The Chemistry of Trichloro[tris(trimethylsilyl)methyl] and Trichloro[tris(dimethylphenylsilyl)methyl] Complexes of Gallium, Indium, and Thallium. Crystal and Molecular Structures of [Li(thf)$_2$(μ-Cl)$_2$GaCl{C(SiMe$_2$Ph)$_3$}]·thf, [Li(thf)$_3$(μ-Cl)InCl$_2${C(SiMe$_3$)$_3$}], and [{(Me$_3$Si)$_3$C}In(μ-Cl)$_2${μ-Fe(CO)$_4$}In{C(SiMe$_3$)$_3$}] (thf = tetrahydrofuran)†

Jerry L. Atwood* and Simon G. Bott
Department of Chemistry, University of Alabama, Alabama 35486, U.S.A.
Peter B. Hitchcock, Colin Eaborn,* Rio S. Shariffudin, J. David Smith,* and Alice C. Sullivan
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Tris(trimethylsilyl)methyl-lithium and tris(dimethylphenylsilyl)methyl-lithium react with gallium(III), indium(III), or thallium(III) chlorides to give alkylmetalates Li(thf)$_n$MCl$_3$R [M = Ga, R = C(SiMe$_3$)$_3$ (**1**) or C(SiMe$_2$Ph)$_3$ (**2**), n = 2; M = In, R = C(SiMe$_3$)$_3$ (**4**) or C(SiMe$_2$Ph)$_3$, (**5**), n = 3; M = Tl, R = C(SiMe$_3$)$_3$ (**11**), n = 1]. *X*-Ray studies show that the gallium compound (**2**) has the structure [Li(thf)$_2$(μ-Cl)$_2$GaCl{C(SiMe$_2$Ph)$_3$}]·thf with two bridging chlorides between Ga and Li but that there is only one bridging chloride in the indium compound [Li(thf)$_3$(μ-Cl)InCl$_2${C(SiMe$_3$)$_3$}] (**4**). The 'alkyltrichlorometalates' are reduced by lithium aluminium hydride to 'alkyltrihydridometalates.' The indium compound can be converted into the chloride hydroxide InCl{C(SiMe$_3$)$_3$}(OH) and the oxide hydroxide [{In[C(SiMe$_3$)$_3$]}$_4$(μ_4-O)(μ-OH)$_6$]. The trichloroindate (**4**) reacts with Na$_2$[Fe(CO)$_4$] to give the yellow complex [{(Me$_3$Si)$_3$C}In(μ-Cl)$_2${μ-Fe(CO)$_4$}In{C(SiMe$_3$)$_3$}], in which the In $\cdots$ In distance is 304.8(1) pm. The trichlorothallate (**11**) decomposes on heating to give first TlCl$_2${C(SiMe$_3$)$_3$} and then {C(SiMe$_3$)$_3$}Cl; it reacts with lithium aluminium hydride to give a trihydrido[tris(trimethylsilyl)methyl]aluminate.

Tris(trimethylsilyl)methyl and tris(dimethylphenylsilyl)methyl derivatives of a range of main-group and transition metals have been described.[1,2] In many cases the bulky silicon-substituted methyl group inhibits nucleophilic attack at the adjacent metal centre and makes possible the isolation of a series of unusual organometallic compounds for which unsubstituted methyl analogues cannot be obtained. This paper describes some of the chemistry of derivatives of gallium, indium, and thallium containing the bulky C(SiMe$_3$)$_3$ or C(SiMe$_2$Ph)$_3$ groups as ligands, the structures of some chloride-bridged species, and the isolation of the first alkylindium hydroxide and the first alkylindium hydride.

Experimental

Air and moisture were excluded from all reactions by the use of Schlenk-tube techniques. Solvents were dried by standard procedures and distilled immediately before use.

N.m.r. spectra were recorded at 360 or 90 MHz. Chemical shifts for ^{1}H spectra are relative to internal SiMe$_4$, for ^{7}Li spectra relative to external LiNO$_3$–C$_6$D$_6$, and for ^{27}Al spectra relative to external aqueous aluminium(III) chloride. The ^{6}Li-{^{1}H} nuclear Overhauser effect (n.O.e.) was examined in gated decoupling experiments with selective radiation centred at intervals of 180 Hz.[3] Unless otherwise stated, mass spectral data were obtained by electron impact at 70 eV ($\approx 1.1 \times 10^{-17}$ J); where relevant the *m*/*z* values refer to ions containing ^{7}Li, ^{35}Cl, ^{69}Ga, ^{115}In, or ^{205}Tl.

Microanalysis for C and H was carried out where possible but was sometimes prevented by the air-sensitivity of the sample. For lithium analysis a sample was hydrolysed with 2 mol dm^{-3} HCl and the solution examined by atomic emission spectroscopy.

Li(thf)$_3$GaCl$_3${C(SiMe$_3$)$_3$} (**1**).—A solution of gallium(III) chloride (0.89 g, 5.05 mmol) in thf (25 cm^3) was treated with Li{C(SiMe$_3$)$_3$}[4] (5.05 mmol) in thf (10 cm^3) at 0 °C. The pale yellow solution was stirred for 12 h at 20 °C and the solvent then removed under vacuum. The solid residue was washed with pentane, then extracted into toluene (50 cm^3). The filtered toluene solution was concentrated and kept at -10 °C for several days to give colourless *crystals* of (**1**) (1.72 g, 54%), m.p. 101 °C; δ_H(C$_6$D$_6$) 0.66 (27 H, s, SiMe$_3$), 1.29 (12 H, m, thf), and 3.5 (12 H, m, thf); δ_{Li} (C$_6$D$_6$) -1.09 p.p.m. (s). The mass spectrum (sample at 30 °C) showed peaks corresponding to GaCl$_2${C(SiMe$_3$)$_3$} (*M*): *m*/*z* 355 (40%, [*M* − Me]$^+$), 335 (45, [*M* − Cl]$^+$), 73 (100, [SiMe$_3$]$^+$). The compound was too air-sensitive for satisfactory C and H analysis.

*Di-μ-chloro-*1*-chloro-*2,2*-bis*(*tetrahydrofuran*)*-*1*-*[*tris*(*dimethylphenylsilyl*)*methyl*]*galliumlithium–Tetrahydrofuran* (1/1), [Li(thf)$_2$(μ-Cl)$_2$GaCl{C(SiMe$_2$Ph)$_3$}]·thf (**2**).—This was made similarly from GaCl$_3$ and Li{C(SiMe$_2$Ph)$_3$}.[5] The sticky yellow residue obtained by removal of solvent from the reaction mixture was washed with pentane, and the resulting powder was dissolved in toluene. After filtration, the toluene solution was concentrated to 50 cm^3, thf (10 cm^3) was added, and the mixture was kept at -30 °C to yield crystals, which were washed with pentane. Yield 92%, m.p. 72—87 °C (see Discussion section); δ_H (C$_6$D$_6$) 1.1 (18 H, s, SiMe$_2$), 1.35 (8

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† Di-μ-chloro-1-chloro-2,2-bis(tetrahydrofuran)-1-[tris(dimethylphenylsilyl)methyl]galliumlithium–tetrahydrofuran (1/1), μ-chloro-1,1-dichloro-2,2,2-tris(tetrahydrofuran)-1-[tris(trimethylsilyl)methyl]indiumlithium, and di-μ-chloro-μ-tetracarbonylferrio-bis{[tris(trimethylsilyl)methyl]indium} respectively.

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H, m, thf), 3.5 (8 H, m, thf), 6.75—7.3 (15 H, m, Ph); δ_{Li} ($C_6D_5CD_3$) −0.58 p.p.m. (s). A crystal suitable for *X*-ray study was obtained by crystallisation from toluene.

Reduction of (**1**) *with* $LiAlH_4$.—An excess of $LiAlH_4$ (0.20 g, 5.0 mmol) was added to (**1**) (0.60 g, 1.0 mmol) in thf (20 cm^3) at −40 °C. The mixture was stirred for several hours and then warmed to 20 °C. The thf was pumped away and the grey residue extracted several times with heptane. The concentrated heptane solution yielded white *crystals* of (**3**) on cooling; m.p. 165—170 °C (decomp.); δ_H($C_6D_5CD_3$) 0.38 (27 H, s, $SiMe_3$), 1.42 (8 H, m, thf), 3.62 (8 H, m, thf), and 3.25 (br, GaHLi, width at half-height $w_{\frac{1}{2}}$ = 2 340 Hz, confirmed by ^6Li-{^1H} n.O.e.[3]); δ_{Li} −0.67 p.p.m. The i.r. spectrum (Nujol) showed broad poorly resolved bands at 1 620—1 690 cm^{-1} [ν(GaH)]. The compound was too reactive towards air and moisture to give satisfactory C and H analyses, but the Li content was found to be 0.8%. $Li(thf)_3GaH_3\{C(SiMe_3)_3\}$ requires Li, 1.33%: $Li(thf)_2Ga_2H_5\{C(SiMe_3)_3\}_2$ requires Li, 0.9%.

