Iodo(methoxydimethylsilyl)bis(trimethylsilyl)methane: a reagent for the preparation of novel organometallic compounds. Crystal structures of $\overline{Mg\{C(SiMe_3)_2(SiMe_2OMe)\}}_2$ and $MgI_2(OEt_2)_2$ [1]

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Abstract

The alkyl chloride $R_2(HMe_2Si)CCl$ (R = $SiMe_3$) reacted with ICl to give the iodide $R_2(ClMe_2Si)Cl$, which with MeOH gave $R_2(MeOMe_2Si)Cl$. This reacted with Mg in Et_2O to give $MgI_2(OEt_2)_2$ (which was isolated and structurally characterised) and the chelated dialkylmagnesium $\overline{Mg\{C(SiMe_3)_2(SiMe_2OMe)\}}_2$, apparently following initial formation of the Grignard reagent $\overline{MeOSiMe_2CR_2MgI}$. The latter compound was isolated from the products of the reaction between the iodide $R_2(MeOMe_2Si)Cl$ and Mg in toluene. The lithium compound $\overline{MeOSiMe_2CR_2Li}$ was made by treatment of the chloride $R_2(MeOMe_2Si)_2CCl$ with BuLi in THF and the chelated structure was confirmed by an X-ray study.

Keywords: Silicon; Magnesium; Lithium; Grignard reagent; Crystal structure

1. Introduction

Organometallic compounds containing the ligands $C(SiMe_3)_3$ and $C(SiMe_2Ph)_3$ show an astonishing variety of new structures and reactions, many of which cannot be observed for derivatives possessing less bulky ligands [1,2]. We considered that it should be possible to obtain a further range of interesting structures by replacing the methyl groups in $C(SiMe_3)_3$ by groups bearing lone pairs, since these could either chelate to the metal and thereby stabilise it against unwanted attack or link organometallic units together to form novel cage structures. This last possibility was realised in the dimeric lithium compound $[Li\{C(SiMe_2OMe)_3\}]_2$ which has an unprecedented cage structure [3,4]. In contrast the organometallic compounds of zinc, cadmium and mercury containing the ligand $C(SiMe_3)_2$-$(SiMe_2OMe)$ showed a metal–oxygen interaction (very weak) only in the case of the zinc compound [5,6]. Our

discovery of a simple and reliable synthesis of $(Me_3Si)_2(MeOMe_2Si)CCl$ has allowed us to explore its potential as a starting material for the preparation of novel organometallic compounds. The crystal structure of a dialkylmagnesium made from the iodide is described here; that of an alkylytterbium iodide is reported elsewhere [7]. During the course of the work we incidentally isolated and determined the crystal structure of the halide complex $MgI_2(OEt_2)_2$; this is used as a reagent for the conversion of cyclopropylmethanols $C_3H_5CRR'OH$ to homoallylic iodides $RR'C = CHCH_2CH_2I$ [8] and has been extensively studied in solution by large-angle X-ray scattering and EXAFS [9], so we include a brief report on its geometry in the solid state.

2. Experimental

Air and moisture were excluded by use of Schlenk tube techniques. Solvents were dried by standard methods. NMR spectra were recorded by use of a Bruker AC-P250 spectrometer; chemical shifts are relative to

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[1] Dedicated to Professor R.J.P. Corriu in recognition of his outstanding innovative contributions to organosilicon chemistry.

SiMe$_4$. Mass spectra (EI) were obtained with a Fisons VG Autospec instrument; intensities (%) are relative to that of the strongest peak.

2.1. Syntheses

(Me$_3$Si)$_2$(HMe$_2$Si)CCl **1**, m.p. 95°C, was made as described previously [5] and recrystallised from methanol. Anal. Found: C, 42.1; H, 9.5. C$_9$H$_{25}$ClSi$_3$ Calc.: C, 42.7; H, 9.96%. δ(H) (C$_6$D$_6$) 0.18 (18H, s, SiMe$_3$), 0.21 (6H, d, ^3J(HH) 3.7 Hz, SiMe$_2$), 4.34 (1H, septet ^3J(HH) 3.7 Hz, SiH); δ(C) 1.15 (SiMe$_3$), −1.32 (SiMe$_2$H); δ(Si) 4.9 (SiMe$_3$), −10.0 (SiMe$_2$H). m/z 252 (10, M) 237, (35, M − Me), 178 (55, M − Me$_3$SiH), 163 (15, M − Me − Me$_3$SiH), 149 (50, M − Me − SiMe$_4$), 129 (100, Me$_2$Si=CHSiMe$_2$), 73 (100, SiMe$_3$), 59 (20, Me$_2$SiH).

