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Silylmethyl and Related Complexes. 7.[1] Bulky, Monomeric, Heavy Group 3 Metal Trialkyls and the Crystal and Molecular Structure of $In[CH(SiMe_3)_2]_3$

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The reaction of $GaCl_3$ or $InCl_3$ with the sterically hindered $Li[CH(SiMe_3)_2]$ (LiR) yields white crystalline MR_3, whereas $InCl_3$ with $Li(CHPh_2)$ gives In, Ph_2CH_2, and $(Ph_2CH)_2$. Treatment of $InCl_3$ with LiR (in a 1:1 or 2:1 ratio) in diethyl ether also gave InR_3 and not an alkylindium(III) chloride. Addition of $Li[N(SiMe_3)_2]$ to InBr or InCl in Et_2O or LiR to InBr in Et_2O at low temperature gives In, with RH + R_2 as the organic coproducts in the LiR experiment. Irradiation of $B(Cl)R_2$ with $[Et\overline{NCH_2CH_2N(Et)C}]_2$ in pyridine in the cavity of an ESR spectrometer yields a broad signal, $g_{av} = 2.0034$, which is persistent at 30 °C, and is believed to be due to $(BR_2^{-}\cdot)(NC_5H_5^{+})$. The structure of the crystalline $In[CH(SiMe_3)_2]_3$ has been determined by X-ray crystallography. It crystallizes (with disordered Et_2O solvent) in the space group $P31c$ with $a = b = 16.302$ (6) Å, $c = 8.890$ (3) Å, and $Z = 2$. The structure was solved by heavy-atom methods and refined to $R = 0.032$ and $R_w = 0.041$ for 1022 observed reflections. The crystal consists of discrete monomer molecules: the In atom is three-coordinate and lies 0.191 Å above the symmetry-related carbon atoms C(1), with CInC angles of 119.3 (2)° and a rather long In–C(1) bond length of 2.196 (6) Å. The compound is of interest as the first crystallographically authenticated monomeric, heavy group 3 metal trialkyl.

Introduction

The structures of the trialkyls of the group 3 metals have been of interest for more than two decades, partly because $(AlMe_3)_2$ has provided one of the simplest models for discussions of electron-deficient bonding.[3] The compound is a dimer in the solid state, in solution, and even in the gas phase except at high temperature. The monomeric group 3 metal trialkyls have an open-shell sextet structure, with the metal center available as a Lewis acid site, not only for coordination by an external nucleophile but also by a bridging alkyl group, as in the dimer. Trimethylboron was originally regarded as atypical in being monomeric, a fact attributed to steric considerations. It is now evident that the heavier group 3 metal trialkyls also have distinct structural features, although in the gas phase they resemble BMe_3 in being monomeric. For example, $InMe_3$ has been examined three times by electron diffraction: the monomer has l(In–C) = 2.093 (6) Å, l(C–H) = 1.14 (3) Å, and $H\hat{C}In$ = 112.7 (8)° on the assumption of a trigonal arrangement about the metal, with a slight nonplanarity (3.0 ± 2.5°) attributed to a shrinkage effect in $r(C\cdots C)$ of 0.004 Å.[4] $GaMe_3$ has a similar structure, with no dimer present at 338 K in the gas phase: l(Ga–C) = 1.967 (2) Å and $C\widehat{Ga}C$ = 118.6 (4)°.[5]

By contrast, in the solid-state trimethylindium may be regarded as a tetramer of S_4 symmetry,[6a] with the coordination about the metal approximating to trigonal bipyramidal. There are three short In–C equatorial bonds ("the monomer") of 2.16 (4), 2.24 (6), and 2.25 (6) Å and two long axial bonds of 3.10 and 3.60 Å;[6b] the equatorial $C\widehat{In}C$ bond angles indicate near planarity at the metal: 120.5 (1.8), 117.3 (1.3), and 122.2 (1.8)°. The closest $In\cdots In$ distances are 5.235 (4) and 5.665 (4) Å within and between tetramer units, respectively.[6a] Crystalline $TlMe_3$ is isostructural, but the difference between the intra- [5.46 (1) Å] and inter- [5.63 (1) Å] tetrameric $M\cdots M$ bridge bond lengths is smaller.[7]

Metal-centered radicals of the group 3 elements are rather poorly characterized and have very short lifetimes. Radicals $\dot{M}Me_2$ (M = Al, Ga, or In) were proposed as intermediates in the gas-phase pyrolysis of MMe_3,[8] whereas an ESR spectrum obtained by irradiation of an $AlMe_3$ glass was attributed to $AlMe_3^{-}\cdot$.[9]

The objectives of the present work were (i) to prepare and characterize bulky, monomeric trialkyls of gallium and indium, (ii) to obtain structural information on the unassociated monomers, and (iii) to examine their potential as sources of the radicals $MR_2^{-}\cdot$ and $\dot{M}R_3$ which were expected to have some kinetic stability. Apart from the lack of data on monomeric GaR_3 or InR_3 molecules, there is no structurally authenticated monomeric, crystalline AlR_3.

