Alkylindium Subhalides Derived from the Tetrahedral Indium(I) Cluster Compound $[In_4\{C(SiMe_3)_3\}_4]$

Werner Uhl* and Sandra Melle[a]

Abstract: Partial oxidation of the tetraalkyltetraindium(I) compound $[In_4\{C(SiMe_3)_3\}_4]$ **1** with halogen donors such as 1,2-dibromoethane and hexachloroethane or with mixtures of bromine and aluminum tribromide afforded novel alkylindium halides in which the indium atoms still possess unusually low oxidation states. Indium–indium single bonds between bivalent indium atoms were found in the compounds $In_2X_2R_2$ ($R = C(SiMe_3)_3$, $X = Cl$ (**2**) or Br (**4**)), which gave dimers in the solid state with all four halogen atoms in a bridging position. The tetrahedral arrangement of four indium atoms in a cluster was retained in the compound $In_4Br_2R_4$ (**3**), in which one bromine atom occupied a μ_3-bridging position above one triangular face of the In_4 tetrahedron. One edge of that triangle was bridged by the second bromine atom. Mixed-valent indium atoms resulted with an average oxidation state of +1.5.

Keywords: cluster compounds · halides · indium · low-valent compounds

Introduction

The tetrahedral tetraindium(I) compound $In_4[C(SiMe_3)_3]_4$ **1** is readily available by the reaction of indium monobromide with tris(trimethylsilyl)methyllithium.[1, 2] Compound **1** exhibits a distinctive chemical reactivity, and many secondary, unprecedented products were isolated and characterized.[3] Two different types of reactions occurred in principle, in which either only the monomeric fragments of the cluster InR were trapped or in which the indium atoms still retained their overall tetrahedral arrangement. The monomer of the cluster (InR) is isolobal to carbon monoxide, and several transition metal carbonyl analogous compounds were obtained with bridging or terminal InR ligands. Among these the tetracarbonylnickel analogues $Ni[InC(SiMe_3)_3]_4$[4] and $Pt[InC(SiMe_3)_3]_4$[5] are of particular interest, because considerable π-back bonding of electron density from the central metal atoms into the empty p orbitals of the indium atoms was verified by quantum-chemical calculations.[6] Furthermore, these monomeric InR fragments were trapped by cycloaddition reactions.[7] Heterocubane-type structures containing four indium atoms in a tetrahedral arrangement were obtained by the complete oxidation of the In_4 cluster with oxygen,[8] sulfur,[9] selenium,[1] or tellurium.[9] Partial oxidation by the careful treatment of **1** with the sulfur atom donor propylene sulfide yielded the remarkable mixed-valent compound $[In_4S\{C(SiMe_3)_3\}_4]$,[10] in which only one face of the In_4 tetrahedron of **1** is bridged by a sulfur atom. Despite this now well-known and fascinating reactivity pattern of **1**, no information existed concerning the reactivity of **1** towards halogens. Such reactions are of particular interest, because in the case of partial oxidation of the indium atoms products would result which are extremely useful for secondary reactions and for the facile generation of cluster derivatives containing indium atoms in an unusually low-oxidation state by salt elimination, for instance. However, treatment of **1** with the free halogens bromine or iodine gave mixtures of several unknown products regardless of the molar ratio of the starting materials. We report here on the synthesis of the first chlorine and bromine derivatives of **1**. A corresponding iodine compound $[In_3I_2\{C(SiMe_3)_3\}_3]$, which contains a chain of three indium atoms connected by In–In single bonds, was described only recently by our group in a preliminary communication.[11]

Results and Discussion

Reaction of 1 with hexachloroethane: synthesis of a dichlorodiindium compound containing bivalent indium atoms: As a mild chlorination agent we employed hexachloroethane, which has been used by several groups, for example, for the oxidation of phosphorus compounds.[12] Equivalent quantities of **1** and C_2Cl_6 were heated in toluene for 25 min to 65 °C to completely consume the tetraindium(I) compound. The color of the solution changed from the deep violet color of **1** to pale yellow, and a small amount of elemental indium precipitated. The product (**2**) was isolated after recrystallization from

