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Notes

Neutral and Cationic Trimethylsilylmethyl Complexes of Indium

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*Summary: The trimethylsilylmethyl indium complex [In(CH_2SiMe_3)$_3$] (**1**) was studied by single-crystal X-ray structure analysis at low temperature and shown to be weakly associated as dimeric units with a long indium−carbon bond in the bridges. The bis(trimethylsilylmethyl) cation [In(CH_2SiMe_3)$_2$(THF)$_3$][B(C_6F_5)$_4$] (**2**) was prepared by protonolysis of the neutral complex [In(CH_2SiMe_3)$_3$] with [$NPhMe_2H$][B(C_6F_5)$_4$] in THF. Crystal structure analysis revealed that mononuclear **2** adopts a square-pyramidal geometry.*

Introduction

Organoindium compounds, in particular allyl indium reagents, are currently attracting interest as a new type of carbanionic reagents with a reactivity profile distinct from that of conventional polar organometallics based on main group elements.[1,2] In the context of investigating cationic organyl complexes of the rare-earth metals, we became interested in comparing the Lewis acidity and electrophilicity of these elements vis-à-vis that of indium, which has an ionic radius (0.800 Å) similar to that of the smaller rare-earth elements (Sc = 0.745 Å; Lu = 0.861 Å; Y = 0.900 Å).[3] Compared with the lighter homologue aluminum, indium shows a pronounced tendency to expand its coordination sphere.[4] While dimeric indium species are typically encountered in heteroleptic derivatives with three-electron-donor ligands in the bridges as in [{$InMe_2$(μ-C≡CMe)}$_2$],[5] [{In^{t}Bu$_2$(μ-OEt)}$_2$],[6] or [{$InMes_2$(μ-Cl)}$_2$],[7] Lewis base coordination leads to discrete molecules with coordination number up to five, as observed in the 10-electron species [In(CH_2Ph)Cl_2(THF)$_2$][8] or [In(η^1-C_5H_5)Cl_2(THF)$_2$].[9] Six-coordination is found in [$InCl_3$(THF)$_3$].[10] Bulky organyl substituents such as mesityl $C_6H_2Me_3$-2,4,6 (Mes)[7] and bis(trimethylsilyl)methyl CH($SiMe_3$)$_2$[11] prevent association in the solid state, giving monomeric species, whereas with sterically less demanding ligands chain-like polymeric structures in the solid state are formed (Table 1). In order to compare the properties of the trimethylsilylmethyl ligand in organorare-earth metal and organoaluminum chemistry,[4,12] we report here on the structure of previously reported [In(CH_2SiMe_3)$_3$] (**1**) and the cation [In(CH_2SiMe_3)$_2$(THF)$_3$][B(C_6F_5)$_4$] (**2**) derived therefrom.

Table 1. Structural Features of Homoleptic Organoindium Compounds

compound	degree of association	In···C (Å)	Σ_{C-In-C} (deg)	ref
[$InMes_3$]	monomeric		359.9	7
[In{CH($SiMe_3$)$_2$}$_3$]	monomeric		357.9	11
[In(CH_2SiMe_3)$_3$] (**1**)	dimeric	3.082(7)	356.0	this work
[$InMe_3$]	tetrameric	3.11(4); 3.59(4)	358	15
[$InPh_3$]	infinite chain	3.07(2)	360	16
[In(CH_2Ph)$_3$]	infinite chain	3.002(6); 3.081(7) [a]	356.3	17
[$InCp_3$]	infinite chain	2.466(8)/2.482(4) [b]	346.6/342.9 [b]	18
[In^{t}Bu$_3$]	infinite chain	3.467(5)	359.6	19

[a] First value for the In···*ortho*-C contact, second for the In···*meta*-C contact. [b] First value from ref 18a, second from ref 18b.

