Hexasupersilyloctaindane $(tBu_3Si)_6In_8$—A Compound with a Novel In_8 Cluster Framework[**]

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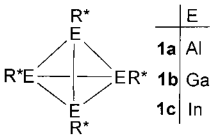
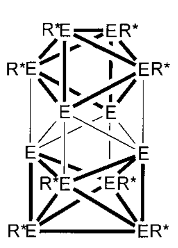
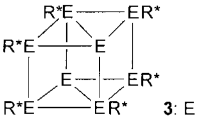
Dedicated to Professor Gerhard Fritz
on the occasion of his 80th birthday

We recently reported[1] that tetrasupersilyldialane $R^*_4Al_2$ and trisupersilyldigallanyl $R^*_3Ga_2$ (a secondary product of the digallane $R^*_4Ga_2$ which is metastable at room temperature) are converted in heptane at 100 °C into tetrasupersilyl-*tetrahedro*-tetraalane (**1a**) and -tetragallane (**1b**), respectively, whereas the thermolysis of tetrasupersilyldiindane $R^*_4In_2$ in heptane at 100 °C did not afford the analogous tetraindane **1c**, but the octasupersilyldodecaindane **2** (R* = supersilyl = tri-*tert*-butylsilyl).







3: E = In

2: E = In

As a continuation of efforts to synthesize **1c** we attempted to generate R*In at low temperature in the hope that it would tetramerize under these conditions. Thus we treated pentamethylcyclopentadienylindium Cp*In with supersilylsodium R*Na in pentane at −78 °C (Cp* = C_5Me_5). After two days the resulting dark green solution was allowed to warm to room temperature, and from this solution we obtained—after replacement of the solvent pentane by benzene—black-green crystals, which, according to X-ray structure analysis,[2] were again not tetrahedrane molecules **1c**, but hexasupersilyloctaindane molecules **3**. The latter are formed together with diindane $R^*_4In_2$, which is consistent with a reaction such as that given in Equation (1).

$$10\,Cp^*In \xrightarrow[-12\,Cp^*Na]{+12\,R^*Na} \underset{\mathbf{3}}{R^*_6In_8} + R^*_4In_2 \qquad (1)$$

Compound **3** is comparatively sensitive to oxidation and hydrolysis. Its solutions are thermally stable up to 100 °C with the exclusion of light; however, in light they tend to deposit an indium mirror on the wall of the flask at room temperature. NMR spectra of the compound in C_6D_6 indicate the presence of only one type of supersilyl group.[3]

Figure 1 gives a more realistic view of the structure of $R^*_6In_8$ in the crystal than the formula **3**. The In–In distances denoted by solid lines range—as for the dodecaindane **2**[1]—from 2.77 to 3.30 Å. They are thus on average shorter than the In–In distances in elemental indium (3.25 – 3.38 Å[1]), but are similar to those in other structurally characterized low-valent neutral indium compounds with In_2 and In_4 cluster frameworks (see ref. [1]). The In–In distances denoted by dashed lines in Figure 1 range between 3.41 and 3.56 Å and are thus weaker but certainly can still be considered as bonding In–In contacts. All the remaining In–In distances are ≥4 Å, which rules out interactions between the respective atoms. The In–Si distances (ca. 2.65 Å) correspond to those in **2** (av 2.68 Å[1]). They are shorter than those in the diindane $R^*_4In_2$ (ca. 2.78 Å[4]), which is consistent with a significantly reduced steric interaction between the supersilyl groups in **3**. Similarly, the Si–C distances (av. 1.948 Å) and the C-Si-C angles of the