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[a] Prof. Dr. W. Uhl, Dr. S. Melle
Fachbereich Chemie der Philipps Universität
Hans-Meerwein-Strasse, 35032 Marburg (Germany)
Fax: (+49) 6421-2825653
E-mail: uhl@chemie.uni-marburg.de

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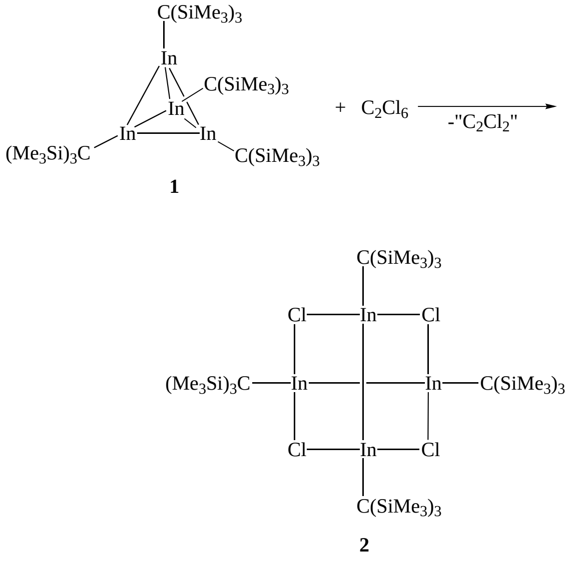
pentafluorobenzene as yellow crystals in 49% yield [Eq. (1)]. Compound **2** is unstable in benzene and decomposes slowly at room temperature to give at least two new secondary products of unknown constitution. The mixture obtained could not be separated by recrystallization. Owing to the instability of **2** in solution the NMR spectroscopic characterization was difficult, and no resonance could be assigned to the inner carbon atoms attached to indium. In contrast, **2** is quite stable in the solid state and decomposes only at 183 °C by the formation of elemental indium. Crystals of **2** are stable at 0 °C for several months.



(1)

The constitution of **2** was clarified by an X-ray crystal structure determination (Figure 1). Four chlorine atoms of hexachloroethane were transferred to **1**, and the indium atoms were oxidized from $+1$ in **1** to $+2$. Formally, dichloroethyne should be a by-product of that reaction, which, however, is quite unstable and may be consumed here by unknown secondary reactions. As expected for compounds with bivalent indium atoms,[13] **2** possesses two In–In single bonds which are arranged perpendicular to one another. The molecular structure of **2** may be derived from that of **1**. Four edges of the In$_4$ tetrahedron of **1** are occupied by chlorine atoms, while two opposite edges become localized In–In single bonds. Compound **2** may further be described as a dimeric dialkyldiindium dichloride, and thus it is the first known organoelement diindane derivative with functional halogeno substituents. A similar digallium compound, [{Ga$_2$Cl$_2$[Si(SiMe$_3$)$_3$]$_2$}$_2$], was obtained by another route and has been reported recently.[14] The In–In distances in **2** (In1–In2 282.1, In3–In4 282.6 pm) are shortened compared to the multicenter In–In interactions in **1** (300.2 pm)[1] and correspond well to the average value usually observed for tetralkyl- or tetraaryldiindane(4) derivatives (R$_2$In–InR$_2$) possessing In–In single bonds.[13] Shorter In–In bonds were reported for inorganic diindium derivatives with electronegative halogeno or chalcogeno substituents.[15] As expected, the intramolecular In–In distances of the chlorine-bridged In$_2$ couples are significantly longer (av 413.5 pm, sum of van der Waals radii 380 pm[16]). Similarly, the intramolecular Cl···Cl distances (367.4 pm) correspond to the sum of the van der Waals radii (340 to 380 pm).[16] Many organoelement compounds bearing In-Cl-In bridges have been described,[17, 18] the In–Cl bond lengths observed for **2** (259.1 to 265.3 pm) are in the normal range. As observed in most secondary products of **1**, the In–C bond lengths are a little shorter than those of the cluster compound **1** (221 compared to 225 pm of **1**). This may be caused by the enhancement of the oxidation state of the central indium atoms. The In-In-C groups approach linearity (angle In-In-C 147.6 to 150.4°), probably owing to the steric repulsion between the bulky tris(trimethylsilyl)methyl substituents, while the Cl-In-Cl angles are close to 90° on average. An almost ideally eclipsed conformation across the In–In bonds is observed with torsion angles C-In-In-C of 3.7 and −8.7° only.