As alkyl group R, the choice fell on bis(trimethylsilyl)methyl, $(Me_3Si)_2CH$, because of its now well-tested properties as a stabilizing ligand for subvalent compounds of the group 4 and 5 elements. Thermally robust alkyls of this type include GeR_2, SnR_2, PbR_2,[10] $\dot{S}iR_3$,[11] $\dot{G}eR_3$, $\dot{S}nR_3$, $\dot{P}R_2$,[12] and $\dot{A}sR_2$; X-ray data are available for three-coordinate main-group metal complexes $(SnR_2)_2$,[10] $[Cr(CO)_5(SnR_2)]$,[13] and $[Cr(CO)_5(GeR_2)]$.[14] The dialkyltin compound, which is isoelectronic with InR_3, has the monomeric, bent ground-state singlet structure in cyclohexane solution but has the metal–metal bond (Sn–Sn = 2.78 Å) in the diamagnetic crystalline dimer.[10] $InR_3^{-}\cdot$ would be isoelectronic and presumably isostructural with the persistent radical $\dot{S}nR_3$ of pyramidal structure.[11] Since this work was completed, Beachley and Rusinko[15] have described the synthesis and characterization of $In(CH_2SiMe_3)_3$. A monomeric, trigonal structure was proposed on the basis of spectroscopic and molecular weight measurements.

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Experimental Section

General Procedures and Materials. Owing to the air sensitivity of the complexes, all preparations and other operations were carried out under a dry and oxygen-free argon atmosphere or in vacuo, by using standard Schlenk techniques. Diethyl ether, or THF, was dried and distilled over sodium/benzophenone, toluene over K, and pentane over $\mathrm{CaH_2}$. LiBu-*n* was obtained as a standard solution from Cortourch Chemicals, $\mathrm{Li(CHPh_2)}$ from $\mathrm{Ph_2CHCl}$ and lithium powder,[16] $\mathrm{Li[CH(SiMe_3)_2]}$ from $\mathrm{(Me_3Si)_2CHCl}$ and lithium powder,[10] and $\mathrm{Li[N(SiMe_3)_2]}$ from $\mathrm{HN(SiMe_3)_2}$ and LiBu-*n*.[17] Indium(III) or gallium(III) chloride was supplied by Johnson-Matthey. $\mathrm{InBr_3}$ was prepared by heating $\mathrm{In_2O_3}$ and an excess of $\mathrm{BBr_3}$ at 60 °C for 24 h in an evacuated T tube and was purified by sublimation in vacuo.[18] Indium(I) chloride was made from $\mathrm{InCl_3 + 2In}$ by heating in a sealed, evacuated tube for 4 days at ca. 290 °C;[19] InBr was prepared similarly by heating $\mathrm{InBr_3 + 2In}$ at 400 °C for 48 h.[19] $\mathrm{BCl\{CH(SiMe_3)_2\}_2}$ was made from $\mathrm{Li[CH(SiMe_3)_2]}$ and $\mathrm{BCl_3}$.[20]

Preparation of Tris[bis(trimethylsilyl)methyl]gallium. Lithiobis(trimethylsilyl)methane in diethyl ether (ca. 1 M) was added dropwise over 1 h to a one-third molar portion of gallium(III) chloride in the same solvent at 0 °C. A white precipitate formed, and the mixture was refluxed for 2 h and then stirred at room temperature for 14 h. Volatiles were removed in vacuo from the filtrate, and pentane was added. Filtration and evaporation of the volatiles from the filtrate yielded white crystals of the title compound (ca. 2.7 g, 82%); mp 90–92 °C. The compound sublimes at 185 °C (10^{-3} mmHg). Anal. Calcd for $\mathrm{C_{21}H_{57}Ga}$: C, 46.0; H, 10.51. Found: C, 46.2; H, 10.27. The mass spectrum (AEI MS30, source temperature = 150 °C, sample temperature = 75 °C) showed that the highest monoisotopic ion was that with *m/e* 531 [i.e., (monomer − $\mathrm{CH_3)^+}$], and other abundant peaks were those attributed to $\mathrm{[Ga\{CH(SiMe_3)_2\}_2]^+}$ (*m/e* 387), $\mathrm{[(Me_3Si_2)CH]^+}$ (*m/e* 159), and $\mathrm{[Ga]^+}$ (*m/e* 69–71). The ^{1}H NMR spectrum in $\mathrm{CDCl_3}$ (with reference to internal $\mathrm{Me_4Si}$) showed resonances at $\tau = 9.95$ (Si–$\mathrm{CH_3}$) and 10.05 (Ga–CH). The ^{13}C NMR spectrum (ppm downfield of $\mathrm{Me_4Si}$) showed resonances at $\tau = 9.95$ (Si–$\mathrm{CH_3}$) and 10.05 (Ga–CH). The ^{13}C NMR spectrum (ppm downfield of $\mathrm{Me_4Si}$) showed resonances at $\delta = 4.62$ (Si–$\mathrm{CH_3}$) and 19.79 (Ga–CH).

