$In_3I_2[C(SiMe_3)_3]_3$: Synthesis of a Diiodotrialkyltriindane(5) Containing Two In−In Single Bonds

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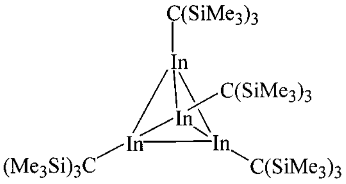
*Summary: Treatment of the tetrahedral indium(I) cluster compound $In_4[C(SiMe_3)_3]_4$ (**1**) with a mixture of AlI_3 and I_2 afforded the yellow diiodotriindium compound $In_3I_2[C(SiMe_3)_3]_3$ (**2**) in 73% yield. **1** contains a chain of three indium atoms connected by In−In single bonds. A trigonal bipyramidal structure resulted in the solid state by two iodide bridges between the terminal indium atoms.*

Introduction

The synthesis of organoelement cluster compounds of the heavier elements of the third main group has been of considerable interest in the past decade.[1,2] Besides their fascinating structures and bonding, these compounds are of particular importance owing to their singular chemical properties.[2] Our efforts have been focused on the investigation of the reactivity of the tetrahedral cluster compounds $E_4[C(SiMe_3)_3]_4$ (E = Ga, In (**1**)), which are readily prepared by the reduction of the corresponding alkyltrichlorogallate with Rieke magnesium[3] or by the reaction of indium(I) bromide with $LiC(SiMe_3)_3 \cdot 2THF$.[4,5] The monomeric fragments of these clusters (E−R) are isolobal with carbon monoxide, and we synthesized many derivatives analogous to transition metal carbonyl complexes. The compounds $M[EC(SiMe_3)_3]_4$ (E = Ga, In; M = Ni, Pt),[6,7] which contain nickel and platinum atoms tetrahedrally coordinated by four E−R ligands, are of particular interest. Considerable π-back-bonding of electron density from filled transition metal orbitals to the vacant p-orbitals of the unsaturated gallium or indium atoms was verified by quantum-chemical calculations.[7,8] Reactions of chalcogens with these group 13 tetrahedrans gave heterocubane type structures,[2] and a remarkable product containing mixed-valent indium atoms was isolated with the sulfur compound $In_4S[C(SiMe_3)_3]_4$.[9] White phosphorus reacted with the tetragallium derivative to yield a Ga_3P_4 cage compound by the insertion of three Ga−R monomers into three P−P bonds.[10] Halogen derivatives of the clusters to date have not been prepared, and we were interested in synthesizing such compounds that retain the gallium or indium atoms in a low oxidation state. Such halogen derivatives may be useful in further development of group 13 cluster chemistry and may open a route to the synthesis of novel compounds with subvalent gallium and indium atoms by salt elimination.

Chart 1



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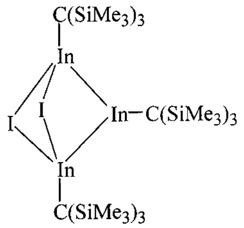

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Results and Discussion

To obtain an iodine derivative of the indium cluster, we treated **1** with equivalent quantities of elemental iodine. But in no case did we succeed in isolating any pure product. Instead mixtures of unknown products together with the starting compound **1** were formed. 1,2-Diiodoethane, a mild halogenation reagent, gave an inseparable mixture of **1** together with an unknown

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product upon reaction in a stoichiometric 1 to 1 ratio in toluene at 60 °C. An excess of 1,2-diiodoethane resulted in the formation of a mixture of unknown products, none of which could be purified by recrystallization. We believe that the reaction with pure iodine failed because the strongly oxidizing halogen molecule may not only attack the $\mathrm{In_4}$ cluster in a nonspecific way but also cleave In−C bonds. Therefore, we hoped to observe a more specific reaction when we employed an $\mathrm{AlI_3/I_2}$ mixture as the iodine source. The aluminum component polarizes the iodine molecules, possibly by forming an intermediate complex $[\mathrm{I_3AlI^{\delta-}\cdots I^{\delta+}}]$,[11] and the iodine atom that bears a partial positive charge may react preferably at the electron-rich cluster center of the molecule. Indeed, we observed a clean reaction with almost quantitative formation of only one product which showed two resonances of trimethylsilyl groups in the ^{1}H NMR spectrum in an intensity ratio of 2 to 1. The product (**2**) was crystallized from toluene to give yellow crystals in 73% yield. Compound **2** is thermally quite stable in the solid state and decomposes only at 200 °C with the formation of elemental indium. It is only marginally stable in solution; indium powder precipitates when it is stored in benzene or cyclohexane at room temperature after about 1 h, forming several new products, none of which could be isolated in pure form. Owing to this instability, the NMR spectroscopic characterization of **2** remained incomplete. The inner carbon atoms attached to indium, which, owing to the quadrupole moment of the indium atoms, usually give very broad signals, could not be detected unambiguously in the ^{13}C NMR spectrum of **2**.