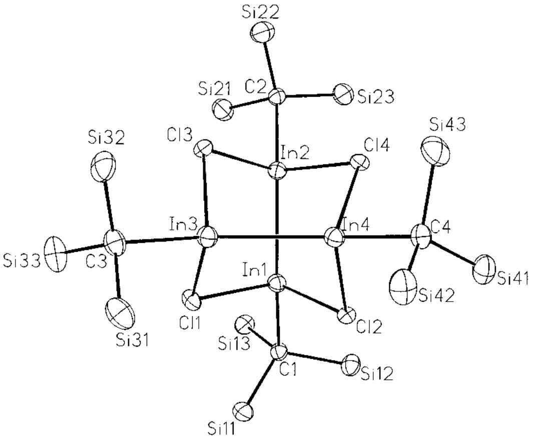
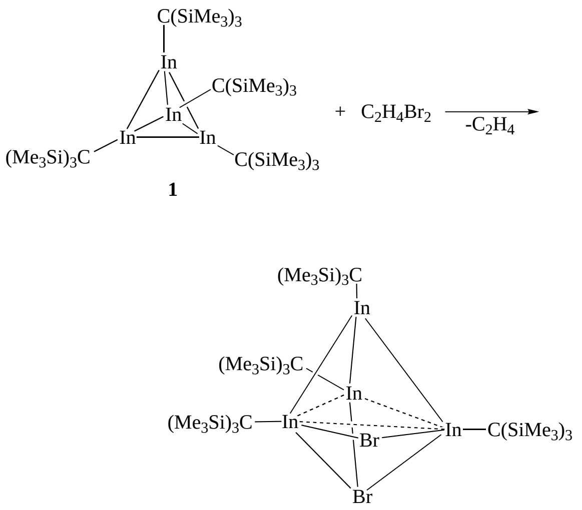


Figure 1. Molecular structure of compound **2** (the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity). Selected bond lengths [pm] and angles [°]: In1–In2 282.09(7), In3–In4 282.56(7), In1–C1 221.7(7), In1–Cl1 259.5(2), In1–Cl2 265.3(2), In2–C2 221.1(7), In2–Cl3 264.0(2), In2–Cl4 259.6(2), In3–C3 222.1(7), In3–Cl1 261.3(2), In3–Cl3 259.1(2), In4–C4 220.7(7), In4–Cl2 260.0(2), In4–Cl4 264.0(2); Cl-In-Cl 89.2 (av), In-Cl-In 104.4 (av), In-In-C 148.7 (av), In-In-Cl (two differing angles each indium atom) 95.7 and 102.5 (av).

Reaction of 1 with dibromoethane: synthesis of a dibromotetraindium compound with mixed-valent indium atoms: In contrast to the chlorination reaction described above only two bromine atoms were transferred upon treatment of the tetraindium compound **1** with 1,2-dibromoethane. The reaction proceeds in hot toluene (60 °C) under similar conditions as given above. The deep violet color of **1** began to disappear after about 10 min, and **1** was completely consumed after a short period of only 20 min [Eq. (2)]. An orange solution was obtained. The partial decomposition of **1** or of the product **3** led to the precipitation of a considerable quantity of elemental indium, and HC(SiMe$_3$)$_3$ was detected by ^{1}H NMR spectroscopy to be the only by-product of the reaction. Orange crystals of **3** were isolated in 33% yield after recrystallization from pentafluorobenzene. Solid **3** is stable up to 164 °C and decomposes above that temperature by the formation of elemental indium. It is much more unstable in solution, and elemental indium precipitated upon storing of solutions in benzene or toluene at room temperature. In



1

(2)

3

toluene, compound **1** was partially reformed (characteristic color and NMR spectroscopy).