Preparation of Tris[bis(trimethylsilyl)methyl]indium. This was prepared (ca. 90%) as a crystalline white solid, mp 107–109 °C, by a procedure similar to that described for the gallium analogue. The compound sublimes at 150 °C (10^{-3} mmHg). Anal. Calcd for $\mathrm{C_{21}H_{57}In}$: C, 42.5; H, 9.71. Found: C, 42.1; H, 9.52. The mass spectrum taken under conditions identical with that for the Ga compound showed the following prominent peaks (monoisotopic): (monomer − $\mathrm{CH_3)^+}$ (*m/e* 577), $\mathrm{[In\{CH(SiMe_3)_2\}_2]^+}$ (*m/e* 433), $\mathrm{[In\{CH(SiMe_3)_2\}]^+}$ (*m/e* 274), $\mathrm{[(Me_3Si)_2CH]^+}$ (*m/e* 159), and $\mathrm{[In]^+}$ (*m/e* 115). The ^{1}H NMR spectrum in $\mathrm{CDCl_3}$ (with reference to internal $\mathrm{Me_4Si}$) showed resonances at $\tau = 9.85$ (Si–$\mathrm{CH_3}$) and 9.96 (In–CH). The ^{13}C NMR spectrum (ppm downfield of $\mathrm{Me_4Si}$) showed resonances at $\delta = 4.62$ (Si–$\mathrm{CH_3}$) and 21.18 (In–CH).

Attempted Preparation of Tris(benzhydryl)indium. The deep red solution of $\mathrm{Li(CHPh_2)}$ in THF (ca. 1 M) was added to $\mathrm{InCl_3}$ in diethyl ether at 0 °C under conditions similar to those for $\mathrm{In[CH(SiMe_3)_2]_3}$. The color of the lithium reagent was immediately discharged, giving way to a pale yellow solution, but as the addition proceeded, the solution became darker. The mixture was set aside for 14 h at 20 °C, whereafter indium metal (98.2%) had precipitated. The supernatant pale yellow solution was shown by ^{1}H NMR to contain $\mathrm{(Ph_2CH)_2}$ and $\mathrm{Ph_2CH_2}$.

Attempted Preparation of Dichloro[bis(trimethylsilyl)methyl]indium and Chlorobis[bis(trimethylsilyl)methyl]indium. An equimolar portion of $\mathrm{Li[CH(SiMe_3)_2]}$ in diethyl ether was added to $\mathrm{InCl_3}$ in the same solvent at 20 °C. A white precipitate instantly formed. Filtration and removal of $\mathrm{Et_2O}$ from the filtrate afforded a white solid. This was extracted with hexane. The hexane-soluble portion was identified as $\mathrm{In[CH(SiMe_3)_2]_3}$ (>90%), whereas the solid material was a mixture of LiCl and an excess of $\mathrm{InCl_3}$.

Similarly, 2:1 addition of $\mathrm{Li[CH(SiMe_3)_2]}$ to $\mathrm{InCl_3}$ yielded $\mathrm{In[CH(SiMe_3)_2]_3}$, $\mathrm{InCl_3}$, and LiCl.

Attempted Preparation of $\mathrm{In[CH(SiMe_3)_2]}$ and $\mathrm{In[N(SiMe_3)_2]}$. To a solution of indium(I) bromide in diethyl ether at −20 °C was added an equivalent portion of $\mathrm{Li[CH(SiMe_3)_2]}$ in the same solvent. When the addition was approximately half completed, the mixture darkened, and upon completion (ca. 1 h) metallic indium (96%) had precipitated. The pale yellow supernatant solution contained $\mathrm{[(Me_3Si)_2CH]_2}$ and $\mathrm{(Me_3Si)_2CH_2}$.

Similarly from $\mathrm{Li[N(SiMe_3)_2]\cdot OEt_2}$ and an equimolar portion of InCl or InBr at −40 °C, indium metal (98.7%) was obtained as a metallic mirror.

Attempted Preparation of $\mathrm{B_2[CH(SiMe_3)_2]_4}$. A solution of $\mathrm{BCl[CH(SiMe_3)_2]_2}$ in toluene was refluxed with a stoichiometric quantity of sodium for 12 h. Filtration and removal of solvent from the filtrate afforded unreacted $\mathrm{BCl[CH(SiMe_3)_2]_2}$ (98%).

Preparation of a Boron-Centered Radical. A solution of $\mathrm{BCl[CH(SiMe_3)_2]_2}$ (100 mg) was dissolved in toluene (2 mL) and introduced into a quartz ESR tube. A few crystals of the electron-rich olefin $\mathrm{[Et\overline{NCH_2CH_2N(Et)C}]_2}$ were added at 20 °C. An ESR signal was not observed, by using a Varian Associates E3 spectrometer with a V-4557 variable-temperature unit. The sample was irradiated in situ with an Osram ME/D 250-W high-pressure mercury lamp, but a signal was not observed even when the temperature was varied from +20 to −80 °C.

