	1.833(6)	Li–C–Si	100.7(3), 106.6(3), 104.1(3)		
Si–Me [b]	1.882(7)	Si–C–Si [b]	114.5(3)		
Si–Ph [b]	1.904(7)	Me–Si–Me [b]	103.8(4)		
$[Li(TMEDA)(\mu\text{-}Br)_2Mg\{C(SiMe_3)_2(SiMe_2Ph)\}(THF)]$ (**6**)					
Li–N [b]	2.06(2)	Li–Br–Mg [b]	82.2(3)		
Li–Br [b]	2.507(13)	Br–Mg–Br	97.25(9)		
Mg–Br [b]	2.530(3)	Br–Li–Br	98.4(5)		
Mg–O	2.056(5)	N–Li–N	89.2(6)		
Mg–C	2.186(8)	Br–Mg–C	120.0(2), 118.5(2)		
C1–Si [b]	1.859(7)	Br–Mg–O	96.2(2). 98.9(2)		
Si–Ph	1.900(8)	C–Mg–O	120.9(3)		
Si–Me [b]	1.875(8)	Si–C–Si	114.4(4), 110.6(4), 111.4(4)		
		Me(Ph)–Si–Me [b]	104.4(4)		
$Li(THF)_3(\mu\text{-}Br)MgBr\{C(SiMe_3)_2(SiMe_2C_5H_4N)\}$ (**8**) [c]					
Li–O1	1.887(11)	Li–Br–Mg	129.2(2)		
Li–O2	1.925(13)	Br–Mg–Br	105.12(6)		
Li–O3	1.933(12)	N–Mg–Br1	100.69(12)		
Li–Br	2.505(10)	N–Mg–C	94.18(16)		
Mg–Br1	2.535(2)	Br–Li–O	105.9(5), 116.2(6), 112.2(5)		
Mg–Br2	2.488(2)	O–Li–O	105.0(5), 110.1(6), 107.1(5)		
Mg–C	2.219(5)	Mg–C1–Si1	96.6(2)		
Mg–N	2.122(4)	C1–Si1–C4	108.0(2)		
C1–Si [b]	1.856(5)	Si1–C4–N	116.3(3)		
Si–C4	1.904(5)	C4–N–Mg	112.6(3)		
Si–Me [b]	1.887(5)	Si–C1–Si [b]	112.4(2)		
		Me–Si–Me	103.9(3)–106.3(2)		
$[Mg(OEt_2)\{C(SiMe_3)_3\}I]_2$ (**10**) and $[Mg(OEt_2)\{C(SiMe_3)_2(SiMe_2Ph)\}I]_2$ (**11**)					
	10	**11**		**10**	**11**
Bond lengths			Bond angles		
Mg–C	2.146(7)	2.181(3)	Mg–I–Mg	90.01(7)	90.34(4)
Mg–I	2.849(3)	2.814(1)	I–Mg–I	89.99(7)	89.66(4)
Mg–I′	2.860(3)	2.842(2)	I–Mg–C	119.2(2) [b]	117.90(10), 123.00(9)
Mg–O	2.080(6)	2.059(3)	I–Mg–O	101.9(2), 100.2(2)	100.04(8), 100.99(8)
C1–Si [b]	1.869(7)	1.870(3)	Si–C–Si	110.0(4) [b]	109.1(2), 110.5(2), 113.5(2)
Si–Me [b]	1.880(9)	1.882(4)	Me–Si–Me	102.2(4)–106.2(4)	101.6(2)–106.9(2)
$[MgBu\{C(SiMe_3)_2(SiMe_2NMe_2)\}\cdot THF]$ (**13**)					
Mg–C(Bu)	2.130(3)	Bu–Mg–O	101.44(13)		
Mg–C1	2.241(2)	N–Mg–O	107.63(8)		
Mg–O	2.069(2)	C1–Mg–N	80.41(8)		
Mg–N	2.203(2)	C(Bu)–Mg–N	118.97(11)		
Si–N	1.829(2)	C(Bu)–Mg–C1	131.60(12)		
Si1–C1	1.831(2)	C1–Mg–O	114.69(9)		
Si2–C1	1.851(2)	Mg–N–Si	88.75(8)		
Si3–C1	1.847(2)	N–Si–C1	103.24(10)		
Si–Me [b]	1.877(3)	Mg–C1–Si1	87.53(9)		
N–C [b]	1.474(3)	Si–C–Si	117.60(12), 114.21(12), 114.49(12)		
		Me–Si–Me	102.07(15)–106.08(18)		

---

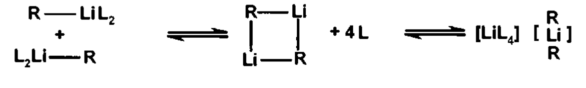
[a] The data are for one of the two independent molecules in the asymmetric unit. Those for the other molecule differ insignificantly.

[b] Average value with e.s.d.s for individual measurements, none of which differs significantly from the mean.

[c] In **8**: N–Mg–Br2 104.01(13); C–Mg–Br2 128.70(14); C–Mg–Br1 118.13(13); Mg–C1–Si2 116.5(2); Mg–C1–Si3 105.3(2).

Si–C bond length (1.833(6) Å) is similar to that in **3** and in other tris(organosilyl)methyl–lithium derivatives, reflecting the delocalisation of anionic charge, but this delocalisation does not affect the lengths of the outer Si–C bonds (mean 1.882(7) Å), which are similar to those (1.875(2) Å) in $SiMe_4$ [17]. The wide Si–C–Si and narrow Me–Si–Me angles are normal [18].

The NMR spectra of **4** at room temperature show sharp peaks assigned to $SiMe_3$, $SiMe_2$ and TMEDA groups. Samples containing an excess of TMEDA gave separate signals for complexed and free TMEDA but chemical exchange was detected by polarisation transfer experiments. We showed previously [12] that the changes in the NMR spectra from solutions of $LiC(SiMe_3)_3$ in THF between 288 and 318 K could be understood in terms of chemical exchange between the ate complex $[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$ and molecular species $Li(THF)_nC(SiMe_3)_3$, as shown in Eq. (1) [L = THF, R = $C(SiMe_3)_3$].



