Some Sterically Hindered Lithium Alkylbromo- and Alkylchloro-magnesates, -cadmates, and -manganates. Crystal and Molecular Structures of $[Li(thf)_2(\mu\text{-}Br)_2Mg\{C(SiMe_3)_3\}(thf)]$, $[Li(thf)_4][\{Cd[C(SiMe_3)_3]\}_3(\mu\text{-}Br)_3(\mu_3\text{-}Br)]\cdot 0.5C_6H_{12}$, $[\{Li(thf)\}_3(\mu_3\text{-}Br)_3(\mu_3\text{-}OSiMe_3)Cd\{C(SiMe_3)_3\}]$, and $[Li(thf)_4][\{Mn[C(SiMe_3)_3]\}_3(\mu\text{-}Cl)_4(thf)]$ (thf = tetrahydrofuran)†

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Tris(trimethylsilyl)methyl-lithium reacts with anhydrous magnesium(II) bromide to give the magnesate $[Li(thf)_2(\mu\text{-}Br)_2Mg\{C(SiMe_3)_3\}(thf)]$ (**1**), which has been shown by an *X*-ray study to have a structure with two bridging bromine atoms between lithium and magnesium. With cadmium(II) bromide, $Li\{C(SiMe_3)_3\}$ gives the tricadmate $[Li(thf)_4][\{Cd[C(SiMe_3)_3]\}_3(\mu\text{-}Br)_3(\mu_3\text{-}Br)]\cdot 0.5C_6H_{12}$ (**2**) (C_6H_{12} = cyclohexane), in which the anion has a structure based on a Cd_3Br_4 cube with one corner missing. In the presence of traces of moisture, the neutral compound $[\{Li(thf)\}_3(\mu_3\text{-}Br)_3(\mu_3\text{-}OSiMe_3)Cd\{C(SiMe_3)_3\}]$ (**3**), also with a cage structure, is obtained. Both (**2**) and (**3**) can be converted into $CdBr\{C(SiMe_3)_3\}$, and $Cd(OH)\{C(SiMe_3)_3\}$. The chloride $CdCl\{C(SiMe_3)_3\}$ is dimeric in the gas phase. The reaction between tris(dimethylphenylsilyl)methyl-lithium and cadmium(II) bromide yields the cadmate $Li(thf)_2CdBr_2\{C(SiMe_2Ph)_3\}$ which can be converted into $Cd(OH)\{C(SiMe_2Ph)_3\}$, $CdBr\{C(SiMe_2Ph)_3\}$, or $Cd(OMe)\{C(SiMe_2Ph)_3\}$. The reaction between $Li\{C(SiMe_3)_3\}$ and anhydrous manganese(II) chloride gives the trimanganate $[Li(thf)_4][\{Mn[C(SiMe_3)_3]\}_3(\mu\text{-}Cl)_4(thf)]$, in which the anion has been shown by *X*-ray diffraction to have a cage structure related to that of the anion in (**2**). In each $C(SiMe_3)_3$ group the three $SiMe_3$ fragments are twisted from fully staggered positions so the group as a whole is chiral. In some tris(trimethylsilyl)methylmetal compounds left- and right-handed $C(SiMe_3)_3$ groups alternate in the crystal lattice; in others chiralities are arranged randomly.

We have described the structures and chemistry of some chlorine-bridged tris(trimethylsilyl)methyl and tris(dimethylphenylsilyl)methyl derivatives of gallium and indium.[1] Similar compounds have been isolated from reactions between $Li\{C(SiMe_3)_3\}$ or $Li\{C(SiMe_2Ph)_3\}$ and the divalent halides of magnesium, zinc, cadmium, and manganese,[2–4] and we give details of the relevant synthetic and structural studies here.

Experimental

Schlenk-tube techniques were used throughout in order to exclude air and moisture as far as possible. Solvents were carefully dried and distilled immediately before use.

Hydrogen-1 n.m.r. spectra were recorded at 360 or 90 MHz. Chemical shifts for ^1H, ^{13}C, and ^{29}Si spectra were relative to internal $SiMe_4$, and those for ^7Li relative to external aqueous $LiNO_3$. Unless otherwise stated, mass spectra were obtained by electron impact (e.i.) at 70 eV; *m*/*z* values are for ions with ^{28}Si, ^{35}Cl, ^{79}Br, and ^{114}Cd isotopes.

Di-μ-bromo-tris(tetrahydrofuran)[tris(trimethylsilyl)methyl]-magnesiumlithium, $[Li(thf)_2(\mu\text{-}Br)_2Mg\{C(SiMe_3)_3\}(thf)]$ (**1**).—Magnesium bromide etherate was made by the slow addition of 1,2-dibromoethane (2.0 g, 10.6 mmol) to a suspension of magnesium turnings (0.25 g) in diethyl ether (20 cm^3). After removal of solvent, the white solid was dissolved in thf and treated with a solution of $Li\{C(SiMe_3)_3\}$[5] (10 mmol) in tetrahydrofuran (thf, 25 cm^3) at 20 °C. The mixture was stirred for 16 h at 20 °C and then for 5 h under reflux. After removal of solvent, the residue was extracted into hot heptane and the filtered extract on cooling gave white *crystals* of (**1**), which did not give a sharp melting point but decomposed at 80—100 °C; $\delta_H(C_6D_5CD_3)$ 0.50 (27 H, s, $SiMe_3$), 1.33 (12 H, m, thf), and 3.63 (12 H, m, thf); $\delta_{Li}(C_6D_5CD_3)$ -0.42 p.p.m. The product was too sensitive for satisfactory C and H analysis, but it was identified by an *X*-ray structure determination. It did not react with an excess of $Li\{C(SiMe_3)_3\}$ to give the dialkylmagnesium analogue of the compounds $M\{C(SiMe_3)_3\}_2$ (M = Zn, Cd, Hg, or Mn).[6–8]

Only unchanged $Li\{C(SiMe_3)_3\}$ was isolated when a mixture of magnesium(II) chloride and $Li\{C(SiMe_3)_3\}$ in thf was heated under reflux for 48 h.

Tetrakis(tetrahydrofuran)lithium Tri-μ-bromo-μ₃-bromo-tris[{tris(trimethylsilyl)methyl}cadmate]–Cyclohexane (1/0.5), $[Li(thf)_4][\{Cd[C(SiMe_3)_3]\}_3(\mu\text{-}Br)_3(\mu_3\text{-}Br)]_3]\cdot 0.5C_6H_{12}$ (**2**).—$Li\{C(SiMe_3)_3\}$ (40 mmol) in diethyl ether–thf (1:1, 35 cm^3) was added during 1 h to a suspension of $CdBr_2$ (12 g, 44 mmol) in thf (100 cm^3). The mixture was stirred for 30 min and the solvent was then removed. The mixture was extracted into boiling cyclohexane and the extract was filtered, concentrated,

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† Di-μ-bromo-1,2,2-tris(tetrahydrofuran)-1-[tris(trimethylsilyl)-methyl]magnesiumlithium, tetrakis(tetrahydrofuran)lithium tri-μ-bromo-μ₃-bromo-tris[{tris(trimethylsilyl)methyl}cadmate(II)]–cyclohexane(1/0.5), 1,2,3;1,2,4;1,3,4-tri-μ₃-bromo-2,3,4-tris(tetrahydrofuran)-2,3,4-μ₃-(trimethylsilyloxy)-1-[tris(trimethylsilyl)methyl]-cadmium-trilithium, and tetrakis(tetrahydrofuran)lithium 1,2;1,3;2,3;2,3-tetra-μ-chloro-1-(tetrahydrofuran)-1,2,3-tris[tris(trimethylsilyl)methyl]-trimanganate(II) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. units employed: eV ≈ 1.60×10^{-19} J, Torr ≈ 133 Pa.

and left to cool to 20 °C, to give white *crystals*, which were shown by an *X*-ray structural determination to contain 0.5 mol of cyclohexane per mol of tricadmate (5 g, 21%), m.p. 105—107 °C (Found: C, 34.6; H, 7.6. $C_{49}H_{119}Br_4Cd_3LiO_4Si_9$ requires C, 34.8; H, 7.1%); $\delta_H(C_6D_6)$ 0.55 (81 H, s, $SiMe_3$), 1.11 (16 H, m, thf), and 3.43 (16 H, m, thf); $\delta_{Li}(C_6D_6)$ 0.92 p.p.m.

Tri-μ_3*-bromo-tris(tetrahydrofuran)-*μ_3*-(trimethylsilyloxy)-[tris(trimethylsilyl)methyl]cadmiumtrilithium*, $[\{Li(thf)\}_3(\mu_3\text{-}Br)_3(\mu_3\text{-}OSiMe_3)Cd\{C(SiMe_3)_3\}]$ (**3**).—The procedure described in the previous experiment was repeated but, after removal of solvent the thick liquid residue was extracted three times with heptane and the extracts were combined and concentrated. After 16 h at −10 °C a *solid* had separated; this was recrystallised from boiling heptane and shown by *X*-ray diffraction to be (**3**) (yield 13%), m.p. 162—165 °C (Found: C, 29.6; H, 6.9. $C_{25}H_{60}Br_3CdLi_3O_4Si_4$ requires C, 33.0; H, 6.6%); $\delta_H(C_6D_6)$ 0.21 (9 H, s, $OSiMe_3$), 0.60 (27 H, s, $SiMe_3$), 1.37 (12 H, m, thf), and 3.65 (12 H, m, thf); $\delta_{Li}(C_6D_6)$ 0.13; $\delta_{Si}(C_6D_6)$ 4.68 ($SiMe_3$) and 6.48 p.p.m. ($OSiMe_3$).

Bromo[tris(trimethylsilyl)methyl]cadmium (**4**).—When compound (**3**) (3.0 g) was heated at 175 °C and 0.01 Torr in a sublimation apparatus white *crystals* of $CdBr\{C(SiMe_3)_3\}$ (**4**) (1.15 g, 70%), m.p. 250 °C (decomp.) were collected on a water-cooled cold-finger (Found: C, 28.4; H, 6.4. $C_{10}H_{27}BrCdSi_3$ requires C, 28.4; H, 6.4%); $\delta_H(CCl_4)$ 0.21 p.p.m. (s); *m/z* 409 (55%, $[M - Me]^+$), 201 {100, $[Me_2Si{=}C(SiMe_3)SiMe_2]^+$}, 73 (60, $[SiMe_3]^+$). Compound (**4**) was similarly obtained in 77% yield when (**2**) was heated at 175 °C/0.01 Torr.