The experiment was repeated by using pyridine as the solvent in place of toluene. A signal was not observed prior to photolysis. However, upon irradiation at −50 °C a broad singlet was observed, $g_{\mathrm{av}} = 2.0034$, which persisted when irradiation ceased even upon warming to +30 °C.

X-ray Crystal Structure Analysis. A hexagonal-prismatic crystal 0.30 mm in diameter by 0.24 mm long was mounted in a Lindemann glass capillary under dry dinitrogen. Laue symmetry ($\bar{3}m$), a choice of space groups, and preliminary unit cell dimensions were determined from Weissenberg and precession photographs. Accurate unit cell dimensions were obtained from the least-squares refinement of the 2θ values of 21 general reflections measured on a General Electric XRD-6 Datex-automated X-ray diffractometer.

Crystal Data. $\mathrm{C_{21}H_{57}InSi_6\cdot C_4H_{10}O}$: $M_{\mathrm{r}} = 667.15$; trigonal; $a = b = 16.302$ (6), $c = 8.890$ (3) Å; $V = 2046.1$ Å^3; $Z = 2$, $\rho_{\mathrm{c}} = 1.083$ g cm^{-3}; $F(000) = 706$; Mo Kα radiation; $\lambda = 0.71069$ Å, μ(Mo Kα) = 7.59 cm^{-1}, space groups $P31c$ (C_{3v}^4, No. 159) or $P\bar{3}1c$ (D_{3d}^2, No. 163) from systematic absences $h,h,\overline{2h},l$, $l = 2n + 1$.

Data Collection. The crystal was mounted with c^* parallel to the ϕ axis of a Datex automated General Electric XRD-6 diffractometer. A total of 2683 reflections were measured ($2.5° \le 2\theta \le 50°$) which reduced to 1378 independent reflections of which 1022 with intensities $> 3\sigma(I)$ above background were considered observed and used for the structure determination. Zirconium-filtered Mo Kα radiation ($\lambda = 0.71069$ Å) was used and the θ–2θ scan method employed with a scan speed of 2°/min. The intensities of three standard reflections, monitored every 100 reflections, diminished by 4% during the course of data collection; these were used to scale the data to a common level. The data were corrected for Lorentz and polarization effects. With $\mu = 7.59$ cm^{-1} for these atoms no absorption correction was deemed necessary.

Structure Solution and Refinement. Considering the choice of space groups, $P\bar{3}1c$ appeared to be unreasonable. With $Z = 2$, the indium atom would be required to occupy either a 32 or $\bar{3}$ site, both of these alternatives seeming very unlikely in view of the expected stereochemistry of the molecule and the anticipated tetrahedral geometry at the metal-coordinated carbon atoms.

The Patterson synthesis was solved for the indium atom occupying a threefold site ($^1/_3$, $^2/_3$, z) in the space group $P31c$, and this choice of space group was supported throughout the refinement of the structure. The two silicon atoms were also located from the Patterson function. A least-squares refinement at this stage gave a residual R of 0.176 ($R = \sum[(|F_o| - |F_c|)/|F_o|]$). The remainder of the $\mathrm{InR_3}$ molecule was located from a Fourier synthesis phased by these three atoms. Considerable false symmetry was observed about the plane of the indium atom ($\pm z$). With the indium and two silicon atoms having anisotropic thermal parameters and the remaining atoms isotropic coefficients, the structure was refined to an R value of 0.104. Conversion of all nonhydrogen atom coefficients to anisotropic thermal parameters and refinement to convergence gave a high residual R of 0.068. At this stage difference Fourier syntheses not only located the $\mathrm{CH(SiMe_3)_2}$ group hydrogen atoms but also indicated a large

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Table I. Atomic Coordinates (Fractional, ×10^4) and B_{iso} for Solvent Carbon Atoms of In$\{CH(SiMe_3)_2\}_3 \cdot (C_2H_5)_2O$[a]

	x	*y*	*z*	
In	3333	6667	2500	
Si(1)	2818 (3)	4526 (3)	926 (3)	
Si(2)	1687 (2)	4532 (2)	3901 (3)	
C(1)	2785 (4)	5138 (4)	2715 (7)	
C(11)	1653 (7)	3970 (8)	−5 (13)	
C(12)	3303 (10)	3712 (8)	1402 (12)	
C(13)	3652 (7)	5383 (8)	−538 (11)	
C(21)	1374 (8)	3282 (8)	4358 (16)	
C(22)	646 (6)	4488 (7)	2984 (12)	
C(23)	1949 (8)	5179 (9)	5743 (12)	
	x	*y*	*z*	B_{iso}, Å^2
O(S)	187 (12)	16 (22)	3134 (15)	
C(S1)	−295	−990	3100	9.0 (7)
C(S2)	150	380	1685	10 (1)
C(S3)	−655	−1355	1500	14 (2)
C(S4)	−725	505	1595	13 (1)

[a] Solvent: multiplicity $^1/_3$. Solvent carbon atom positions not refined.

