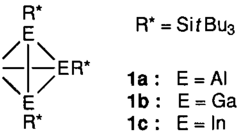
Dodecaindane $(tBu_3Si)_8In_{12}$—A Compound with an In_{12} Deltapolyhedron Framework**

Nils Wiberg,* Thomas Blank, Heinrich Nöth, and Werner Ponikwar

Dedicated to Professor Helmut Werner
on the occasion of his 65th birthday

We recently reported that the thermolysis of tetrasupersilyldialane $R^*_2Al-AlR^*_2$ ("supersilyl" $R^* =$ tri-*tert*-butylsilyl) in heptane at 100 °C initially gives trisupersilyldialanyl $R^*_3Al_2$, which is metastable at room temperature, and then leads to the red-violet tetrasupersilyl-*tetrahedro*-tetraalane **1a**.[1] Analogously, trisupersilyldigallanyl $R^*_3Ga_2$ thermolyzes in heptane at 100 °C to give the deep violet tetrasupersilyl-*tetrahedro*-tetragallane **1b**.[2] The enlargements of the element clusters according to Equations (1), and (2), accordingly are initiated by thermal dissociations of element – supersilyl bonds, which in the case of the digallane $R^*_2Ga-GaR^*_2$ are so facile that so far instead of $R^*_4Ga_2$ only the supersilyl-poorer $R^*_3Ga_2$ compound could be isolated.[3] The resulting supersilyl radicals R* dimerize *quickly* to give "superdisilane" R*–R* [Eq. (3)], which is *slowly* converted at 100 °C in heptane into "supersilane" R*–H by H-uptake.[4]

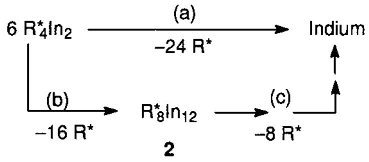


$$2R^*_4Al_2 \rightarrow R^*_4Al_4 + 4R^* \tag{1}$$

$$2R^*_3Ga_2 \rightarrow R^*_4Ga_4 + 2R^* \tag{2}$$

$$R^*{-}R^* \rightleftharpoons 2R^*\,(+\,2H \rightarrow 2R^*{-}H) \tag{3}$$

As a continuation of our studies we set out to synthesize tetrasupersilyl-*tetrahedro*-tetraindane **1c** as a further indatetrahedrane in addition to the two known tetraorganyl-*tetrahedro*-tetraindanes R_4In_4 ($R = C(SiMe_3)_3$ and $C(SiMe_2Et)_3$[6]) by thermolysis of tetrasupersilyldiindane $R^*_2In-InR^*_2$.[5] The diindane in question, which is readily accessible from $InCl_3$ and R*Na in THF (see Experimental Section), indeed completely thermolyzes in boiling heptane (ca. 100 °C) after 22 h to give supersilane R*H and an indium-containing product. From the dark reaction solution black-violet, water- and air-sensitive crystals precipitate at room temperature in the course of days after substituting benzene for the heptane. These crystals are thermally comparably stable and are almost insoluble in heptane, benzene, or toluene even at 100 °C. Surprisingly, according to X-ray structural analyses[7] these crystals are not of **1c** but of octasupersilyldodecaindane **2**. Thus, thermolysis of the diindane $R^*_4In_2$ at 100 °C is accompanied by elimination of more supersilyl radicals than that of the dialane $R^*_4Al_2$ or that of the digallanyl $R^*_3Ga_2$. Consequently the former case leads to a more pronounced enlargement of the element cluster than the latter two. In other words, the thermal decomposition of the diindane, which finally leads to indium (Scheme 1, Reaction (a)), initially stops at an element-richer cluster level (Scheme 1, Reaction (b)) than that of the dialane or that of the digallanyl.



Scheme 1. Thermal cluster enlargements starting from $R^*_4In_2$ ($R^* = SitBu_3$).

Figure 1 shows the X-ray crystal structure of **2** (local symmetry approximately S_4), in which all H atoms have been omitted for clarity. It reveals a closed polyhedron framework of 20 triangular faces and 12 In atoms, which does not exhibit a spherical form, such as the icosahedrally shaped $B_{12}H_{12}^{2-}$,[8] but resembles a stretched ellipsoid. The four In atoms at the ends of the ellipsoid each carry one supersilyl group and the four In atoms in the middle of the ellipsoid carry no supersilyl group. The four spherical $SitBu_3$ groups at the end of the ellipsoid display distorted-tetrahedral packing. This illustrates the tendency (attributed to van der Waals interactions[4]) of the