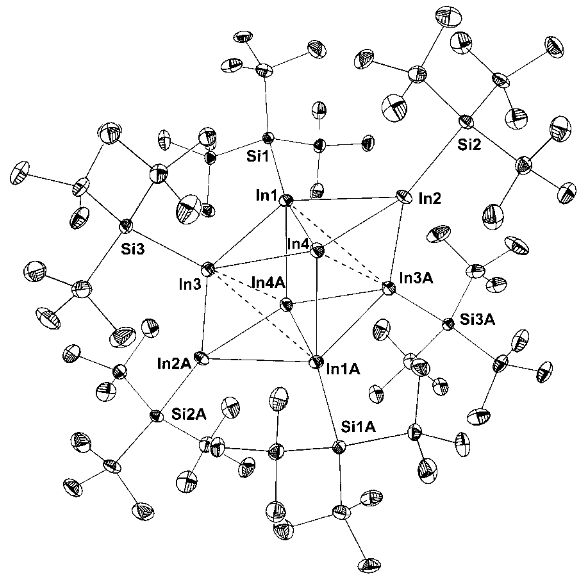


Figure 1. Molecular structure of **3** in the crystal (ORTEP; 25 % thermal probability ellipsoids, hydrogen atoms are omitted for clarity). Selected distances [Å] and angles [°]: In1–In2 3.303(1), In1–In3 3.104(1), In1–In4 3.041(1), In1–In4A 2.957(1), In1–In3A 3.565(1), In1–In1A 4.497(1), In2–In3A 2.770(1), In2–In4 2.835(1), In3–In4 2.910(1), In3–In2A 2.770(1), In3–In4A 3.413(1), In4–In1A 2.957(1), In4–In4A 3.971(1), In1–Si1 2.683(1), In2–Si2 2.615(1), In3–Si3 2.665(2), Si–C (av) 1.948; In4A-In1-In4 82.90(3), In4A-In1-In3 68.50(2), In4-In1-In3 56.52(2), In4A-In1-In2 98.68(2), In4-In1-In2 52.89(1), In3-In1-In2 109.28(2), In3A-In2-In4 75.01(2), In3A-In2-In1 71.27(2), In4-In2-In1 58.82(2), In2A-In3-In4 113.62(2), In2A-In3-In1 105.68(2), In4-In3-In1 60.66(2), In2-In4-In3 130.91(2), In2-In4-In1A 107.97(2), In3-In4-In1A 74.83(2), In2-In4-In1 68.29(2), In3-In4-In1 62.82(1), In1A-In4-In1 97.10(3), Si1-In1-In4A 115.15(4), Si1-In1-In4 161.78(3), Si1-In1-In3 130.48(3), Si1-In1-In2 118.11(3), Si2-In2-In3A 153.47(4), Si2-In2-In4 119.35(4), Si2-In2-In1 134.89(4), Si3-In3-In2A 126.55(4), Si3-In3-In4 110.75(3), Si3-In3-In1 121.46(4), C-Si-C (av) 111.5.

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supersilyl groups (av. 111.5°) lie in the normal ranges of 1.94–1.95 Å and 110–112°,[5] respectively (cf. $R^*_4In_2$: 1.95 Å, 109.7°[4]).

Figure 1 also reveals that the eight In atoms in **3** form a cube stretched along one body diagonal (local symmetry of the In_8 cluster: C_i; see Table 1 for details with regard to the lengths of the four body diagonals of the cluster) and the six supersilyl groups form a distorted octahedron. These groups surround the indium cluster as a broad belt, as clearly illustrated in the space-filling model in Figure 2. The supersilyl-free In atoms are located above and below in the belt openings.

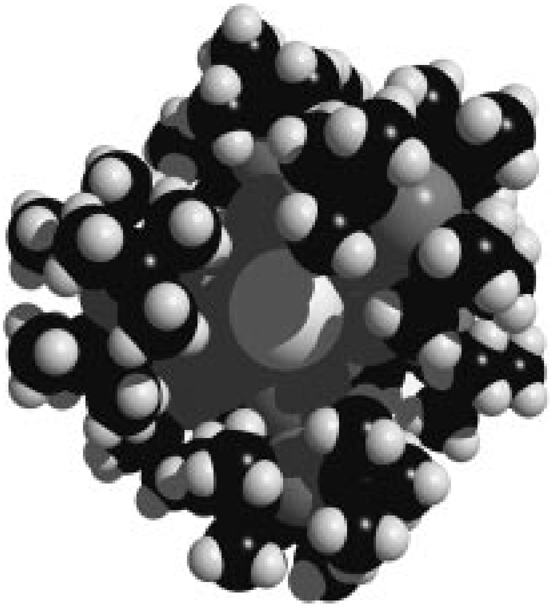

Figure 2. Space-filling model of the octaindane **3**; "naked" In atoms: white; R*-linked In atoms: gray.