Table II. Hydrogen Atom Atomic Coordinates (Fractional, ×10^3) and B_{iso} for In$\{CH(SiMe_3)_2\}_3 \cdot (C_2H_5)_2O$

	x	*y*	*z*	B_{iso}, Å^2
H(1)	338	521	341	6 (2)
H(111)	113	321	73	8 (3)
H(112)	165	344	−103	11 (4)
H(113)	139	425	−29	10 (3)
H(121)	366	391	241	6 (3)
H(122)	390	385	71	17 (6)
H(123)	283	300	129	17 (6)
H(131)	376	501	−139	8 (3)
H(132)	339	578	−93	8 (3)
H(133)	435	581	−11	12 (4)
H(211)	140	319	556	12 (4)
H(212)	192	308	395	14 (5)
H(213)	67	282	416	14 (5)
H(221)	81	514	258	12 (4)
H(222)	35	390	221	17 (6)
H(223)	14	428	380	10 (4)
H(231)	244	509	635	10 (3)
H(232)	219	595	555	17 (6)
H(233)	129	495	641	10 (4)

Table III. Anisotropic Thermal Parameters (×10^4) for Skeletal Atoms of In$\{CH(SiMe_3)_2\}_3 \cdot (C_2H_5)_2O$[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
In	38.9 (4)	38.9	107.3 (8)	19.4	0	0
Si(1)	61 (2)	49 (2)	174 (4)	32 (2)	−23 (2)	−21 (2)
Si(2)	53 (2)	49 (2)	170 (4)	20 (2)	11 (2)	26 (2)
C(1)	46 (4)	42 (3)	134 (10)	22 (3)	2 (5)	7 (5)
C(11)	85 (7)	80 (6)	261 (19)	24 (6)	−34 (10)	−52 (10)
C(12)	148 (12)	89 (7)	274 (21)	88 (8)	−41 (14)	−35 (10)
C(13)	82 (7)	92 (7)	160 (14)	51 (6)	12 (7)	−30 (8)
C(21)	83 (7)	69 (6)	476 (32)	31 (6)	22 (12)	106 (12)
C(22)	46 (5)	80 (7)	277 (18)	21 (5)	5 (8)	25 (10)
C(23)	84 (8)	117 (10)	183 (15)	44 (7)	8 (9)	−6 (10)
O(S)	20 (9)	29 (5)	214 (21)	14 (5)	−2 (13)	1 (26)

[a] The form of the anisotropic thermal parameters is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

residual electron density about the *c* axis including a major peak at (0, 0, 0.31) with as much electron density as that exhibited by the previously located methyl carbon atoms (~4.85 e Å^{-3}). This electron density had been noted in previous Fourier maps, but no coherent molecular picture emerged in these earlier inspections. Experimentally diethyl ether had been used as a reaction solvent, but the solid was recrystallized from anhydrous pentane. Attempts to simulate the observed electron density pattern by inclusion of carbon atoms of a pentane skeleton did not produce a featureless difference map. Various efforts to fit a disordered hydrocarbon to the electron density maxima were never entirely satisfactory. Consideration was then given to the possibility that the trapped solvent molecule was diethyl ether. Incorporation of an oxygen atom in the synthesis significantly reduced the *R* value; the remaining electron density could then be fitted to the carbon atoms of a threefold disordered ether molecule. A close examination of the behavior of the oxygen atom indicated a best position just off the *c* axis, and the atoms were allowed to refine to this position. In final Fourier maps hydrogen atoms and the atoms of the solvent of crystallization were included with fixed positions. Convergence was obtained at an *R* value of 0.032 with the weighted residual R_w ($R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$) of 0.041. The weighting scheme, derived from the program RANGER had weights $w^{-1} = 2.5 - 0.12|F_o| + 0.0025|F_o|^2$. A final difference Fourier synthesis indicated a maximum residual electron density of 0.30 e Å^{-3} in the vicinity of the indium atom and 0.28 e Å^{-3} in the solvent cavity. Although the space group *P*31*c* is polar, the major contributor to anomalous dispersion is the indium atom which occupies a special position. Thus reversal of the coordinates *x*, *y*, *z* to *x*, *y*, −*z* and rerefinement to convergence led to no significant change in the *R* factor. The handedness of the crystal was thus not determined.

Computer programs used in the calculations have been described in ref 21. Scattering factor tables including corrections for the anomalous dispersion of indium were taken from ref 22. Hydrogen atom scattering factors were those due to Stewart et al.[23] A table of observed and calculated structure factors is available as supplementary data.[24] Final atomic positions are listed in Table I for heavy atoms and in Table II for hydrogen atoms. Heavy-atom anisotropic thermal parameters appear in Table III.