(1)

We therefore sought evidence for the presence of similar species in the case of **4**. As samples in toluene-d_8 were cooled, the NMR spectra remained sharp until the temperature was 220 K, then the signals attributed to $SiMe_3$ and $SiMe_2$ protons each split into two of equal intensity ($\Delta G^{\ddagger} = 42$ kJ mol^{-1} at 202 K). This suggests that there is a single species **4** in solution, since exchange between species of the kind envisaged for $LiC(SiMe_3)_3$ would be likely to result in changes in the NMR spectra at temperatures higher than 220 K. The observed splitting probably arises from restricted rotation about C–$SiMe_2$Ph bonds at low temperatures. It is likely but not certain that the predominant species in solution is the ate complex present in the crystal. This would be expected to give two signals in the ^{7}Li spectrum, but only one sharp peak was detected. However, as the Li signal from the lithate anion $[Li\{C(SiMe_3)_3\}_2]^-$ is broad and difficult to detect [12], it would not be surprising if the only clear signal from **4** was that from the cation at δ 0.54 [3]. The alternative explanation that there is rapid exchange of lithium between the cation and dialkyllithate cannot be ruled out, but it seems unlikely in view of the considerable chemical reorganisation required (Eq. (1)).

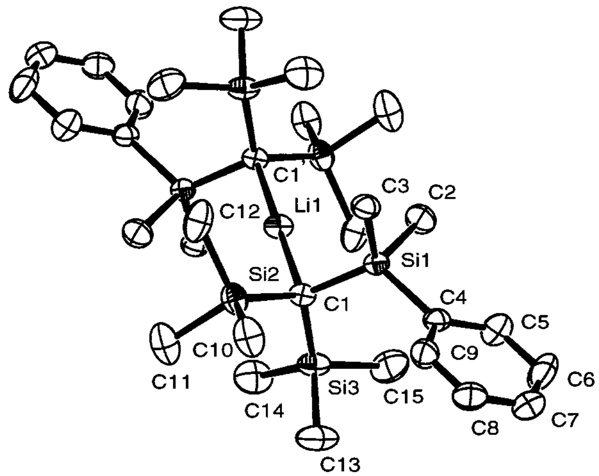
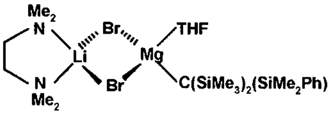


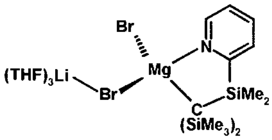
Fig. 2. Structure of the anion of $[Li(TMEDA)_2][Li\{C(SiMe_3)_2(SiMe_2Ph)\}_2]$ (**4**).

The formation of an ate rather than a molecular complex upon treatment of **3** with TMEDA reflects the greater basicity towards Li of the amine than of the ether ligand, as shown also in the formation of **1** from **2**. Possible Li···Ph interactions are insufficiently strong to compete with the strongly basic TMEDA and the phenyl groups point away from the central lithium atom. In the presence of only the more weakly basic diethyl ether, however, Li···Ph interactions are sufficiently strong to stabilise the molecular species **3**. In the case of $LiC(SiMe_3)_3$, both THF and TMEDA are sufficiently basic to give species with the ate structure, and (weak) Li···Me interactions are seen only in the absence of donor solvents [19]. In contrast, the NMe_2 group in **1** and **2** is able to compete successfully with TMEDA for space in the coordination sphere of lithium, and formation of molecular species is favoured over that of ate complexes.

The presently available structural data on $LiL_2\{C(SiMe_3)_2(SiMe_2X)\}$ show that molecular species are formed, i.e. the equilibrium of Eq. (1) lies to the left, when X has high and L has low coordinating power. Ate complexes are formed when X has low and L has high coordinating power. (There are fewer data for sodium analogues but it appears that the stronger interaction of phenyl with sodium than with lithium gives a molecular species in the presence of TMEDA. Introduction of a second phenyl group does not, however, lead to displacement of TMEDA, and $[Na(TMEDA)\{C(SiMe_3)(SiMe_2Ph)_2\}]$ has a molecular structure in which one phenyl group interacts with sodium and the other hangs free [3].)



6



8

2.3. The lithium magnesates *6* and *8*

The use of the lithium compound **3** to attach the $C(SiMe_3)_2(SiMe_2Ph)$ group to silicon [20] and cadmium [21] has been described previously. The TMEDA derivative **4** was employed similarly for the synthesis of the lithium organodibromomagnesate **6**, obtained pure but in poor yield from reaction with $MgBr_2$ in THF.

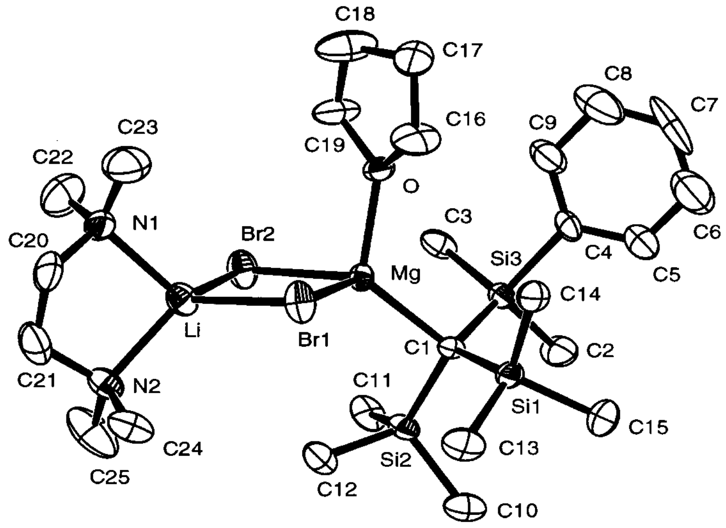
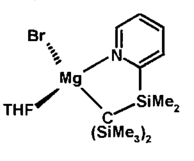
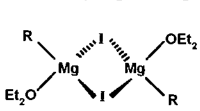


Fig. 3. Molecular structure of $[\mathrm{Li(TMEDA)(\mu\text{-}Br)_2Mg\{C(SiMe_3)_2(SiMe_2Ph)\}(THF)}]$ (**6**).