Hydroxo[tris(trimethylsilyl)methyl]cadmium (**5**).—A solution of (**2**) (1 g, 0.61 mmol) in thf (30 cm^3) was heated under reflux with 10% aqueous NaOH (5 cm^3) for 3 h. The solvent was evaporated, and the residue extracted with light petroleum (b.p. 30—40 °C, 50 cm^3). The extract was dried ($MgSO_4$) and concentrated, and the white crystals which separated at 20 °C were filtered off and recrystallised from CH_2Cl_2–MeOH to give $Cd(OH)\{C(SiMe_3)_3\}$ (**5**) (0.5 g, 77%), m.p. 305 °C (decomp.) (Found: C, 32.9; H, 7.7. $C_{10}H_{28}CdOSi_3$ requires C, 33.3; H, 7.8%); $\delta_H(CCl_4)$ 0.70 (27 H, s, $SiMe_3$) and 0.92 (1 H, s, OH; disappeared upon shaking with D_2O); ν(OH) at 3 700 cm^{-1}; *m/z* 345 (9%, $[M - OH]^+$), 231 (20, $[C(SiMe_3)_3]^+$), 201 (100), 129 {60, $[Me_2Si{=}CHSiMe_2]^+$}, and 73 (100, $[SiMe_3]^+$).

$Li(thf)CdCl_2\{C(SiMe_3)_3\}$ (**6**).—A solution of $Li\{C(SiMe_3)_3\}$ (17.2 mmol) in thf (20 cm^3) was added to a suspension of $CdCl_2$ (3.7 g, 20 mmol) in thf (60 cm^3) and the mixture was stirred for 16 h. The solvent was removed and the residue extracted with cold heptane (80 cm^3); the heptane-insoluble part was then extracted with cold toluene (50 cm^3). The heptane fraction yielded on evaporation a white solid which was shown by ^1H n.m.r. spectroscopy ($C_6D_5CD_3$) to consist of two compounds in the ratio 7:3. (Signals from these in CH_2Cl_2 or CH_2Cl_2–CCl_4 were not separated at 90 MHz.) The compounds could be separated by further fractional extractions with cold heptane. The more soluble compound was $Cd\{C(SiMe_3)_3\}_2$, identified by its m.p. and n.m.r. and mass spectrometry; the second was judged to be compound (**6**) (4.2 g, 50%) (Found: C, 33.4; H, 8.3. $C_{14}H_{35}CdCl_2LiOSi_3$ requires C, 34.0; H, 7.1%); $\delta_H(C_6D_5CD_3)$ 0.37 (27 H, s, $SiMe_3$), 1.31 (4 H, m, thf), and 3.49 (4 H, m, thf); δ_{Li} −0.24 p.p.m. In another experiment the toluene extract was concentrated and cooled to give crystals of a different compound, which was possibly $[\{Li(thf)\}_2\{Cd[C(SiMe_3)_3]\}_2(\mu_3\text{-}Cl)_3(\mu_3\text{-}OSiMe_3)]$ (Found: C, 33.3; H, 7.2. $C_{31}H_{79}Cd_2Cl_3Li_2O_3Si_7$ requires C, 35.8; H, 7.6%); $\delta_H(C_6D_6)$ 0.16 (9 H, s, $OSiMe_3$), 0.50 (54 H, s, $SiMe_3$), 1.29 (8 H, m, thf), and 3.57 p.p.m. (8 H, m, thf).

Chloro[tris(trimethylsilyl)methyl]cadmium (**7**).—When the lithium compound (**6**) (1.0 g, 2.0 mmol) was heated at 170 °C/0.01 Torr the products were thf (identified spectroscopically) and a white sublimate (0.57 g, 74%). This was extracted with methanol and the extract was concentrated and cooled to give colourless *crystals* of $CdCl\{C(SiMe_3)_3\}$ (**7**), m.p. >280 °C (decomp.) (Found: C, 31.4; H, 7.3. $C_{10}H_{27}CdClSi_3$ requires C, 31.7; H, 7.2%); $\delta_H(CCl_4)$ 0.15 p.p.m. (s); *m/z* 745 (20%, $[2M$ (dimer) $- Me]^+$), 365 ($[M - Me]^+$), and 201 {100, $[Me_2Si{=}C(SiMe_3)SiMe_2]^+$}.

Lithium chloride (0.02 g, 0.47 mmol) was added to (**7**) (0.14 g, 0.37 mmol) in thf (10 cm^3) and the mixture was heated under reflux for 3 h. The solvent was removed under vacuum and the solid obtained was taken up in cold heptane. The n.m.r. spectrum ($C_6D_5CD_3$) of the solid obtained by evaporation of the heptane extract showed only (**7**) without any lithium compound (**6**).

$Li(thf)_2CdBr_2\{C(SiMe_2Ph)_3\}$ (**8**).—A solution of $Li\{C(SiMe_2Ph)_3\}$[9] (20 mmol) in thf–diethyl ether (2:1, 45 cm^3) was added to $CdBr_2$ (6 g, 20 mmol) in thf (100 cm^3) during 1 h. After stirring for 30 min the solvent was removed and the thick liquid residue was extracted with heptane to remove any $CH(SiMe_2Ph)_3$, then three times with boiling toluene. The toluene extracts were combined, then filtered, concentrated, and allowed to cool to give colourless *crystals* of (**8**) (6 g, 75%), m.p 137—139 °C (Found: C, 47.2; H, 5.8. $C_{33}H_{49}Br_2CdLiO_2Si_3$ requires C, 47.1; H, 5.8%); $\delta_H(C_6D_6)$ 0.59 (18 H, s, $SiMe_2$), 1.39 (8 H, m, thf), 3.57 (8 H, m, thf), 7.1—7.3 and 7.5—7.64 (15 H, m, Ph); δ_{Li} −3.41 p.p.m.

Bromo[tris(dimethylphenylsilyl)methyl]cadmium (**9**).—Compound (**8**) was heated at 175 °C/0.01 Torr to give a white *sublimate* of $CdBr\{C(SiMe_2Ph)_3\}$ (**9**) (86%), m.p. 192—194 °C (Found: C, 49.3; H, 5.6. $C_{25}H_{33}BrCdSi_3$ requires C, 49.2; H, 5.4%); $\delta_H(CH_2Cl_2)$ 0.37 (18 H, s, $SiMe_2$) and 7.15—7.70 (15 H, m, Ph); *m/z* 610 (10%, $[M]^+$); 595 (30, $[M - Me]^+$).

Hydroxo[tris(dimethylphenylsilyl)methyl]cadmium.—A solution of (**8**) (1 g) in a mixture of thf (30 cm^3) and 10% aqueous NaOH (5 cm^3) was heated under reflux for 3 h. The solvent was removed and the residue was extracted with light petroleum. Solvent was evaporated from the extract and methanol added to the thick liquid residue to give the crystalline *product* (0.56 g, 86%), m.p. 142—144 °C (Found: C, 54.4; H, 6.2. $C_{25}H_{34}CdOSi_3$ requires C, 54.9; H, 6.2%); $\delta_H(CCl_4)$ 0.55 (18 H, s, $SiMe_2$), 1.65 (1 H, s, OH; disappeared on shaking with D_2O), and 6.65—6.70 (15 H, m, Ph); ν(OH) at 3 700 cm^{-1}; *m/z* (chemical ionisation, NH_3) 548 ($[M]^+$), (e.i.) 533 ($[M - Me]^+$).

Methoxo[tris(dimethylphenylsilyl)methyl]cadmium (**10**).—A solution of NaOMe (0.5 mmol) in MeOH (0.5 cm^3) was added with stirring to (**9**) (0.3 g, 0.5 mmol) in thf (10 cm^3). After 0.5 h the solvent was removed and the residue was extracted with boiling heptane. The extract was filtered and concentrated, then cooled to give white *crystals* of $Cd(OMe)\{C(SiMe_2Ph)_3\}$ (**10**) (0.15 g, 53%), m.p. 158—160 °C (Found: C, 55.3; H, 6.1. $C_{26}H_{36}CdOSi_3$ requires C, 55.7; H, 6.4%); $\delta_H(CCl_4)$ 0.35 (18 H, s, $SiMe_2$), 3.57 (3 H, s, OMe), and 7.1—7.5 (15 H, m, Ph).

Tetrakis(tetrahydrofuran)lithium Tetra-μ*-chloro-(tetrahydrofuran)tris[tris(trimethylsilyl)methyl]trimanganate*, $[Li(thf)_4][\{Mn[C(SiMe_3)_3]\}_3(\mu\text{-}Cl)_4(thf)]$ (**11**).—Pale yellow crystals of this compound were obtained as described earlier.[4] Upon heating, they became opaque and lost thf at *ca.* 146 °C, leaving a yellow solid, m.p. 180—186 °C, ν(MnCl) at 280 cm^{-1}. The mean magnetic moment (3.8 μ_B) was much lower than expected for

Table 1. Fractional atomic co-ordinates ($\times 10^4$) in compound (**1**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Br(1)	1 384(2)	1 239(1)	4 525(1)	C(10)	−2 928(23)	1 964(18)	2 635(9)
Br(2)	−930(3)	3 429(2)	4 641(1)	C(11)	−3 672(23)	1 722(16)	4 120(10)
Si(1)	839(7)	1 667(4)	2 897(2)	C(12)	−4 309(22)	940(21)	4 409(10)
Si(2)	1 256(8)	3 677(4)	3 306(3)	C(13)	−3 694(26)	121(17)	4 229(12)
Si(3)	−1 795(8)	2 998(5)	2 845(3)	C(14)	−2 286(23)	394(15)	4 123(10)
Mg	−499(6)	2 217(4)	3 972(2)	C(15)	−1 154(35)	1 477(17)	5 719(11)
O(1)	−2 274(12)	1 375(9)	4 043(5)	C(16)	−2 037(28)	1 641(21)	6 127(12)
O(2)	32(16)	2 005(10)	5 749(5)	C(17)	−1 083(35)	2 204(21)	6 453(10)
O(3)	2 648(15)	3 181(9)	5 430(6)	C(18)	102(31)	2 443(23)	6 197(9)
C(1)	−70(19)	2 682(11)	3 198(7)	C(19)	4 049(29)	2 936(19)	5 473(12)
C(2)	−29(21)	518(12)	3 044(7)	C(20)	5 035(30)	3 729(21)	5 591(14)
C(3)	2 851(21)	1 518(15)	3 140(8)	C(21)	4 034(35)	4 454(19)	5 664(14)
C(4)	659(22)	1 718(14)	2 167(8)	C(22)	2 662(31)	4 105(19)	5 572(16)
C(5)	2 302(25)	3 928(14)	2 732(9)	Li	942(53)	2 462(26)	5 155(14)
C(6)	2 678(22)	3 535(13)	3 867(8)	Si(1a)	−418(58)	1 712(27)	2 732(14)
C(7)	277(30)	4 837(13)	3 434(10)	Si(2a)	1 963(36)	2 995(40)	3 203(17)
C(8)	−3 030(23)	3 714(15)	3 238(8)	Si(3a)	−1 234(44)	3 712(29)	3 037(15)
C(9)	−1 547(24)	3 740(16)	2 236(9)				