2.1.1. (Me$_3$Si)$_2$(ClMe$_2$Si)Cl. 8

A solution of (Me$_3$Si)$_2$(HMe$_2$Si)CCl (7.83 g, 0.031 mol) and ICl (5.2 g, 0.032 mol) in CCl$_4$ (30 cm^3) was stirred at 20°C. The progress of the reaction was monitored by GLC, which showed that after 30 min all the silicon hydride had disappeared to give a 9:1 mixture of (Me$_3$Si)$_2$(ClMe$_2$Si)CI and (Me$_3$Si)$_2$(ClMe$_2$Si)CCl. Solvent and the excess of ICl were removed in vacuum and the residue was fractionally sublimed to give (Me$_3$Si)$_2$(ClMe$_2$Si)CCl (0.5 g) and (Me$_3$Si)$_2$-(ClMe$_2$Si)CI (9.0 g, 77%), subl. 100–120°C at 0.01 Torr, m.p. 134°C. Anal. Found: C, 28.2; H, 6.2. C$_9$H$_{24}$ClISi$_3$ Calc.: C, 28.5; H, 6.4%. δ(H) 0.34 (18H, s, SiMe$_3$), 0.71 (6H, s, SiMe$_2$); δ(C) 4.1 (SiMe$_3$), 7.5 (SiMe$_2$); δ(Si) 6.3 (SiMe$_3$), 23.1 (SiMe$_2$Cl).

2.1.2. (Me$_3$Si)$_2$(MeOMe$_2$Si)Cl, 9

A mixture of (Me$_3$Si)$_2$(ClMe$_2$Si)CI (2.0 g, 5.3 mmol), CH$_2$Cl$_2$ (40 cm^3) and MeOH (40 cm^3) was stirred for 24 h at 20°C. Analysis by GLC showed the presence of only one silicon-containing product, and solvents were removed in vacuum to give (Me$_3$Si)$_2$-(MeOMe$_2$Si)CI, (1.8 g, 81%), m.p. 227°C. Anal. Found: C, 31.9; H, 7.1. C$_{10}$H$_{27}$IOSi$_3$ Calc.: C, 32.1; H, 7.3%. δ(H) (CDCl$_3$) 0.26 (18H, s, SiMe$_3$), 0.37 (6H, s, SiMe$_2$), 3.47 (3H, s, OMe); δ(C) 2.5 (SiMe$_2$), 3.9 (SiMe$_3$), 51.7 (OMe); δ(Si) 5.0 (SiMe$_3$), 15.2 (SiMe$_2$). m/z 374 (36, M), 359 (100, M − 15), 270 (33, M − Me$_3$SiOMe), 143 (83, M − Me$_3$SiOMe − I), 73 (75, SiMe$_3$), 59 (43%, Me$_2$SiH).

2.1.3. Reaction of (Me$_3$Si)$_2$(MeOMe$_2$Si)Cl with magnesium

(a) In ether. The reaction between magnesium metal (50 mg, 2.1 mmol) and (Me$_3$Si)$_2$(MeOMe$_2$Si)CI (400 mg, 1.1 mmol) was initiated with a crystal of iodine. The mixture was stirred for 48 h, then filtered, and the filtrate was concentrated to 10 cm^3 and cooled to

−30°C. The first crystals formed showed only signals ascribed to Et$_2$O in the ^{1}H NMR spectrum and were judged to be MgI$_2$ · nEt$_2$O **14** (ca. 50 mg). This (with $n = 2$) was confirmed by an X-ray structural determination. The mother liquor was cooled to yield colourless hexagonal plates which were shown by an X-ray study to be Mg{C(SiMe$_3$)$_2$(SiMe$_2$OMe)}$_2$ **12** (150 mg, 50%); δ(H) (tolu ne-d_8) 0.21 (s, 6H, SiMe$_2$), 0.26 (s, 18H, SiMe$_3$), 2.94 (s, 3H, OMe). A third crop of crystals appeared to be a mixture of the bis-alkylmagnesium and a new compound containing coordinated ether; δ(H) (C$_6$D$_6$) 0.24 (s, 6H, SiMe$_2$), 0.35 (s, 18H, SiMe$_3$), 0.89 (t, 15H) and 3.47 (q, 10H, Et), 2.95 (s, 3H, OMe); δ(C) 2.57 (SiMe$_3$), 7.35 (SiMe$_2$), 10.2 (CSi$_3$), 14.1 and 66.5 (Et), 50.9 (OMe); δ(Si) −4.72 (SiMe$_3$), −4.51 (SiMe$_2$).