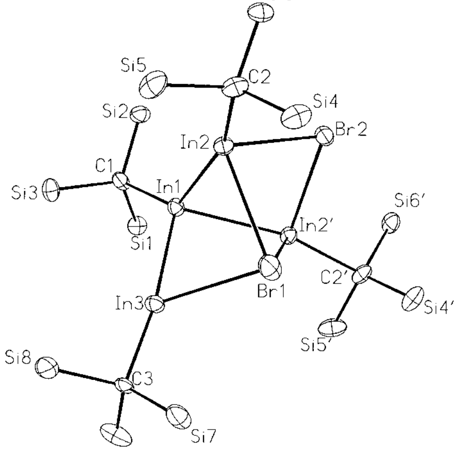


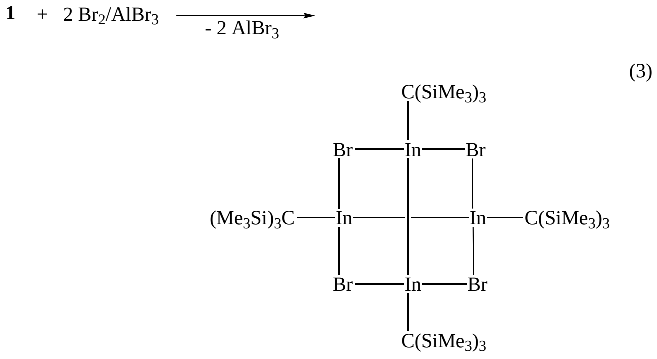
Figure 2. Molecular structure of compound **3** (the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity). Selected bond lengths [pm] and angles [°]: In1–In2 284.17(9), In1–In3 290.4(1), In1–C1 224(1), In2–C2 222.6(8), In3–C3 222(1), Br1–In2 303.6(1), Br1–In3 292.7(2), Br2–In2 278.0(1); In2-Br1-In3 86.15(3), In2-Br2-In2′ 81.08(4), In2-In1-In2′ 78.95(3), In2-In1-In3 90.29(3), In1-In2-Br1 77.87(3), In1-In2-Br2 91.33(3), In1-In3-Br1 78.70(4); In2′ generated by x, $-y+1/2$, z.

The unprecedented molecular structure of **3** is depicted in Figure 2. It may be derived from the In_4 tetrahedron of the starting compound **1**, one triangular face of which is bridged by a μ_3-bromine atom, while a second μ_2-bromine atom bridges one edge of that particular triangle. Compound **3** is a mixed-valent compound, and the average oxidation state of the indium atoms in **3** is +1.5. In this respect, **3** is similar to the monosulfur derivative $[In_4S\{C(SiMe_3)_3\}_4]$, which was mentioned above[10] and which has one sulfur atom bridging one face of the In_4 tetrahedron. The In–In distances of the bridged face of **3** (361 and 407 pm) are much longer than those of the starting compound **1** (300.2 pm) and are in the range of twice the van der Waals radius of indium (380 pm).[16] Thus, bonding interactions between these indium atoms seem to be negligible. The longest distance belongs to the bromine-bridged edge of the In_3 triangle. The fourth indium atom at the top of the cluster does not bond to a bromine atom. It has three short distances (284.2 and 290.4 pm) to the remaining indium atoms, which correspond to In–In single bonds.[13] Thus, the strength of In–In interactions in the cluster is dramatically changed by partial oxidation. Compound **1** has delocalized bonding with six almost equidistant In–In contacts. In contrast, three In–In distances in **3** are very long and out of the range of significant bonding interactions, while the remaining ones are shorter than in **1** and similar to the localized single bonds. This observation is in accordance with the three electron pairs in the cluster of **3** (four in the cluster of **1**). The distances of the μ_2-bridging bromine atom to indium (278.0 pm) are in accordance with standard values of organoelement compounds.[18, 19] The In–Br distances to the μ_3-bridging bromine atom are much longer (In3–Br1 292.7 pm; In2/In2′-Br1 303.6 pm). To the best of our knowledge, a comparable μ_3-situation has not been observed before in organoelement indium chemistry. The longest In–C bond length is observed to In1 at the top of the cluster, which formally has an oxidation number of +1 similar to **1**. However, the large standard deviation prevents a more detailed discussion about a possible and interesting correlation of In–C bond lengths and oxidation state of the indium atoms.