Table 2. Intramolecular distances (Å) and angles (°) in compound (**1**) with estimated standard deviations in parentheses

Br(1)–Mg	2.551(6)	Br(1)–Li	2.46(4)	O(1)–C(11)	1.42(2)	O(1)–C(14)	1.42(2)
Br(2)–Mg	2.515(6)	Br(2)–Li	2.49(4)	O(2)–C(15)	1.33(3)	O(2)–C(18)	1.32(3)
Si(1)–C(1)	1.89(2)	Si(1)–C(2)	1.88(2)	O(2)–Li	1.95(4)	O(3)–C(19)	1.34(3)
Si(1)–C(3)	1.91(2)	Si(1)–C(4)	1.89(2)	O(3)–C(22)	1.37(3)	O(3)–Li	1.95(5)
Si(2)–C(1)	1.88(2)	Si(2)–C(5)	1.90(2)	C(11)–C(12)	1.50(4)	C(12)–C(13)	1.40(4)
Si(2)–C(6)	1.87(2)	Si(2)–C(7)	1.93(2)	C(13)–C(14)	1.42(3)	C(15)–C(16)	1.42(4)
Si(3)–C(1)	1.81(2)	Si(3)–C(8)	1.91(2)	C(16)–C(17)	1.41(4)	C(17)–C(18)	1.39(4)
Si(3)–C(9)	1.94(2)	Si(3)–C(10)	1.86(3)	C(19)–C(20)	1.47(4)	C(20)–C(21)	1.42(4)
Mg–O(1)	2.061(13)	Mg–C(1)	2.19(2)	C(21)–C(22)	1.36(4)		
Mg–Br(1)–Li	80.3(9)	Mg–Br(2)–Li	80.4(8)	C(15)–O(2)–Li	125(2)	C(18)–O(2)–Li	124(2)
C(1)–Si(1)–C(2)	111.5(9)	C(1)–Si(1)–C(3)	114.3(9)	C(19)–O(3)–C(22)	104(2)	C(19)–O(3)–Li	129(2)
C(1)–Si(1)–C(4)	113.0(9)	C(2)–Si(1)–C(3)	105.0(9)	C(22)–O(3)–Li	126(2)	Si(1)–C(1)–Si(2)	109.2(9)
C(2)–Si(1)–C(4)	104.1(9)	C(3)–Si(1)–C(4)	108.2(9)	Si(1)–C(1)–Si(3)	113.0(9)	Si(1)–C(1)–Mg	106.2(8)
C(1)–Si(2)–C(5)	114.1(9)	C(1)–Si(2)–C(6)	115.3(9)	Si(2)–C(1)–Si(3)	114.4(9)	Si(2)–C(1)–Mg	105.9(8)
C(1)–Si(2)–C(7)	111(1)	C(5)–Si(2)–C(6)	105(1)	Si(3)–C(1)–Mg	107.6(9)	O(1)–C(11)–C(12)	103(2)
C(5)–Si(2)–C(7)	105(1)	C(6)–Si(2)–C(7)	105(1)	C(11)–C(12)–C(13)	105(2)	C(12)–C(13)–C(14)	105(2)
C(1)–Si(3)–C(8)	114.2(9)	C(1)–Si(3)–C(9)	111.9(9)	O(1)–C(14)–C(13)	109(2)	O(2)–C(15)–C(16)	114(2)
C(1)–Si(3)–C(10)	112.9(9)	C(8)–Si(3)–C(9)	106(1)	C(15)–C(16)–C(17)	100(2)	C(16)–C(17)–C(18)	109(2)
C(8)–Si(3)–C(10)	103(1)	C(9)–Si(3)–C(10)	108(1)	O(2)–C(18)–C(17)	110(2)	O(3)–C(19)–C(20)	113(2)
Br(1)–Mg–Br(2)	98.0(2)	Br(1)–Mg–O(1)	97.6(4)	C(19)–C(20)–C(21)	101(2)	C(20)–C(21)–C(22)	109(3)
Br(1)–Mg–C(1)	120.0(5)	Br(2)–Mg–O(1)	98.8(4)	O(3)–C(22)–C(21)	112(2)	Br(1)–Li–Br(2)	101(1)
Br(2)–Mg–C(1)	118.8(5)	O(1)–Mg–C(1)	118.9(6)	Br(1)–Li–O(2)	114(2)	Br(1)–Li–O(3)	115(2)
Mg–O(1)–C(11)	124(1)	Mg–O(1)–C(14)	128(1)	Br(2)–Li–O(2)	106(2)	Br(2)–Li–O(3)	113(2)
C(11)–O(1)–C(14)	108(2)	C(15)–O(2)–C(18)	106(2)	O(2)–Li–O(3)	107(2)		

high-spin Mn^{II} indicating that there was some interaction between the Mn atoms.[4] Solutions in thf and single crystals of (**11**) both gave broad, featureless e.s.r. spectra centred on $g = 2$, with no evidence for hyperfine coupling even at 77 K. Similar spectra have been reported for several other alkylmanganese compounds.[10]

Compound (**11**) reacted rapidly with traces of moisture or air to give $CH(SiMe_3)_3$ (identified by its n.m.r. spectrum) and an unidentified brown solid.

Crystal Structure Determinations.—All crystals were sealed in thin walled capillaries under argon; for (**11**) a small amount of mother-liquor was included.

(*a*) *Crystal data for* $[Li(thf)_2(\mu\text{-}Br)_2Mg\{C(SiMe_3)_3\}(thf)]$ (**1**). $C_{22}H_{51}Br_2LiMgO_3Si_3$, $M = 638.9$, monoclinic, space group $P2_1/n$, $a = 9.256(2)$, $b = 14.284(2)$, $c = 24.944(1)$ Å, $\beta = 96.24(2)°$, $U = 3\,410$ Å^3, $Z = 4$, $D_c = 1.25$ g cm^{-3}, $F(000) = 1\,336$, monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 24.9$ cm^{-1}.

Data were measured on an Enraf-Nonius CAD4 diffractometer using a crystal of size 1.5 × 0.5 × 0.2 mm. Preliminary cell dimensions were found by use of the SEARCH and INDEX routines of the CAD4 and final values were calculated from the setting angles of 25 reflections with $\theta \approx 14°$. Intensities for $h, k, \pm l$ reflections with $2 < \theta < 21°$ were measured by a θ–2θ scan with $\Delta\theta = (0.8 + 0.35 \tan\theta)°$. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lorentz and polarisation effects but not for absorption; 2 180 reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement.

The structure was solved by routine heavy-atom methods with full-matrix least-squares refinement of non-hydrogen atoms by use of anisotropic thermal parameters. A difference map showed that the silicon atoms in the $C(SiMe_3)_3$ groups were disordered, in the same way as in a number of other [tris(trimethylsilyl)methyl]metal compounds.[1,2,11,12] Occupancies of 85 and 15% were found for the two sites. With hydrogen atoms at calculated positions and $B = 6.0$ Å^2,

Table 3. Fractional atomic co-ordinates (× 10^4) in compound (**2**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cd	5 069(2)	2 816(1)	2 519(1)	C(8)	4 219(25)	1 242(27)	933(22)
Br(1)	6 666	3 333	1 561(3)	C(9)	2 153(24)	802(28)	904(24)
Br(2)	6 134(2)	4 417(2)	3 322(2)	C(10)	2 896(27)	135(21)	2 267(26)
Si(1)	3 697(7)	3 298(7)	1 463(7)	C(11)	4 055(33)	8 346(35)	4 438(27)
Si(2)	2 892(7)	2 151(9)	2 980(7)	C(12)	3 177(34)	8 481(35)	3 503(27)
Si(3)	3 249(7)	1 205(7)	1 562(7)	C(13)	3 019(40)	8 858(39)	4 195(26)
O(1)	3 333	6 666	2 236(25)	C(14)	3 740(42)	9 016(36)	4 648(33)
O(2)	3 502(19)	7 866(16)	3 782(16)	C(19)[a]	225(28)	−695(33)	5 136(42)
C(1)	3 599(15)	2 324(18)	2 077(16)	Li	3 333	6 666	3 359(65)
C(2)	4 234(24)	3 270(31)	456(20)	C(15)[b]	3 125	7 285	1 660
C(3)	2 463(19)	3 205(22)	1 255(22)	C(16)[b]	3 125	6 875	996
C(4)	4 503(25)	4 543(20)	1 845(26)	C(17)[b]	3 125	6 250	996
C(5)	3 207(19)	1 601(25)	3 816(22)	C(18)[b]	3 750	6 250	1 660
C(6)	1 540(22)	1 392(28)	2 804(24)				
C(7)	3 154(23)	3 422(25)	3 406(24)				

[a] Cyclohexane solvate. [b] Atoms fixed with occupancy 33%.

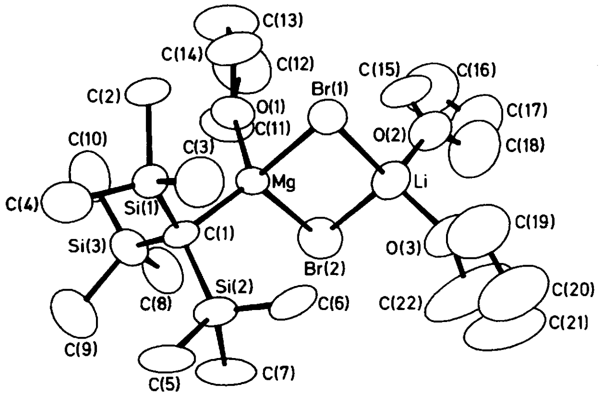


Figure 1. Molecular structure of (**1**)

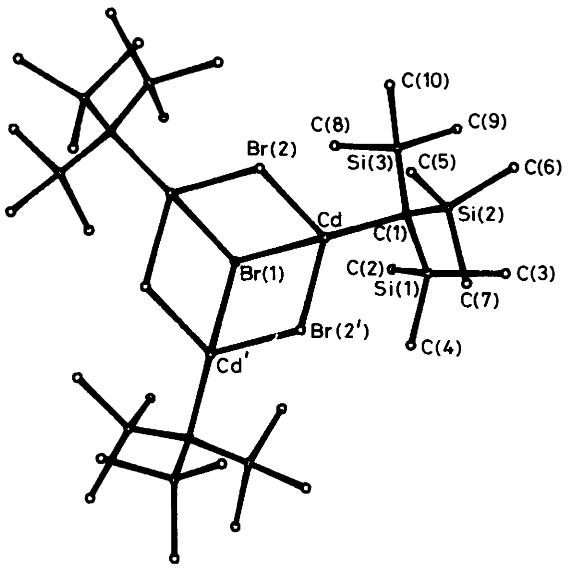


Figure 2. Structure of the anion of (**2**)

refinement converged at R $(\Sigma||F_o| - |F_c||/\Sigma|F_o|) = 0.092$, R' $\{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\} = 0.107$. A final difference map had two peaks of 0.8 e Å^{-3} near the Br atoms but was featureless elsewhere.