Elemental indium precipitated in the course of that reaction, and $\mathrm{H{-}C(SiMe_3)_3}$ was detected by an ^{1}H NMR spectrum of the crude product. Owing to the integration of the spectrum, a 2 to 1 molar ratio resulted between the product **2** and the alkane derivative. That alkane is known as a decomposition product of the cluster and may be formed via a radical intermediate after cleavage of an In−C bond and the reaction of the radical with the solvent, for instance. Interestingly, $\mathrm{AlI_3}$ alone gave the same product (**2**) upon treatment with **1**; however, owing to unknown impurities, we did not succeed in isolating the pure compound.

The molecular structure of **2** (Figure 1) comprises a short, nonlinear chain of three indium atoms which are connected by In−In single bonds. Each indium atom is bonded to one $\mathrm{C(SiMe_3)_3}$ substituent, and the terminal indium atoms also are attached to iodine atoms. The iodine atoms bridge the terminal indium atoms, and a trigonal bipyramidal cage structure results that has both iodine atoms and one indium atom (In(2)) in the equatorial plane and the remaining indium atoms (In(1) and In(3)) in the apical positions. Thus, In1 and In3 are coordinatively saturated with coordination number 4, while In2 is attached only to three atoms (In1, In3, C2) in an almost ideal planar coordination geometry (sum of the angles = 359.7°). A diphosphorus-trigallium compound of similar structure with a chain of three gallium atoms has been reported. However, it, surprisingly, has a strongly asymmetric, poorly understood structure with one very long Ga−Ga distance.[12] A chain of three gallium atoms in a noncage structure was observed for a trigallium pentaiodide in which all gallium atoms are coordinatively saturated by the coordination of triethylphosphane ligands.[13] The In−In bond lengths (2.814 Å on average) of **2** are shorter than the In−In distances of the cluster compound **1** (3.002 Å),[4] which has a multicenter bonding situation. They are in the normal range of In−In single bonds observed for tetraalkyldiindium derivatives, $\mathrm{R_2In{-}InR_2}$.[14,15] Shorter ones were observed in the remarkable triangular triindium compound $\mathrm{In(InR_2)_3}$ (R = 2,4,6-$i\mathrm{Pr_3C_6H_2}$).[15] The In−I separations deviate only slightly from the average value of 3.008 Å. They are similar to those in other symmetrically bridged dimetallic species.[16] Despite the different coordination geometries and oxidation states (+1 at In2, +2 at In1 and In3) of the indium atoms, the In−C bond lengths are almost indistinguishable (2.221 Å on average). A similarly long In−C distance was observed in the starting indium(I)

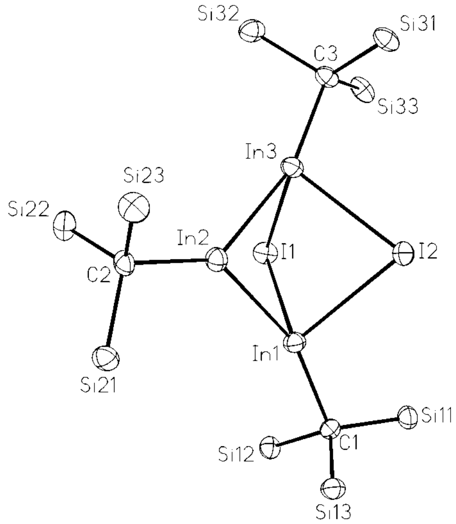

Figure 1. Molecular structure of **2**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups are omitted for clarity. Important bond lengths (Å) and angles (deg): In(1)−In(2) 2.8099(4), In(2)−In(3) 2.8186(4), In(1)−I(1) 2.9880(4), In(1)−I(2) 3.0218(4), In(3)−I(1) 3.0189(4), In(3)−I(2) 3.0034(4), In(1)−C(1) 2.218(4), In(2)−C(2) 2.225(4), In(3)−C(3) 2.220(4), In(1)−In(2)−In(3) 82.44(1), In(1)−I(1)−In(3) 76.26(1), In(1)−I(2)−In(3) 75.98(1).

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compound **1** (2.25 Å)[4] and in an adduct of the tetraalkyldiindium(II) compound $R_2In{-}InR_2$ (R = $CH(SiMe_3)_2$), in which one indium atom was tetracoordinated by the addition of an ethynyl ligand (In−C 2.26 Å).[17] The intramolecular contact distances between indium and iodine atoms (In1⋯In3 3.709 Å, In2⋯I1, I2 3.859 Å on average, I1⋯I2 4.178 Å) are similar to the sum of the van der Waals radii (3.80, ~3.90, and ~4.00 Å)[18] and confirm a localized bonding situation. Owing to the steric interaction between the bulky alkyl substituents, the apical In−C bonds are tilted toward the iodine bridges.