(b) In toluene. Magnesium metal (40 mg, 1.7 mmol) and a crystal of iodine were added to a solution of (Me$_3$Si)$_2$(MeOMe$_2$Si)CI (400 mg, 1.10 mmol) in toluene (20 cm^3) and the mixture was stirred at 80°C for 3 h then at 25°C overnight. The excess of metal was filtered off and the filtrate was concentrated to 5 cm^3 and cooled to −10°C to give colourless plates (39 mg, 80%), m.p. 211–213°C. Anal. Found: C, 29.7; H, 6.75. C$_{10}$H$_{27}$IMgOSi$_3$ **16** Calc.: C, 30.1; H, 6.78%. δ(H) (C$_6$D$_6$) 0.18 (s, 6H, SiMe$_2$), 0.41 (s, 18H, SiMe$_3$), 2.90 (s, 3H, MeO); δ(C) 3.1 (SiMe$_2$), 6.3 (CSi$_3$), 7.2 (SiMe$_3$), 50.9 (OMe); δ(Si) −4.7 (SiMe$_3$), 0.5 (SiMe$_2$). m/z 398 (10%, M), 383 (70, M − Me).

2.1.4. Preparation of (Me$_3$Si)$_2$(Me$_2$MeOSi)CLi · 2THF

Butyllithium (5.6 mmol) in hexane (3 cm^3) was added dropwise to a solution of (Me$_3$Si)$_2$(MeO-Me$_2$Si)CCl^6 (0.50 g, 1.8 mmol) in THF (20 cm^3) at −78°C and the mixture was stirred at −78°C for 2 h. The solvent was removed in vacuum below 0°C and the residue recrystallised from heptane–THF (95:5) to give colourless crystals of Li{C(SiMe$_3$)$_2$(SiMe$_2$OMe)} · 2THF. δ(H) (C$_6$D$_6$) 0.44 (18H, s, SiMe$_3$), 0.45 (6H, s, SiMe$_2$), 1.29 (4H, m, THF) and 3.38 (4H, m, THF), 3.06 (3H, s, OMe); δ(C) 3.1 (SiMe$_2$), 7.1 (CSi$_3$, J(CSi) 49.6 Hz), 7.7 (SiMe$_3$), 25.0 and 68.4 (THF), 49.8 (OMe); δ(Li) 0.2; δ(Si) −7.9 (SiMe$_3$), 0.7 (SiMe$_2$OMe).

2.2. Crystal structure determinations

2.2.1. Mg{C(SiMe$_3$)$_2$(SiMe$_2$OMe)}$_2$, 12

Crystal data: C$_{20}$H$_{54}$MgO$_2$Si$_6$, $M = 519.5$, trigonal, $P3_121$, $a = 9.320(3)$, $c = 31.605(11)$ Å, $U = 2377.5(14)$ Å^3, $Z = 3$, $D_c = 1.09$ Mg m^{-3}, $F(000) = 858$. Monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, $\mu = 0.30$ mm^{-1}, $T = 173(2)$ K.

Intensities were measured on an Enraf-Nonius CAD4 diffractometer from a crystal of size 0.2 × 0.2 × 0.05 mm^3. Data for 2179 reflections with h, $-k$, l and

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **12**

Atom	x	y	z	U_{eq}
Mg	3933(3)	0	3333	24(1)
Si(1)	5580(3)	2191(3)	2660(1)	27(1)
Si(2)	1908(3)	1199(3)	2577(1)	32(1)
Si(3)	3003(3)	−1360(3)	2361(1)	31(1)
O	6222(6)	1720(6)	3118(2)	34(1)
C(1)	3413(8)	493(9)	2676(2)	23(2)
C(2)	7933(9)	2544(12)	3243(3)	81(4)
C(3)	6041(10)	4373(9)	2746(3)	46(3)
C(4)	6981(10)	2310(10)	2232(3)	45(3)
C(5)	2298(11)	2423(11)	2082(3)	58(3)
C(6)	1871(10)	2501(11)	3018(3)	52(3)
C(7)	−295(9)	−521(10)	2523(3)	47(3)
C(8)	4744(10)	−1826(10)	2351(3)	46(3)
C(9)	2515(11)	−1254(11)	1801(3)	60(3)
C(10)	1240(10)	−3292(9)	2589(3)	54(3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