A PDP 11/34 computer and the Enraf-Nonius Structure Determination Package were used for the structure solution and refinement.[3] Scattering factors were from ref. 13. Final atomic co-ordinates are given in Table 1 and bond lengths and angles in Table 2; the molecule is shown in Figure 1.

(*b*) *Crystal data for* $[Li(thf)_4][\{Cd[C(SiMe_3)_3]\}_3(\mu\text{-}Br)_3(\mu_3\text{-}Br)]\cdot 0.5C_6H_{12}$ (**2**). $C_{49}H_{119}Br_4Cd_3LiO_4Si_9$, M = 1 689.0, trigonal, space group $P\bar{3}$, a = 16.145(3), c = 17.478(6) Å, U = 3 945.5 Å^3, Z = 2, D_c = 1.42 g cm^{-3}, $F(000)$ = 1 716, Mo-K_α radiation, λ = 0.710 69 Å, μ = 29.7 cm^{-1}.

Data collection, from a crystal of size 0.5 × 0.35 × 0.5 mm, was similar to that for (**1**): intensities for reflections with $2 < \theta < 21°$ and h, $\pm k$, $\pm l$ were measured in the θ–2θ mode. A correction was made for absorption based on ψ-scan measurements. There were 5 193 reflections with $|F^2| > \sigma(F^2)$ where $(F^2) = [\sigma^2(I) + (0.02I)^2]^{\frac{1}{2}}/Lp$. After averaging symmetry equivalent reflections ($R_{av.}$ = 0.05), 2 029 unique reflections were used in the final refinement.

The structure was initially solved in $P\bar{1}$. The Cd and Br atoms were found using MULTAN[14] and the remaining non-hydrogen atoms from difference maps. However, both cation and anion had three-fold symmetry so the space group was changed to $P\bar{3}$ for the final refinement. The cation has Li and O(1) on the three-fold axis with the thf containing O(1) disordered about the axis. Atoms of this disordered fragment were located from the electron density map and held fixed with B_{iso} = 6.0 Å^2. There was also a molecule of cyclohexane solvent centred on a site of $\bar{3}$ symmetry. Refinement by full-matrix least-squares methods with anisotropic thermal parameters and unit weights converged at R = 0.138 and R' = 0.130; hydrogen atoms were omitted. Final atomic co-ordinates and bond lengths and angles are given in Tables 3 and 4, and the anion is shown in Figure 2.

(*c*) *Crystal data for* $[\{Li(thf)\}_3(\mu_3\text{-}Br)_3(\mu_3\text{-}OSiMe_3)Cd\{C(SiMe_3)_3\}]$ (**3**). $C_{25}H_{60}Br_3CdLi_3O_4Si_4$, M = 910.1, orthorhombic, space group *Pnam*, a = 23.875(5), b = 12.261(6), c = 14.990(5) Å, U = 4 387.2 Å^3, Z = 4, D_c = 1.38 g cm^{-3}, $F(000)$ = 1 840, Mo-K_α radiation, λ = 0.710 69 Å, μ = 35.2 cm^{-1}.

Data, from a crystal measuring 0.5 × 0.45 × 0.3 mm, were collected as above. Intensities for *hkl* reflections with $2 < \theta < 25°$ [1 919 reflections with $|F^2| > \sigma(F^2)$] were used in the structure refinement. Systematic absences (*hk*0 for $h + k$ odd and *h*0*l* for l odd) were consistent with space group $Pna2_1$

Table 4. Intramolecular distances (Å) and angles (°) for the anion of (**2**) with estimated standard deviations in parentheses*

Cd–Br(1)	2.829(4)	Cd–Br(2)	2.677(3)	Si(2)–C(1)	1.88(3)	Si(2)–C(5)	1.91(4)
Cd–Br(2′)	2.698(4)	Cd–C(1)	2.23(2)	Si(2)–C(6)	1.92(3)	Si(2)–C(7)	2.02(4)
Si(1)–C(1)	1.85(3)	Si(1)–C(2)	1.97(4)	Si(3)–C(1)	1.84(3)	Si(3)–C(8)	1.89(5)
Si(1)–C(3)	1.95(4)	Si(1)–C(4)	1.89(3)	Si(3)–C(9)	1.93(4)	Si(3)–C(10)	1.96(4)

Br(1)–Cd–Br(2)	88.5(1)	Br(1)–Cd–Br(2′)	88.1(1)	C(3)–Si(1)–C(4)	106(2)	C(1)–Si(2)–C(5)	115(2)
Br(1)–Cd–C(1)	123.5(7)	Br(2)–Cd–Br(2′)	95.8(1)	C(1)–Si(2)–C(6)	112(2)	C(1)–Si(2)–C(7)	111(1)
Br(2)–Cd–C(1)	125.5(8)	Br(2′)–Cd–C(1)	124.6(7)	C(5)–Si(2)–C(6)	108(2)	C(5)–Si(2)–C(7)	103(2)
Cd–Br(1)–Cd′	88.6(1)	C(9)–Si(3)–C(10)	105(2)	C(6)–Si(2)–C(7)	108(2)	C(1)–Si(3)–C(8)	114(1)
Cd–Br(2)–Cd′	94.6(1)	C(1)–Si(1)–C(2)	111(2)	C(1)–Si(3)–C(9)	114(2)	C(1)–Si(3)–C(10)	112(2)
C(1)–Si(1)–C(3)	113(1)	C(1)–Si(1)–C(4)	115(2)	C(8)–Si(3)–C(9)	106(2)	C(8)–Si(3)–C(10)	105(2)
C(2)–Si(1)–C(3)	106(2)	C(2)–Si(1)–C(4)	105(2)				

* Primed atoms are related by the symmetry elements $1-y$, $x-y$, z.

Table 5. Fractional atomic co-ordinates ($\times 10^3$ for Li, $\times 10^4$ for other atoms) in compound (**3**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cd	7 998.0(6)	304.6(13)	2 500	C(3)	10 077(14)	322(28)	2 500
Br(1)	7 053.7(11)	1 541.1(20)	2 500	C(4)	9 232(7)	76(15)	685(12)
Br(2)	7 613.6(7)	−1 043.1(14)	3 804.6(12)	C(6)	9 500(8)	2 679(16)	1 259(14)
Si(1)	9 310(4)	52(7)	3 027(6)	C(8)	8 322(7)	2 012(14)	4 281(12)
Si(2)	8 738(4)	2 322(8)	3 275(6)	C(9)	8 384(11)	3 493(24)	2 500
Si(3)	8 980(4)	1 449(8)	1 333(7)	C(11)	5 952(14)	1 302(30)	4 436(24)
Si(4)	5 776(3)	−1 484(5)	2 500	C(12)	5 980(12)	1 869(24)	5 258(20)
Li(1)	669(1)	−8(2)	340(2)	C(13)	6 326(12)	1 328(25)	5 873(22)
Li(2)	701(2)	−191(4)	250	C(14)	6 573(12)	529(24)	5 277(22)
O(1)	6 410(5)	−996(11)	2 500	C(15)	7 094(10)	−4 196(20)	3 290(16)
O(2)	6 312(5)	493(10)	4 454(9)	C(16)	6 775(9)	−5 193(18)	3 001(15)
O(3)	7 024(7)	−3 526(14)	2 500	C(17)	5 653(7)	−2 323(15)	3 529(13)
C(1)	8 829(8)	1 078(17)	2 500	C(18)	5 239(11)	−349(23)	2 500
C(2)	9 143(10)	−1 368(21)	2 500				

Table 6. Intramolecular distances (Å) and angles (°) in compound (**3**) with estimated standard deviations in parentheses*

Cd–Br(1)	2.717(2)	C(13)–C(14)	1.45(2)	Si(1)–C(4′)	2.18(2)	Si(4)–O(1)	1.629(7)
Cd–C(1)	2.199(10)	Cd–Br(2)	2.719(1)	Si(2)–C(6′)	1.97(2)	Si(4)–C(18)	1.891(15)
Br(2)–Li(1)	2.568(13)	Br(1)–Li(1)	2.556(14)	Si(3)–C(8′)	2.13(2)	Li(1)–O(2)	1.95(2)
Si(1)–C(1)	1.879(11)	Br(2)–Li(2)	2.66(2)	Li(1)–O(1)	1.88(2)	Li(2)–O(3)	1.98(3)
Si(1)–C(3)	2.02(2)	Si(1)–C(2)	1.954(13)	Li(2)–O(1)	1.81(2)	O(2)–C(14)	1.38(2)
Si(2)–C(8)	1.845(10)	Si(2)–C(1)	1.930(10)	O(2)–C(11)	1.31(2)	C(11)–C(12)	1.42(2)
Si(3)–C(1)	1.843(6)	Si(2)–C(9)	2.031(13)	O(3)–C(15)	1.451(13)	C(12)–C(13)	1.40(2)
Si(3)–C(6)	1.957(11)	Si(3)–C(4)	2.034(11)	C(15)–C(16)	1.50(2)	C(16)–C(16′)	1.50(2)
Si(4)–C(17)	1.877(10)			C(13)–C(14)	1.45(2)		