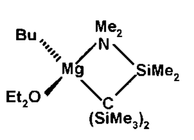
The crystal contains molecular species (Fig. 3) and the structure is very similar to that of the previously reported $[\mathrm{Li(THF)_2(\mu\text{-}Br)_2Mg\{C(SiMe_3)_3\}(THF)}]$ (**7**) [22], which appears to be the only analogous bromide-bridged lithium–organomagnesium compound previously reported. The bond lengths and angles in **6** are more precisely determined than those in **7**, but there is no significant difference between the corresponding parameters in the two species. The wide endocyclic angles at lithium and magnesium and narrow angles at bromine reflect lower inner electron repulsion between Li and Mg than between Br and Br, and the wide exocyclic C–Mg–O angle can be attributed to repulsion between the large organic group and THF. The Li–N bond lengths (2.06(2) Å) are similar to those in the cation of **4** (2.125(9) Å) but significantly shorter than those in **1**, probably because there is less crowding round the lithium atom. The Mg–C and Mg–O bond lengths are in the usual range [23,24].



9



10 R = $\mathrm{C(SiMe_3)_3}$
11 R = $\mathrm{C(SiMe_3)_2(SiMe_2Ph)}$



13

The lithium magnesate **8** was obtained from the reaction between the lithium reagent $\overline{\mathrm{Li(THF)\{C(SiMe_3)_2(SiMe_2C_5H_4N}}\mathrm{\text{-}2)\}}$ and $[\mathrm{MgBr_2(OEt_2)_2}]$ [25]. It was previously reported to have the composition $\mathrm{Li(THF)_2MgBr_2C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)}$ [26], but an X-ray structure determination has shown that in the crystalline compound there is a third molecule of THF and a single bridging bromine between Li and Mg. The molecular structure is shown in Fig. 4, and the most important bond lengths and angles are given in Table 1. The Mg–Br2, Mg–C and Mg–N distances are not significantly different from those (2.487(3), 2.189(9) and 2.097(9) Å, respectively) in the Grignard reagent **9**. The wide C1–Mg–Br angles, and the configuration of the $\overline{\mathrm{MgCSiCN}}$ ring are very similar in the two compounds. The Mg–Br1 bond length is significantly greater than that of Mg–Br2 but it is similar to that of the Mg–Br bonds in the doubly-bridged compounds **6** and **7**. The Li–Br distance is similar to those in **6**, even though the Li–Br–Mg and Br–Mg–Br angles are wider. The isolation of **8** confirms that the coordinating power of Br attached to Mg is similar to that of THF, since quite small changes in the coordination of the magnesium cause the disruption of the four-membered $\mathrm{LiBr_2Mg}$ rings found in **6** and **7**.

*2.4. The Grignard reagents **10** and **11***

The Grignard reagent $\mathrm{(Me_3Si)_3CMgCl}$ was made some time ago by reaction between the anthracene derivative $\mathrm{Mg(C_{14}H_{10})(THF)_3}$ and $\mathrm{(Me_3Si)_3CCl}$ [27]. The corresponding bromide was obtained from $\mathrm{(Me_3Si)_3CBr}$ and magnesium metal and found to react as a ligand transfer reagent with benzyl chloride and $\mathrm{HgCl_2}$ [28]. In neither case was the Grignard reagent isolated. When the organomagnesium bromide was made in THF a crystalline compound could be isolated, but this was shown to be a Grignard reagent–$\mathrm{MgBr_2}$ complex $[\mathrm{(Me_3Si)_3CMg(\mu\text{-}Br)_3Mg(THF)_3}]$ (**12**) [29]. We have now found that the iodides RI [R = $\mathrm{C(SiMe_3)_3}$ or $\mathrm{C(SiMe_2Ph)_3}$] react with activated magnesium metal to give the Grignard reagents RMgI, **10** and **11**, which readily crystallise as diethyl ether complexes. The iodides are conveniently obtained by treatment of the lithium compounds LiR with 1,2-diiodoethane; this appears to be a general method for synthesis of iodides RI [R = $\mathrm{C(SiMe_3)_n(SiMe_2X)_{3-n}}$] from the corresponding RH (see, e.g. Ref. [30]).

The structures of **10** and **11** are shown in Figs. 5 and 6, respectively, and selected bond lengths and angles are given in Table 1. The compounds crystallise as centrosymmetrical halide-bridged dimers. Despite the importance of Grignard reagents in organic synthesis, the structures of only a few dimeric organomagnesium halides have been reported [23]. They are found when the Lewis basicity of the solvent is similar to that of the halide. Mononuclear structures [$\mathrm{MgRXL_n}$] are obtained in the presence of stronger donors L, and more complex halide bridged structures when the basicity of the donor is low or the amount available is insufficient. As far as we are aware, no other dimeric organomagnesium iodide, has been structurally characterised previously, though some ytterbium analogues [$\mathrm{Yb\{C(SiMe_3)_2(SiMe_2X)\}I]_2}$ (X = Me, CH=CH$_2$ or OMe) have been reported [31,32]. The Mg–C bond in **11** is slightly longer and the Mg–I bonds are slightly shorter than the corresponding bonds in **10**, and the $\mathrm{Mg_2I_2}$ ring is slightly less symmetrical than that in **10**. Taken together these data suggest that there is greater crowding in **11** from interactions between the tris(organosilyl)methyl group and diethyl ether. The other bond lengths and angles in **10** are not significantly different from the corresponding values in **11**, and within each molecule no individual value differs significantly from the average values given in Table 1. The Mg–C bond lengths (2.146(7) Å in **10** and 2.181(3) Å in **11**) are similar to those in [$\mathrm{Mg\{CH(SiMe_3)_2\}Cl(OEt_2)}$] (2.131(8) Å) [33], **6**, **12** and other compounds (2.094(11)–2.18 Å (no e.s.d. given)) containing (μ-Br)$_2$ [34–37] or (μ-Cl)$_2$ bridges [38]. The Mg–O bonds in **10** and **11** are also similar to those in **6** and related compounds (2.012(4)–2.09(2) Å).