μ-*Chloro*-1,1-*dichloro*-2,2,2-*tris*(*tetrahydrofuran*)-1-[*tris*(*trimethylsilyl*)*methyl*]*indiumlithium*, $[Li(thf)_3(\mu\text{-}Cl)InCl_2\{C(SiMe_3)_3\}]$ (**4**).—This was made from $InCl_3$ and $Li\{C(SiMe_3)_3\}$ by the procedure described for (**1**). White crystals suitable for *X*-ray determination were obtained from toluene–thf (6:1). Yield 87%, m.p. 152—155 °C (Found: C, 38.6; H, 7.6. $C_{22}H_{51}Cl_3InLiO_3Si_3$ requires C, 39.1; H, 7.6%); δ_H(C_6D_6) 0.54 (27 H, s, $SiMe_3$), 1.39 (12 H, m, thf), and 3.54 (12 H, m, thf); δ_{Li}(C_6D_6) −0.94 p.p.m.(s). Peaks at *m*/*z* 401 ($[InCl_2\{C(SiMe_3)_3\} - Me]^+$) and 387 ($[InCl_2\{C(SiMe_3)_3\} - Cl]^+$) were observed in the mass spectrum (sample at 100 °C): there was no peak indicating formation of $\{C(SiMe_3)_3\}Cl$ by reductive elimination, as observed for the thallium analogue (**11**) (see below).

$Li(thf)_3InCl_3\{C(SiMe_2Ph)_3\}$ (**5**).—A solution of $Li\{C(SiMe_2Ph)_3\}$ (7.0 mmol) in thf (10 cm^3) was added dropwise to a suspension of $InCl_3$ (1.55 g, 7.0 mmol) in Et_2O (25 cm^3) at 0 °C. The grey mixture was stirred overnight at 20 °C and the solvent was removed under vacuum. The residue was washed with heptane then extracted with toluene, and after filtration the yellow extract was concentrated to 50 cm^3 and diluted with thf (10 cm^3). Long colourless *needles* (5 g, 83%), m.p. 143 °C, formed on cooling (Found: C, 50.9; H, 6.7. $C_{37}H_{57}Cl_3InLiO_3Si_3$ requires C, 51.5; H, 6.7%); δ_H(C_6D_6) 1.03 (18 H, s, $SiMe_2$), 1.4 (12 H, m, thf), and 3.6 (12 H, m, thf); δ_{Li}($C_6D_5CD_3$) −0.78 p.p.m. (s). Mass spectrum (sample at 150 °C) (+ve NH_3 chemical ionisation): *m*/*z* 609 (40%, $[LiInCl_2\{C(SiMe_2Ph)_3\}]^+$) and 567 (100, $[InCl\{C(SiMe_2Ph)_3\}]^+$).

Di-μ-*chloro*-μ-*tetracarbonylferrio*-*bis*{[*tris*(*trimethylsilyl*)-*methyl*]*indium*}, $[\{(Me_3Si)_3C\}In(\mu\text{-}Cl)_2\{\mu\text{-}Fe(CO)_4\}In\{C(SiMe_3)_3\}]$ (**6**).—A suspension of $Na_2[Fe(CO)_4]\cdot1.5(diox)$ (1.17 g, 3.4 mmol) (diox = dioxane) in thf (25 cm^3) was added to a solution of $[Li(thf)_3(\mu\text{-}Cl)InCl_2\{C(SiMe_3)_3\}]$ (4.56 g, 6.86 mmol) in thf (25 cm^3) at −78 °C. As the solution was allowed to warm up it became orange. After removal of thf the residue was extracted with toluene and the filtered toluene solution was kept at −20 °C, to give yellow *crystals* (3.39 g, 96%), m.p. 235 °C; δ_H 0.32 (s, $SiMe_3$); ν(CO) at 2 030, 2 000, 1 990, and 1 980 cm^{-1}.

$[Li(thf)_2(\mu\text{-}H)_2\{InH[C(SiMe_3)_3]\}_2(\mu\text{-}H)]$ (**7**).—A suspension of $LiAlH_4$ (0.91 g, 24 mmol) in thf (30 cm^3) was added to a solution of (**4**) (3.25 g, 4.8 mmol) in thf (40 cm^3) at −40 °C. After 1 h the mixture was allowed to warm to 20 °C; it was then stirred overnight, and the solvent was removed. The grey residue was extracted with toluene and the concentrated extract yielded a white gum which after washing with pentane became a powder. This was recrystallised from the minimum volume of toluene at −20 °C, to give the *product*, (**7**) (4.8 g, 85%), m.p. 115 °C (decomp.) (Found: Li, 0.83. $C_{28}H_{75}In_2LiO_2Si_6$ requires Li, 0.82%). The compound was too reactive towards air and moisture to give satisfactory C and H analyses but its identity has been confirmed by an *X*-ray structural determination[6]); δ_H 0.55 (27 H, s, $SiMe_3$); 1.38 (4 H, m, thf), 3.55 (4 H, m, thf), 4.7 [vbr, $w_{\frac{1}{2}}$ = 900 Hz from n.O.e. (InHLi)]; δ_{Li} −0.8 p.p.m.; ν(InH) at 1 635, 1 660, 1 695, and 1 725 cm^{-1}.

Reactions of (**7**).—(*a*) *With* (**4**). A suspension of (**7**) (0.56 g, 0.66 mmol) in thf (40 cm^3) was added dropwise to a solution of (**4**) (0.44 g, 0.64 mmol) in thf (20 cm^3) at −70 °C. After several hours at −70 °C a grey solid separated as the mixture warmed to 20 °C. The thf was pumped away and the grey residue extracted with heptane. The solvent was removed from the filtered extract to leave a yellow-brown solid, which gave yellow, extremely air-sensitive crystals from pentane or toluene. These proved to be difficult to handle; on exposure to air they gave a white solid, which appeared to be *chloro*(*hydroxo*)[*tris*(*trimethylsilyl*)*methyl*]*indium*, $InCl\{C(SiMe_3)_3\}(OH)$, (**8**), m.p. 250 °C (decomp.) (Found: C, 30.5; H, 6.7. $C_{10}H_{28}ClInOSi_3$ requires C, 30.1; H, 7.0%); δ_H 0.32 (s, $SiMe_3$); ν(OH) at 3 610 cm^{-1}.

(*b*) *With methanol*. When MeOH (0.139 g, 4.3 mmol) was added to a solution of (**7**) (0.62 g, 0.73 mmol) in thf at 0 °C, gas (presumably H_2) was immediately evolved. After several hours the solvent was removed under vacuum, the residue was extracted with pentane, and the solvent evaporated from the filtered extract to leave a pale yellow solid. A sample in a sealed n.m.r. tube gave δ_H($C_6D_5CD_3$) 0.28 p.p.m., but, surprisingly, the solution appeared to be unstable since a black solid slowly separated. The yellow solid was therefore treated with wet toluene. The slight precipitate was filtered off and white crystals of *hexa*-μ-*hydroxo*-μ_4-*oxo*-*tetrakis*{(*tris*(*trimethylsilyl*)*methyl*]-*indium*}, (**9**), m.p. 257 °C, were obtained from the concentrated solution (Found: C, 32.0; H, 7.5. $C_{40}H_{114}In_4O_7Si_{12}$ requires C, 32.0; H, 7.2%); δ_H (90 MHz, $C_6D_5CD_3$) 0.32 p.p.m. (s, $SiMe_3$); ν(OH) at 3 650 (sharp) and 3 410br cm^{-1}. The structure of (**9**) has been confirmed by an *X*-ray study.[7]

No signals from hydroxide protons were found in the 90-MHz n.m.r. spectra of (**8**) or (**9**): more work is required on this point.

(*c*) *With* 1-*phenylpropan*-2-*one*. Hydrogen was evolved when a solution of (**7**) (2.2 g, 2.6 mmol) in thf (25 cm^3) was treated with one of 1-phenylethylamine (0.63 g, 5.2 mmol) in thf (10 cm^3) at −60 °C. The thf was pumped away and the residue extracted with toluene to give a white solid, which was washed with pentane and identified as (**10**); δ_H (90 MHz, $C_6D_5CD_3$) 0.43 (54 H, s, $SiMe_3$), 1.45 (16 H, m, thf), 3.76 (16 H, m, thf), 1.69 (3 H, d, *J* = 6 Hz, Me), and 4.58 (1 H, q, CH); δ_{Li} −0.47 p.p.m. A solution of $PhCH_2COMe$ (0.148 g, 1.1 mmol) in thf (10 cm^3) was added to a suspension of (**10**) (1.22 g) in thf (20 cm^3) at −78 °C, and after 1 h the solvent was pumped away. The residue was treated with aqueous thf until effervescence ceased, then with 2 mol dm^{-3} HCl, and the products were extracted into ethyl acetate and chromatographed on silica [Merck Kieselgel 60 Art 9395 with ethyl acetate–light petroleum (b.p. 60—80 °C) (1 : 4) as eluant] to give 1-phenylpropan-2-ol (0.142 g, 95%); δ_H (60 MHz) 1.23 (3 H, d, *J* = 7), 1.72 (1 H, s, OH), 2.71 (2 H, d, *J* = 7), 3.99 (1 H, tq, *J* = 7 Hz), and 7.2 (5 H, m); α(293.15 K, 589.3 nm, 2.8 g per 100 g of solution, Et_2O) = +0.4°, corresponding to 2% more *S* than *R* isomer.[8] The cage compound (**9**) (identified from its ^1H n.m.r. and i.r. spectra and m.p.) was eluted from the column with methanol.