$2° < \sigma < 23°$ were corrected for Lorentz and polarisation effects but not for absorption, and 1950 were independent. The structure was solved by direct methods and full-matrix least-squares refinement on all F^2 gave $R_1 = 0.062$ (from 1391 reflections with $I > 2\sigma(I)$), $wR_2 = 0.142$ (all data) [10]. Goodness of fit 1.04. Non-hydrogen atoms were anisotropic and hydrogens were included in the riding mode with $U_{iso}(H) = 1.5 U_{eq}(C)$. Atomic coordinates are listed in Table 1. Anisotropic displacement parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

2.2.2. $MgI_2(OEt_2)_2$, **15**

Crystal data: $C_8H_{20}I_2MgO_2$, $M = 426.4$, triclinic, $P\bar{1}$, $a = 7.650(2)$, $b = 8.036(4)$, $c = 12.710(7)$ Å, $\alpha = 99.98(4)$, $\beta = 96.46(4)$, $\gamma = 93.00(4)°$, $U = 762.6(6)$ Å^3, $Z = 2$, $D_c = 1.86$ Mg m^{-3}, $F(000) = 404$, Mo Kα radiation, $\lambda = 0.71073$ Å, $\mu = 4.14$ mm^{-1}. Data from

2675 reflections with h, $\pm k$, $\pm l$ and $2° < \sigma < 25°$ were collected as for **12**. The structure was solved by direct methods and full-matrix least-squares refinement on all F^2 gave $R_1 = 0.055$ (from 2295 reflections with $I > 2\sigma(I)$), $wR_2 = 0.146$ (all data). All non-H atoms were isotropic and hydrogens were included in the riding mode with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for Me groups. Atomic coordinates are given in Table 2.

2.2.3. $Li\{C(SiMe_3)_2(SiMe_2OMe)\} \cdot 2THF$, **4** $\cdot$ $2THF$

Crystal data: $C_{18}H_{43}LiO_3Si_3$, $M = 398.7$, orthorhombic, $Pna2_1$, $a = 16.964(2)$, $b = 9.727(5)$, $c = 16.215(2)$ Å, $U = 2675.6(14)$ Å^3, $Z = 4$, $D_c = 0.99$ Mg m^{-3}, $F(000) = 880$, Mo Kα radiation, $\lambda = 0.71073$ Å, $\mu = 0.19$ mm^{-1}. Data from 4021 reflections with h, k, l and $2° < 2\sigma < 30°$ were collected as for **12**. Full-matrix least-squares refinement on all F^2 gave $R_1 = 0.102$ (from 929 reflections with $I > 2\sigma(I)$) and $wR_2 = 0.396$ (all data). All non-H atoms were anisotropic and hydro-

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **14**

Atom	x	y	z	U_{eq}
I(1)	2548.1(7)	8336.1(7)	417.7(4)	32(1)
I(2)	2971.4(7)	7851.9(6)	3931.0(4)	34(1)
Mg	1593(3)	9348(3)	2351(2)	22(1)
O(1)	2107(6)	11833(6)	2857(4)	25(1)
O(2)	−1017(7)	9098(7)	2247(4)	30(1)
C(1)	1637(11)	13006(10)	2116(6)	33(2)
C(2)	3166(13)	13556(11)	1601(7)	43(2)
C(3)	3009(10)	12698(10)	3898(5)	29(2)
C(4)	1746(13)	13284(12)	4681(7)	42(2)
C(5)	−2131(11)	7932(11)	1393(7)	36(2)
C(6)	−2427(20)	6260(14)	1700(11)	75(4)
C(7)	−1929(11)	9940(12)	3107(6)	36(2)
C(8)	−2828(12)	11476(13)	2800(7)	47(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

gens were included in the riding mode with U_{iso} (H) = $1.2U_{eq}$(C). Details have been deposited at the Cambridge Crystallographic Data Centre.

3. Discussion

We previously used the organolithium compound **4** in the syntheses of the Group 12 organometallic compounds **5–7** by the reaction sequence (i)–(v) in Scheme 1 [5,6]; compound **4** was not isolated at that time. It was found to be very soluble in both aliphatic and aromatic hydrocarbons as well as diethyl ether and THF, but we have now obtained a single crystal from heptane/THF and determined the structure by X-ray diffraction. The data are not sufficiently precise ($R_1 = 0.102$) to merit publication, but they show unambiguously that the crystal consists of isolated molecules of **4 · 2THF** in which the silicon-containing organic group is bound through both carbon and oxygen. The NMR spectra indicate that this structure persists in benzene solution. The THF can be removed under vacuum but we have not been able to determine the structure of the residue.