Results and Discussion

Synthesis of Gallium(III) and Indium(III) Alkyls. From the appropriate metal(III) chloride and lithiobis(trimethylsilyl)methane,[10,25] the metal(III) alkyl MR_3 was obtained (eq 1)

$$MCl_3 + 3Li[CH(SiMe_3)_2] \rightarrow M[CH(SiMe_3)_2]_3 + 3LiCl \quad (1)$$

irrespective of the relative stoichiometry of reagents. We infer, therefore, that the mixed chloroalkyls $MCl_n[CH(SiMe_3)_2]_{3-n}$ (M = Ga or In, *n* = 1 or 2) are surprisingly unstable with respect to disproportionations (eq 2) under the conditions of

$$3MCl_n[CH(SiMe_3)_2]_{3-n} \rightarrow nMCl_3 + (3-n)M[CH(SiMe_3)_2]_3 \quad (2)$$

reaction which were employed, namely, diethyl ether as solvent. This may be due to the relative Lewis acid strengths decreasing in the sequence $InCl_3$ > $InCl_2[CH(SiMe_3)_2]$ > $InCl[CH(SiMe_3)_2]_2$ > $In[CH(SiMe_3)_2]_3$, which is the inverse of solubility in Et_2O or *n*-C_6H_{14}. No attempt was made to examine the position of equilibrium in diethyl ether solution. An alternative explanation is that the mixed chloroalkyls are more reactive to the alkylating agent than $InCl_3$ or $GaCl_3$, resulting in rapid conversion of mixed species to the trialkyls. With the less bulky alkyl ligand $Me_3SiCH_2^-$ it has been possible to prepare the mixed alkyl indium chlorides $InCl(CH_2SiMe_3)_2$ and $InCl_2(CH_2SiMe_3)$ by reacting the trialkyl with $InCl_3$ or HCl.[15]

It is interesting that attempted alkylation of $InCl_3$ by $Li(CHPh_2)$ in place of $Li[CH(SiMe_3)_2]$ results instead in reduction to indium metal. Similar relative reducing capabilities of these lithium reagents were observed in the reaction of $[V(\eta\text{-}C_5H_5)_2Cl_2]$ with LiR to give $[V(\eta\text{-}C_5H_5)_2]$ and $(Ph_2CH)_2$ with lithiobis(diphenyl)methane but $[V(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}]$ with $Li[CH(SiMe_3]$.[26] As the red color of the

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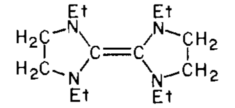
lithium reagent was at first discharged to yield a pale yellow solution and indium metal was only later deposited, eq 3 may be indicated.

$$\mathrm{InCl_3 + 2LiR \xrightarrow{-2LiCl} InClR_2 \rightarrow InCl + R_2 \xrightarrow{LiR} In + LiCl + (RH + R_2)} \quad (3)$$

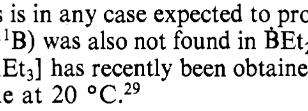
Attempted Preparation of Subvalent Alkyls or Amides of Indium or Boron. In view of earlier success in stabilizing subvalent states of group 4 or 5 metals by means of the ligand $(Me_3Si)_2CH^-$ or $(Me_3Si)_2N^-$, an indium(I) halide was reacted with either $Li[CH(SiMe_3)_2]$ or $Li[N(SiMe_3)_2]$. However, even at low temperature, indium metal was deposited. The formation of bis(trimethylsilyl)methane and 1,1,2,2-tetrakis(trimethylsilyl)ethane in the former case suggests that an unstable indium(I) alkyl decomposes via M–C homolysis, as do the univalent coinage metal alkyls.

We have previously shown that organometallic one-electron reductions may be affected by reduction of an organometallic chloride, especially by use of an electron-rich olefin such as **1** under UV irradiation;[27] for example $SnCl[CH(SiMe_3)_2]_3$



1

gave $\dot{S}n[CH(SiMe_3)_2]_3$, and $PCl[CH(SiMe_3)_2]_2$ yielded $\dot{P}[CH(SiMe_3)_2]_2$.[12] However, under conditions which had earlier served for the reduction of chloroalkyls of Ge^{IV}, Sn^{IV}, P^{III}, or As^{III}, there was no direct ESR evidence for the formation of a persistent $\mathbf{B}^{II}$ radical, $\dot{B}[CH(SiMe_3)_2]_2$. However, like the Si^{III} analogue $\dot{S}i[CH(SiMe_3)_2]_3$,[11] this might have been expected readily to abstract a hydrogen atom from solvent since the B–H bond strength (like that of SiH) is relatively high. When the photolysis of $BCl[CH(SiMe_3)_2]_2$ and the olefin **1** was carried out in pyridine as solvent in the cavity of an ESR spectrometer, an ESR signal was observed which was indefinitely persistent even at +30 °C. Although hyperfine coupling to ^{11}B ($I = {}^3/_2$) or ^{10}B ($I = 3$) was not observed, the signal was broad. The g_{av} value of 2.0034 is similar to that (2.003) attributed to $\dot{B}Et_2{\cdot}NC_5H_5$.[28] We therefore suggest that the signal is due to the radical **2**, which is kinetically stable



$$(Me_3Si)_2CH\dot{B}^{-}(CH(SiMe_3)_2)(^{+}NC_5H_5)$$

2

due to the steric shielding around the boron atom and to the relatively energetically inaccessible intramolecular decomposition pathways. Quadrupolar broadening by the $^{10}B/^{11}B$ nuclei may be partly the cause of failure to observe boron hyperfine coupling, but interaction with ^{14}N, α ^1H's, and pyridine protons is in any case expected to produce a 162-line spectrum; a ($^{10/11}B$) was also not found in $\dot{B}Et_2{\cdot}NC_5H_5$.[28] The compound $K[AlEt_3]$ has recently been obtained from $(AlEt_3)_2$ and K in hexane at 20 °C.[29]