$Li(thf)TlCl_3\{C(SiMe_3)_3\}$ (**11**).—Thallium(III) chloride was dehydrated with thionyl chloride. A solution of $Li\{C(SiMe_3)_3\}$ (17.2 mmol) in thf (30 cm^3) was added slowly with stirring to a solution of $TlCl_3$ (5.36 g, 21.5 mmol) in thf (20 cm^3) at −78 °C.

Table 1. Fractional atomic co-ordinates with estimated standard deviations in parentheses for $[Li(thf)_2(\mu\text{-}Cl)_2GaCl\{C(SiMe_2Ph)_3\}]\cdot thf$ (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ga	0.283 3(1)	0.105 4(1)	0.262 49(8)
Si(1)	0.462 0(3)	0.209 7(3)	0.326 4(2)
Si(2)	0.537 0(3)	0.022 2(3)	0.229 6(2)
Si(3)	0.432 3(3)	0.236 7(3)	0.130 1(2)
Cl(1)	0.199 1(3)	0.056 6(3)	0.158 0(2)
Cl(2)	0.271 6(3)	−0.044 5(3)	0.352 7(2)
Cl(3)	0.151 7(4)	0.205 2(4)	0.309 9(3)
C(1)	0.438 2(9)	0.144 9(8)	0.234 0(7)
C(2)	0.394(1)	0.344(1)	0.314 3(8)
C(3)	0.401(1)	0.140(1)	0.431 4(6)
C(4)	0.612(1)	0.220(1)	0.342 4(7)
C(5)	0.673(1)	0.292(1)	0.292 0(7)
C(6)	0.785(1)	0.299(1)	0.304 3(9)
C(7)	0.837(1)	0.238(1)	0.374(1)
C(8)	0.774(1)	0.169(1)	0.426 4(8)
C(9)	0.665(1)	0.159(1)	0.414 9(7)
C(10)	0.570(1)	−0.053(1)	0.336 6(8)
C(11)	0.477(1)	−0.072(1)	0.177 4(8)
C(12)	0.678(1)	0.040 5(9)	0.173 7(7)
C(13)	0.761(1)	0.075(1)	0.210 9(8)
C(14)	0.870(1)	0.086(1)	0.171 7(9)
C(15)	0.894(1)	0.056(1)	0.092(1)
C(16)	0.813(1)	0.025(1)	0.054 1(9)
C(17)	0.705(1)	0.012(1)	0.093 4(8)
C(18)	0.444(1)	0.168(1)	0.039 0(6)
C(19)	0.294(1)	0.322(1)	0.122 0(8)
C(20)	0.541(1)	0.326(1)	0.106 5(6)
C(21)	0.518(1)	0.433(1)	0.109 9(8)
C(22)	0.600(2)	0.498(1)	0.094 9(9)
C(23)	0.711(2)	0.462(2)	0.073 8(9)
C(24)	0.734(1)	0.356(2)	0.067 5(8)
C(25)	0.654(1)	0.292(1)	0.0836(7)
Li	0.151(2)	−0.092(2)	0.259(2)
O(1)	0.016 8(9)	−0.112 4(8)	0.322 6(7)
C(26)	−0.023(2)	−0.054(2)	0.391(1)
C(27)	−0.112(2)	−0.128(2)	0.436(2)
C(28)	−0.118(2)	−0.207(2)	0.395(2)
C(29)	−0.064(2)	−0.182(2)	0.308(2)
O(2)	0.207 1(9)	−0.215 6(8)	0.223 9(7)
C(30)	0.249(2)	−0.304(2)	0.286(1)
C(31)	0.320(2)	−0.373(2)	0.241(2)
C(32)	0.311(2)	−0.333(2)	0.151(2)
C(33)	0.233(2)	−0.235(1)	0.136(1)
O(3)	0.886 7	0.588 6	0.206 7
C(35)	0.989 9	0.529 0	0.164 3
C(36)	0.984 9	0.609 5	0.073 1
C(37)	0.887 4	0.710 7	0.076 2
C(38)	0.812 7	0.690 3	0.169 5

Table 2. Bond lengths (pm) and angles (°) with estimated standard deviations in parentheses for $[Li(thf)_2(\mu\text{-}Cl)_2GaCl\{C(SiMe_2Ph)_3\}]\cdot thf$ (**2**)

Ga–Cl(1)	230.2(4)	Ga–Cl(2)	227.4(4)	Si(2)–C(1)	192(1)	Si(2)–C(10)	190(1)
Ga–Cl(3)	213.9(5)	Ga–C(2)	200(1)	Si(2)–C(11)	189(2)	Si(2)–C(12)	189(1)
Li–Cl(1)	243(3)	Li–Cl(2)	243(3)	Si(3)–C(1)	191(1)	Si(3)–C(18)	188(1)
Li–O(1)	187(3)	Li–O(2)	189(3)	Si(3)–C(19)	191(1)	Si(3)–C(20)	185(2)
Si(1)–C(1)	194(1)	Si(1)–C(2)	187(1)	Mean O–C(thf)	150(2)	Mean C–C(thf)	149(4)
Si(1)–C(3)	193(1)	Si(1)–C(4)	189(1)	Mean C–C(Ph)	141(3)		
Cl(1)–Ga–Cl(2)	95.1(1)	Cl(1)–Ga–Cl(3)	101.3(2)	C(13)–C(12)–C(17)	118(1)	C(12)–C(13)–C(14)	123(1)
Cl(2)–Ga–Cl(3)	103.0(2)	Cl(1)–Ga–C(1)	116.2(3)	C(13)–C(14)–C(15)	117(1)	C(14)–C(15)–C(16)	121(1)
Cl(2)–Ga–C(1)	114.8(3)	Cl(3)–Ga–C(1)	122.2(4)	C(15)–C(16)–C(17)	122(1)	C(12)–C(17)–C(16)	119(1)
Cl(1)–Li–Cl(2)	88(1)	Cl(1)–Li–O(1)	129(1)	Si(3)–C(20)–C(21)	123(1)	Si(3)–C(20)–C(25)	121(1)
Cl(2)–Li–O(1)	105(1)	Cl(1)–Li–O(2)	112(1)	C(21)–C(20)–C(25)	116(1)	C(20)–C(21)–C(22)	122(1)
Cl(2)–Li–O(2)	112(1)	O(1)–Li–O(2)	108(1)	C(21)–C(22)–C(23)	120(2)	C(22)–C(23)–C(24)	117(2)
Ga–Cl(1)–Li	87.2(7)	Ga–Cl(2)–Li	87.9(6)	C(23)–C(24)–C(25)	123(2)	C(20)–C(25)–C(24)	121(1)
C(1)–Si(1)–C(2)	112.1(5)	C(1)–Si(1)–C(3)	112.6(6)	O(1)–C(26)–C(27)	96(2)	C(26)–C(27)–C(28)	113(2)
C(2)–Si(1)–C(3)	106.0(6)	C(1)–Si(1)–C(4)	115.5(5)	C(27)–C(28)–C(29)	108(2)	O(1)–C(29)–C(28)	99(2)
C(2)–Si(1)–C(4)	104.3(6)	C(3)–Si(1)–C(4)	105.5(6)	O(2)–C(30)–C(31)	108(2)	C(30)–C(31)–C(32)	107(2)
C(1)–Si(2)–C(10)	113.3(5)	C(1)–Si(2)–C(11)	113.0(6)	C(31)–C(32)–C(33)	112(2)	O(2)–C(33)–C(32)	101(2)
C(10)–Si(2)–C(11)	104.2(6)	C(1)–Si(2)–C(13)	115.7(5)	C(10)–Si(8)–C(12)	104.2(6)	C(11)–Si(2)–C(12)	105.4(6)
C(10)–Si(2)–C(12)	104.2(6)	C(18)–Si(3)–C(19)	105.2(6)	C(11)–Si(2)–C(12)	105.4(6)	C(1)–Si(3)–C(20)	116.1(5)
C(1)–Si(3)–C(18)	112.3(5)	C(18)–Si(3)–C(20)	105.4(6)	C(1)–Si(3)–C(19)	111.9(5)	C(19)–Si(3)–C(20)	105.0(6)
Si(1)–C(1)–Si(2)	112.7(5)	Ga–C(1)–Si(3)	105.6(5)	C(1)–Si(3)–C(18)	112.3(5)	C(1)–Si(3)–C(19)	111.9(5)
Si(1)–C(1)–Si(3)	113.6(6)	Si(2)–C(1)–Si(3)	113.7(5)	C(18)–Si(3)–C(19)	105.2(6)	C(1)–Si(3)–C(20)	116.1(5)
Si(1)–C(4)–C(5)	122.1(9)	Si(1)–C(4)–C(9)	120.2(9)	C(18)–Si(3)–C(20)	105.4(6)	C(19)–Si(3)–C(20)	105.0(6)
C(5)–C(4)–C(9)	117(1)	C(4)–C(5)–C(6)	122(1)	Li–O(1)–C(26)	122(1)	Li–O(1)–C(29)	124(2)
C(5)–C(6)–C(7)	120(1)	C(6)–C(7)–C(8)	117(1)	C(26)–O(1)–C(29)	114(1)	Li–O(2)–C(30)	120(1)
C(7)–C(8)–C(9)	123(1)	C(4)–C(9)–C(8)	119(1)	Li–O(2)–C(33)	128(1)	C(30)–O(2)–C(33)	112(1)
Si(2)–C(12)–O(13)	121.3(9)	Si(2)–C(12)–C(17)	120(1)	Ga–C(1)–Si(1)	102.3(5)	Ga–C(1)–Si(2)	107.9(5)