4 · 2THF   **12**

When the hydride **1** was treated with ICl [step (vi)] the product was unexpectedly the alkyl iodide **8** together with a small amount of the expected chloride $(Me_3Si)_3(ClMe_2Si)CCl$ (the mechanism of this unusual conversion of an alkyl chloride to an alkyl iodide merits investigation). Treatment of the iodide **8** with MeOH gave a good yield of the methoxy compound **9**, which reacted with magnesium or ytterbium metal to give the alkylmetal iodides **10** and **11**.

The reaction between **9** and magnesium in diethyl ether gave three products, which were separated by fractional crystallisation. The least soluble compound was the complex $MgI_2 \cdot 2OEt_2$ **14**, which was characterised by an X-ray diffraction study. After the crystals of this compound had been filtered off, the mother liquor was concentrated and cooled to $-30°C$ to give hexagonal plates which were shown by an X-ray structural determination to be the dialkylmagnesium **12**. A third crop, of irregularly shaped crystals, shown by NMR spectroscopy to contain diethyl ether as well as methyl groups attached to silicon and oxygen, probably consisted of the Grignard reagent **10**, which was partially converted during recrystallisation into the dialkylmagnesium and magnesium diiodide as shown in Eq. (1). This reaction could be facilitated by the low solubil-

ity of **14** and/or the stabilisation of **12** by internal coordination.

$$[MgRI(OEt_2)]_2 \rightarrow MgR_2 + MgI_2(OEt_2)_2 \qquad (1)$$
10   **12**   **14**

$$R = C(SiMe_3)_2(SiMe_2OMe)$$

The structure of the solvent-free compound **12** is shown in Fig. 1 and bond lengths and angles in Table 3. The four-coordinate magnesium atom lies on a two-fold symmetry axis and the methoxy oxygen atoms are linked to the metal to give four-membered, almost planar rings with dimensions similar to those in $[LiC(SiMe_3)_2(SiMe_2OMe)(THF)_2]$ and $[LiC(SiMe_2OMe)_3]_2$ [4]. Previously reported examples of internal coordination of methoxy groups to magnesium centres involve five-membered rings [11,12].

Comparision of the structure with that of the compound $Mg\{C(SiMe_2)_3\}_2$ **15** reveals the following features.

(a) The Mg–C bond in **12** is significantly longer that those in **15** (2.116(2) Å) [13], $(Me_3CCH_2)_2Mg$ (2.126(6) Å) [14], in which the coordination number of magnesium is 2, or common Grignard reagents (2.09–2.25 Å), in which the coordination number is 4–6 [15,16]. The Mg–O bonds are in the usual range (2.0–2.1 Å).

(b) One silicon atom of each CSi_3 fragment in **12** is pulled in towards the magnesium (Mg–C1–Si1 = 86.8(3)°). The C–Mg–C axis is bent and the coordination sphere at Mg is intermediate between the linear arrangement of **15** and the tetrahedral arrangement expected for four-coordination. The O–Mg–O angle is considerably narrower than the tetrahedral value.

(c) The CSi_3 framework is slightly flatter in **12** (mean Si–C–Si 113.6(4)°) than it is in **15** (mean Si–C–Si 112.6(1)°) and the C–Si bonds are slightly shorter (mean 1.850(7) Å in **12**, 1.877(3) Å in **15**), possibly indicating a small but significant increase in the delocalisation of negative charge from the central carbon, but none of these bond lengths or angles in either compound differs significantly from the mean. Thus there is remarkably little distortion of the CSi_3 framework as the coordination number of magnesium is increased from 2 to 4. The distortions arising from formation of the four-membered chelate rings are almost entirely in Mg–C–Si angles, which range from 86 to 121°.

(d) The lengths of the outer Si–C bonds are normal. As expected as a result of coordination of the oxygen to the magnesium, the Si–O bond (1.705(6) Å) in **12** is lengthened compared with those commonly found (1.62–1.66 Å) in $R_3Si–OR^1$ species [17]. Similar long Si–O bonds are found in $[LiC(SiMe_2OMe)_3]_2$ [18].