Based on the molecular structure of **3**, three chemically different $C(SiMe_3)_3$ substituents are expected; however, only one resonance signal for methyl groups was detected in the ^1H and ^{13}C NMR spectra. The proton resonance is broadened compared to the signal of **1**. The broadening increased upon cooling of toluene solutions to −80°C, but no splitting in clearly separated resonance signals was observed. A sharp signal was obtained at elevated temperatures. NMR experiments in $[D_{10}]$diethyl ether were not successful owing to the rapid decomposition of **3** in organic donor solvents. Usually, the chemical shifts of **1** and of its secondary products differ only slightly, and in most cases differences of less than 0.02 ppm were observed. These very narrow shifts possibly prevent the observation of dynamic processes by the splitting of resonance signals at low temperature.

Reaction of 1 with a bromine/aluminum tribromide mixture: Elemental bromine reacts with **1** leading to the formation of an inseparable mixture of at least four unknown products. Decomposition was an important side reaction; elemental indium precipitated and $HC(SiMe_3)_3$ was detected in considerable concentration. The alkane derivative was possibly formed by the cleavage of an In–C bond and the reaction of a radical intermediate with the solvent, for instance. Evidently, the attack of the bromine molecules on **1** proceeds unspecifically and may not only be directed towards the cluster center of the molecule, but may also lead to the cleavage of In–C bonds. We hoped to prevent these side reactions by polarizing the bromine molecule by the addition of $AlBr_3$.

Equimolar quantities of $AlBr_3$ and bromine were mixed in *n*-hexane at room temperature to yield a brown suspension, which was treated with the tetraindium compound **1** dissolved in the same solvent. In an optimized procedure the starting materials were employed in a 3:1 molar ratio with an excess of the oxidizing agent. The mixture was stirred for 40 min and heated to 80 °C for a further 15 min in a prewarmed oil bath to complete the reaction. A yellow-greenish suspension resulted which contained considerable quantities of elemental indium. After filtration and evaporation the crude product was recrystallized from pentafluorobenzene to give yellow crystals of **4** in 28 % yield [Eq. (3)].



(3)

4

Compound **4** crystallizes isotypic to the chloro compound **2** described above, and thus it has the same molecular structure with two In–In single bonds bridged by four μ_2-bromine atoms (Figure 3). The In–In bonds (284.8 and 284.2 pm) are slightly longer than those of **2**, but are still in the range usually observed for organoelement diindium derivatives (see above).[13] The In–Br distances (267.7 to 274.0 pm) are in the normal range for bridging bromine atoms.[18, 19] They are little shorter than those of the In_4Br_2 cluster compound **3** discussed before.