After 20 h at 20 °C the solvent was removed and the residue extracted into toluene. On cooling the solution gave pale yellow *crystals* of (**11**) (2.0 g, 45%), m.p. 120 °C (Found: C, 22.6; H, 5.6. $C_{14}H_{35}Cl_3OSi_3Tl$ requires C, 22.2; H, 5.6%); δ_H 0.46 (27 H, s, $SiMe_3$), 1.4 (8 H, m, thf), and 3.6 (8 H, m, thf); $\delta_{Li}(C_6D_6)$ −0.55 p.p.m. The mass spectrum gave peaks corresponding to $TlCl_2\{C(SiMe_3)_3\}$ (*M*) at *m*/*z* 491 ($[M - Me]^+$) and 471 ($[M - Cl]$). When a small sample of (**11**) was heated at *ca.* 120—130 °C under vacuum the white crystalline sublimate was shown to be $\{C(SiMe_3)_3\}Cl$, m.p. 130 °C (lit.,[9] 125—126 °C) (Found: C, 46.0; H, 9.9. Calc. for $C_{10}H_{27}ClSi_3$: C, 45.0; H, 10.1%); *m*/*z* 251 ($[M - Me]^+$).

Reaction of (**11**) *with* $LiAlH_4$.—A suspension of (**11**) (0.5 g, 0.8 mmol) in thf (25 cm^3) was treated with an excess of $LiAlH_4$ (1.22 g, 32 mmol) in thf at −78 °C. The mixture immediately turned black. The solution was allowed to warm to 20 °C, then the solvent was removed and heptane was added to the black residue. After filtration the heptane solution was concentrated to yield crystalline $Li(thf)_3AlH_3\{C(SiMe_3)_3\}$;[10] $\delta_H(C_6D_5CD_3)$ 0.38 (27 H, s, $SiMe_3$), 1.43 (12 H, m, thf), and 3.70 (12 H, m, thf); $\delta_{Al}(C_6D_5CD_3)$ 118.4 p.p.m.

Crystal Structure Determinations.—(*a*) *Crystal data for* $[Li(thf)_2(\mu\text{-}Cl)_2GaCl\{C(SiMe_2Ph)_3\}]\cdot thf$ (**2**). $C_{37}H_{57}Cl_3$-

Table 3. Fractional atomic co-ordinates with estimated standard deviations in parentheses for [Li(thf)$_3$(μ-Cl)InCl$_2${C(SiMe$_3$)$_3$}] (**4**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
In	0.276 8(2)	0.313 4(1)	0.872 56(6)	C(7)	0.227(3)	0.079(2)	0.866(1)
Cl(1)	0.306 0(8)	0.478 1(4)	0.879 0(3)	C(8)	−0.031(3)	0.386(2)	0.934(1)
Cl(2)	0.092 3(9)	0.302 3(7)	0.803 6(3)	C(9)	−0.014(3)	0.243(2)	1.021(1)
Cl(3)	0.492 7(7)	0.272 0(5)	0.832 3(3)	C(10)	−0 089(3)	0.177(2)	0.911(1)
Si(1)	0.356 4(7)	0.303 3(6)	0.997 3(3)	C(11)	0.669(3)	0.646(2)	0.794(1)
Si(2)	0.282 5(7)	0.122 8(4)	0.934 9(3)	C(12)	0.825(5)	0.626(3)	0.803(2)
Si(3)	0.033 5(6)	0.263 3(5)	0.953 5(3)	C(13)	0.841(4)	0.542(3)	0.819(2)
O(1)	0.597(1)	0.573(1)	0.815 4(7)	C(14)	0.699(3)	0.504(2)	0.834(1)
O(2)	0.299(2)	0.679(1)	0.819 3(6)	C(15)	0.236(3)	0.708(2)	0.865 8(9)
O(3)	0.325(2)	0.526(1)	0.742 3(6)	C(16)	0.188(4)	0.805(3)	0.857(1)
Li	0.383(4)	0.562(2)	0.808(1)	C(17)	0.219(4)	0.828(2)	0.803(1)
C(1)	0.236(2)	0.248(1)	0.945 2(7)	C(18)	0.281(4)	0.747(2)	0.783(1)
C(2)	0.283(3)	0.418(2)	1.017(1)	C(19)	0.394(5)	0.476(4)	0.711(2)
C(3)	0.384(3)	0.227(2)	1.058(1)	C(20)	0.320(5)	0.440(4)	0.671(2)
C(4)	0.546(3)	0.333(2)	0.975 0(9)	C(21)	0.193(4)	0.454(3)	0.677(2)
C(5)	0.499(3)	0.102(2)	0.944(1)	C(22)	0.184(4)	0.515(3)	0.716(2)
C(6)	0.190(3)	0.041(2)	0.983(1)				

Table 4. Bond lengths (pm) and angles (°) with estimated standard deviations in parentheses for [Li(thf)$_3$(μ-Cl)InCl$_2${C(SiMe$_3$)$_3$}] (**4**)

In–Cl(1)	243.2(6)	In–Cl(2)	236.7(7)	Si(2)–C(5)	200(3)	Si(3)–C(1)	190(2)
In–Cl(3)	238.9(6)	In–Cl(1)	217(2)	Si(2)–C(7)	192(3)	Si(3)–C(9)	186(3)
Cl(1)–Li	237(3)	Si(1)–C(1)	186(2)	Si(3)–C(8)	195(3)	Si(3)–C(10)	198(3)
Si(1)–C(2)	190(3)	Si(2)–C(1)	191(2)	Mean Li–O	190(4)	Si(1)–C(4)	193(2)
Si(1)–C(3)	193(3)	Si(2)–C(6)	196(3)	Mean O–C(thf)	139(3)	Mean C–C(thf)	139(4)
Cl(1)–In–Cl(2)	108.8(3)	Cl(2)–In–Cl(3)	102.7(3)	C(1)–Si(3)–C(10)	112(1)	C(8)–Si(3)–C(10)	107(1)
Cl(1)–In–Cl(3)	101.0(2)	Cl(2)–In–C(1)	117.5(5)	C(9)–Si(3)–C(10)	105(1)	Cl(1)–Li–O(1)	109(2)
Cl(1)–In–C(1)	113.8(5)	Cl(3)–In–C(1)	118.3(5)	Cl(1)–Li–O(2)	102(1)	O(1)–Li–O(2)	109(2)
In–Cl(1)–Li	120.1(9)	C(1)–Si(1)–C(2)	112(1)	Cl(1)–Li–O(3)	120(2)	O(1)–Li–O(3)	109(2)
C(1)–Si(1)–C(3)	112(1)	C(2)–Si(1)–C(3)	109(1)	O(2)–Li–O(3)	108(7)	In–C(1)–Si(2)	104.3(8)
C(1)–Si(1)–C(4)	112(1)	C(2)–Si(1)–C(4)	103(1)	In–C(1)–Si(1)	107.7(8)	In–C(1)–Si(3)	106.5(8)
C(3)–Si(1)–C(4)	108(1)	C(1)–Si(2)–C(5)	111(1)	Si(1)–C(1)–Si(2)	113(1)	Si(2)–C(1)–Si(3)	111.2(9)
C(1)–Si(2)–C(6)	113(1)	C(5)–Si(2)–C(6)	108(1)	Si(1)–C(1)–Si(3)	113.2(9)	Mean C–C–C	108(3)
C(1)–Si(2)–C(7)	114(1)	C(5)–Si(2)–C(7)	104(1)	Mean Li–O–C	127(2)	Mean C–O–C	105(3)
C(6)–Si(2)–C(7)	106(1)	C(1)–Si(3)–C(8)	111(1)	Mean O–C–C	109(2)		
C(1)–Si(3)–C(9)	113(1)	C(8)–Si(3)–C(9)	107(1)				

GaLiO$_3$Si$_3$, M = 817.2, triclinic, space group $P\bar{1}$, a = 12.104(4), b = 13.409(6), c = 16.396(9) Å, α = 79.26(4), β = 84.75(4), γ = 83.03(3)°, U = 2 588 Å^3, Z = 2, D_c = 1.04 g cm^{-3}, $F(000)$ = 860, monochromated Mo-K_α radiation, λ = 0.710 69 Å, μ = 7.73 cm^{-1}.