(e) The structure of **12** is very different from those of the Zn, Cd and Hg analogues **5–7** [5,6]. In **5** the Zn $\cdots$ O distance is 2.93 Å, indicating that any inter-

$(Me_3Si)_2CCl_2$ $\xrightarrow{\text{(i)}}$ $(Me_3Si)_2(HMe_2Si)CCl$ **1**

$(Me_3Si)_2(BrMe_2Si)CCl$ **2** $\xleftarrow{\text{(ii)}}$ $\qquad$ $(Me_3Si)_2(ClMe_2Si)CI$ **8** $\quad$ (vi)↓

(iii)↓

$(Me_3Si)_2(MeOMe_2Si)CCl$ **3** $\qquad$ $(Me_3Si)_2(MeOMe_2Si)CI$ **9** $\quad$ (vii)↓

(iv)↓

$(Me_3Si)_2(MeOMe_2Si)CLi$ **4** $\qquad$ $[(Me_3Si)_2(MeOMe_2Si)CMI(OEt_2)]_2$ $\quad$ (viii)↓

$\qquad$ M = Mg **10**, Yb **11**

(v)↓

$\{(Me_3Si)_2(MeOMe_2Si)C\}_2M$ $\qquad$ $\{(Me_3Si)_2(MeOMe_2Si)C\}_2M$ $\quad$ (ix)↓

M = Zn **5**, Cd **6**, Hg **7** $\qquad$ M = Mg **12**, Yb **13**

$MgI_2(OEt_2)_2$ **14** $\qquad\qquad$ $\{(Me_3Si)_3C\}_2Mg$ **15**

(i) BuLi, $-110°$, then $SiMe_2HCl$; (ii) Br_2 in CCl_4/CH_2Cl_2; (iii) MeOH; (iv) BuLi, $-110°$; (v) $ZnBr_2$, $CdCl_2$ or $HgBr_2$; (vi) ICl, CCl_4; (vii) MeOH; (viii) Mg or Yb metal in Et_2O; (ix) warm.

Scheme 1.

action is very weak, and the Si–C–Zn skeleton is very similar to that in the oxygen-free dialkyl $\{(Me_3Si)_3C\}_2Zn$ [19].

Crystals of the diiodide bisetherate **14** consist of discrete molecules as shown in Fig. 2; there is no

evidence for the dimer formation postulated on the basis of large-angle X-ray scattering from ethereal solutions [9]. In contrast the MgI_2 complex obtained from THF has an Mg : THF ratio of 1 : 4 [20]. Bond lengths and angles for **14** are given in Table 4. Although the
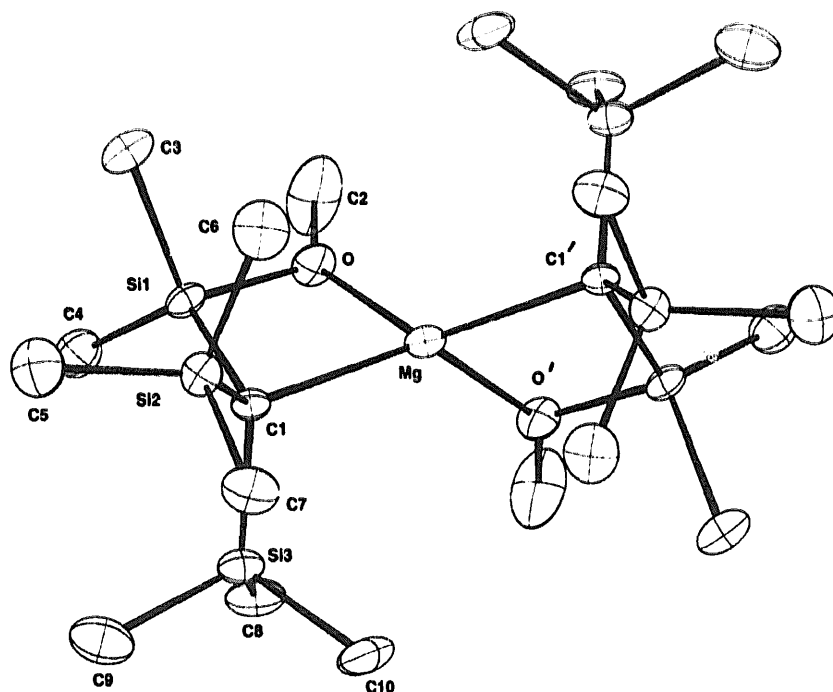
Fig. 1. The molecular structure of $\{(Me_3Si)_2(MeOMe_2Si)C\}_2Mg$ **12**.