The compound $R^*_6In_8$ (**3**) is after $R^*_8In_{12}$ (**2**) a further rare cluster structure for boron and its homologues. In accord with the structural formula shown for **2**, the dodecaindane, which can be described as *conjuncto*-indane, consists of two $R^*_4In_6$ clusters with distorted In_6 octahedral frameworks. Unfortunately, an In_6 cluster of this type has not yet been isolated as a solid. However, with $R^*_6In_8$ a related indane has now been obtained.[6] If the six R*In groups in **3** are each considered to provide two electrons and the two "naked" In atoms to provide one electron for the In_8 framework, there are $14 = 2n - 2$ framework electrons available (n = number of framework atoms; in the counting it was considered that from every cluster atom two electrons are used in bonding to one ligand or as a lone pair of electrons). According to the counting rules of Wade[7] and Mingos[8] for framework electrons, **3** is classified as a doubly capped *closo* compound ("*hypoprecloso* compound"), thus its framework would be a doubly capped octahedron. The experimentally determined structure (Figure 1; consideration of the solid and dashed lines) corresponds to this description.[9]

The interpretation of the structure as an $R^*_4In_6$ octahedron, whose electron deficiency is compensated for by the double capping with R*In groups, is also supported by density functional calculations (Table 1).[10, 11] The capping groups R*In2/R*In2A are the furthest apart, and the remaining $R^*_4In_6$ octahedron is also stretched: R*In1/In4/R*In1A/In4A form the corners of the—almost square—base and R*In3/R*In3A the apexes of the octahedron. The comparison of calculated and experimentally determined distances in Table 1 confirms the good agreement despite the simplification used (e.g. ECP basis sets).

Table 1. In–In distances [Å] in $(H_3Si)_6In_8$ and $(tBu_3Si)_6In_8$ calculated with density functional methods and average In–C distances [Å] in $(tBu_3Si)_6In_8$ determined by X-ray crystallography. For the numbering of the In atoms see Figure 1.

[a]	$(H_3Si)_6In_8$ calcd		$(tBu_3Si)_6In_8$ calcd		$(tBu_3Si)_6In_8$ found	
I	In2–In2A	6.59	In2–In2A	7.05	In2–In2A	6.75
II	In4–In4A	5.42	In3–In3A	5.04	In3–In3A	4.95
III	In1–In1A	4.34	In1–In1A	4.52	In1–In1A	4.50
III	In3–In3A	4.32	In4–In4A	4.10	In4–In4A	3.57
IV	In1–In3	3.20	In1–In4	3.11	In1–In4	3.04
IV	In1–In3A	2.92	In1–In4A	3.00	In1–In4A	2.96

[a] Types of In–In distance: I = between the capping atoms; II = between the atoms located at the apexes of the octahedron; III = between the atoms lying on opposite sides of the base of the octahedron; IV = between the atoms forming one edge of the base of the octahedron.

For the sterically less demanding octaindane $(H_3Si)_6In_8$ a slightly different geometry is calculated (see Table 1): The groups furthest apart, thus the groups forming the caps are identical (In2/In2A), and the remaining $(H_3Si)_4In_6$ octahedron is likewise stretched, but this time with the silyl-group-free In4/In4A at the apexes of the octahedron and (H_3Si)In1/(H_3Si)In3/(H_3Si)In1A/(H_3Si)In3A at the corners of the—almost square—base. Evidently $(H_3Si)_6In_8$ adopts the electronically most favorable, $R^*_6In_8$ the sterically most favorable geometry. The silyl-group-free In atoms visible in Figure 2 in the second case are immersed slightly deeper in the "belt openings" than in the first case. According to ab initio calculations, only by applying considerable energy can the "naked" In atoms be extracted from the belt openings in the sense of a formulation $(In^+)_2In_6R_6{}^{2-}$ (R = SiH_3, SitBu$_3$).