A crystal of size 0.3 × 0.5 × 1.2 mm was used and data were measured on an Enraf-Nonius CAD4 diffractometer. Preliminary cell dimensions were found using the SEARCH and INDEX routines and final values were calculated using 24 accurately centred reflections. Intensities for h, $\pm k$, $\pm l$ reflections with $1 < \theta < 20°$ were measured as described previously.[11] Three standard reflections monitored every hour showed no significant variation. Data were corrected for Lorentz and polarisation effects and for absorption; 3 340 reflections with $|F^2| > 2\sigma(F^2)$ were used in the structure refinement.

The position of the gallium was found from a Patterson map, and a subsequent difference map gave the positions of other non-hydrogen atoms. Three regions of unassigned electron density remained: one was refinable as a molecule of thf. Attempts to assign the others as partially weighted molecules of thf were unsuccessful, though calculations[12] showed that there was room for thf in the lattice. With anisotropic thermal parameters for non-hydrogen atoms the refinement converged at $R = (\Sigma||F_o| - |F_c||)/(\Sigma|F_o|) = 0.085$, $R' = \{[\Sigma w(|F_o| - |F_c|)^2]/\Sigma w|F_o|^2\}^{\frac{1}{2}} = 0.092$. Neutral-atom scattering factors were from ref. 13 and the factor for hydrogen from ref. 14. Scattering for heavier elements was corrected for anomalous dispersion[15] and SHELX computer programs[16] were used throughout. Final fractional atomic co-ordinates are given in Table 1 and bond lengths and angles in Table 2.

(*b*) *Crystal data for* [Li(thf)$_3$(μ-Cl)InCl$_2${C(SiMe$_3$)$_3$}] (**4**). C$_{22}$H$_{51}$Cl$_3$InLiO$_3$Si$_3$, M = 676, monoclinic, space group $P2_1/c$, a = 9.191(4), b = 14.682(4), c = 26.051(9) Å, β = 94.52(3)°, U = 3 504 Å^3, Z = 4, D_c = 1.29 g cm^{-3}, $F(000)$ = 1 408, Mo-K_α radiation, λ = 0.710 69 Å, μ = 10.21 cm^{-1}.

The general procedure was as described for (**2**). Data for h, k, $\pm l$ reflections with $1 < \theta < 22°$ were collected from a large crystal of size 1.2 × 0.9 × 4.5 mm and 2 474 reflections with $|F^2| > 2\sigma(F^2)$ were used in the structure determination. The position of the indium was found from a Patterson map and the remaining non-hydrogen atoms from a difference Fourier map. With hydrogen atoms at calculated positions and anisotropic thermal parameters for atoms except carbon and hydrogen, the structure converged at R = 0.085, R' = 0.091. No feature >0.5 e A^{-3} was observed in a final difference map. Fractional atomic co-ordinates and bond lengths and angles are given in Tables 3 and 4, respectively.

(*c*) *Crystal data for* [{(Me$_3$Si)$_3$C}In(μ-Cl)$_2${μ-Fe(CO)$_4$}In{C(SiMe$_3$)$_3$}], (**6**). C$_{24}$H$_{54}$Cl$_2$FeIn$_2$O$_4$Si$_6$, M = 931.7, triclinic,

Table 5. Fractional atomic co-ordinates with estimated standard deviations in parentheses for [{(Me$_3$Si)$_3$C}In(μ-Cl)$_2${μ-Fe(CO)$_4$}In{C(SiMe$_3$)$_3$}] (**6**)*

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
In(1)	0.758 46(7)	0.600 57(5)	0.216 36(4)	C(12)	0.740(1)	0.636 8(9)	−0.026 5(6)
In(2)	0.800 49(7)	0.384 22(4)	0.304 06(4)	C(13)	0.473(1)	0.584 7(9)	0.091 6(7)
Fe	0.927 5(1)	0.529 43(9)	0.331 02(8)	C(14)	0.462(1)	0.793 7(8)	−0.000 4(7)
Cl(1)	0.843 9(3)	0.438 1(2)	0.149 0(1)	C(15)	0.336(1)	0.760(1)	0.219 0(8)
Cl(2)	0.545 6(4)	0.504 3(3)	0.292 1(2)	C(16)	0.483(1)	0.942 1(8)	0.148 2(7)
Si(1)	0.590 1(3)	0.687 0(2)	0.052 3(2)	C(17)	0.578(1)	0.804 5(8)	0.295 2(6)
Si(2)	0.522 6(3)	0.807 5(2)	0.195 5(2)	C(18)	1.013(1)	0.700 2(8)	0.063 8(7)
Si(3)	0.843 1(3)	0.794 0(2)	0.089 0(2)	C(19)	0.897(1)	0.864 6(8)	0.158 6(7)
Si(4)	0.917 7(5)	0.153 6(3)	0.274 2(2)	C(20)	0.812(1)	0.888 0(8)	−0.001 9(7)
Si(5)	0.792 0(5)	0.197 2(3)	0.447 8(3)	C(21)	0.769 7(9)	0.226 5(6)	0.338 0(5)
Si(6)	0.567 9(5)	0.219 3(3)	0.321 8(3)	C(22)	0.967(1)	0.017 9(7)	0.324 0(7)
O(1)	0.652 1(9)	0.568 2(6)	0.440 4(5)	C(23)	0.846(2)	0.158 1(9)	0.172 0(6)
O(2)	1.171 1(8)	0.476 6(6)	0.203 9(5)	C(24)	1.100(1)	0.207 9(8)	0.254 0(7)
O(3)	1.091 9(9)	0.407 7(6)	0.458 1(5)	C(25)	0.712(1)	0.298 3(8)	0.502 8(6)
O(4)	1.011(1)	0.721 1(6)	0.344 5(5)	C(26)	0.701(1)	0.082 8(8)	0.499 2(7)
C(1)	0.756(1)	0.552 2(7)	0.394 9(6)	C(27)	1.014(2)	0.168(1)	0.451 9(9)
C(2)	1.072(1)	0.497 4(8)	0.251 7(7)	C(28)	0.514(1)	0.286 0(8)	0.223 6(6)
C(3)	1.028(1)	0.453 3(8)	0.407 9(6)	C(29)	0.557(1)	0.082 2(8)	0.320 3(9)
C(4)	0.980(1)	0.646 8(9)	0.336 7(6)	C(30)	0.429(1)	0.269(1)	0.408(1)
C(11)	0.670(1)	0.730 2(6)	0.132 1(5)				

* Only the Si sites with higher occupancy are given.

Table 6. Bond lengths (pm) and angles (°) with estimated standard deviations in parentheses for [{(Me$_3$Si)$_3$C}In(μ-Cl)$_2${μ-Fe(CO)$_4$}In{C(SiMe$_3$)$_3$}] (**6**)

In(1)···In(2)	304.8(1)	In(1)–Fe	263.1(1)	Si(3)–C(18)	186(1)	Si(3)–C(19)	186(1)
In(1)–Cl(1)	264.4(3)	In(1)–Cl(2)	256.9(4)	Si(3)–C(20)	185(1)	Si(4)–C(21)	186(1)
In(1)–C(11)	218.7(8)	In(2)–Fe	262.4(2)	Si(4)–C(22)	190(1)	Si(4)–C(23)	196(1)
In(2)–Cl(1)	262.1(3)	In(2)–Cl(2)	259.0(4)	Si(4)–C(24)	189(1)	Si(5)–C(21)	190(1)
In(2)–C(21)	218.7(8)	Fe–C(1)	177(1)	Si(5)–C(25)	181(1)	Si(5)–C(26)	190(1)
Fe–C(2)	179(1)	Fe–C(3)	179(1)	Si(5)–C(27)	198(1)	Si(6)–C(21)	192(1)
Fe–C(4)	178(1)	Si(1)–C(11)	189(1)	Si(6)–C(28)	186(1)	Si(6)–C(29)	191(1)
Si(1)–C(12)	189(1)	Si(1)–C(13)	187(1)	Si(6)–C(30)	193(1)	O(1)–C(1)	114(1)
Si(1)–C(14)	188(1)	Si(2)–C(11)	188(1)	O(2)–C(2)	115(1)	O(3)–C(3)	114(1)
Si(2)–C(15)	188(1)	Si(2)–C(16)	187(1)	O(4)–C(4)	114(2)		
Si(2)–C(17)	187(1)	Si(3)–C(11)	191(1)				