Table 3
Bond lengths (Å) and angles (deg) for 12

Mg-O	2.041(5)	Mg-C(1)	2.233(7)
Si(1)-O	1.705(6)	Si(1)-C(1)	1.842(7)
Si(1)-C(4)	1.844(8)	Si(1)-C(3)	1.877(7)
Si(2)-C(1)	1.849(7)	Si(2)-C(6)	1.859(9)
Si(2)-C(5)	1.862(9)	Si(2)-C(7)	1.877(8)
Si(3)-C(9)	1.841(9)	Si(3)-C(1)	1.860(7)
Si(3)-C(10)	1.871(8)	Si(3)-C(8)	1.879(7)
O-C(2)	1.437(8)		
O-Mg-O'	98.5(3)	O-Mg-C(1)	77.1(2)
O-Mg-C(1)'	129.8(2)	C(1)-Mg-C(1)'	142.7(4)
O-Si(1)-C(1)	97.5(3)	O-Si(1)-C(4)	108.0(3)
C(1)-Si(1)-C(4)	120.8(4)	O-Si(1)-C(3)	103.7(3)
C(1)-Si(1)-C(3)	119.0(3)	C(4)-Si(1)-C(3)	105.6(4)
C(1)-Si(2)-C(6)	111.8(4)	C(1)-Si(2)-C(5)	114.2(4)
C(6)-Si(2)-C(5)	106.9(4)	C(1)-Si(2)-C(7)	114.3(4)
C(6)-Si(2)-C(7)	104.8(4)	C(5)-Si(2)-C(7)	104.0(4)
C(9)-Si(3)-C(i)	114.0(4)	C(9)-Si(3)-C(10)	107.5(4)
C(1)-Si(3)-C(10)	111.2(4)	C(9)-Si(3)-C(8)	105.2(4)
C(1)-Si(3)-C(8)	115.0(4)	C(10)-Si(3)-C(8)	103.2(4)
C(2)-O-Si(1)	122.3(5)	C(2)-O-Mg	140.6(5)
Si(1)-O-Mg	97.0(2)	Si(1)-C(1)-Si(2)	113.0(4)
Si(1)-C(1)-Si(3)	114.3(4)	Si(2)-C(1)-Si(3)	113.6(4)
Si(1)-C(1)-Mg	86.8(3)	Si(2)-C(1)-Mg	120.8(4)
Si(3)-C(1)-Mg	105.8(3)		

Symmetry transformations used to generate equivalent atoms: ' $x - y, - y, - z + 2/3$.

molecule has no crystallographically imposed symmetry there is no significant difference between the two Mg–OEt₂ bonds nor between the two Mg–I bonds. There are small variations in the conformation of the ethyl groups, as seen in the range of Mg–O–C angles. The mean Mg–I bond length (2.654(3) Å) is significantly longer than that (2.52(2) Å) in gaseous MgI₂ [21], but

similar to those deduced for solutions by X-ray scattering (2.65 Å) or EXAFS (2.75 Å) [9]. The I–Mg–I angle, like the C–Mg–I angle in Grignard reagents with Et₂O solvation [16], is wide and the O–Mg–O angle is narrow, reflecting differences in size between iodine and oxygen or differences in polarity between Mg–I and Mg–O bonds. As is common in other Et₂O com-
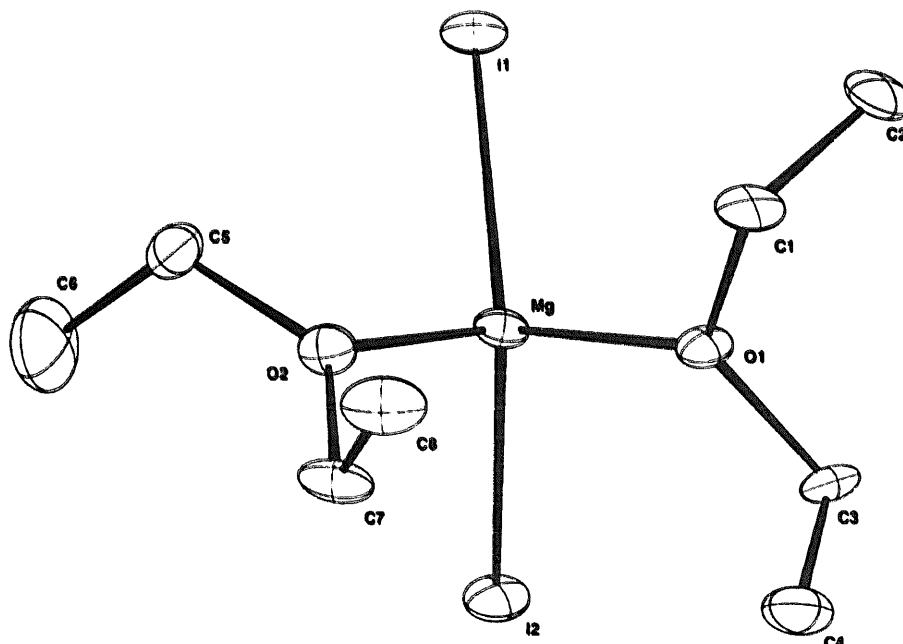

Fig. 2. The molecular structure of MgI₂(OEt₂)₂ 14.