Br(1)–Cd–Br(2)	93.38(3)	Br(2)–Cd–Br(2′)	91.94(5)	C(1)–Si(3)–C(8′)	112.2(5)	C(6)–Si(3)–C(8′)	102.2(5)
Br(1)–Cd–C(1)	120.5(3)	Br(2)–Cd–C(1)	124.5(1)	C(4)–Si(3)–C(8′)	107.9(4)	O(1)–Si(4)–C(17)	110.3(3)
Cd–Br(1)–Li(1)	81.2(3)	Cd–Br(2)–Li(1)	80.9(3)	O(1)–Si(4)–C(18)	111.1(5)	C(17)–Si(4)–C(17′)	110.5(6)
Br(1)–Li(1)–Br(2)	101.06(5)	Br(2)–Li(2)–Br(2′)	94.8(8)	C(17)–Si(4)–C(18)	107.3(4)	O(1)–Li(2)–O(3)	130(1)
Cd–Br(2)–Li(2)	84.2(4)	Li(1)–Br(2)–Li(2)	62.9(3)	O(1)–Li(1)–O(2)	129.0(8)	Li(1)–O(1)–Li(1′)	92.0(9)
Li(1)–Br(1)–Li(1′)	64.1(7)	C(1)–Si(1)–C(3)	106.3(6)	Si(4)–O(1)–Li(1)	123.4(5)	Li(1)–O(2)–C(14)	121(1)
C(1)–Si(1)–C(2)	107.6(5)	C(2)–Si(1)–C(3)	100.0(6)	Si(4)–O(1)–Li(2)	120.2(9)	Li(2)–O(3)–C(15)	124.6(6)
C(1)–Si(1)–C(4′)	110.4(4)	C(3)–Si(1)–C(4′)	118.3(4)	Li(1)–O(1)–Li(2)	95.1(7)	C(15)–O(3)–C15′)	110(1)
C(2)–Si(1)–C(4′)	113.3(4)	C(1)–Si(2)–C(8)	112.9(4)	Li(1)–O(2)–C(11)	124(1)	C(11)–C(12)–C(13)	112(2)
C(1)–Si(2)–C(6′)	106.3(5)	C(6′)–Si(2)–C(8)	104.5(5)	C(11)–O(2)–C(14)	107(1)	O(2)–C(14)–C(13)	113(2)
C(1)–Si(2)–C(9)	105.1(4)	C(8)–Si(2)–C(9)	112.9(5)	O(2)–C(11)–C(12)	109(2)	C(15)–C(16)–C(16′)	106.8(8)
C(6)–Si(2)–C(9)	115.1(5)	C(1)–Si(3)–C(6)	111.6(5)	C(12)–C(13)–C(14)	99(2)	O(3)–C(15)–C(16)	100(1)
C(1)–Si(3)–C(4)	107.9(5)	C(4)–Si(3)–C(6)	115.0(5)				

* Primed atoms are related by the symmetry elements x, y, $\frac{1}{2}-z$.

or *Pnam*. The former was assumed initially, but it was clear that the molecule had a mirror plane through Li(2), O(1), Cd, and Br(1) and that the Si atoms of the $C(SiMe_3)_3$ group were disordered equally between two sets of sites related by the mirror plane (Figure 3). The space group was changed to *Pnam* to complete the full-matrix least-squares refinement with Cd and Br anisotropic. Convergence was at $R = 0.076$, $R' = 0.093$; a final difference map had a peak at 0.7 e Å^{-3} near the Cd atom. Final atomic co-ordinates and bond lengths and angles are given in Tables 5 and 6; the molecule is shown in Figure 3.

(*d*) *Crystal data for* $[Li(thf)_4][\{Mn[C(SiMe_3)_3]\}_3(\mu\text{-}Cl)_4(thf)]$ (**11**). $C_{50}H_{121}Cl_4LiMn_3O_5Si_9$, M = 1 368.8, monoclinic, space group $P2_1/m$, a = 14.445(3), b = 18.996(5), c = 14.892(4) Å, β = 95.72(2)°, U = 4 065.6 Å^3, Z = 2, D_c = 1.19 g cm^{-3},

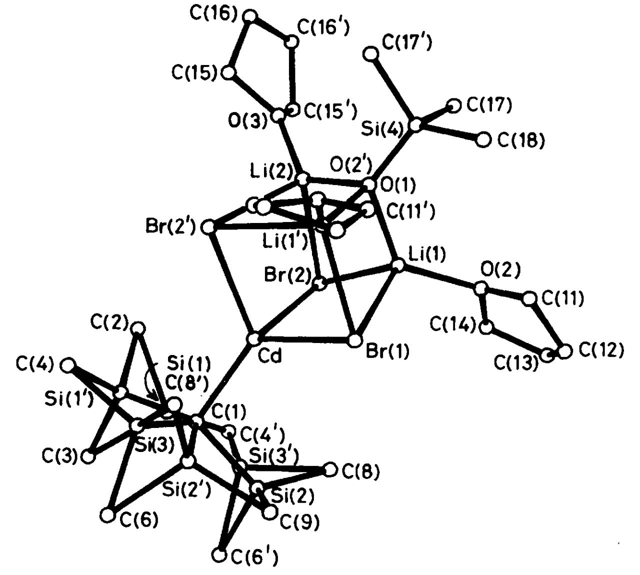


Figure 3. Molecular structure of (3): the crystallographic mirror plane passes through Li(2), O(1), Br(1), Cd, O(3), Si(4), C(18), C(1), C(9), C(2), and C(3)

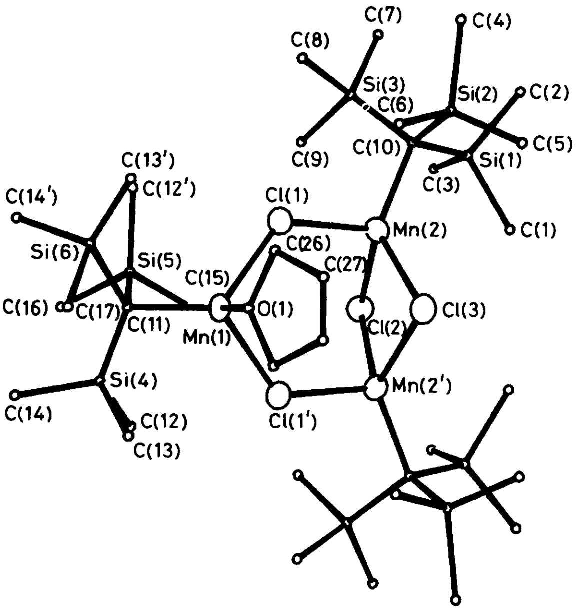


Figure 4. Structure of the anion of (**11**)

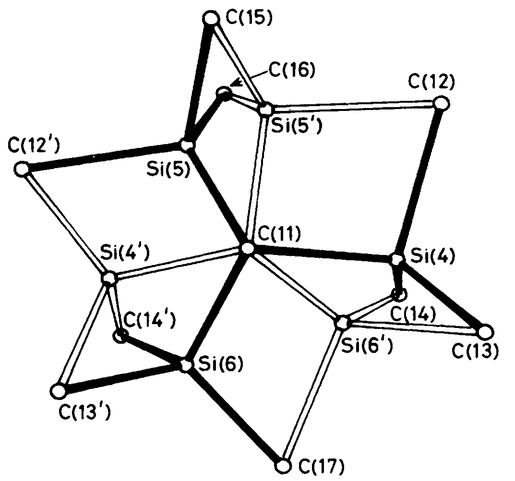
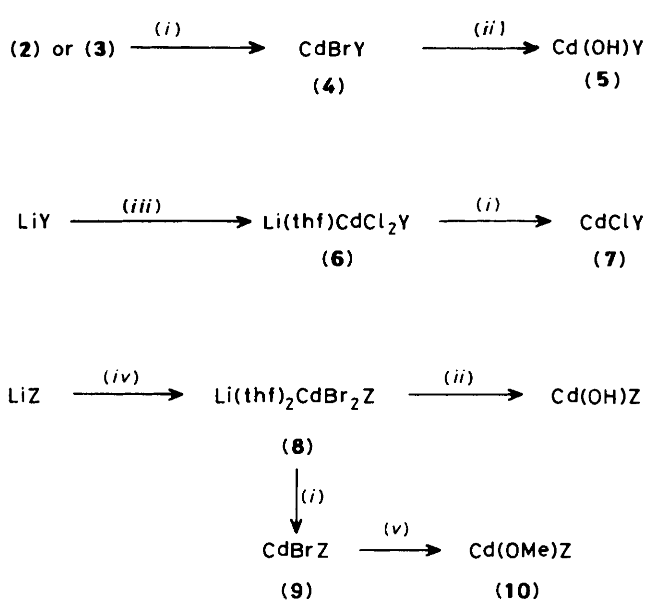


Figure 5. The $C(SiMe_3)_3$ group, Y', of (**11**) showing the crystallographic mirror plane introduced by the disorder in the silicon sites. The bonds shown in black and white are in $C(SiMe_3)_3$ groups of opposite chirality



Scheme 1. Y = $C(SiMe_3)_3$, Z = $C(SiMe_2Ph)_3$. (*i*) 175 °C/0.01 Torr or under reflux in aqueous or methanolic thf; (*ii*) 10% aqueous NaOH in thf (1 : 6) under reflux; (*iii*) $CdCl_2$ in thf–ether; (*iv*) $CdBr_2$ in thf–ether; (*v*) 1 mol dm^{-3} NaOMe in MeOH at 20 °C

$F(000) = 1\,466$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 7.4$ cm^{-1}.

Data were collected as previously from a crystal of size 0.8 × 0.4 × 0.4 mm, and 3 854 reflections ($2 < \theta < 23°$) were used in the refinement. The space group was initially assumed to be $P2_1$ and the structure was solved in that space group using routine heavy-atom methods. However, it was apparent that both anion and cation had approximate mirror symmetry across a plane perpendicular to *b*. The $C(SiMe_3)_3$ group on Mn(1) (Figures 4 and 5) was thus disordered, with the Si atoms distributed equally between two sets of sites related by the mirror plane. The space group was changed to $P2_1/m$. This revealed further disorder in the $C(SiMe_3)_3$ group attached to Mn(2), and refinement of occupancies suggested that these should be in the ratio of 2:1. There was further disorder in the thf in the cation and pairs of sites with 50% occupancy were allotted to several C atoms. This procedure was not entirely satisfactory since the thf bond lengths and angles were not well defined, but no improvement resulted from refinement of an ordered model in $P2_1$. The final block-diagonal least-squares refinement was therefore in $P2_1/m$, with Mn and Cl atoms anisotropic and the remaining atoms isotropic. The high residuals ($R = 0.156$, $R' = 0.214$) probably result from disorder and from loss of thf during the mounting of the crystal. Final atomic co-ordinates and bond lengths and angles are given in Tables 7 and 8.