Fe–In(1)–Cl(1)	93.17(7)	Cl(1)–In(1)–Cl(2)	83.2(1)	C(11)–Si(3)–C(19)	113.2(5)	C(18)–Si(3)–C(19)	106.2(5)
Fe–In(1)–Cl(2)	91.2(1)	Fe–In(1)–C(11)	147.9(3)	C(11)–Si(3)–C(20)	112.5(5)	C(18)–Si(3)–C(20)	108.2(5)
Cl(1)–In(1)–C(11)	111.5(3)	Cl(2)–In(1)–C(11)	111.3(2)	C(19)–Si(3)–C(20)	105.0(5)	C(21)–Si(4)–C(22)	111.8(5)
Fe–In(2)–Cl(1)	93.89(7)	Cl(1)–In(2)–Cl(2)	83.2(1)	C(21)–Si(4)–C(23)	109.3(5)	C(22)–Si(4)–C(23)	110.0(6)
Fe–In(2)–Cl(2)	90.9(1)	Fe–In(2)–C(21)	146.7(3)	C(21)–Si(4)–C(24)	111.0(5)	C(22)–Si(4)–C(24)	106.1(5)
Cl(1)–In(2)–C(21)	111.6(2)	Cl(2)–In(2)–C(21)	112.3(2)	C(23)–Si(4)–C(24)	108.5(8)	C(21)–Si(5)–C(25)	114.8(4)
In(1)–Fe–In(2)	70.91(4)	In(1)–Fe–C(1)	84.4(4)	C(21)–Si(5)–C(26)	110.7(5)	C(25)–Si(5)–C(26)	107.3(5)
In(2)–Fe–C(1)	82.4(4)	In(1)–Fe–C(2)	84.3(4)	C(21)–Si(5)–C(27)	105.7(5)	C(25)–Si(5)–C(27)	108.1(6)
In(2)–Fe–C(2)	85.7(4)	C(1)–Fe–C(2)	165.7(6)	C(26)–Si(5)–C(27)	110.2(5)	C(21)–Si(6)–C(28)	114.7(5)
In(1)–Fe–C(3)	166.3(4)	In(2)–Fe–C(3)	95.4(4)	C(21)–Si(6)–C(29)	108.0(5)	C(28)–Si(6)–C(29)	103.7(6)
C(1)–Fe–C(3)	94.5(5)	C(2)–Fe–C(3)	94.4(5)	C(21)–Si(6)–C(30)	108.1(6)	C(28)–Si(6)–C(30)	111.1(5)
In(1)–Fe–C(4)	96.0(3)	In(2)–Fe–C(4)	166.3(3)	C(29)–Si(6)–C(30)	111.2(6)	Fe–C(1)–O(1)	174(1)
C(1)–Fe–C(4)	92.7(5)	C(2)–Fe–C(4)	97.1(5)	Fe–C(2)–O(2)	176(1)	Fe–C(3)–O(3)	178(1)
C(3)–Fe–C(4)	97.7(5)	In(1)–Cl(1)–In(2)	70.7(1)	Fe–C(4)–O(4)	176.5(9)	In(1)–C(11)–Si(1)	110.2(4)
In(1)–Cl(2)–In(2)	72.4(1)	C(11)–Si(1)–C(12)	113.6(5)	In(1)–C(11)–Si(2)	104.4(4)	Si(1)–C(11)–Si(2)	113.0(5)
C(11)–Si(1)–C(13)	113.7(5)	C(12)–Si(1)–C(13)	105.4(5)	In(1)–C(11)–Si(3)	103.8(4)	Si(1)–C(11)–Si(3)	111.7(4)
C(11)–Si(1)–C(14)	110.5(5)	C(12)–Si(1)–C(14)	107.0(5)	Si(2)–C(11)–Si(3)	113.0(5)	In(2)–C(21)–Si(4)	107.1(4)
C(13)–Si(1)–C(14)	106.1(5)	C(11)–Si(2)–C(15)	113.2(5)	In(2)–C(21)–Si(5)	103.4(5)	Si(4)–C(21)–Si(5)	114.3(4)
C(11)–Si(2)–C(16)	112.8(4)	C(15)–Si(2)–C(16)	106.7(6)	In(2)–C(21)–Si(6)	107.1(4)	Si(4)–C(21)–Si(6)	112.8(5)
C(11)–Si(2)–C(17)	112.2(5)	C(15)–Si(2)–C(17)	103.9(6)	Si(5)–C(21)–Si(6)	111.4(4)		
C(16)–Si(2)–C(17)	107.3(5)	C(11)–Si(3)–C(18)	111.3(4)				

space group $P\bar{1}$, $a = 9.063(7)$, $b = 13.751(6)$, $c = 17.307(5)$ Å, $\alpha = 78.89(3)$, $\beta = 80.49(5)$, $\gamma = 79.45(6)°$, $U = 2\,062$ Å^3, $Z = 2$, $D_c = 1.50$ g cm^{-3}, $F(000) = 944$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 17.66$ cm^{-1}.

A crystal of size 0.2 × 0.15 × 0.9 mm was used. Data for h, $\pm k$, $\pm l$ reflections with $1 < \theta < 20°$ were measured as described for (**2**), and 3 439 reflections with $|F^2| > 2\sigma(F^2)$ were used in the structure determination. Standard heavy-atom techniques revealed the positions of the indium atoms and the remaining non-hydrogen atoms were found from a difference Fourier map. The silicon atoms in one of the C(SiMe$_3$)$_3$ groups were disordered, as found in a number of related crystal structures, and with separate refinement of positional and thermal parameters the occupancy factors were found to be 0.65 and 0.35. After refinement of all non-hydrogen atoms with anisotropic thermal parameters except for the disordered silicon

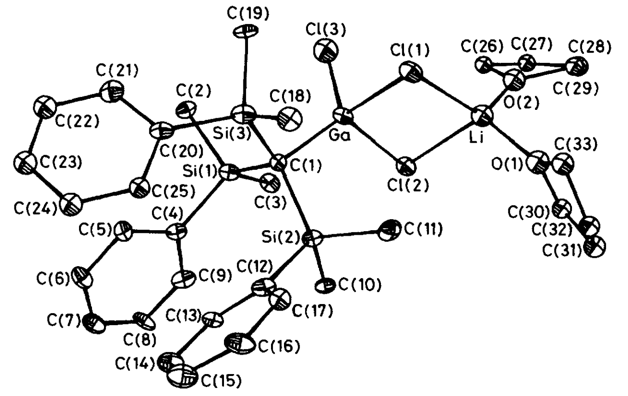

Figure 1. The structure of $[Li(thf)_2(\mu\text{-}Cl)_2GaCl\{C(SiMe_2Ph)_3\}]\cdot thf$ (2) with hydrogen atoms omitted

Table 7. Li–Cl bond lengths

Compound[a]	Co-ordination number Cl	Li	Angle at Cl (°)	Li–Cl/pm	Ref.
LiCl (s)	6	6	90	257	*b*
(2)	2	4	87.5	243	*c*
$[\{LiCl[OP(NMe_2)_3]\}_4]$	3	4	78—81	236—244	*d*
(4)	2	4	120	237	*c*
$LiCl\cdot 2py\cdot H_2O$	1	4		233	*e*
$[\{Li(pmeta)\}_2Cl]^+$	2	4	180	217	*f*
LiCl (g)	1	1		202	*g*

[a] py = Pyridine, pmdien = *NNN'N''N''*-pentamethyldiethylenetriamine. [b] A.S.T.M. (American Society for Testing and Materials) Powder Diffraction File. [c] This work. [d] D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 79. [e] F. Durant, P. Piret, and M. Van Meerssche, *Acta Crystallogr.*, 1967, **22**, 52. [f] N. H. Buttrus, C. Eaborn, P. B. Hitchcock, J. D. Smith, J. G. Stamper, and A. C. Sullivan, *J. Chem. Soc., Chem. Commun.*, 1986, 969. [g] E. F. Pearson and W. Gordy, *Phys. Rev.*, 1969, **177**, 52.

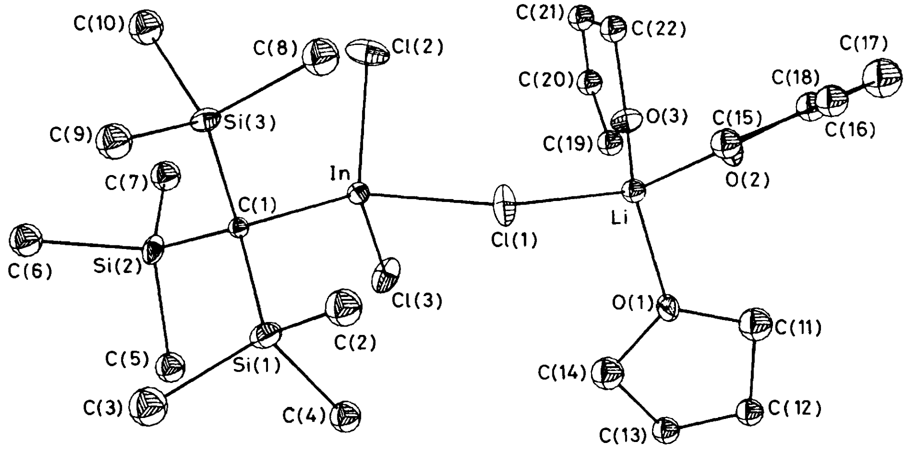

Figure 2. The structure of $[Li(thf)_3(\mu\text{-}Cl)InCl_2\{C(SiMe_3)_3\}]$ (4) with hydrogen atoms omitted

atoms, a low-angle difference map revealed the positions of all hydrogen atoms except those on one carbon atom. Refinement converged at $R = 0.039$, $R' = 0.043$. Except for small ripples of 0.33 e $Å^{-3}$ about In(2), no feature >0.1 e $Å^{-3}$ was observed on the final difference map. Fractional atomic co-ordinates and bond lengths and angles are given in Tables 5 and 6, respectively.