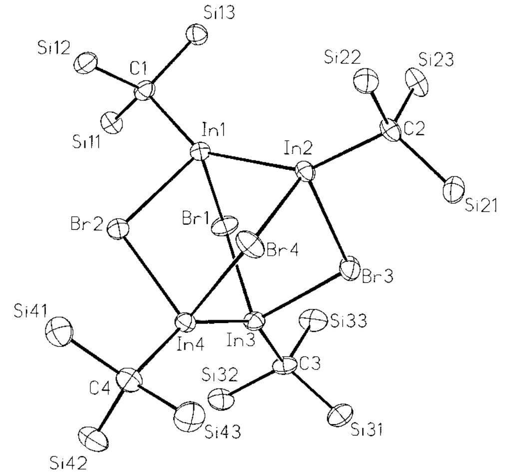


Figure 3. Molecular structure of compound **4** (the thermal ellipsoids are drawn at the 40 % probability level; methyl groups are omitted for clarity). Selected bond lengths [pm] and angles [°]: In1–In2 282.75(6), In3–In4 284.16(6), In1–C1 221.9(5), In1–Br1 268.14(7), In1–Br2 273.40(7), In2–C2 222.0(5), In2–Br3 272.15(7), In2–Br4 267.67(7), In3–C3 222.3(6), In3–Br1 271.94(7), In3–Br3 268.13(7), In4–C4 222.1(6), In4–Br2 268.37(7), In4–Br4 274.00(7); Br-In-Br 88.8 (av), In-Br-In 103.4 (av), In-In-C 147.7 (av), In-In-Cl (two differing angles each indium atom) 96.0 and 103.3 (av).

Compound **4** is stable in nonpolar solvents such as hexane or benzene, but decomposes in donor solvents such as THF. Owing to its low solubility in toluene or benzene the NMR spectroscopic characterization succeeded only with very dilute solutions, and the resonance signal of the inner carbon atoms attached to indium could not be detected in the ^{13}C NMR spectrum. For the same reason, we were not able to determine the molar mass and the degree of association in solution by cryoscopy. Two unknown by-products were formed and detected by ^{1}H NMR spectroscopy ($\delta = 0.43$ and 0.31). They could not be isolated in a pure form up to now. Treatment of **1** with $AlBr_3/Br_2$ in a 1:1 molar ratio afforded compound **4** as the main product, but it was isolated from that reaction with some difficulty in a very poor yield only. Compound **3** with the less oxidized In_4Br_2 cluster as a possible intermediate could not be identified by NMR spectroscopy. The reactions of the organic halogen donors hexachloroethane [Eq. (1)] and 1,2-dibromoethane [Eq. (2)] with the gallium analogue of **1**, $[Ga_4\{C(SiMe_3)_3\}_4]$,[20] were unsuccessful, and only inseparable mixtures of unknown components were formed. Owing to the particular importance of these halogeno derivatives of subvalent alkylindium or alkylgallium compounds for secondary reactions, we hope to synthesize the corresponding alkylgallium derivatives by employing AlX_3/X_2 mixtures according to the new method described in Equation (3). Investigations concerning the synthesis of such gallium compounds and the application of these novel reagents in salt elimination reactions are in progress.

Experimental Section

General: All procedures were carried out under purified argon in dried solvents (toluene over Na/benzophenone, *n*-hexane over $LiAlH_4$, pentafluorobenzene over molecular sieves). Compound **1** was obtained according to a literature procedure.[1] Commercially available hexachloroethane and aluminum tribromide were further purified by sublimation. 1,2-Dibromoethane was distilled and stored over molecular sieves.