Table 7. Fractional atomic co-ordinates (× 10^4) in compound (**11**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn(1)	2 239(2)	2 500	9 673(2)	C(8)	2 480(17)	5 402(14)	11 145(17)
Mn(2)	2 154(1)	3 417(1)	12 285(1)	C(9)	4 114(14)	4 513(12)	12 078(13)
Cl(1)	2 252(3)	3 500(2)	10 673(3)	C(10)	2 158(10)	4 456(8)	12 892(10)
Cl(2)	3 329(4)	2 500	12 703(4)	C(11)	3 217(14)	2 500	8 657(13)
Cl(3)	924(4)	2 500	12 335(4)	C(12)	4 229(19)	1 095(15)	9 233(18)
Si(1)^{a}	2 530(5)	4 345(4)	14 110(5)	C(13)	2 119(16)	1 064(13)	8 145(16)
Si(1A)^{b}	1 888(27)	4 222(21)	14 159(26)	C(14)	3 588(16)	1 491(11)	7 013(15)
Si(2)^{a}	889(5)	4 764(4)	12 752(5)	C(15)	4 562(17)	2 500	10 433(16)
Si(2A)^{b}	3 220(13)	4 881(10)	12 690(12)	C(16)	5 436(23)	2 500	8 604(22)
Si(3)^{a}	2 971(5)	5 036(4)	12 280(5)	C(17)	1 651(31)	2 500	6 943(31)
Si(3A)^{b}	989(11)	4 944(8)	12 381(10)	C(18)^{c}	−3 790(30)	1 942(23)	4 952(28)
Si(4)	3 308(8)	1 655(6)	8 254(7)	C(18A)^{c}	−4 340(29)	1 968(24)	4 305(28)
Si(5)	4 317(7)	2 912(5)	9 238(6)	C(19)	−4 294(26)	2 200(25)	5 361(26)
Si(6)	2 669(7)	3 210(6)	7 768(7)	C(20)^{c}	−2 238(31)	1 133(25)	2 366(29)
O(1)	716(12)	2 500(38)	9 320(11)	C(20A)^{c}	−2 161(33)	3 369(26)	1 990(32)
O(2)	−3 720(12)	2 500(40)	4 195(11)	C(21)	−2 543(23)	1 226(17)	1 265(22)
O(3)	−2 806(9)	1 707(7)	2 601(8)	C(22)	−3 397(22)	1 039(18)	1 483(21)
O(4)	−1 662(11)	2 500(34)	4 208(10)	C(23A)^{c}	−2 941(93)	3 721(63)	2 164(88)
C(1)	2 018(15)	3 449(11)	14 557(14)	C(23)^{c}	−3 217(51)	1 159(40)	2 223(49)
C(2)	2 226(16)	5 112(13)	14 852(15)	C(24)^{c}	−851(26)	2 077(19)	4 172(25)
C(3)	3 840(18)	4 230(14)	14 337(17)	C(24A)^{c}	−1 626(31)	2 005(22)	5 158(29)
C(4)	798(15)	5 807(12)	12 849(15)	C(25)	−591(28)	2 197(31)	5 605(26)
C(5)	131(18)	4 389(15)	13 492(17)	C(26)	−210(22)	1 875(19)	9 448(21)
C(6)	306(16)	4 561(12)	11 514(14)	C(27)	−764(17)	2 165(13)	9 665(17)
C(7)	3 442(16)	5 803(13)	13 038(16)	Li	−2 670(34)	2 500	3 425(31)

^{a} Occupancy 67%. ^{b} Occupancy 33%. ^{c} Occupancy 50%.

Table 8. Selected bond lengths (Å) and angles (°) in the anion of (**11**) with estimated standard deviations in parentheses*

Mn(1)–Cl(1)	2.412(4)	Mn(1)–C(11)	2.17(2)	Si(3)–C(10)	1.91(2)	Si(4)–C(11)	1.72(1)
Mn(1)–O(1)	2.21(2)	Mn(2)–Cl(1)	2.423(4)	Si(4)–C(12)	2.15(3)	Si(4)–C(13)	2.04(3)
Mn(2)–Cl(2)	2.468(4)	Mn(2)–Cl(3)	2.495(4)	Si(4)–C(14)	1.95(3)	Si(5)–C(11)	1.90(2)
Mn(2)–C(10)	2.17(2)	Si(1)–C(1)	2.00(2)	Si(5)–C(12′)	1.89(3)	Si(5)–C(15)	1.94(2)
Si(1)–C(2)	1.91(2)	Si(1)–C(3)	1.90(3)	Si(5)–C(16)	2.10(3)	Si(6)–C(11)	2.00(2)
Si(1)–C(10)	1.85(2)	Si(2)–C(4)	1.99(2)	Si(6)–C(13′)	1.71(3)	Si(6)–C(14′)	1.91(3)
Si(2)–C(5)	1.78(3)	Si(2)–C(6)	1.99(2)	Si(6)–C(17)	2.26(4)	O(1)–C(26)	1.42(4)
Si(2)–C(10)	1.92(2)	Si(3)–C(7)	1.93(2)	C(26)–C(27)	1.57(4)	C(27)–C(27′)	1.27(3)
Si(3)–C(8)	1.90(3)	Si(3)–C(9)	1.97(2)				
Cl(1)–Mn(1)–Cl(1′)	103.9(2)	Cl(1)–Mn(1)–O(1)	95.4(3)	C(6)–Si(2)–C(10)	111(1)	C(7)–Si(3)–C(8)	109(1)
Cl(1)–Mn(1)–C(11)	117.7(3)	O(1)–Mn(1)–C(11)	122.4(7)	C(7)–Si(3)–C(9)	103(1)	C(7)–Si(3)–C(10)	111(1)
Cl(1)–Mn(2)–Cl(2)	100.9(2)	Cl(1)–Mn(2)–Cl(3)	100.8(3)	C(8)–Si(3)–C(9)	107(1)	C(8)–Si(3)–C(10)	116(1)
Cl(1)–Mn(2)–C(10)	110.8(4)	Cl(2)–Mn(2)–Cl(3)	88.5(1)	C(9)–Si(3)–C(10)	110(1)	C(11)–Si(4)–C(12)	107(1)
Cl(2)–Mn(2)–C(10)	124.3(4)	Cl(3)–Mn(2)–C(10)	126.5(4)	C(11)–Si(4)–C(13)	117(1)	C(11)–Si(4)–C(14)	120(1)
Mn(1)–Cl(1)–Mn(2)	124.2(2)	Mn(2)–Cl(2)–Mn(2′)	89.8(2)	C(12)–Si(4)–C(13)	104(1)	C(12)–Si(4)–C(14)	113(1)
Mn(2)–Cl(3)–Mn(2′)	88.6(2)	Mn(1)–O(1)–C(26)	119(1)	C(13)–Si(4)–C(14)	95(1)	C(11)–Si(5)–C(12′)	111(1)
Mn(2)–C(10)–Si(1)	107.0(7)	Mn(1)–C(11)–Si(4)	108.7(8)	C(11)–Si(5)–C(15)	109(1)	C(11)–Si(5)–C(16)	107(1)
Mn(2)–C(10)–Si(2)	105.6(7)	Mn(1)–C(11)–Si(5)	104.8(9)	C(12′)–Si(5)–C(15)	114(1)	C(12′)–Si(5)–C(16)	115(1)
Mn(2)–C(10)–Si(3)	107.6(7)	Mn(1)–C(11)–Si(6)	102.7(8)	C(15)–Si(5)–C(16)	101(1)	C(11)–Si(6)–C(13′)	119(1)
C(1)–Si(1)–C(2)	110(1)	C(1)–Si(1)–C(10)	110(1)	C(11)–Si(6)–C(14′)	110(1)	C(11)–Si(6)–C(17)	99(1)
C(1)–Si(1)–C(3)	104(1)	C(2)–Si(1)–C(10)	115(1)	C(13′)–Si(6)–C(14′)	109(1)	C(13′)–Si(6)–C(17)	111(1)
C(2)–Si(1)–C(3)	106(1)	C(4)–Si(2)–C(5)	108(1)	C(14′)–Si(6)–C(17)	108(1)	C(26)–C(27)–C(27′)	110(2)
C(3)–Si(1)–C(10)	112(1)	C(4)–Si(2)–C(10)	111(1)	Si(1)–C(10)–Si(2)	108.8(8)	Si(4)–C(11)–Si(5)	117.0(11)
C(4)–Si(2)–C(6)	104(1)	C(5)–Si(2)–C(10)	117(1)	Si(1)–C(10)–Si(3)	113.7(8)	Si(4)–C(11)–Si(6)	115.9(11)
C(5)–Si(2)–C(6)	105(1)			Si(2)–C(10)–Si(3)	113.6(8)	Si(5)–C(11)–Si(6)	106.4(6)

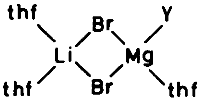
* Primed atoms are related by the symmetry element *x*, $\frac{1}{2} - y$, *z*.

Results and Discussion

The initial products from the reactions between Li{C(SiMe$_3$)$_3$} and the bromides MBr$_2$ (M = Mg or Cd) or chlorides MCl$_2$ (M = Zn,[2] Cd, or Mn) were lithium alkylbromo- or alkylchloro-metalate complexes. The presence of bulky alkyl groups makes these metalate complexes soluble in heptane or toluene. Similar compounds were isolated from the reactions between Li{C(SiMe$_3$)$_3$} and the halides MI (M = Cu or Ag)[15] or MCl$_3$ (M = Ga, In, or Tl).[1] The metalate complexes decompose to lithium-free alkylmetal halides on sublimation or on heating in organic solvents. However, an attempt to form the metalate complex Li(thf)CdCl$_2${C(SiMe$_3$)$_3$} (**6**) by heating CdCl{C(SiMe$_3$)$_3$} (**7**) with LiCl in thf was not successful. This suggests that initial reaction between Li{C(SiMe$_3$)$_3$} and CdCl$_2$ is an addition to give (**6**) rather than a displacement of Cl by C(SiMe$_3$)$_3$ to give (**7**). At low temperatures the kinetically

Table 9. Mean Si–C bond lengths (Å) with estimated standard deviations in parentheses

Compound	(1)	(2)	(3)	(11)
C–SiMe$_3$	1.86(2)	1.87(2)	1.88(1)	1.89(2)
Si–Me	1.90(2)	1.93(3)	1.94(1)	1.96(3)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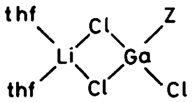
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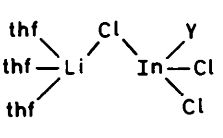
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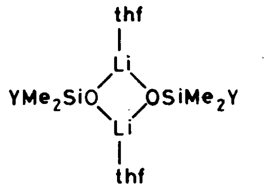
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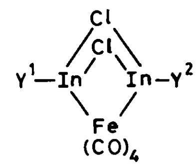
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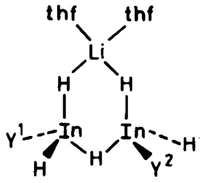
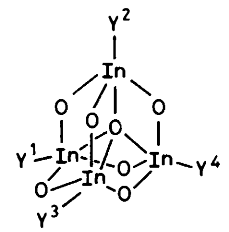

(17)

Y = C(SiMe$_3$)$_3$, Z = C(SiMe$_2$Ph)$_3$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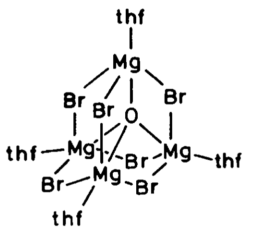
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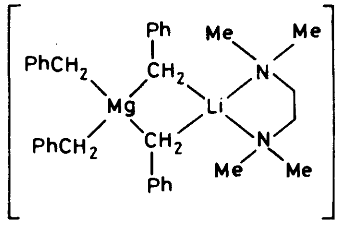
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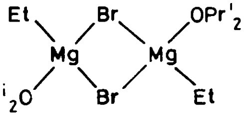
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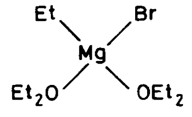
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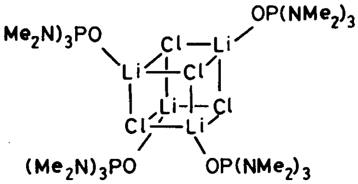
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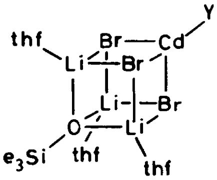
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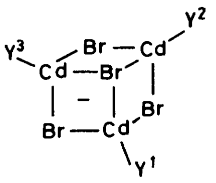
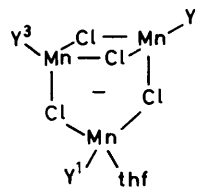

anion of **(2)**


anion of **(11)**

Y = C(SiMe$_3$)$_3$

controlled product (**6**) can be isolated; at higher temperatures this decomposes to the thermodynamically more stable LiCl and (**7**) (Scheme 1).