Results and Discussion

The products isolated from the reaction between $Li\{C(SiMe_3)_3\}$ or $Li\{C(SiMe_2Ph)_3\}$ and the chlorides MCl_3 (M = Ga, In, or Tl) were the 'alkyltrichlorometalates'* $Li(thf)_nMCl_3R$, with $n = 1, 2,$ or 3 and R = $C(SiMe_3)_3$ or $C(SiMe_2Ph)_3$, rather than the dichlorides MCl_2R. The lithium chloride formed in the alkylation of the metal was not precipitated; instead it formed a complex with the alkylmetal product and the lyophilic R groups made this soluble in heptane or toluene. Lithium alkylchlorometalates were also isolated from the reaction between $Li\{C(SiMe_3)_3\}$ or $Li\{C(SiMe_2Ph)_3\}$ and the dichlorides MCl_2 (M = Zn, Cd, or Mn), but dialkylmetalates from $Li\{C(SiMe_3)_3\}$ or $Li\{C(SiMe_2Ph)_3\}$ and the iodides MI (M = Cu or Ag).[1,17] Packing diagrams for the alkylchlorometalates of Groups 7 (Mn) or 2 (Cd) and the dialkylmetalates of Group 1 (Cu, Ag) show that the solid-state structures consist of discrete cations and anions held together by long-range electrostatic attraction.[10] In contrast, in the lithium alkyltrichloro-gallate and -indate described here, one cationic fragment is linked to a particular anionic fragment. In the gallate (Figure 1) two chlorides participate in the co-ordination around both Li and Ga; in the indate (Figure 2) one chloride is bound to both Li and In. The compounds (2) and (4) are thus molecular species, $[Li(thf)_2(\mu\text{-}Cl)_2GaCl\{C(SiMe_2Ph)_3\}]\cdot thf$ and $[Li(thf)_3(\mu\text{-}Cl)InCl_2\{C(SiMe_3)_3\}]$. Other recently described examples of molecules comprising tightly linked cationic and anionic moieties are the hydride-bridged species $[Li(thf)_3(\mu\text{-}H)_3B\{C(SiMe_2Ph)_3\}]$[18] and (7),[6] $[(tmen)Li(PMe_2CH_2)_2AlMe_2]$,[19] and $[\{(tmen)Li(PhCH_2S(Ph)O_2)\}_2]$[20] (tmen = *NNN'N'*-tetramethylethylenediamine).

The Solid-state Structures.—The molecular parameters (Tables 2, 4, and 6) in compounds (2), (4), and (6) are unremarkable; the M–Cl, M–C, and Si–C bond lengths are

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* The compounds described in this paper are referred to generally as lithium alkylchlorometalates; however the crystal structures of (2) and (4) indicate these species to be molecular, neutral, chloride-bridged lithium-gallium and -indium complexes, respectively.

similar to those in related compounds. As expected, terminal M–Cl bonds are shorter than bridging M–Cl bonds, and these in turn are longer the smaller the M–Cl–Li angle. The Li–Cl bond lengths show a similar trend (Table 7). There is no significant difference between the C–Si and Me–Si bond lengths within $C(SiMe_3)_3$ or $C(SiMe_2Ph)_3$ groups, in contrast to the situation in most other compounds containing these groups.[21] As in all such compounds so far studied, the Si–C–Si angles (*ca.* 113°) are greater and the Me–Si–Me angles (105—107°) less than the tetrahedral value. In (**4**) and (**6**) the $SiMe_3$ groups are twisted by *ca.* 20° from staggered positions, and in (**2**) the phenyl groups are slightly but significantly distorted so that the C–C–C angle adjacent to Si is only 117° (*cf.* ref. 22).

Although the configuration at Ga in (**2**) is roughly tetrahedral, the bulk of the $C(SiMe_2Ph)_3$ group forces the Ga–Cl bonds together (mean Cl–Ga–Cl 100°), making possible the displacement of thf from the co-ordination sphere of the lithium and formation of a $(\mu\text{-}Cl)_2$ bridge to Ga. The awkwardly shaped ion pairs pack in such a way as to leave large cavities in the crystal lattice (Figure 3). These are almost certainly occupied by disordered thf molecules which show as unresolved electron density in the crystal structure determination and account for the indefinite melting point. The Cl–In–Cl angles (mean 101.5°) in (**4**) are similarly reduced below the tetrahedral value by steric hindrance from the $C(SiMe_3)_3$ group. However, the longer M–Cl bonds apparently place the chlorines too far apart to occupy two co-ordination sites around lithium. The chloride-bridged ion pairs then pack neatly like typical molecules in space group $P2_1/c$; there is no room for extra solvent in the lattice, and the m.p. is much sharper than that of (**2**). The fact that the chemically similar $[Li(thf)_2(\mu\text{-}Cl)_2GaCl\{C(SiMe_2Ph)_3\}]\cdot thf$ (**2**) and $[Li(thf)_3(\mu\text{-}Cl)InCl_2\{C(SiMe_3)_3\}]$ (**4**) adopt different structures suggests that breaking a chloride bridge by co-ordination of thf makes little difference to the stability of the system (see ref. 1*b* for another illustration of this point).

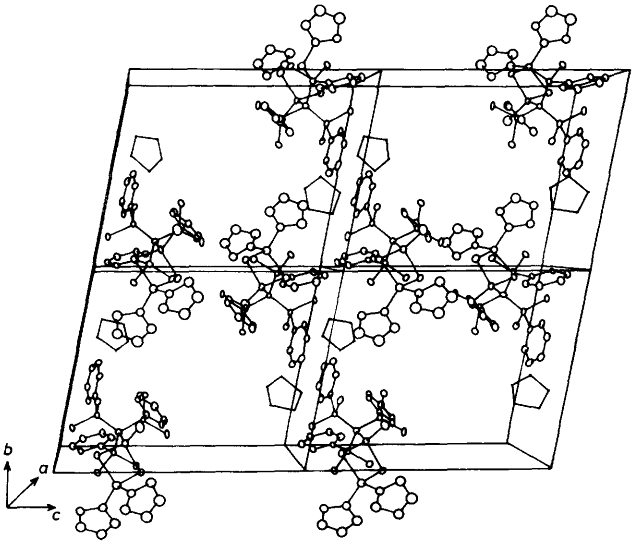


Figure 3. Packing diagram for $[Li(thf)_2(\mu\text{-}Cl)_2GaCl\{C(SiMe_2Ph)_3\}]\cdot thf$ (**2**) showing space occupied by disordered solvent

As is common, the carbon atoms of $C(SiMe_3)_3$ groups have larger thermal parameters than those in $C(SiMe_2Ph)_3$ groups, so that the standard deviations for bond lengths in (**4**) are greater than those in (**2**), but this does not affect the conclusions drawn here.

Compound (**6**) (Figure 4) has no crystallographically required symmetry, but if the $C(SiMe_3)_3$ groups are excluded the framework has within experimental error a mirror plane through Cl(1), Cl(2), Fe, C(1), O(1), C(2), and O(2). The difference between the In(1)–Cl and In(2)–Cl bond lengths is puzzling, but it may not be significant. The $Fe(CO)_4$ group has local C_{2v} symmetry consistent with four carbonyl stretching absorptions in the i.r.[23] The co-ordination around indium is highly distorted from tetrahedral, with the bulky $C(SiMe_3)_3$ and $Fe(CO)_4$ groups compressing the Cl–In–Cl angle to 83°. However, the conformation is such that there is no contact between methyl and carbonyl groups which is significantly below the sum of van der Waals radii. The In-Fe distance is similar to that in $[\{(CO)_5Mn\}In\{\mu\text{-}Fe(CO)_4\}_2In\{Mn(CO)_5\}]$ (**12**) [266.2(1) pm],[24] and the co-ordination at Fe is like that in $H_2Fe(CO)_4$,[25] with the carbonyls C(1)O(1) and C(2)O(2) bent towards the indium atoms. The In ••• In distance in (**6**) (304.8 pm) is surprisingly short, and only a little larger than twice the covalent radius (142 pm).[26] The shortest In–In distances in indium metal are 325 pm, in (**12**) 325 pm, in $[\{\mu_3\text{-}Co(CO)_3\}(\mu\text{-}Br)_3\{InCo(CO)_4\}_3]$ 329 pm,[26] in (**7**) 348 pm,[6] and in four