Results and Discussion

The trimethylsilylmethyl indium complex [In(CH_2SiMe_3)$_3$] (**1**) was synthesized according to the procedure previously reported by Beachley et al. and isolated as a colorless oil.[13] The solid state structure of [In(CH_2SiMe_3)$_3$] (**1**), obtained from single crystals grown in a microcapillary, revealed the presence of a weakly associated dimer in the lattice with a distorted trigonal-planar environment around the indium center (Figure

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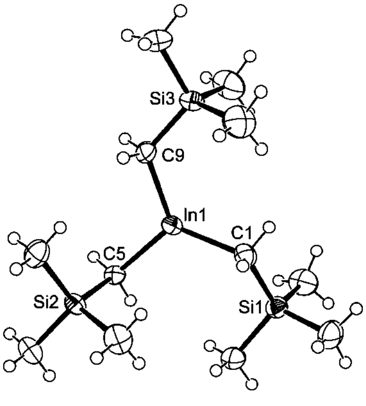


Figure 1. ORTEP view of [In(CH_2SiMe_3)$_3$] (**1**). Displacement ellipsoids are drawn at the 50% probability level. Selected bond angles (Å) and angles (deg): In1−C1 2.171(8), In1−C5 2.189(7), In1−C9 2.175(8), C1−Si1 1.850(8), C5−Si2 1.870(7), C9−Si3 1.843(8); C1−In1−C5 119.9(3), C5−In1−C9 116.2(3), C9−In1−C1 119.9(3), In1−C1−Si1 124.6(4), In1−C5−Si2 110.7(3), In1−C9−Si3 121.3(4).

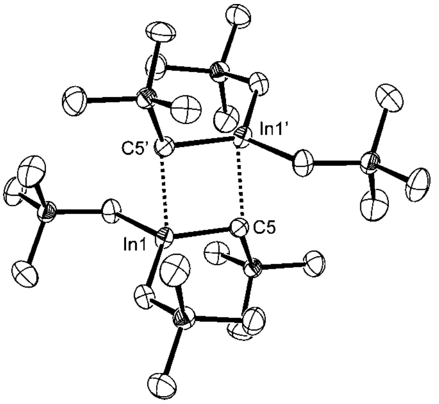
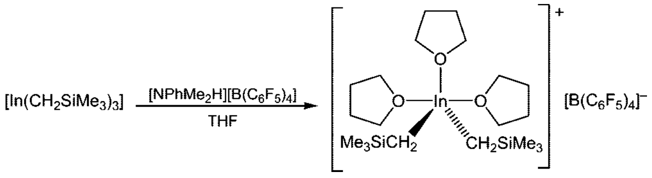


Figure 2. ORTEP view of [In(CH_2SiMe_3)$_3$] (**1**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): In1···In1′ 3.6668(14), In1−C5 2.189(7), In1···C5′ 3.082(7); In1−C5−In1′ 86.4(2), C5−In1−C5′ 93.6(2). Primed atoms are related to unprimed atoms by the symmetry operation 1−*x*, 1−*y*, 1−*z*.

1). In contrast to the perfect trigonal-planar geometry observed in [InMes$_3$] (Σ_{C-In-C} = 359.9°),[7] the sum of the angles around the indium center in **1** (Σ_{C-In-C} = 356.0°) presents a slight deviation from planarity. Thus, the central atom is found 0.2527(6) Å above the plane subtended by the carbon atoms C1, C5, and C9. Similarly, the indium center in [In{CH(SiMe$_3$)$_2$}$_3$] is found 0.191 Å above the plane defined by the three carbon atoms directly bound to the metal (Σ_{C-In-C} = 357.9°).[11] In **1**, a weak interaction of each indium atom with a carbon atom of a neighboring molecule [In1···C5′ = 3.082(7) Å] in the solid state leads to formation of a dimeric structure (Figure 2). This short interaction represents the only contact involving interatomic distances significantly shorter than the sum of the van der Waals radii.[14] The dimeric nature of **1** is reminiscent of that of its aluminum congener [Al(CH_2SiMe_3)$_3$], where the metal is situated 0.4748(6) Å above the C1−C2−C3 plane (Σ_{C-Al-C} = 343.3°).[4] The deviation from planarity in **1** is however less pronounced. Conversely, the boron and gallium analogues were found to be monomeric in the solid state.[4]