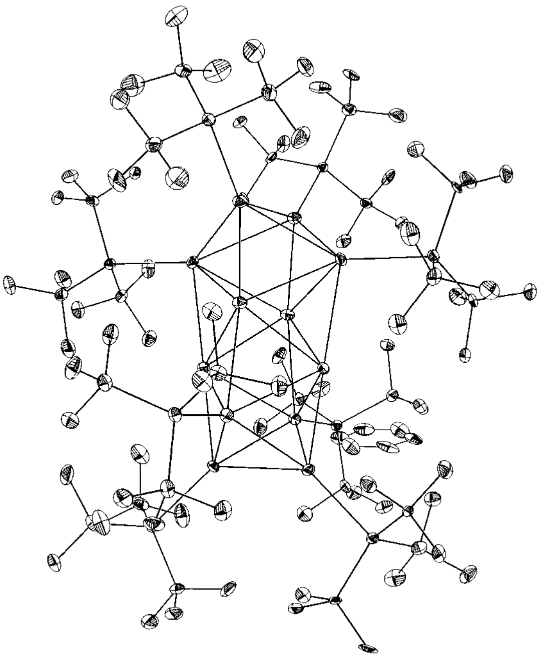


Figure 1. View of the crystal structure of $R^*_8In_{12}$ (ORTEP plot, 25% thermal probability ellipsoids, hydrogen atoms are omitted for clarity).

---

[*] Prof. Dr. N. Wiberg, Dipl.-Chem. T. Blank, Prof. Dr. H. Nöth, Dipl.-Chem. W. Ponikwar
Institut für Anorganische Chemie der Universität
Meiserstrasse 1, D-80333 München (Germany)
Fax: (+49) 89-5902-578
E-mail: Niw@anorg.chemie.uni-muenchen.de

[**] Compounds of Silicon, Part 125: Supersilyl Compounds of the Triels, Part 8. This work was supported by the Deutsche Forschungsgemeinschaft. Part 124: N. Wiberg, H. Auer, H. Nöth, J. Knizek, K. Polborn, *Angew. Chem.* **1998**, *110*, 3030; *Angew. Chem. Int. Ed.* **1998**, *37*, 2869; Part 7: ref. [2].

supersilyl groups to form the densest possible packing arrangement. The arrangement of the In atoms at the ends of the In_{12} cluster has to “submit” to this tendency. The Si*t*Bu$_3$ groups play a structure-determining role in the structure of the In_{12} cluster, which can be described as a section of elemental indium (distorted cubic closest packing[8, 9]). The longitudinal diameter of the In_{12} cluster is about 750 pm. Thus cluster **2**, which is formed in the course of the thermolysis (b), approaches the realm of nanostructured materials; this area is then passed through in the course of the thermolysis (c) (Scheme 1), which has still to be studied in detail.

The presentation of the In_{12} polyhedron shown in Figure 2 gives a better insight into the present structures. The In_{12} cluster consists of two distorted octahedral In_6 building blocks, which when considered as separate entities can be classified as *closo* compounds.[10] Thus, the dodecaindane **2** can be described as a *conjuncto* indane (cf. the boron hydride $B_{20}H_{16}$[8]). Therefore it seems possible that **2** is formed from the diindane $R^{*}_{4}In_2$ via hexaindane as an intermediate product $R^{*}_{4}In_6$, which dimerizes to give the dodecaindane **2**. Indeed, in the synthesis described above insoluble **2** is formed from a soluble precursor, which is initially detectable in the reaction mixture, and which we are currently trying to isolate.[11]