Synthesis of $[\{In_2Cl_2R_2\}_2]$ (2): A solution of **1** (0.379 g, 0.274 mmol) in toluene (50 mL) was treated with a solution of hexachloroethane (0.065 g, 0.274 mmol) in toluene (15 mL). The deep violet solution was warmed to 65 °C for 25 min. The color changed to pale yellow, and elemental indium precipitated. After filtration the solvent was distilled off in vacuum, and the residue was thoroughly evacuated to 10^{-3} Torr. The remaining solid was extracted with warm (45 °C) pentafluorobenzene (15 mL) (if necessary, several times). Yellow crystals of the product $\mathbf{2} \cdot C_6F_5H$ were obtained upon cooling of the solutions to 0 °C. Yield: 0.228 g (49 %), m.p. (argon, sealed capillary): 183 °C (decomp); ^{1}H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 0.46$ (s, $SiMe_3$); ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): $\delta = 6.5$ ($SiMe_3$), InC not detected; IR (CsBr, paraffin): $\tilde{\nu}$ [cm^{-1}] = 1285 w, 1268 s, 1260 vs, 1251 vs δCH$_3$; 1178 w, 1137 vw pentafluorobenzene; 1072 m, 956 w, 942 w, 857 vs, 845 vs, 775 s, 719 w ρCH$_3$(Si); 673 s, 651 s ν_{as}SiC; 615 w ν_sSiC; 601 s, 566 w νInC; 360 vw, 312 vw δSiC; UV/vis (*n*-hexane): λ_{max} (log ε) = 240 (4.3), 295 nm (4.4); elemental analysis calcd (%) for $C_{40}H_{108}Si_{12}Cl_4In_4 \cdot C_6F_5H$ (1695.5): In 27.1, C 32.6, H 6.5; found: In 26.6, C 32.0, H 6.5.

Synthesis of $[In_4Br_2R_4]$ (3): A solution of **1** (0.332 g, 0.240 mmol) in toluene (40 mL) was added to 1,2-dibromoethane (0.045 g, 0.240 mmol). The solution was warmed to 60 °C for 20 min. The deep violet color of **1** changed to yellow-orange, and elemental indium precipitated. After filtration and

Table 1. Crystal data, data collection parameters, and structure refinement of compounds **2**, **3**, and **4**.[a]

	2	**3**	**4**
formula	$C_{46}H_{108}Cl_4F_5In_4Si_{12}$	$C_{58}H_{108}Br_2F_{15}In_4Si_{12}$	$C_{46}H_{108}Br_4F_5In_4Si_{12}$
crystal system	monoclinic	monoclinic	monoclinic
space group	$C2/c$; no. 15[21]	$P2_1/m$; no. 11[21]	$C2/c$; no. 15[21]
Z	8	2	8
temperature [°C]	-80	-80	-80
ρ_{calcd} [$g\,cm_{-}^{3}$]	1.425	1.578	1.556
a [pm]	2893.5(2)	1332.1(2)	2903.2(2)
b [pm]	1976.47(8)	1872.1(1)	1984.5(1)
c [pm]	2762.5(2)	1769.1(2)	2774.3(2)
β [°]	90.010(7)	102.42(2)	90.317(8)
V [$10^{-30}\,m^3$]	15799(2)	4308.6(8)	15984(2)
μ [mm^{-1}]	1.509	1.578	3.358
crystal size [mm]	0.20 × 0.15 × 0.12	0.60 × 0.30 × 0.03	0.90 × 0.60 × 0.54
diffractometer	STOE IPDS	CAD-4	STOE IPDS
radiation	$Mo_{K\alpha}$; graphite monochromator		
2Θ range [°]	$3.9 \leq 2\Theta \leq 52.0$	$4.9 \leq 2\Theta \leq 46.1$	$3.9 \leq 2\Theta \leq 52.1$
index ranges	$-35 \leq h \leq 35$	$-14 \leq h \leq 14$	$-35 \leq h \leq 35$
	$-24 \leq k \leq 23$	$-20 \leq k \leq 0$	$-24 \leq k \leq 24$
	$-33 \leq l \leq 33$	$-19 \leq l \leq 0$	$-34 \leq l \leq 33$
independent reflections	15355	6225	15197
reflections $F > 4\sigma(F)$	8211	4726	10417
parameters	687	521	745
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma\lvert F_o\rvert\ (F > 4\sigma(F))$	0.0486	0.0515	0.0486
$wR^2 = \{\Sigma w(F_o^2 - F_c^2)^2 / \Sigma\, w(F_o^2)^2\}^{1/2}$ (all data)	0.1165	0.1511	0.0977
max./min. residual [$10^{30}\,e\,m^{-3}$]	2.02/ − 0.78	2.23/ − 0.90	1.12/ − 0.86