The metalate complexes may be of two structural types. In type (A), *e.g.* the magnesium compound (**1**) and the Group 13 * compounds (**12**) and (**13**), the lithium is linked to the other metal by bridging halogen atoms and gaps in the co-ordination spheres are filled by thf. The Li(thf)$_n$ cation interacts strongly with only one metalate anion. In type (B), *e.g.* the Cd and Mn derivatives (**2**) and (**11**), cationic and anionic fragments are quite distinct; in the lattice as a whole each ion interacts strongly with several of opposite sign. It is not at present possible to predict which of the two structural types will result from the reaction between Li{C(SiMe$_3$)$_3$} and any particular halide, since there is probably only a small energy difference between the structures with paired and those with distinct ions.

The Solid-state Structures.—(*a*) *The* C(SiMe$_3$)$_3$ *group.* The molecular parameters of the C(SiMe$_3$)$_3$ group have been discussed elsewhere.[15,16] The bond lengths and angles have large uncertainties because in (**1**), (**2**), and (**11**) the silicon atoms are disordered over two sites and the corresponding carbon and hydrogen positions are nearly (but not quite) coincidental. In compound (**3**) the asymmetric unit is very large, so that there are many independent atom positions to be refined.

Nevertheless, the C–SiMe$_3$ bonds are consistently shorter than the Si–Me bonds (Table 9). This pattern of bond lengths is found in the metalate complexes $[M\{C(SiMe_3)_3\}_2]^-$ (M = Li, Cu, or Ag)[5,15] but not in EC(SiMe$_3$)$_3$ (E = B,[17] Si or Sn[16]) derivatives, in which C–SiMe$_3$ bonds are usually longer than Si–Me bonds. It seems that the compounds (**1**), (**2**), (**3**), and (**11**) have C(SiMe$_3$)$_3$ configurations which are intermediate between those in the B, Si, or Sn compounds and those in the strongly

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* Refers to the 18-group format of the Periodic Table.

carbanionic metalate complexes. However, the uncertainties in the structural parameters make it impossible to discern a clear trend in Si–C bond lengths as the metal is changed from the more electropositive Mg or Mn to the less electropositive Cd. As in other $C(SiMe_3)_3$ compounds, the Si–C–Si angles are significantly larger and the Me–Si–Me angles significantly smaller than the tetrahedral value.

Steric interactions in compounds $M\{C(SiMe_3)_3\}$ are partly relieved by twisting of $SiMe_3$ groups, as shown by the deviation of the M–C–Si–C torsion angles (Table 10) from those for staggered positions (60, 180, and −60°).[*] Within a particular $C(SiMe_3)_3$ group the twists are all in the same direction,[17] so that the $SiMe_3$ groups interlock, and the $C(SiMe_3)_3$ group as a whole becomes chiral. The chirality has also been detected in low-temperature n.m.r. studies of $C(SiMe_3)_3$ compounds.[18] In some cases, *e.g.* in (**3**), in Y^1 [$Y = C(SiMe_3)_3$] of (**11**) (Figure 5), or in $[\{Li(thf)[OSiMe_2C(SiMe_3)_3]\}_2]$ (**14**), right- and left-handed $C(SiMe_3)_3$ groups are arranged randomly so that the groups appear in an *X*-ray structural determination to have mirror symmetry: in (**3**) and (**11**) this is indicated by the space group but in (**14**) it is not. In other cases, *e.g.* (**13**), $BPh_2C(SiMe_3)_3$ (**15**), or Y^1 of (**16**), right- and left-handed $C(SiMe_3)_3$ groups are arranged alternately, in an ordered way: chiralities are balanced over two equivalent positions in the space group rather than disordered at one. Partial segregation of $C(SiMe_3)_3$ chiralities is found in (**1**), in Y^2 and Y^3 of (**11**), Y^2 of (**16**), or (**17**).[19]

The data in Table 10 suggest that there is no simple relationship between the extent of disorder and the asymmetry of the bonds at the atom to which the $C(SiMe_3)_3$ group is attached: whether the molecules in a particular crystalline compound pack best with random or alternate chiralities probably depends on the conformation, within the crystal, of the molecule as a whole. This is not easy to predict.

Where there is only one $C(SiMe_3)_3$ group per molecule, the signs of the torsion angles in Table 10 are without significance. Where there are several $C(SiMe_3)_3$ groups the signs show their relative chiralities. In the anion of (**2**) all the $C(SiMe_3)_3$ groups have the same 'hand' and the compound crystallises as a racemate. The introduction of a fourth $C(SiMe_3)_3$ group as in $[\{In[C(SiMe_3)_3]\}_4O(OH)_6]$ (**18**),[2] leads to disorder in *one* $C(SiMe_3)_3$ group (Y^2) and to two left- and one right-handed configurations in the other three (Table 10).

It is not easy to understand this result. The Cd ··· Cd distance in the anion of (**2**) is 3.95 Å, and between $C(SiMe_3)_3$ groups there are three C ··· C contacts of <4.5 Å (at 3.9, 4.3, and 4.3 Å). The In ··· In distance in (**18**) is 3.5 Å, and between $C(SiMe_3)_3$ groups there are several C ··· C contacts in the range 3.6—4.5 Å [*cf.* C ··· C distances in (**18**): within an $SiMe_3$ group, 3.0—3.1 Å; between $SiMe_3$ groups in a particular $C(SiMe_3)_3$ group, 3.4—3.7 Å]. Between Y^4 and Y^1 or Y^3 in (**18**), *i.e.* between $C(SiMe_3)_3$ groups of opposite hands (Table 10), there are two C ··· C contacts <4.0 Å; between Y^1 and Y^3, which have the same hand, there is only one contact <4.0 Å. It seems therefore that steric interactions between $C(SiMe_3)_3$ groups of the same hand are only slightly smaller than those between $C(SiMe_3)_3$ groups of opposite hands; the chirality arises internally from the positions of the Si atoms while the positions of the peripheral C atoms in D and L forms are essentially identical. A random distribution of left- and right-handed $C(SiMe_3)_3$ groups would give combinations LLLL, LLLD, LLDD, LDDD, and DDDD in the ratio 1:4:6:4:1. If the molecules are arranged in two separate disordered combinations (LLLD, LLDD) and (LLDD, LDDD) a racemate is produced in which the asymmetric unit appears to have disorder (57:43) in only one $C(SiMe_3)_3$ group. This is close to what is found in (**18**). Although the percentage occupancies were refined, the standard deviations were such that there was no significant difference between 57:43 and the 50:50 assumed, and the data were insufficient to exclude the possibility that small amounts of the combinations LLLL and DDDD also cocrystallised. If, however, the energy differences between non-bonding D,D and D,L interactions are small, the pattern adopted in a particular crystal may again be determined by molecular packing. This is a point that may be further clarified as more structures are solved and site occupancies more accurately refined.

The Magnesate (**1**).—As far as we are aware, this is the first alkylhalogenomagnesate to be characterised by *X*-ray diffraction, though related structures with alkyl instead of halogen bridges have been postulated for alkali magnesates $MMgR_3$ (M = Li or Na, R = Bu^s or Bu^t) in hydrocarbon solution,[20] and the structure of the ion (**19**) has been established.[21] The mean Mg–Br distance [2.533(6) Å] in (**1**) is a little shorter than that in $[\{MgEtBr(OPr^i_2)\}_2]$ (**20**) [2.579(3) Å][22] or $[\{Mg(thf)\}_4OBr_6]$ (**21**) [2.602(8) Å],[23] and longer than that [2.48(1) Å] in $MgEtBr(OEt_2)_2$ (**22**), which is monomeric.[24] The Mg–O and Mg–C distances in (**1**) [2.06(1) and 2.19(2) Å, respectively] are also unremarkable [*cf.* 2.019(6) and 2.094(11) Å in (**20**),[22] and 2.04(2) and 2.15(2) Å in (**22**)];[24] the Mg–O (thf) distance in (**21**) is 2.11(2) Å. The Li–Br distance in (**1**) is close to the sum of the covalent radii (2.48 Å).[25] Other Li–Br distances are given in Table 11. The four-membered $LiBr_2Mg$ ring has smaller angles at Br (80°) and larger angles at the metal atoms (98° at Mg and 101° at Li), as is common for compounds with halogen bridges between positive atoms.[26]

The Cage Anions in (**2**) *and* (**11**), *and the Neutral Molecule* (**3**).—There are few values of Cd–C bond distances in the literature.[16] Those in (**2**) [2.23(2) Å] and (**3**) [2.20(1) Å] are similar to that in $Cd\{C(SiMe_3)_2(SiMe_2CH{=}CH_2)\}_2$ [2.172(3) Å].[16] Table 12 shows some Cd–Br bond lengths. The Cd_3Br_4 core of (**2**) is almost identical with a fragment of the rhombohedral structure of $CdBr_2$, but, as expected, bonds to two-co-ordinate Br are shorter than those to three-co-ordinate Br. In the anion of (**11**) the Mn–Cl(1) bonds are shorter than the Mn–Cl(2) or Mn–Cl(3) bonds (Table 8); all are longer than the Mn–Cl bond in $[Mn(CO)_5Cl]$[27] and are slightly shorter than those in α- or β-$RbMnCl_3$, which contain μ-Cl and (μ-Cl)$_2$ bridges, respectively.[28] The mean Mn–C distance [2.17(2) Å] corresponds to a covalent radius for Mn of 1.40 Å, which is close to the values (1.39, 1.38 Å) given in refs. 25 and 27. The distance is, however, longer than that in $Mn\{C(SiMe_3)_3\}_2$ [2.102(4) Å],[8] $Mn(CH_2CMe_3)_2$ [2.104(6) Å],[29] $Mn(C_6H_2Me_3\text{-}2,4,6)_3$ [2.11(1) Å],[30] and many carbonyl compounds.[27] Comparison of (**1**) and (**11**) provides further evidence for the suggestion that Mg^{II} and high-spin Mn^{II} are similar in size.[29]

The cations in (**2**) and (**11**) are similar to those in many other compounds[31] and require no comment.