Scheme 1



The In−C bond lengths in **1** ranging from 2.171(8) and 2.189(7) Å fall into the range of values observed in earlier studies about the solid state structures of tri(alkyl) indium compounds.[7,11,15−19] As a result of the steric congestion induced by the close contact between both molecules, the In−C5−Si2 angle (110.7(3)°) is significantly smaller compared to In−C1−Si1 (124.6(4)°) and In−C9−Si3 (121.3(4)°). The bond of the alkyl group that shows a close interaction with the neighboring molecule is slightly elongated (In1−C5 = 2.189(7) Å). Similarly, the C5−Si2 bond (1.870(7) Å) is slightly elongated (cf. C1−Si1 1.850(8) Å and C9−Si3 1.843(8) Å), although the significance of this comparison is limited by the rather high standard uncertainties.

Since cationic dialkyl complexes of the inherently Lewis acidic group 3 and 13 metals are of interest,[12,20] we have studied the formation of the monocationic derivative of **1**. Only few cationic diorganoindium complexes have been reported so far.[21−23] The reaction of **1** with the strong Brønsted acid [NPhMe$_2$H][B(C$_6$F$_5$)$_4$] in THF gave the bis(trimethylsilylmethyl)indium(III) cation by protonolysis of one alkyl group and abstraction of tetramethylsilane (Scheme 1). Weaker acids such as [NEt$_3$H][B(C$_6$F$_5$)$_3$] failed to protonolyze **1**.

The cationic complex **2** was isolated as colorless, thermally robust crystals soluble in benzene. Variable-temperature ^{1}H NMR spectra suggest labile THF ligands. The charge-separated

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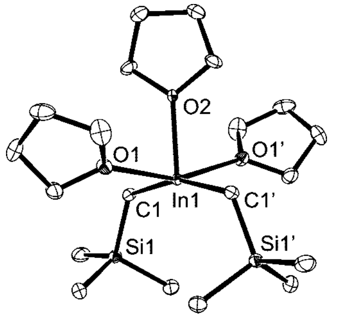

Figure 3. ORTEP view of the cationic part of one of the two independent ion pairs in [In(CH_2SiMe_3)$_2$(THF)$_3$][B(C_6F_5)$_4$] (**2**). Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): In1−C1 2.136(11), In1−O1 2.425(7); C1−In1−C1′ 159.0(6), C1−In1−O2 100.5(3), O1−In1−O1′ 158.3(4), O1−In1−O2 79.15(18).

Table 2. Selected Indium−Carbon Distances in Ionic Organoindium Compounds

compound	In−C (Å)	ref
[In(^{i}Pr)$_2$(THF)$_2$][BF_4]	2.128(6)	21a
[In(Mes)$_2$][BF_4]	2.130(10)	21b
[In(CH_2SiMe_3)$_2$(THF)$_3$][B(C_6F_5)$_4$] (**2**)	2.136(11), 2.133(10)	this work
[K][$InMe_4$]	2.239(3)	22
[K][In(CH_2SiMe_3)$_4$]	2.236(4), 2.234(4), 2.235(4), 2.251(4)	24

ion pair crystallized in the monoclinic space group *P*2/*c* (No. 13) with the indium center as well as the oxygen atom O2 on a crystallographic C_2 axis and two independent molecular cations within the unit cell (Figure 3). The indium atom is coordinated to two σ-bound alkyl groups and three oxygen atoms of the THF molecules in a square-pyramidal geometry, in which the O2 oxygen atom occupies the axial position. Selected In−C bond lengths of ionic indium(III) complexes are compiled in Table 2. The values of 2.230(3)−2.239(3) Å in tetrahedral indates are ca. 0.1 Å larger than in the cationic indium organyls with distances of 2.13 Å, which is attributed to the positive charge on the metal atom. The apical THF ligands in **2** are stronger coordinated than the basal THF ligands. As expected, the cationic complexes show shorter In−C bond lengths.