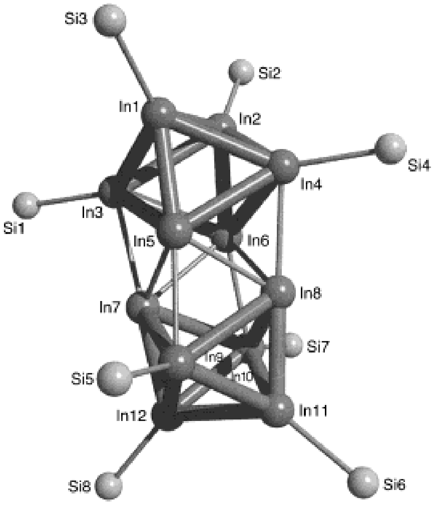


Figure 2. View of the crystal structure of $R^{*}_{8}In_{12}$, which is divided into two $R^{*}_{4}In_6$ octahedra, and atom numbering system used (local symmetry approximately S_4; SCHAKAL plot; atoms with arbitrary radii; *t*Bu groups are omitted for clarity). Selected bond lengths [Å] and angles [°] (in each case only one distance and angle are given for one set of bond and angles; however, the underlying S_4 symmetry is merely an approximation): In1–In2 3.091(2), In1–In3 2.948(1), In1–In4 3.173(2), In1–In5 2.814(2), In3–In5 3.191(1) (the equivalent distances In4–In6/In7–In10/In9–In12 are 3.192(2)/3.267(1)/3.307(2)), In3–In6 3.141(2), In3–In7 3.037(2), In5–In7 3.004(1), In5–In8 3.009(1), In5–In9 3.059(2), In1–Si3 2.668(3), In3–Si1 2.685(3), Si–C (mean) 1.94; In5-In1-In3 67.21(3), In5-In1-In2 94.41(3), In3-In1-In4 93.40(5), In3-In1-In2 64.06(3), In5-In1-In4 62.49(3), In2-In1-In4 55.81(3), In1-In3-In7 111.63(4), In1-In3-In6 90.82(4), In7-In3-In5 57.62(3), In7-In3-In2 109.25(4), In5-In3-In2 85.37(4), In7-In3-In6 58.32(3), In1-In3-In5 54.38(3), In6-In3-In5 68.73(4), In1-In3-In2 60.13(4), In1-In5-In7 116.62(4), In7-In5-In8 72.42(4), In7-In5-In9 61.59(3), In1-In5-In4 64.41(3), In1-In5-In8 121.77(4), In1-In5-In9 173.68(4), In8-In5-In9 64.07(3), In7-In5-In4 109.27(4), In8-In5-In4 59.06(4), In1-In5-In3 58.41(3), In8-In5-In3 107.68(4), In4-In5-In3 89.87(4), In9-In5-In4 121.84(4), In7-In5-In3 58.61(4), In9-In5-In3 118.73(4), Si3-In1-In2 135.62(7), Si1-In3-In1 136.22(8), C-Si-C (mean) 111.3.

The In–In distances in **2** range from almost 2.80 to 3.30 Å. On average they are shorter than the In–In bond lengths in indium metal and longer than those in other low-valent uncharged indium compounds (Table 1). The In–In distances differ slightly within the two In_6 clusters; in contrast, the In–In distances between the two In_6 octahedra are both about 3.00 Å. The Si–In distances of about 2.68 Å are shorter than those in the diindane $R^{*}_{4}In_2$ (ca. 2.78 Å[5]), which indicates that the supersilyl groups in the dodecaindane sterically inhibit one another less than in the diindane. The same tendency is indicated by the Si–C distances and the C-Si-C angles of the supersilyl groups, which are on average 1.94 Å and 111.3°, and lie in the normal range of 1.94–1.95 Å and 110–112°[4] (cf. $R^{*}_{4}In_2$: 1.95 Å and 109.7°[5]).

Table 1. Bond lengths *d*(In–In) in indium metal and in several uncharged indium compounds (Dsi = $CH(SiMe_3)_2$, Tsi = $C(SiMe_3)_3$, Tip = 2,4,6-$iPr_3C_6H_2$, R* = Si*t*Bu$_3$).

Compound	*d*(In–In) [Å]	Ref.
In metal	3.252/3.377	[9]
Dsi_4In_2	2.828(1)	[12]
Tip_4In_2	2.775(2)	[13]
$R^{*}_{4}In_2$	2.922(1)	[5]
$(Tip_2In)_3In$	2.696(2)	[13]
Tsi_4In_4	3.002(1)	[6]
$R^{*}_{8}In_{12}$	2.80–3.30	this work

To date there are only a few donor-free, uncharged molecular compounds with clusters from boron homologues (cf. ref. [5]). In the case of indium, these include diindanes R_4In_2 with In_2 frameworks (cf. among others ref. [5, 12, 13] and Table 1), the tetraindanes $(Tip_2In)_3In$ with an acyclic In_3In framework (cf. ref. [13] and Table 1), and tetraindanes R_4In_4 with a tetrahedral In_4 framework (cf. ref. [6] and Table 1). The In–In interactions are only very weak (cf. ref. [5]; Cp* = C_5Me_5; Cp** = $C_5(CH_2Ph)_5$) in the compounds $(Cp^{*}In)_6$ and $(Cp^{**}In)_2$. The *conjuncto*-$R^{*}_{8}In_{12}$ compound represents a unique E_{12} polyhedron structure for boron and its homologues and will naturally stimulate the search for compound homologues R_8E_{12} (E = B, Al, Ga, Tl) as well as for other donor-free and uncharged polyhedral compounds $R_{<n}E_n$ of the boron homologues.

According to the space-filling model the surface of the central In_{12} cluster of $R^{*}_{8}In_{12}$ is almost completely covered by eight supersilyl groups. This probably plays a major role in determining the outcome of the thermolysis of $R^{*}_{4}In_2$. Owing to their smaller surface the corresponding Ga_{12} and Al_{12} polyhedra offer less space for eight supersilyl groups, thus compounds of the type $R^{*}_{8}Ga_{12}$ and $R^{*}_{8}Al_{12}$ should be more thermolabile than $R^{*}_{8}In_{12}$ or only accessible with sterically less demanding substituents such as *i*Pr$_3$Si.