The population analysis revealed that the twelve three-center–two-electron bonds on the triangular faces both in $(H_3Si)_6In_8$ and in $R^*_6In_8$ contribute nearly equally to the stabilization of the In_8 cluster. The eight In atoms are approximately neutral.

Finally it should be noted that among the triels and tetrels tetrasupersilylated tetrahedranes $R^*_4E_4$ of the elements Al and Ga[1] and Si and Ge,[12] respectively, are accessible as stable products, but not the analogous In_4 and Sn_4 clusters, respectively.[12] In the latter case larger clusters are formed, which is perhaps attributable to the fact that these E_4 tetrahedra cannot be completely covered by four supersilyl groups and therefore react to give larger element clusters with simultaneous reduction of the cluster strain energy.

Experimental Section

A solution of tBu_3SiNa (0.182 g, 0.818 mmol) in pentane (20 mL) was added dropwise over 3 h to a pale yellow suspension of Cp*In (0.208 g, 0.832 mmol) in pentane (20 mL) cooled to −120 °C. The resulting dark brown suspension was stirred for 48 h at −78 °C during which time it turned dark green. The NMR spectrum recorded for the dark green solution obtained after the reaction mixture had been allowed to warm to room temperature and the solvent pentane had been exchanged for C_6D_6 revealed in addition to small amounts of tBu$_3$SiH (hydrolysis product of tBu$_3$SiNa; identification by comparison with an authentic sample[5]), $R_2^*In{-}InR_2^*$ (identification by comparison with an authentic sample[4]) and **3** in a molar ratio of about 1:1. After removal of insoluble products (Cp*Na) from the original solution in pentane by filtration, removal of all volatile components under an oil pump vacuum (tBu$_3$SiH, pentane), and dissolution of the dark green residue in benzene (10 mL), **3** (0.072 g, 0.034 mmol, 32 %) crystallized as dark green parallelpipeds in the course of 7 d at room temperature. ^{1}H NMR (C_6D_6, TMS internal): $\delta = 1.362$ (s; 6 SitBu$_3$); ^{13}C{^{1}H} NMR (C_6D_6, TMS internal): $\delta = 29.29/33.09$ (18 CMe$_3$/18 CMe_3); ^{29}Si NMR (C_6D_6, TMS external): $\delta = 80.95$ (6 SitBu$_3$).

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[1] N. Wiberg, T. Blank, H. Nöth, W. Ponikwar, *Angew. Chem.* **1999**, *111*, 887; *Angew. Chem. Int. Ed.* **1999**, *38*, 839, and references therein.

[2] Crystal structure analysis of **3**: STOE-IPDS diffractometer, $Mo_{K\alpha}$ irradiation, measurement temperature 200(2) K. The crystal was mounted in perfluoropolyether. Crystal dimensions: $0.5 \times 0.4 \times 0.2$ mm^3, monoclinic, space group $C2/c$ with $a = 24.657(5)$, $b = 16.648(3)$, $c = 27.798(6)$ Å, $\beta = 115.50(3)°$, $V = 10299(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.465$ Mg m^{-3}, $\mu = 1.863$ mm^{-1}, $\theta = 3.84–51.84°$, $-30 \leq h \leq 30$, $-20 \leq k \leq 20$, $-34 \leq l \leq 33$, 9911 measured reflections, of which 9911 independent; 6929 with $I > 4\sigma(I_0)$ included in the refinement, numerical absorption correction by local scaling (transmission: max. 0.8202, min. 0.6404), $R1 = 0.0293$, $wR2 = 0.0881$, GOOF 0.916, no restraints, 469 parameters, residual electron density: max. 1.218, min. −0.728 e Å^{-3}. The structure was solved by direct methods and refined against F^2 for all observed reflections (structure solution with SHELXS 94, refinement with SHELXL 93). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114210. 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).