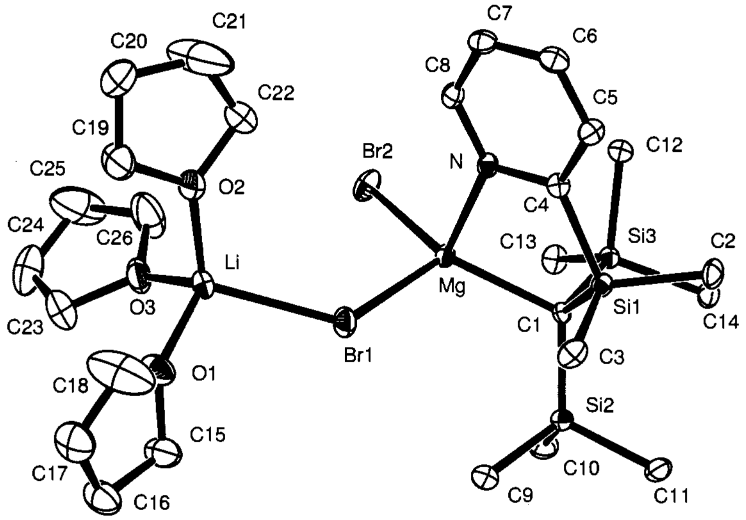


Fig. 4. Molecular structure of $\mathrm{Li(THF)_3(\mu\text{-}Br)}\overline{\mathrm{MgBr\{C(SiMe_3)_2(SiMe_2C_5H_4N)}}\mathrm{\}}$ (**8**).

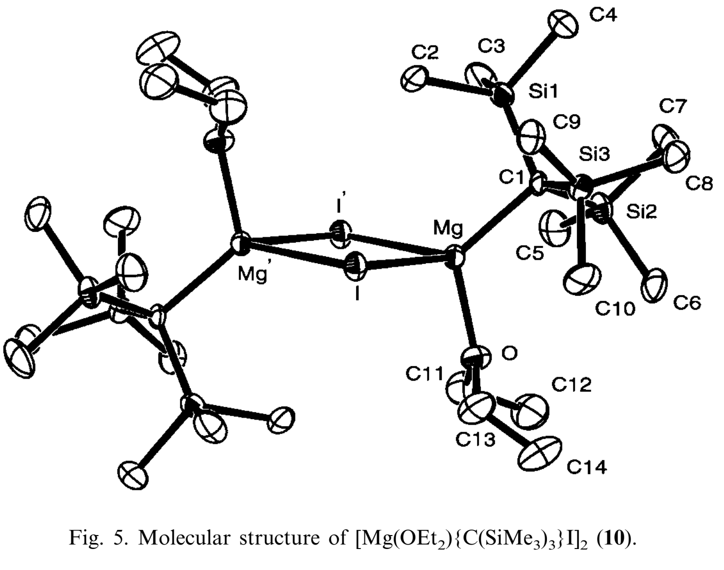


Fig. 5. Molecular structure of $\mathrm{[Mg(OEt_2)\{C(SiMe_3)_3\}I]_2}$ (**10**).

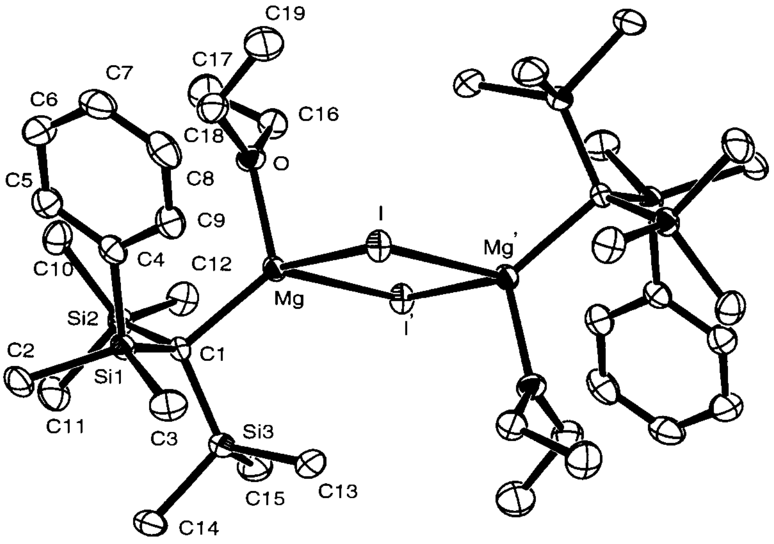


Fig. 6. Molecular structure of $[Mg(OEt_2)\{C(SiMe_3)_2(SiMe_2Ph)\}I]_2$ (**11**).

The Mg_2I_2 ring, like the Mg_2Br_2 ring in dimeric organomagnesium bromides, is almost square, reflecting the greater transannular inner-shell repulsion between the Mg atoms in **10** and **11** than between Li and Mg in **6**.