The In−O bond lengths to the basal THF ligands in **2** (2.425(7) and 2.458(7) Å) are ca. 0.2 Å longer than the equatorial THF ligands in the octahedral [$InCl_3$(THF)$_3$] complex (2.235(10) and 2.223(11) Å).[10] The distances to the apical THF ligands in **2** (2.223(12) and 2.253(10) Å) are similar to the bond length of indium to the axial THF ligand (2.304(9) Å) in [$InCl_3$(THF)$_3$].[10]

In summary, we have structurally characterized the parent neutral tris(trimethylsilylmethyl)indium [In(CH_2SiMe_3)$_3$] (**1**) along with the bis(trimethylsilylmethyl) cation [In(CH_2SiMe_3)$_2$(THF)$_3$][B(C_6F_5)$_4$] (**2**) and illustrated the tendency to higher coordination number for the trivalent indium center. This is in agreement with previously studied organoindium cations stabilized by noncoordinating anions.[23]

Table 3. Crystal Data and Convergence Results for [In(CH_2SiMe_3)$_3$] (1) and [In(CH_2SiMe_3)$_2$(THF)$_3$][B(C_6F_5)$_4$] (2)

	1	2
empirical formula	$C_{12}H_{33}InSi_3$	$C_{20}H_{46}InO_3Si_2$,$C_{24}BF_{20}$
M_r (g mol^{-1})	376.47	1184.62
cryst size (mm)	0.5 × 0.3 × 0.3	0.43 × 0.34 × 0.23
cryst color and habit	colorless rod	colorless block
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2/c$
a (Å)	10.353(3)	25.692(3)
b (Å)	10.358(3)	10.8489(13)
c (Å)	10.386(2)	18.007(2)
α (deg)	74.22(2)	
β (deg)	77.787(19)	104.287(2)
γ (deg)	67.66(2)	
V (Å^3)	984.0(4)	4863.9(10)
Z	2	4
D_{calc} (g·cm^{-3})	1.271	1.618
T (K)	213(2)	130(2)
μ(Mo Kα) (mm^{-1})	1.366	0.651
F(000)	392	2384
θ range (deg)	2.05−26.01	0.82−22.76
no. of reflns collected	8000	40 604
no. of reflns obsd [$I > 2\sigma(I)$]	2828	5867
no. of indep reflns (R_{int})	3855 (0.0841)	6560 (0.0638)
no. of data/restraints/params	3855/0/154	6560/0/648
goodness-of-fit on F^2	1.077	1.191
R_1, wR_2 [$I > 2\sigma(I)$]	0.0634, 0.1311	0.0812, 0.2065
R_1, wR_2 (all data)	0.0970, 0.1384	0.0876, 0.2094
largest diff in peak and hole (e·Å^{-3})	0.986 and −0.836	2.403 and −1.618

Experimental Section

General Considerations. All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. THF and pentane were distilled from sodium benzophenone ketyl and sodium benzophenone ketyl triglyme, respectively. Deuterated THF and toluene were dried over sodium, distilled, and degassed prior to use; deuterated dichloromethane was dried over CaH_2, distilled, and degassed prior to use. Anhydrous $InCl_3$ (ABCR) and [$NPhMe_2H$][B(C_6F_5)$_4$] (Boulder Scientific) were used as received. All other chemicals were commercially available and used after appropriate purification. NMR spectra were recorded on a Bruker DRX 400 spectrometer (^{1}H 400.1 MHz, ^{13}C 100.6 MHz) or on a Varian Unity 500 spectrometer (^{1}H, 499.6 MHz; ^{13}C, 125.6 MHz; ^{11}B, 160.3 MHz; ^{19}F, 376.4 MHz) at room temperature unless otherwise stated. All chemical shifts are given in ppm. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported relative to $SiMe_4$. ^{11}B NMR spectra were referenced externally to a 1 M solution of $NaBH_4$ in D_2O. ^{19}F NMR spectra were referenced externally to neat $CFCl_3$.