Description and Discussion of the Structure of In[CH(SiMe$_3$)$_2$]$_3$. An ORTEP II plot of the molecular structure, excluding hydrogen atoms, is shown in Figure 1. The crystal consists of discrete molecules separated by normal van der Waals contacts. Bond lengths and angles are compiled in Table IV. The indium atom is three-coordinated, but unexpectedly the immediate stereochemistry at the metal is not trigonal planar. The indium atom lies 0.191 Å above the plane defined by the symmetry-related carbon atoms defined by C(1). This result is surprising since the monomeric tris[bis(trimethylsilyl)amido]aluminum[30] which crystallizes in the centrosymmetric space group $P\bar{3}1c$ has a planar D_3 structure. Other tris(amido) complexes are also planar.[30] The only other examples of nonplanar MR_3 compounds known to us are (i) $InMe_3$ in the gas phase,[4] where electron diffraction results show

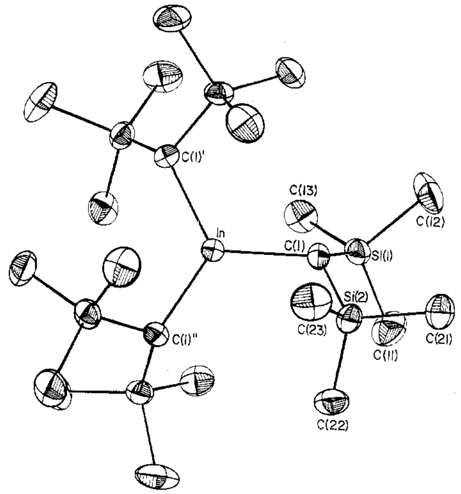


Figure 1. Perspective view of one monomer of $In[CH(SiMe_3)_2]_3$ drawn to illustrate the trigonal stereochemistry at indium. Ellipsoids represent 30% probabilities.

Table IV. Bond Lengths (Å) and Angles (Deg) for $In\{CH(SiMe_3)_2\}_3{\cdot}(C_2H_5)_2O$

(a) Skeleton Bond Lengths and Angles

In–C(1)	2.196 (6)	Si(1)–C(13)	1.90 (1)
C(1)–Si(1)	1.892 (7)	Si(2)–C(21)	1.88 (1)
C(1)–Si(2)	1.878 (8)	Si(2)–C(22)	1.85 (1)
Si(1)–C(11)	1.86 (1)	Si(2)–C(23)	1.88 (1)
Si(1)–C(12)	1.90 (2)		

C(1)–In–C(1′)	119.3 (2)	C(11)–Si(1)–C(13)	107.1 (5)
In–C(1)–Si(1)	115.0 (1)	C(12)–Si(1)–C(13)	105.8 (5)
In–C(1)–Si(2)	112.7 (1)	C(1)–Si(2)–C(21)	111.2 (4)
Si(1)–C(1)–Si(2)	117.8 (1)	C(1)–Si(2)–C(22)	112.8 (3)
C(1)–Si(1)–C(11)	115.2 (4)	C(1)–Si(2)–C(23)	107.8 (4)
C(1)–Si(1)–C(12)	108.2 (4)	C(21)–Si(2)–C(22)	107.9 (5)
C(1)–Si(1)–C(13)	112.8 (3)	C(21)–Si(2)–C(23)	106.5 (5)
C(11)–Si(1)–C(12)	107.2 (5)	C(22)–Si(2)–C(23)	110.6 (5)

(b) Solvent Bond Lengths and Angles

O(S)–C(S1)	1.42	C(S1)–C(S3)	1.54
O(S)–C(S2)	1.43	C(S2)–C(S4)	1.54

C(S1)–O(S)–CS(2)	110.2	O(S)–C(S2)–C(S4)	105.6
O(S)–C(S1)–C(S3)	110.5		

(c) Carbon–Hydrogen Bond Lengths

C(1)–H(1)	1.11	C(21)–H(211)	1.08
C(11)–H(111)	1.11	C(21)–H(212)	1.15
C(11)–H(112)	1.07	C(21)–H(213)	1.03
C(11)–H(113)	1.06	C(22)–H(221)	1.02
C(12)–H(121)	1.03	C(22)–H(222)	1.08
C(12)–H(122)	1.08	C(22)–H(223)	1.02
C(12)–H(123)	1.03	C(23)–H(231)	1.03
C(13)–H(131)	1.04	C(23)–H(232)	1.13
C(13)–H(132)	1.00	C(23)–H(233)	1.12
C(13)–H(133)	1.06		