The reaction of **10** with $SiMe_3Cl$ at room temperature was incomplete after 1 h and $C(SiMe_3)_4$ was obtained in low (23%) yield. The reaction with $LiC(SiMe_3)_3$ for 1 h gave $Mg\{C(SiMe_3)_3\}_2$ (13%) and $CH(SiMe_3)_3$ (29%) as well as unchanged $LiC(SiMe_3)_3$ (32%) and **10** (26%). The low reaction rates can be attributed to steric hindrance. The compound **11** appeared to be stable for more than one year in the solid state in the absence of air and moisture, but ^1H-NMR signals from a sample in C_6D_6 rapidly broadened and the spectra showed that decomposition to $CD(SiMe_3)_2(SiMe_2Ph)$ was complete in 5 h. It is likely that free-radical processes are involved.

2.5. *The dialkylmagnesium* ***13***

In an attempt to make a dialkylmagnesium from **2** and $[MgBr_2(OEt_2)_2]$, a mixture of **2** and butyl–lithium was inadvertently used. The product was the unsymmetrical dialkyl $[MgBu\{C(SiMe_3)_2(SiMe_2NMe_2)\}(THF)]$, seemingly obtained because the LiBu reacts much faster than the sterically hindered **2**. We have not studied the conditions for the formation of this compound in detail, nor explored its chemistry, but we give details of its structure because there are very few data in the literature for unsymmetrical compounds of this type. The closest analogues appear to be the metallacycles $[MgEt\{\mu\text{-}(CH_2)_3NMeR\}]_2$ (R = Me (**14a**) or cyclohexyl (**14b**)), which dimerise through electron deficient dialkylaminopropyl bridges [39].

The structure is shown in Fig. 7 and some molecular parameters are given in Table 1. The Mg–C(Bu) bond length (2.130(3) Å) is similar to that of the Mg–Et bonds in **14** (2.142(3), 2.129(3) Å) and almost as short as the bonds in compounds in which the magnesium is two-coordinate (2.116(2) Å in $[Mg\{C(SiMe_3)_3\}_2]$ [40,41] and 2.126(6) Å in $[Mg\{CH_2CMe_3\}_2]$ [42]). The Mg–C1 bond length (2.241(2) Å) is significantly longer than the Mg–Bu bond, longer also than those in the Grignard reagents **10** and **11**, but shorter than those in the three-centre bonds of **14**. Within the MCSiN rings, the Mg–C bond in **13** is shorter than the Li–C bond in **1** (2.315(8) Å), but the Si–C (1.831(2) Å) and Si–N (1.829(2) Å) bonds are longer in **13** (cf. 1.803(4) and 1.790(4) Å, respectively, in **1**), reflecting the greater transfer of charge from lithium than from magnesium to the carbanionic centre. In **1**, **13** and other compounds containing the same chelate ring [2], the C1–Si1 bonds are significantly shorter than the other two C1–Si bonds, indicating that the $SiMe_2NMe_2$ is more effective than the $SiMe_3$ group in accommodating the carbanionic charge. The wide C1–Mg–C12 angle is characteristic of dialkylmagnesium complexes with ether and amine donors, as discussed elsewhere [23].

3. Experimental

Air and moisture were excluded as far as possible from all reactions by the use of Schlenk techniques, flame-dried glassware and Ar as blanket gas. NMR spectra from samples in C_6D_6 were recorded at 300.1 (^1H), 75.4 (^{13}C), 99.4 (^{29}Si) and 116.6 MHz (^7Li); chemical shifts are given relative to $SiMe_4$ and aqueous LiCl. At the time most of the work was done we did not have

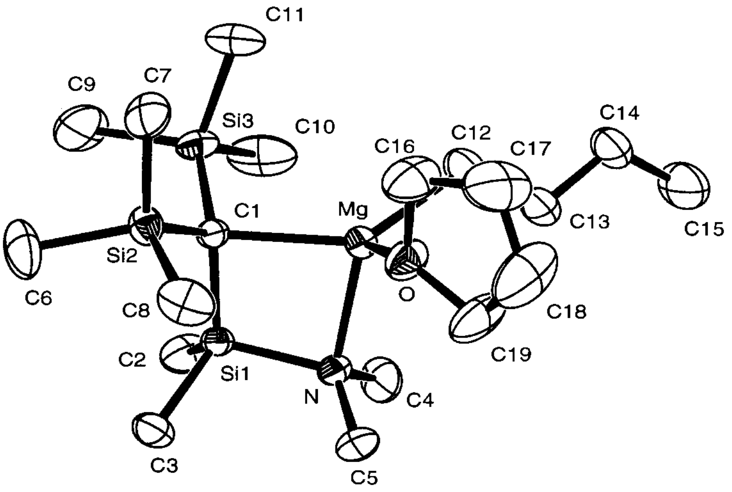


Fig. 7. Molecular structure of [MgBu{C(SiMe$_3$)$_2$(SiMe$_2$NMe$_2$)}·THF] (**13**).

access to satisfactory C, H, and N analyses for air- and moisture-sensitive compounds, so had to rely on clean NMR spectra, consistent with the structures determined by X-ray crystallography, as evidence that the compounds were obtained pure.

3.1. *[Li(TMEDA)C(SiMe$_3$)$_2$SiMe$_3$NMe$_2$] (**1**)*

Dry TMEDA (0.085 g, 0.73 mmol) was added dropwise to a solution of **2** [2] (0.29 g, 0.70 mmol) in hexanes (10 cm^3) at room temperature (r.t.). The clear mixture was reduced in volume to 5 cm^3 and kept at − 30 °C to give colourless crystals of **1** (0.20 g, 74%). δ (H): 0.44 (6H, s, SiMe$_2$), 0.45 (18H, s, SiMe$_3$), 2.2 (6H, s, NMe$_2$), 1.85, (16H, m, TMEDA). δ (C): 3.9 (SiMe$_2$), 3.9 (detected by the INEPT pulse sequence, q, $^1J_{\text{CLi}} =$ 11.6 Hz, CSi$_3$), 8.9 (s, SiMe$_3$), 40.6 (s, NMe$_2$), 46.4 and 57.3 (TMEDA). δ (Si): − 10.2 (SiMe$_3$), 5.5 (SiMe$_2$). δ (Li): 0.23 ($\Delta\nu_{1/2}$ 2 Hz).