Table 4
Bond lengths (Å) and angles (deg) for 14

Mg-O(2)	1.983(6)	Mg-O(1)	1.993(5)
Mg-I(1)	2.648(3)	Mg-I(2)	2.661(3)
O(1)-C(3)	1.461(8)	O(1)-C(1)	1.474(8)
O(2)-C(7)	1.451(9)	O(2)-C(5)	1.462(10)
C(1)-C(2)	1.487(12)	C(3)-C(4)	1.499(11)
C(5)-C(6)	1.476(14)	C(7)-C(8)	1.531(12)
O(2)-Mg-O(1)	102.3(2)	O(2)-Mg-I(1)	108.8(2)
O(1)-Mg-I(1)	112.0(2)	O(2)-Mg-I(2)	109.2(2)
O(1)-Mg-I(2)	106.5(2)	I(1)-Mg-I(2)	116.98(9)
C(3)-O(1)-C(1)	112.9(5)	C(3)-O(1)-Mg	127.7(4)
C(1)-O(1)-Mg	119.4(4)	C(7)-O(2)-C(5)	115.3(6)
C(7)-O(2)-Mg	120.6(5)	C(5)-O(2)-Mg	123.8(5)
O(1)-C(1)-C(2)	112.5(6)	O(1)-C(3)-C(4)	112.4(7)
O(2)-C(5)-C(6)	111.1(8)	O(2)-C(7)-C(8)	111.8(6)

plexes the coordination at oxygen is planar. The structure may be compared with those of ether complexes of magnesium halides. Thus the published data for $MgBr_2(OEt_2)_2$ [23] show that the crystal contains discrete molecules; the O–Mg–O angles are said to be wide and the Br–Mg–Br angles narrow, but these results must be treated with scepticism since there are wide discrepancies in the geometry of the two independent molecules in the asymmetric unit. In contrast $MgBr_2(THF)_2$ forms a polymeric solid in which six-coordinate Mg atoms are linked by bromide bridges [22]. The related complex $BeCl_2(OEt_2)_2$, like 14, adopts a molecular structure in the solid with a wide Cl–Br–Cl angle (117°) [24].

The alkylytterbium iodide 11, isolated as diethyl etherate from the reaction between the iodide 9 and ytterbium metal, has been shown by an X-ray diffraction study [7] to form ether-solvated iodide-bridged dimers in the solid state. Like the Grignard compound 10, it is readily converted into the metal dialkyl and diiodide. Although ethers, at least in catalytic amounts, are normally considered to be essential for formation of Grignard reagents [16,25], we reasoned that the built-in methoxy group in the iodide 9 might facilitate the formation of discrete molecular species of a Grignard reagent in toluene solution without the addition of further ether to solvate the magnesium. We found that, after initiation with a crystal of iodine, the reaction between 9 and magnesium did indeed proceed readily in toluene at 80°C, to give a white crystalline product. The structure was determined by an X-ray diffraction study and, although the data are not sufficiently precise for a full report, there is no doubt that it comprises iodide-bridged dimers 16 with four-membered MgCSiO rings similar to those in 12. A similar halide-bridged structure was found for $[EtMgBr(O^iPr_2)]_2$ [26]. Work in this area is continuing. We note that the Grignard reagent $(Me_3Si)_3CMgBr$ has been obtained in ether solution [27], but it has so far been characterised in the solid

state only as an ate complex with lithium [28] or magnesium [29] bromide.
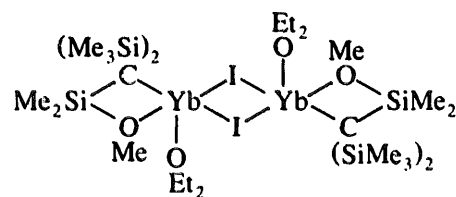
11
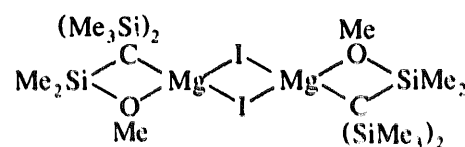
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