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a very slight nonplanarity attributed to a shrinkage effect of ~0.004 Å in C···C, and (ii) crystalline $[Cr\{CH(SiMe_3)_2\}_3]$, where the chromium atom deviates by 0.32 Å from the plane defined by the attached carbon atoms.[31] The origin of these distortions toward pyramidal stereochemistry in molecules with high crystallographic symmetry is intriguing since a priori a planar stereochemistry is expected in the absence of secondary inter- or intramolecular bonding. With indium atoms separated by 8.99 Å, with no intermolecular In···C contacts of <5.0 Å, and with the observation that intramolecular interactions are unimportant in InR_3[32] or in the chromium complex,[31] it seems possible that a subtle electronic effect may be responsible for the deviation from planarity. In this regard it is interesting that, for the group 5 element MR_3 species, s orbital character tends to accumulate in the metal lone pair as the electronegativity of the group 5 atom decreases. It is tempting to suggest that in $In[CH(SiMe_3)_2]_3$ the formally empty $5p_z$ orbital of indium retains some 5s character while the bonding orbitals have greater "p" character than that implied by fully hybridized sp^2. This argument however is at odds with the usual valence-shell electron pair repulsion assumption that three bonding pairs should produce a trigonal-planar stereochemistry! It will be fascinating to see if further examples of crystalline nonplanar MR_3 molecules appear for other heavy metals in the future. The C–In–C angle is 119.3 (2)°, consistent with slight nonplanarity at the indium atom. The angles subtended by the heavy atoms at C(1) [In–C(1)–Si(1) = 115.0 (1)°, In–C(1)–Si(2) = 112.7 (1)°, Si(1)–C(1)–Si(2) = 117.8 (1)°] are all considerably larger than the tetrahedral value, presumably to minimize nonbonded contacts between bulky substituents.

The In–C(1) bond length of 2.196 (6) Å is significantly longer than the electron diffraction value for *l*(In–C) [2.093 (6) Å][4] but compares favorably with the intramolecular In–C distances of 2.16 (4), 2.24 (6), and 2.25 (6) Å in the crystalline $InMe_3$ tetramer.[6] In the latter structure, however, intermolecular In···C interactions of 3.10 and 3.60 Å are present between monomers while in $In[CH(SiMe_3)_2]_3$ there are no intermolecular In–C or In–Si distances of less than 4.0 Å. Significant intermolecular In···C contacts are also present in $InPh_3$[33] where essentially trigonal molecules (In–C = 2.13 Å average) are linked into chains by 3.07 Å interactions involving the metal atom and the ortho carbon atom of a neighboring phenyl ring. Several other alkyl- and arylindium derivatives have recently been examined by X-ray crystallography.[34–41] The tetrahedral salts $K[InMe_4]$, $Na[InPh_4]$, and $Me_4As[InCl_3Me]$ have In–C distances of 2.239 (3),[34] 2.230 (3),[36] and 2.183 (6) Å,[40] respectively. The shortest reported In–C bond length is found in $InCl_2Me$ [2.052 (6) Å] where indium is five-coordinate.[38] In contrast, for the ionic lattice of $InBrMe_2$, which consists of $InMe_2{}^+$ cations and Br^- anions, the reported In–C bond lengths are 2.116 (6) and 2.226 (7) Å.[39] Tris(cyclopentadienyl)indium is a polymer at −100 °C, with approximately tetrahedral indium atoms and terminal and bridging C_5H_5 groups. The shortest In–C bond lengths to terminal ligands are 2.237 (9) and 2.243 (9) Å.[35] It is thus apparent that intramolecular In–C bond lengths lie within the fairly narrow range of 2.05–2.25 Å for a variety of structural types and coordination numbers.

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Note Added in Proof. The following modified procedure is preferred for the synthesis of tris[bis(trimethylsilyl)methyl]gallium.

To a solution of gallium trichloride (1.48 g, 8.41 mmol) in degassed diethyl ether (60 mL) was added dropwise [bis(trimethylsilyl)methyl]lithium (42.1 mL, 25.23 mmol) in ether over a period of 1 h at room temperature. The solution changed from colorless to pale yellow, and a white precipitate was formed. After the solution had stirred overnight at room temperature, ether was pumped off and replaced by toluene (60 mL). The reaction mixture was heated to reflux for 24 h and then filtered, and solvent was removed. The pale yellow residue was sublimed at 185 °C (10^{-2} mmHg) to give 3.8 g, 82.4%, of the required product (mp 90–92 °C) as a white solid.

Registry No. 2, 74929-98-9; $In[CH(SiMe_3)_2]_3\cdot(C_2H_5)_2O$, 74929-99-0; $Ga[CH(SiMe_3)_2]_3$, 74930-00-0; $BCl[CH(SiMe_3)_2]_2$, 67373-59-5.

Supplementary Material Available: A listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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(32) The shortest intramolecular contacts in the present structure [In···C(13) of 3.61 (1) Å and In···C(23) of 3.72 (1) Å] compare with the van der Waals radii sum for indium and carbon of ~3.60 Å. In crystalline $InMe_3$[6] and $InPh_3$[33] there are much shorter intermolecular In···C interactions of 3.10 and 3.07 Å, respectively.

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