3.2. *[Li(TMEDA)$_2$][Li{C(SiMe$_3$)$_2$(SiMe$_2$Ph)}$_2$] (**4**)*

The preparation of this compound has been described previously [3]. Crystals suitable for an X-ray structural determination were obtained from a concentrated solution in benzene that had been kept at r.t. for several months.

3.3. *Li(TMEDA)(μ-Br)$_2$Mg{C(SiMe$_3$)$_2$-(SiMe$_2$Ph)}(THF) (**6**)*

A sample of [MgBr$_2$(OEt$_2$)$_2$] (0.31 g, 0.95 mmol) (made from Mg turnings and 1,2-dibromoethane) [43] was heated in a Schlenk tube under vacuum to remove Et$_2$O and the resulting solid was dissolved in THF (5 cm^3) then cooled to − 80 °C. A solution of complex **4** (0.50 g, 0.6 mmol) in THF (5 cm^3) was added slowly. The clear yellow mixture was stirred for 1 h at − 80 °C, allowed to warm to r.t., and stirred for a further hour. The solvent was removed under vacuum and the residue extracted with warm (40 °C) hexanes (4 × 5 cm^3). The extract was reduced to 5 cm^3 and kept at 5 °C overnight to give colourless crystals of **6** (0.11 g, 22%). δ (H): 0.42 (18H, s, SiMe$_3$), 0.64 (6H, s, SiMe$_2$), 1.41 and 3.57 (4H, s, THF), 1.5–2.2 (16H, m, TMEDA), 7.63–7.77 (5H, m, Ph). δ (Li): 1.98.

3.4. *Li(THF)$_3$(μ-Br)MgBr{C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2)} (**8**)*

The isolation, ^{1}H-, and ^{7}Li-NMR spectra were reported previously. δ (C): 1.3 (CSi$_3$), 3.3 (SiMe$_3$), 4.7 (SiMe$_2$), 7.2 and 25.4 (THF), 123.8, 129.1, 133.4, 150.1, 170.2 (C$_5$H$_4$N).

3.5. *[Mg{C(SiMe$_3$)$_3$}I(OEt$_2$)]$_2$ (**10**)*

Magnesium turnings (0.70 g, 29.2 mmol) were stirred overnight under Ar in a flame-dried Schlenk vessel to break up the metal surface and a solution of (Me$_3$Si)$_3$CI (2.0 g, 5.6 mmol) in Et$_2$O (30 cm^3) was added. The mixture was stirred for 30 min, then the excess of magnesium was filtered off and the filtrate concentrated to 15 cm^3 and kept at − 30 °C to give colourless crystals of **10**, which were recrystallised from toluene (2.26 g, 89%). δ H (toluene-d_8): 0.38–0.53 (27H, broad, SiMe$_3$), 0.77 (6H, t) and 3.57 (4H, broad, Et). δ (C): 7.1 (SiMe$_3$), 3.6 and 12.8 (Et). m/z: 382 (2%, [M] − Et$_2$O), 367 (21, [M] − Me − Et$_2$O), 217 [100, CH(SiMe$_3$)$_3$ − Me], 201 (60), 185 (10), 129 (60).

Chlorotrimethylsilane (0.25 cm^3, 2.0 mmol) was added from a syringe to a stirred solution of **10** (2.0 mmol) in Et$_2$O (12 cm^3) at r.t.. After 30 min the solvent was removed from the mixture, the residue extracted

Table 2
Crystal data and structure refinement parameters for the compounds studied

	1	**4**·2C_6H_6	**6**	**8**	**10**·$C_6H_5CH_3$	**11**	**13**
Empirical formula	$C_{17}H_{46}LiN_3Si_3$	$C_{54}H_{102}Li_2N_4Si_6$	$C_{25}H_{53}Br_2LiMgN_2OSi_3$	$C_{26}H_{52}Br_2LiMgNO_3Si_3$	$C_{35}H_{82}I_2Mg_2O_2Si_6$	$C_{38}H_{78}I_2Mg_2O_2Si_6$	$C_{19}H_{47}MgNOSi_3$
Formula weight	383.8	989.8	673.0	702.0	1006.0	1038.0	414.2
Temperature (K)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic	Orthorhombic	Monoclinic	Triclinic
Space group	$P\bar{1}$ no. 2	$C2/c$ no. 15	$P\bar{1}$ no. 2	$P2_12_12_1$ no. 19	*Pbca* no 61	$P2_1/n$ no 14	$P\bar{1}$ no. 2
Unit cell dimensions							
a (Å)	9.415(1)	15.188(7)	11.375(3)	9.7103(2)	13.564(3)	15.238(5)	9.108(2)
b (Å)	15.202(1)	19.117(9)	11.439(6)	13.1308(5)	24.903(7)	11.122(3)	9.7455(12)
c (Å)	17.712(2)	22.205(9)	14.094(3)	28.1309(19)	15.047(5)	16.412(11)	15.8928(12)
α (°)	90.03(1)	90	95.04(3)	90	90	90	98.971(9)
β (°)	92.74(1)	91.19(3)	96.87(2)	90	90	112.07(3)	96.576(14)
γ (°)	91.31(1)	90	103.37(3)	90	90	90	105.393(15)
V (Å^3)	2531.5(4)	6446(5)	1758.7(11)	3586.8(2)	5083(3)	2578(2)	1325.2(4)
Z	4	4	2	4	4	2	2
μ (mm^{-1})	0.19	0.16	2.44	2.40	1.43	1.41	0.21
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.051$, $wR_2 = 0.125$	$R_1 = 0.095$, $wR_2 = 0.207$	$R_1 = 0.069$, $wR_2 = 0.125$	$R_1 = 0.047$, $wR_2 = 0.089$	$R_1 = 0.055$, $wR_2 = 0.139$	$R_1 = 0.029$, $wR_2 = 0.074$	$R_1 = 0.055$, $wR_2 = 0.134$
R indices (all data)	$R_1 = 0.082$, $wR_2 = 0.161$	$R_1 = 0.172$, $wR_2 = 0.241$	$R_1 = 0.155$, $wR_2 = 0.159$	$R_1 = 0.064$, $wR_2 = 0.096$	$R_1 = 0.074$, $wR_2 = 0.156$	$R_1 = 0.038$, $wR_2 = 0.081$	$R_1 = 0.083$, $wR_2 = 0.151$
Reflections measured/independent	6176/6176	5906/5662 [$R_{int} = 0.054$]	6190/6190	11298/5988, [$R_{int} = 0.043$]	3099/3099	4698/4524, [$R_{int} = 0.032$]	6346/6346
Reflections with [$I > \sigma(I)$]	4515	3136	3368	4978	2360	3888	4564