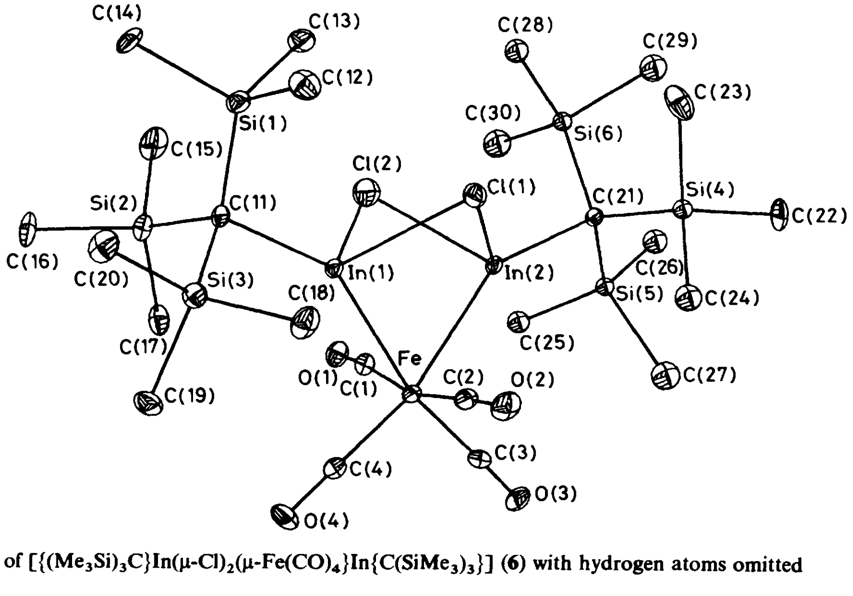
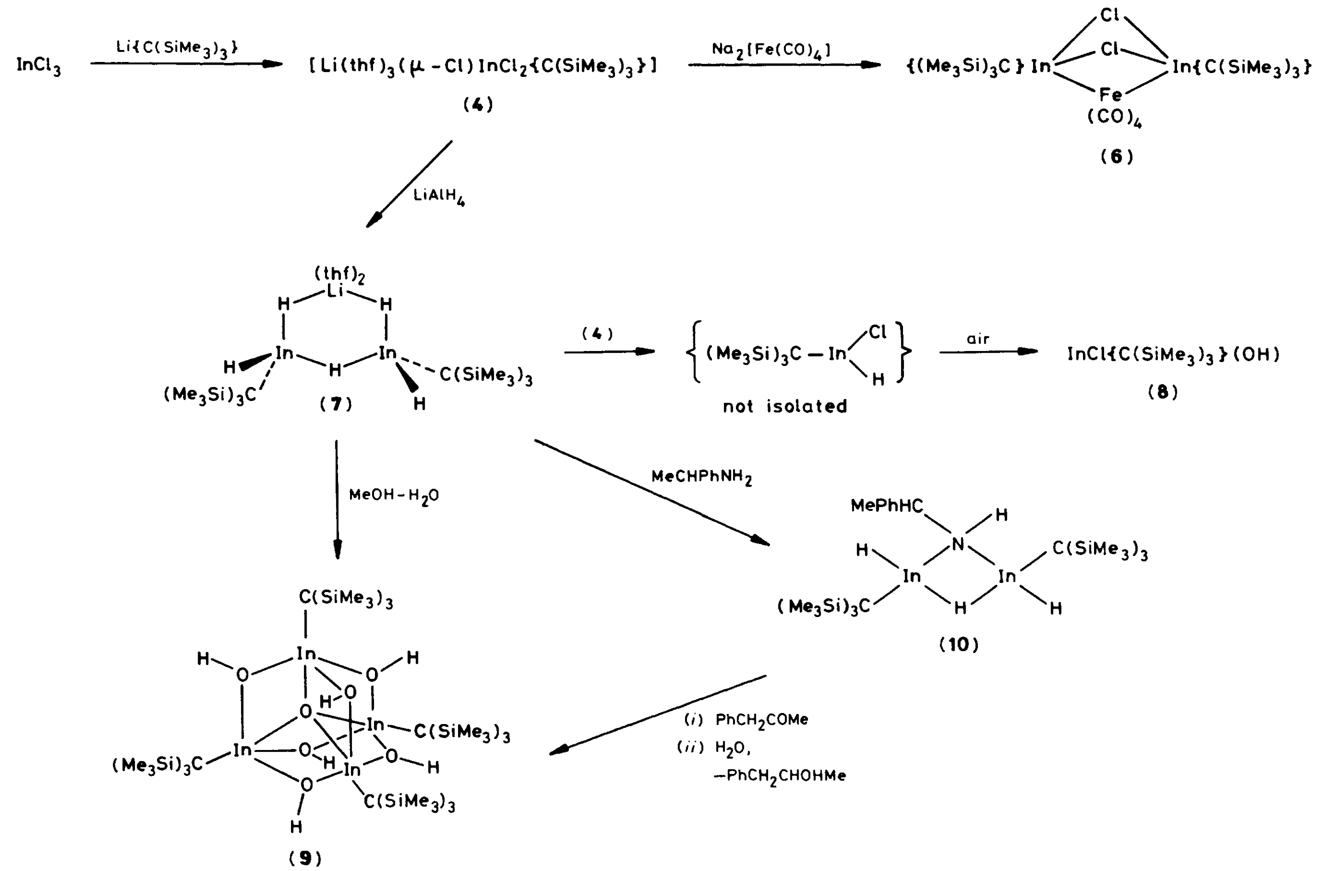


Figure 4. The structure of $[\{(Me_3Si)_3C\}In(\mu\text{-}Cl)_2(\mu\text{-}Fe(CO)_4\}In\{C(SiMe_3)_3\}]$ (**6**) with hydrogen atoms omitted



Scheme.

membered In_2Cl_2 rings > 400 pm. If there is assumed to be no interaction between the indium atoms in (**6**) the 'one angle' radius[27] for In (In ··· In) must be close to 154 pm. An alternative view of (**6**) is that of a cluster with 18 valence electrons; in accord with Wade's rules[28] the five cluster atoms form a dodecahedron with three missing corners.

The Chemistry of the Alkylmetalates.—The reactions of tris(trimethylsilyl)methylindium compounds described in this paper are summarised in the Scheme. Gallium compounds (**1**) and (**3**), analogous respectively to (**4**) and (**7**), have also been characterised, as have tris(dimethylphenylsilyl)methyl derivatives of gallium, (**2**), and indium, (**5**), analogous to (**4**).

The formation of the compounds MCl_2R [R = $C(SiMe_3)_3$ or $C(SiMe_2Ph)_3$; M = Ga, In, or Tl] from heated samples of $Li(thf)_nMCl_3R$ has been detected by mass spectroscopy, but attempts to exploit this decomposition on a preparative scale have been unsuccessful. At pressures obtainable in our vacuum line [*ca.* 10^{-3} Torr (≈ 0.13 Pa)] the breakdown of the gallium and indium compounds appears to require high temperatures, at which side reactions intervene. It may be possible to obtain the thallium compound $TlCl_2\{C(SiMe_3)_3\}$ under very carefully controlled conditions but reductive elimination of $\{C(SiMe_3)_3\}Cl$ with formation of TlCl occurs readily. That lithium can be removed from the alkylmetalates is demonstrated by the formation of (**6**), which may be viewed as a combination of $InCl_2\{C(SiMe_3)_3\}$ and $In\{Fe(CO)_4\}\{C(SiMe_3)_3\}$. Reactions of this kind merit further investigation.

The reduction of the trichlorometalates (**1**) and (**4**) to the hydridometalates (**3**) and (**7**) is readily effected with $LiAlH_4$, but the corresponding reaction with the trichlorothallate (**11**) results in transfer of the $C(SiMe_3)_3$ group to aluminium. Similar transfers of $C(SiMe_3)_3$ and $C(SiMe_2Ph)_3$ groups from zinc and cadmium to aluminium have been observed.[29] The thallium-containing product in the reduction of (**11**) is presumably a hydride, which rapidly decomposes to thallium metal and dihydrogen. It is likely that the hydrides (**3**) and (**7**) can be used to generate a wide range of organometallic compounds by reactions with protic species, as illustrated by the formation of compounds (**8**)—(**10**). The crystal and molecular structure of (**8**) is at present unknown. In the other cases studied so far the indium has achieved at least four-co-ordination. The formation of the oxide hydroxide (**9**) is not surprising, since InO(OH) has been known for a long time[30] but the cage structure is unusual. Although indium is normally four- or six-co-ordinate, five-co-ordination, as in (**9**), is not uncommon.[31] The preliminary experiments on the reduction of 1-phenylpropan-2-one by (**7**) suggest that hydridometalates with bulky alkyl substituents may have potential as selective (and, with suitable modification, asymmetric) reducing agents. This possibility is being explored with the cheaper boron and aluminium derivatives.

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