The cages in (**2**), (**3**), and (**11**) are related to a large class of cages based on cubane frameworks $(AB)_4$.[32] Most of those so far characterised have been tetramers such as (**23**),[33] alkoxides {*e.g.* $[\{Li(thf)(OR)\}_4]$ [R = cyclopropyl or $C(Bu^t){=}CH_2$][34] or $[\{MR(OR)\}_4]$ (M = Mg, Zn, Cd, or Hg)[32]}, or imido compounds {*e.g.* $[\{AlR(NR)\}_4]$[32] or $[\{Li(py)(N{=}CPh_2)\}_4]$ (py = pyridine).[33] The formation of compounds (**3**) and $\{Li(OEt_2)\}_4(cyclo\text{-}C_3H_5)_2Br_2$[35] suggests that it should be possible to obtain more species with the frameworks $(AB)_3(A'B')$ or $(AB)_2(A'B')_2$. At present, these compounds are

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[*] Similar twisting of $SiMe_3$ groups has been observed in an electron diffraction study of $PH_2C(SiMe_3)_3$ (A. H. Cowley, J. E. Kilduff, E. A. V. Ebsworth, D. W. H. Rankin, H. E. Robertson, and R. Seip, *J. Chem. Soc., Dalton Trans.*, 1984, 689).

Table 10. Mean M–C–Si–C(Me) torsion angles (°) in $C(SiMe_3)_3$ groups (Y)

Compound	M	Group	Angles[a]	Occupancy (%)	Ref.
(1)	Mg		42, −78, 160	85:15	*b*
(2)	Cd	Y^1	−41, 77, −164	100	*b*
(3)	Cd		±(−43, 80, −153)	50:50	*b*
(11)	Mn	Y^1	±(−39, 82, −155)	50:50	*b*
		Y^2	(−43, 78, −159	7:33	
(13)	In		−39, 78, −160	100	1
(14)	Si		−40, 78, −160	50:50	11
(15)	B		42, −79, 162	100	17
(16)	In	Y^1	41, −78, 162	100	1
		Y^2	40, −81, 159	65:35	
(17)	In	Y^1	−38, 81, −162	70:30	19
		Y^2	42, −75, 156	70:30	
(18)	In	Y^1	37, −80, 161	100	2
		Y^2	−45, 79, −155	50:50	
		Y^3	40, −80, 161	100	
		Y^4	−39, 80, −161	100	

[a] ± Indicates equal occupancy shown by crystallographic mirror plane. [b] This work.

Table 11. Lithium–bromine bond lengths

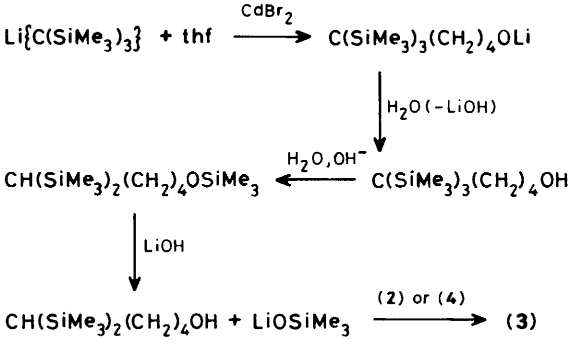
Compound	C.n.(Br)[a]	C.n.(Li)[a]	Li–Br (Å)	Ref.
LiBr (s)	6	6	2.751	*b*
(3)	3	4	2.594(15)	*c*
$\{Li(OEt_2)\}_4(C_3H_5)_2Br_2$	3	4	2.58(2)	35
$(PhLiOEt_2)_3LiBr$	3	4	2.538(5)	*d*
(1)	2	4	2.47(4)	*c*
LiBr (g)	1	1	2.170 4(1)	*e*

[a] C.n. = Co-ordination number. [b] A.S.T.M. Powder Diffraction File, 1965, no. 6-0319. [c] This work. [d] H. Hope and P. P. Power, *J. Am. Chem. Soc.*, 1983, **105**, 5320. [e] A. Honig, M. Mandel, M. L. Stitch, and C. H. Townes, *Phys. Rev.*, 1954, **96**, 629.

Table 12. Cadmium–bromine bond lengths

Compound	C.n.(Br)[a]	C.n.(Cd)[a]	Cd–Br (Å)	Ref.
$CdBr_2$ (s)	3	6	2.82	*b*
(2)	3	4	2.829(4)	*c*
(2)	2	4	2.688(4)	*c*
(3)	3	4	2.718(2)	*c*
$CdBr_2$ (g)	1	2	2.39(4)	*b*

[a] C.n. = Co-ordination number. [b] B. J. Aylett in J. C. Bailar, H. J. Emeleus, and R. Nyholm (eds.), 'Comprehensive Inorganic Chemistry,' Pergamon, Oxford, 1973, vol. 2. [c] This work.



Scheme 2.

isolated fortuitously (see below), and much more work is required to develop rational and controlled syntheses.

Mass spectrometric measurements suggest that (7) is dimeric in the gas phase. The structure in solution is not established with certainty nor are the structures of alkylcadmium halides with smaller alkyl groups. Ethylzinc chloride and bromide, however, have been shown by cryoscopy to be tetrameric in benzene, and cubane structures $(ZnEtX)_4$ (X = Cl or Br) have been proposed.[36,*] The anion of (2) may be regarded as derived from an analogous cubane, $\{CdBr[C(SiMe_3)_3]\}_4$ by removal of a $[Cd\{C(SiMe_3)_3\}]^+$ fragment. The anion of (11) may similarly be regarded as derived from a hypothetical cubane, $\{MnCl[C(SiMe_3)_3]\}_4$, by removal of $[Mn\{C(SiMe_3)_3\}]^+$ and breaking of one metal–halogen bond by co-ordination of an extra solvent molecule. Likewise, the metal–halogen framework of (12) is related to that of (13) by breaking of one metal–halogen bond and co-ordination of an extra solvent molecule. It seems likely that it will be possible to obtain a series of anionic and perhaps cationic metal–halogen cages structurally related to cubanes $(MRX)_4$ (M = divalent metal, X = halogen) by removal of MR^+ or X^-. At present it is not possible to predict which cage will be formed in a particular reaction, or to assess how the size of M influences the cage structure. For example, the adoption of the structure (11) rather than (2) may be a result of the slightly smaller covalent radius of Mn (1.39 Å) compared with that of Cd (1.42 Å).

The Formation of (3).—The ionic compound (2) and the neutral compound (3) were isolated in low yield from reactions between $Li\{C(SiMe_3)_3\}$ and $CdBr_2$ under apparently identical conditions. It is possible that both were formed in both experiments but that different products were isolated by chance on work-up. No attempt was made to optimise the conditions for obtaining one compound rather than the other, but we think that (3) was formed as a consequence of the accidental admission of traces of moisture in the early stage of the reaction. $Li\{C(SiMe_3)_3\}$ is known to cleave ethylene oxide[37] and, in the presence of boron and aluminium halides, thf;[38,39] in each case an $SiMe_3$ group of the alcohol formed on hydrolysis migrates from carbon to oxygen in the presence of base. If the cleavage of thf is likewise catalysed by cadmium(II) bromide (Scheme 2), the resulting alkoxide could be hydrolysed to the alcohol $C(SiMe_3)_3(CH_2)_4OH$, which can undergo a base-catalysed 1,5-rearrangement to $CH(SiMe_3)_2(CH_2)_4OSiMe_3$.[39] With LiOH this would give $Li(OSiMe_3)$, which could then be incorporated into the cage structure (3). Why some metal halides cause thf cleavage in reactions with $Li\{C(SiMe_3)_3\}$ and others apparently do not is not at present clear, but cleavage has so far only been found with BF_3, $AlCl_3$, and $CdBr_2$.

The Chemistry of $CdX\{C(SiMe_3)_3\}$ *and* $CdX\{C(SiMe_2Ph)_3\}$ *Derivatives.*—Both (2) and (3) are converted on heating at 175 °C into $CdBr\{C(SiMe_3)_3\}$, which can be sublimed on to a cold-finger. $CdBr\{C(SiMe_3)_3\}$ was also formed when (2) or (3) was treated with aqueous thf, but when the thf contained aqueous alkali the product isolated in good yield was $Cd(OH)\{C(SiMe_3)_3\}$. The $Cd–C(SiMe_3)_3$ bond is evidently resistant to attack under these conditions. The structure of (6) is unknown.

Both electron impact and chemical ionisation (c.i.) mass spectrometry of the bromide and hydroxide showed only monomeric species. The strongest peaks apparently resulted from disila-allyl ions; for example, the peak at *m/z* 201 [218 in

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[*] *Note added in proof*: compound (7) has a tetrameric cubane structure in the solid state.

c.i. (NH_3) spectra], from $[Me_2Si{=}C(SiMe_3)SiMe_2]^+$, was more intense than that at *m/z* 73 from $[SiMe_3]^+$. Molecular complexities in solution have not been established. As the chloride $CdCl\{C(SiMe_3)_3\}$ has been shown to be dimeric in the vapour it is possible that the bromide and hydroxide are also.

Similar reactions between cadmium(II) bromide and $Li\{C(SiMe_2Ph)_3\}$, which is known to be less reactive than $Li\{C(SiMe_3)_3\}$,[40] are shown in Scheme 1. The structure of compound (**8**) has not been verified by *X*-ray diffraction, but it is probably the same as that of (**1**) without the co-ordinated thf on cadmium. The breakdown on heating to $CdBr\{C(SiMe_2Ph)_3\}$ and the subsequent hydrolysis and methanolysis are similar to the reactions of the $C(SiMe_3)_3$ derivatives. Only monomers were detected in mass spectra, in which especially strong peaks were given (presumably) by disila-allyl cations, *e.g.* at *m/z* 325 $\{[Me_2Si{=}C(SiMe_2Ph)SiMePh]^+$ or an isomer$\}$ and at 309 (derived from the peak at *m/z* 325 by elimination of methane). Peaks at *m/z* 387 $\{[PhMeSi{=}C(SiMe_2Ph)SiMePh]^+\}$ and 263 $\{[Me_2Si{=}C(SiMe_2Ph)SiMe_2]^+\}$ were also prominent, but smaller than that at *m/z* 135 ($[SiMe_2Ph]^+$). Molecular complexities in solution remain uncertain. The zinc compound $Zn(OH)\{C(SiMe_2Ph)_3\}$ is, however, known to be dimeric in the solid.[2]

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