with benzene, and the extract filtered. The solvent was removed from the filtrate to give a sticky solid, which was shown by ^{1}H-NMR spectroscopy to consist of $C(SiMe_3)_4$ (23%), $CH(SiMe_3)_3$ (44%), and unchanged **10** (32%).

A solution of $[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$ (0.75 g, 0.98 mmol) in Et_2O (29 cm^3) was added to a stirred solution of **10** (2.0 mmol) in Et_2O (12cm^3). After 30 min the solvent was removed from the mixture, the residue extracted with toluene, and the extract filtered. The sticky solid obtained after removal of the toluene from the extract was shown by NMR spectroscopy to contain $Mg\{C(SiMe_3)_3\}_2$ (13%), $CH(SiMe_3)_3$ (29%), as well as unidentified products, unchanged $[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$ and **10**.

3.6. *$[Mg\{C(SiMe_3)_2(SiMe_2Ph)\}I(OEt_2)]_2$* (**11**)

Magnesium turnings (0.24 g, 10 mmol) were activated as above, then Et_2O (20 cm^3) and a crystal of iodine were added. A solution of $(Me_3Si)_2(PhMe_2Si)CI$ [32] (2.1 g., 5.0 mmol) in Et_2O (20 cm^3) was added dropwise and the mixture stirred for 1 h. The precipitated solids were filtered off and extracted with toluene (2 × 10 cm^3) at 50 °C and the extract left at r.t. to give colourless crystals of **11** (0.69 g, 31%). The Et_2O was pumped from the filtrate to leave a sticky solid, which was shaken with hexanes (20 cm^3) and washed with heptane at -50 °C to leave a white powder that showed the same ^{1}H-NMR spectrum as the crystals. δ (H): 0.48 (18H, s, $SiMe_3$), 0.69 (6H, s, $SiMe_2$), 0.74 (6H, t) and 3.41 (4H, q, Et_2O), 7.25 (3H, m, *m*- and *p*-H), 7.91 (2H, d, *o*-H). δ (C): 2.7 (CSi_3), 3.4 ($SiMe_3$), 7.9 ($SiMe_2$), 15.3 and 65.8 (Et_2O), 125.6, 129.3, 135.8 and 142.5 (Ph). δ (Si): -9.6 ($SiMe_2$), -6.0 ($SiMe_3$). *m*/*z*: 429 (20%, [M] − Me − THF), 279 [100, $CH(SiMe_3)_2(SiMe_2Ph) - Me$].

3.7. *$[MgBu\{C(SiMe_3)_2(SiMe_2NMe_2)\}(THF)]$* (**13**)

A solution of LiBu (8.7 mmol) in hexanes (3.5 cm^3) was added dropwise to a stirred solution of $(Me_3Si)_2(Me_2NMe_2Si)CCl$ (1.86 g, 6.31 mmol) [2] in THF (40 cm^3) at -78 °C. The mixture was stirred for 2 h and then added dropwise to a stirred solution of $[MgBr_2(OEt_2)_2]$ (0.79 g, 2.40 mmol) in THF (20 cm^3) at -120 °C. The mixture was allowed to warm to r.t. and the solvent was pumped away to leave a sticky brown residue, which was extracted with hexanes. The extract was concentrated to 15 cm^3, then kept at -30 °C to give yellow crystals of **13** (0.95 g, 95% based on $MgBr_2$), m.p. 147–154 °C. δ (H): -0.13 (2H, t, CH_2Mg), 0.29 (6H, s, $SiMe_2$), 0.41 (18H, s, $SiMe_3$), 1.19–1.23 (7H, m, THF and CH_3), 1.66 and 1.76 (2H, m, CH_2), 2.09 (6H, s, NMe_2), 3.42 (4H, m, THF). δ (C): 3.5 ($SiMe_2$), 8.1 ($SiMe_3$), 8.7 ($^1J_{CSi} = 41.5$ Hz, CSi_3), 9.4 (CH_2), 14.6 (CH_3), 25.1 (THF), 32.6 and 33.8 (CH_2), 40.4 (NMe_2), 69.3 (THF). δ (Si): -7.6 ($SiMe_3$), 15.1 ($SiMe_2$).

3.8. *Crystallography*

Data for **1, 4**, **6**, **10**, **11** and **13** were recorded on a CAD4 and for **8** on a Kappa CCD diffractometer by use of Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Further details are given in Table 2. Structural analysis was by direct methods (SHELXS-86 or SHELXS-97) and refinement by full least-squares on all data (SHELXL-93 or SHELXL-97). Non-H atoms were anisotropic and H atoms were included in riding mode. In **4**, there are two molecules of occluded benzene in the asymmetric unit; the high *R* factors result from the weak high angle diffraction. In **10** there is a molecule of toluene disordered across an inversion centre and the H atoms in this were omitted.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 162000–162006 for compounds **1**, **4**·$2C_6H_6$, **6**, **8**, **10**·$C_6H_5CH_3$, **11** and **13**, 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; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the EPSRC and the EU for financial support and the Governments of Saudi Arabia and Libya, respectively, for granting study leave to S.S.Al-J. and S.M.El-H.