Experimental Section

All procedures were carried out under purified argon. *n*-Hexane was dried over $LiAlH_4$, and toluene over Na/benzophenone. $In_4[C(SiMe_3)_3]_4$ (**1**) was obtained according to a literature procedure.[4] AlI_3 and I_2 were freshly sublimed prior to use.

Synthesis of Compound 2. A solution of 0.113 g (0.445 mmol) of I_2 in 60 mL of *n*-hexane was added dropwise to a suspension of 0.182 g (0.445 mmol) of AlI_3 in 25 mL of *n*-hexane at room temperature. The mixture was stirred for 40 min, and a solution of 0.617 g (0.445 mmol) of $In_4[C(SiMe_3)_3]_4$ (**1**) in 50 mL of *n*-hexane then was added. After 5 min at room temperature the mixture was heated at 80 °C in a prewarmed oil bath for 10 min. A solid with gray metallic and colorless particles precipitated. After filtration the yellow solution was evaporated at reduced pressure, and the oily residue was crystallized from toluene (20/−70 °C) to yield yellow crystals of **2**. Yield: 0.420 g (73% based on I_2). **2** was obtained free of toluene after thorough evacuation of the solid product; it is only moderately stable in solution. Decomposition (toluene free product, argon, sealed capillary): 200 °C. Anal. Calcd for $C_{30}H_{81}Si_9In_3I_2$ (1293.0): C, 27.9; H, 6.3. Found: C, 28.2; H, 6.3. ^1H NMR (C_6D_6, 200 MHz): δ 0.50 (54 H, s, $SiMe_3$ of terminal In atoms), 0.31 (27 H, s, $SiMe_3$ of bridging In atom). ^1H NMR (C_6D_{12}, 200 MHz): δ 0.37 (54 H, s, $SiMe_3$ of terminal In atoms), 0.31 (27 H, s, $SiMe_3$ of bridging In atom). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 6.5 ($SiMe_3$ of the bridging In atom), 6.1 ($SiMe_3$ of the terminal In atoms); InC not detected owing to the instability with time of **2** in solution. IR (CsBr plates, paraffin, cm^{-1}): 1300 w, 1252 s δCH_3; 1175 vw, 1156 vw, 1078 vw, 1008 vw; 858 vs, 840 vs, 774 w, 722 m $\rho CH_3(Si)$; 675 w, 648 w $\nu_{as}SiC$; 615 vw ν_sSiC; 590 w νInC; 375 vw, 318 vw δSiC. UV/vis (*n*-hexane): λ_{max} (nm) (log ϵ) 225 (3.4), 304 (2.9).

Crystal Structure Determination of 2·Toluene. Single crystals of **2**·toluene were obtained on cooling of a saturated solution in toluene to −20 °C; the crystals include one molecule of toluene in each formula unit of **2**. The crystallographic data were collected with a STOE IPDS diffractometer. $C_{37}H_{89}I_2In_3Si_9$: monoclinic, $P2_1$, no. 4,[19] Flack parameter −0.008(13), $Z = 2$, temperature 193(2) K, $D_{calcd} = 1.534$ g/cm^3, $a = 9.1269(5)$ Å, $b = 24.8574(10)$ Å, $c = 13.5416(8)$ Å, $\beta = 102.491(5)°$, $V = 2999.5(3) \times 10^{-30}$ m^3, $\mu = 2.375$ mm^{-1}, numerical absorption correction, crystal dimensions 0.27 × 0.24 × 0.045 mm, radiation Mo Kα, graphite monochromator, 2θ range $3.2° \le 2\theta \le 51.7°$, index ranges $-11 \le h \le 11$, $-30 \le k \le 30$, $-16 \le l \le 15$; number of unique reflections 11 505; number of parameters 501. The structure was solved by direct methods and refined with the program SHELXL-97[20] by a full-matrix least-squares method based on F^2. R1 (10 721 reflections $I > 2\sigma(I)$) = 0.0238; wR2 (all data) = 0.0701; max./min. residual electron density = 1.57/−0.37 × 10^{30} e/m^3. The $C(SiMe_3)_3$ group of the inner indium atom In2 is slightly disordered; the silicon atoms were refined on split positions with occupation factors of 0.88 and 0.12.

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Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and all bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org. Further details of the crystal structure determination are available from the Cambridge Crystallographic Data Center on quoting the depository number CCDC-160148.

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