[a] Program: SHELXTL-Plus, SHELXL-97;[22] solutions by direct methods; full-matrix refinement with all independent structure factors.

evaporation of the solvent an orange solid remained, which was thoroughly dried in vacuum, dissolved in pentafluorobenzene (20 mL), and filtered. Slow cooling to 0 °C afforded orange crystals of **3**. Yield: 0.122 g (33%; based on solvent-free **3**), m.p. (argon, sealed capillary): 164 °C (decomp); ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 0.46$ (s, $SiMe_3$); ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): $\delta = 6.9$ ($SiMe_3$), InC not detected; IR (CsBr, paraffin): $\tilde{\nu}$[cm^{-1}] = 1292 vw, 1261 sh, 1251 s δCH_3; 1155 vw, 1072 vw; 860 vs, 840 vs, 775 w, 722 w $\rho CH_3(Si)$; 675 w, 650 w $\nu_{as}SiC$; 616 vw ν_sSiC; 588 w, 565 sh, 432 vw νInC; 311 vw δSiC; UV/vis (n-hexane): λ_{max} (log ε) = 210 (4.2), 285 nm (br., 4.2). Owing to the partial loss of solvent molecules from the powdered samples of **3**, elemental analyses did not give satisfactory results.

Synthesis of [{In$_2$Br$_2$R$_2$}$_2$] (4): A solution of bromine (0.157 M, 9.75 mL, 1.53 mmol) in n-hexane was added to a suspension of $AlBr_3$ (0.408 g, 1.53 mmol) in n-hexane (50 mL) at room temperature. The brownish mixture was stirred for 30 min. A solution of **1** (0.705 g, 0.51 mmol) in n-hexane (50 mL) was added. After 40 min at room temperature the violet suspension was heated to 80 °C in a prewarmed oil bath for 15 min. The color changed to yellow, and elemental indium precipitated. After filtration a yellow solution was obtained. The solvent was removed in vacuum, and the remaining solid was recrystallized from pentafluorobenzene (20/ − 30 °C). Yield: 0.270 g (28%), m.p. (argon, sealed capillary): 220 °C (decomp); ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 0.47$ (s, $SiMe_3$); ^{13}C NMR (75.5 MHz, C_6D_6, 25 °C): $\delta = 6.7$ ($SiMe_3$), InC not detected; IR (CsBr, paraffin): $\tilde{\nu}$[cm^{-1}] = 1268 s, 1259 s, 1252 s δCH_3; 1169 vw, 1156 vw, 1077 vw; 856 vs, 840 vs, 775 m, 742 w, 722 w $\rho CH_3(Si)$; 675 m, 651 m $\nu_{as}SiC$; 615 vw ν_sSiC; 597 w νInC; 358 vw, 308 vw δSiC; UV/vis (n-hexane): λ_{max} (log ε) = 310 nm (3.5); elemental analysis calcd (%) for $C_{40}H_{108}Si_{12}In_4Br_4 \cdot C_6F_5H$ (1873.3): In 24.5, C 29.5, H 5.9; found: In 24.2, C 29.1, H 5.8.

Crystal structure determinations: Single crystals of all compounds were obtained by slow cooling of saturated solutions in pentafluorobenzene to 0 °C. Crystal data and structure refinement parameters are given in Table 1.[23] The crystals include different numbers of solvent molecules (**2**: one, **3**: three, **4**: one molecule per formula unit). Compound **3** is located on a crystallographic mirror plane across the central atoms In1, In3, Br1, and Br2. One trimethylsilyl group of **3** (Si8) and one tris(trimethylsilyl)methyl group of **4** (C2) showed a disorder; silicon atoms and methyl groups were refined on split positions.

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[23] The crystallographic data of **2**, **3**, and **4** (excluding structure factors) were deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos CCDC-163321 (**2**), CCDC-163322 (**3**), and CCDC-163323 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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