References

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

[2] S.S. Al-Juaid, C. Eaborn, S.M. El-Hamruni, P.B. Hitchcock, J.D. Smith, Organometallics 18 (1999) 45.

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

[4] U. Schümann, J. Kopf, E. Weiss, Angew. Chem. Int. Ed. Engl. 24 (1985) 215.

[5] T. Maetzke, D. Seebach, Helv. Chim. Acta 72 (1989) 624.

[6] M.F. Lappert, L.M. Engelhardt, C.L. Raston, A.H. White, J. Chem. Soc. Chem. Commun. (1982) 1323.

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

[8] C. Eaborn, P.B. Hitchcock, J.D. Smith, S.E. Sözerli, Organometallics 17 (1998) 4322.
[9] 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.
[10] C. Eaborn, P.B. Hitchcock, J.D. Smith, A.C. Sullivan, J. Chem. Soc. Chem. Commun. (1983) 827.
[11] R. Boese, P. Paetzold, A. Tapper, Chem. Ber. 120 (1987) 1069.
[12] 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.
[13] G. Wittig, F.J. Meyer, G. Lange, Liebigs Ann. Chem. 571 (1951) 167.
[14] N.H. Buttrus, C. Eaborn, P.B. Hitchcock, J.D. Smith, J.G. Stamper, A.C. Sullivan, J. Chem. Soc. Chem. Commun. (1986) 969.
[15] C. Eaborn, Z.-R. Lu, P.B. Hitchcock, J.D. Smith, Organometallics 15 (1996) 1651.
[16] C. Eaborn, S.M. El-Hamruni, P.B. Hitchcock, J.D. Smith, Chem. Commun. (1998) 1277.
[17] B. Beagley, J.J. Monaghan, T.G. Hewitt, J. Mol. Struct. 8 (1971) 401.
[18] P.T. Brain, M. Mehta, D.W.H. Rankin, H.E. Robertson, C. Eaborn, J.D. Smith, A.D. Webb, J. Chem. Soc. Dalton Trans. (1995) 349.
[19] W. Hiller, M. Layh, W. Uhl, Angew. Chem. Int. Ed. Engl. 30 (1991) 324.
[20] C. Eaborn, K.L. Jones, P.D. Lickiss, J. Organomet. Chem. 466 (1994) 35.
[21] S.S. Al-Juaid, C. Eaborn, A. Habtemariam, P.B. Hitchcock, J.D. Smith, J. Organomet. Chem. 437 (1992) 41.
[22] N.H. Buttrus, C. Eaborn, M.N.A. El-Kheli, P.B. Hitchcock, J.D. Smith, A.C. Sullivan, K. Tavakkoli, J. Chem. Soc. Dalton Trans. (1988) 381.
[23] P.R. Markies, O.S. Akkerman, F. Bickelhaupt, W.J.J. Smeets, A.L. Spek, Adv. Organomet. Chem. 32 (1991) 147.
[24] C.E. Holloway, M. Melnik, J. Organomet. Chem. 465 (1994) 1.
[25] H. Schibilla, M.T. Le Bihan, Acta Crystallogr. 23 (1967) 332.
[26] S.S. Al-Juaid, C. Eaborn, P.B. Hitchcock, M.S. Hill, J.D. Smith, Organometallics 19 (2000) 3224.
[27] S. Harvey, P.C. Junk, C.L. Raston, G. Salem, J. Org. Chem. 53 (1988) 3134.
[28] C.L. Smith, L.M. James, K.L. Sibley, Organometallics 11 (1992) 2938.
[29] S.S. Al-Juaid, C. Eaborn, P.B. Hitchcock, A.J. Jaggar, J.D. Smith, J. Organomet. Chem. 469 (1994) 129.
[30] C. Eaborn, A. Farook, P.B. Hitchcock, J.D. Smith, Organometallics 16 (1997) 503.
[31] C. Eaborn, P.B. Hitchcock, K. Izod, Z.-R. Lu, J.D. Smith, Organometallics 15 (1996) 4783.
[32] C. Eaborn, P.B. Hitchcock, K. Izod, J.D. Smith, J. Am. Chem. Soc. 116 (1994) 12071.
[33] P.B. Hitchcock, J.A.K. Howard, M.F. Lappert, W.-P. Leung, S.A. Mason, J. Chem. Soc. Chem. Commun. (1990) 847.
[34] J. Toney, G.D. Stucky, J. Chem. Soc. Chem. Commun. (1967) 1168.
[35] A.L. Spek, P. Voorbergen, G. Schat, C. Blomberg, F. Bickelhaupt, J. Organomet. Chem. 77 (1974) 147.
[36] J.J. Ellison, P.P. Power, J. Organomet. Chem. 526 (1996) 263.
[37] H. Bock, K. Ziemer, C. Näther, J. Organomet. Chem. 511 (1996) 29.
[38] D.E. Hibbs, C. Jones, A.F. Richards, J. Chem. Soc. Dalton Trans. (1999) 3531.
[39] B. Bogdanović, G. Koppetsch, C. Krüger, R. Mynott, Z. Naturforsch. Teil B 41 (1986) 617.
[40] S.S. Al-Juaid, C. Eaborn, P.B. Hitchcock, C.A. McGeary, J.D. Smith, J. Chem. Soc. Chem. Commun. (1989) 273.
[41] S.S. Al-Juaid, C. Eaborn, P.B. Hitchcock, K. Kundu, C.A. McGeary, J.D. Smith, J. Organomet. Chem. 480 (1994) 199.
[42] E.C. Ashby, L. Fernholt, A. Haaland, R. Seip, R.S. Smith, Acta Chem. Scand. Ser. A 34 (1980) 213.
[43] J.P. McCormick, D.L. Barton, J. Org. Chem. 45 (1980) 2566.