[3] The structural formula indicates several types of supersilyl groups for the compound which is only sparingly soluble at room temperature and almost insoluble at lower temperatures in organic media. Thus, **3** possibly behaves in a fluctional manner in solution.

[4] N. Wiberg, K. Amelunxen, H. Nöth, M. Schmidt, H. Schwenk, *Angew. Chem.* **1996**, *108*, 110; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 65.

[5] N. Wiberg, *Coord. Chem. Rev.* **1997**, *163*, 217.

[6] Nothing definitive can be said about the mechanism of the formation of **3** from Cp*In and R*Na in pentane. However, initially the Cp* group is replaced by a supersilyl group, resulting in R*In and NaCp*. The monomeric supersilylindium could then be converted into the tetrahedrane $R_4^*In_4$ **1c** via $R_2^*In_2$ and the former could then dimerize with elimination of supersilyl groups to give the octaindane $R_6^*In_8$ (**3**). The supersilyl groups eliminated could react with R*In to give the indanyl R_2^*In and this then subsequently gives the diindane $R_4^*In_2$.

[7] K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1; see also R. W. Rudolph, *Acc. Chem. Res.* **1976**, *9*, 446, as well as R. E. Williams, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67.

[8] D. M. P. Mingos, *Nature* **1972**, *236*, 99; D. M. P. Mingos, *Acc. Chem. Res.* **1984**, *17*, 311; see also M. McPartlin, *Polyhedron* **1984**, *3*, 1279.

[9] Accordingly, $R_6^*In_8$ (**3**) cannot be described as a supersilyl derivative of the *closo*-indate $In_8H_8^{2-}$, a homologue of the isolable *closo*-borate $B_8H_8^{2-}$, lacking two hydride ions.

[10] Turbomole program: E. Eichhorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283; SVP basis sets: A. Schäfer, H. Horn, R. Ahlrichs, *Z. Phys. Chem.* **1992**, *97*, 2751.

[11] The computer-intensive studies (230 atoms!) could not be shortened either by symmetry restrictions (e.g. D_{3d}) or by the use of smaller ligands (transfer to In_8H_6) (in the second case structures are obtained with bridging hydrogen atoms).

[12] N. Wiberg, H.-W. Lerner, H. Nöth, W. Ponikwar, *Angew. Chem.* **1999**, *111*, 1176; *Angew. Chem. Int. Ed.* **1999**, *38*, 1103, and references therein.

Terthienyl-Based Redox-Switchable Hemilabile Ligands: Transition Metal Polymeric Complexes with Electrochemically Tunable or Switchable Coordination Environments?**

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Herein we report the synthesis and characterization of the first transition metal complexes (**4a,b**) formed from redox-switchable terthienyl-based hemilabile ligands (**1a,b**) (Scheme 1). These ligands were designed to possess several key features. First, they are hemilabile when bound to Ru^{II} centers in a κ^2 fashion by virtue of their phosphane and terthienyl moieties.[1] Second, the redox-active terthienyl group in **4b** can be electrochemically polymerized at an oxidation potential lower than that of the Ru^{II} centers, allowing the generation of an electroactive film of poly-**4b** with the metal centers still intact. Terthienyl-based polymers can be reversibly oxidized, thereby providing electrochemical control over the binding constant of the polymeric ligand in poly-**4b** for transition metal centers dispersed along its thienyl backbone. Although others have grafted metal centers onto the backbone of preformed conducting polymers to form substitutionally inert linkages[2a,b] or polymerized metal-containing monomers,[2c–h] **4b** is the first isolable, polymerizable monomer suitable for forming a polymeric metal ligand

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