[In(CH_2SiMe_3)$_3$] (1). This compound was synthesized according to the published procedure[13] and isolated as a colorless liquid in 74% yield; mp −42 °C. ^{1}H NMR (CD_2Cl_2): δ −0.37 (s, 3 × 2 H, InCH_2), 0.01 (s, 3 × 9 H, Si(CH_3)$_3$). ^{1}H NMR (200 MHz, THF-d_8): δ −0.50 (s, 3 × 2 H, InCH_2), 0.01 (s, 3 × 9 H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 2.47 (Si(CH$_3$)$_3$), 10.79 (InCH$_2$).

[In(CH_2SiMe_3)$_2$(THF)$_3$][B(C_6F_5)$_4$] (2). To a solution of [In(CH_2SiMe_3)$_3$] (200 mg, 512 μmol) in 3 mL of THF was added a solution of [$NPhMe_2H$][B(C_6F_5)$_4$] (416 mg, 512 μmol) in 3 mL of THF, and the mixture was stirred at 60 °C for 17 h. After removing the solvent *in vacuo*, the white precipitate was repeatedly washed with pentane and dried under reduced pressure to give 550 mg (503 μmol) of a colorless solid; yield 95%; mp 157−158 °C. Crystals were grown from a THF/pentane solution at −30 °C within one week. ^{1}H NMR (THF-d_8): δ 0.14 (s, 2 × 9 H, Si(CH_3)$_3$), 0.15 (s, 2 × 2 H, InCH_2), 1.78 (m, 2 × 4 H, β-THF), 3.62 (m, 2 × 4 H, α-THF). ^{13}C{^{1}H} NMR (THF-d_8): δ 0.0 (InCH$_2$SiCH$_3$), 3.7 (InCH$_2$SiCH$_3$), 23.1 (β-THF), 65.1 (α-THF), 126.6 (br, Ph-1), 134.4 (d, $^1J_{CF}$ = 230 Hz, Ph-4), 135.9 (Ph-3), 147.1 (d, $^1J_{CF}$ = 264 Hz, Ph-2). ^{11}B{^{1}H} NMR (THF-d_8): δ −16.6. ^{19}F NMR (THF-d_8): δ −168.8, −165.1, −132.8. ^{1}H NMR (toluene-d_8, −60 °C): δ −0.47 (s, 2 × 2 H, InCH_2), −0.02 (s, 2 × 9 H, Si(CH_3)$_2$), 1.29 (br, 3 × 4 H, β-THF), 3.31 (br, 3 × 4 H, α-THF). ^{1}H NMR (toluene-d_8, 60 °C): δ −0.23 (s, 2 × 2 H, InCH_2), −0.08 (s, 2 × 9 H, (SiCH_3)$_2$), 1.40 (m, 3 × 4 H, β-THF), 3.36 (m, 3 × 4 H, α-THF). Anal. Calcd for $C_{44}H_{46}BF_{20}InO_3Si_2$: C, 44.61; H, 3.91; In 9.69. Found: C, 44.69; H, 3.88; In, 9.49.

Crystal Structure Determination of 1 and 2. In view of the low melting point, a single crystal of compound **1** was directly grown on a NONIUS CAD4 diffractometer. A capillary containing ca. 2 μL of the compound was exposed in appropriate geometry ($\chi = 90°$) to a cold stream of N_2; the sample completely solidified. The temperature of the gas stream was gradually increased to the melting point, retaining only a small fraction of solid in the tip of the capillary. Slow cooling resulted in a crystalline sample. The procedure was repeated until a single crystal of satisfactory quality was obtained; its diffraction pattern was directly registered on the CAD4 diffractometer. X-ray diffraction measurement of **2** was performed on a Bruker AXS diffractometer. Due to the low crystal quality and the resulting low diffraction intensities at higher θ angles, the measurement of **2** was performed only up to a maximum θ value of 22.8°. Crystal data and convergence results are given in Table 3. Intensity data for **2** were corrected for absorption by the multiscan method as implemented in PLATON.[25] The structures were solved by direct methods and refined against all F^2 data.[26] Hydrogen atoms were treated as riding in idealized geometry. For the graphical representation, the program ORTEP was used as implemented in the program system WinGX.[27] The data for CCDC reference numbers 690488 (**1**) and 690487 (**2**) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: Crystallographic data for **1** and **2** as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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