Experimental Section

$R^{*}_{4}In_2$: *t*Bu$_3$SiNa(THF)$_2$ (10.5 mmol) in THF (10 mL) was added dropwise to a suspension of $InCl_3$ (0.778 g, 3.50 mmol) in THF (30 mL), which had been cooled to −78 °C. The reaction mixture was stirred for 20 h at −78 °C. On slowly allowing the mixture to warm to room temperature, the solution turned deep violet. The mixture was then stirred for 5 h at room temperature. According to the ^1H NMR spectrum (C_6D_6) the solution contained exclusively $R^*_4In_2$ and R*–R* in the molar ratio 1:1 ($2\,InCl_3 + 6\,R^*Na \rightarrow R^*_4In_2 + R^*{-}R^* + 6\,NaCl$; identification of the products by comparison with authentic samples[2, 5]). After removal of all volatile components in an oil pump vacuum, the residue was taken up in toluene (80 mL), the insoluble components (NaCl) were filtered, and the filtrate was concentrated to 20 mL, deep violet $R^*_4In_2$ (1.12 g, 1.09 mmol; 63 %) crystallized from the solution at −23 °C.[5]

$R^*_8In_{12}$: A solution of $R^*_4In_2$ (0.370 g, 0.360 mmol) in heptane (45 mL) was heated under reflux (ca. 100 °C) for 22 h. According to the ^{1}H, ^{13}C{^{1}H}, and ^{29}Si NMR spectra of the reaction solution, the diindane completely decomposed after replacement of C_6D_6 for heptane, leading to supersilane tBu$_3$SiH (identified by comparison with authentic sample[2]) and an indium- and supersilyl-containing product (two different types of SitBu$_3$ groups in the ratio 1:1); ^{1}H NMR: $\delta = 1.419$ and 1.271 (ratio of areas ca. 1:1); ^{13}C{^{1}H} NMR: $\delta = 33.72/25.47$ and 32.60/26.59 (each CMe_3/CMe$_3$); ^{29}Si NMR: $\delta = 64.2$ and 50.9). After removal of all volatile components in an oil pump vacuum, the residue was taken up in benzene (40 mL), and the solution was concentrated to 10 mL, $R^*_8In_{12}$ (0.05 g, 0.02 mmol; ca. 30 %) crystallized from the solution in the course of a few days at room temperature. Crystals suitable for the X-ray structural analysis were grown from C_6D_6. They do not dissolve in heptane, benzene, or toluene, either at room temperature or at 95 °C (no NMR signals). Thus the original thermolysis solution evidently did not contain dodecaindane but precursors of this cluster, from which $R^*_8In_{12}$ was formed.

Received: November 6, 1998 [Z12627IE]
German version: Angew. Chem. **1999**, *111* 887–890

Keywords: cluster compounds · indium · silicon

---

[1] N. Wiberg, K. Amelunxen, T. Blank, H. Nöth, J. Knizek, *Organometallics* **1998**, *17*, 5431.

[2] N. Wiberg, K. Amelunxen, H.-W. Lerner, H. Nöth, W. Ponikwar, H. Schwenk, *J. Organomet. Chem.* **1998**, in press.

[3] N. Wiberg, K. Amelunxen, H. Nöth, H. Schwenk, W. Kaim, A. Klein, T. Scheiring, *Angew. Chem.* **1997**, *109*, 1258; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1213.

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

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

[6] W. Uhl, R. Graupner, M. Layh, U. Schütz, *J. Organomet. Chem.* **1995**, *493*, C1; W. Uhl, A. Jantschak, W. Saak, M. Kaupp, R. Wartchow, *Organometallics* **1998**, *17*, 5009.

[7] Crystal structure analysis of $R^*_8In_{12} \cdot C_6D_6$: Siemens P4 diffractometer, $Mo_{K\alpha}$ radiation, graphite monochromator, CCD area detector, crystal dimensions $0.02 \times 0.3 \times 0.4$ mm^3. The crystal was mounted in perfluoro ether oil, $T = 183(2)$ K, $C_{102}H_{216}D_6In_{12}Si_8$, $M_r = 3051.36$, black-violet platelets, monoclinic, $a = 18.329(7)$, $b = 32.02(2)$, $c = 22.454(8)$ Å, $\beta = 97.74(1)^\circ$, $V = 13059(10)$ Å^3, $Z = 4$; space group $P2_1/n$, $\rho_{calcd} = 1.552$ Mg m^{-3}, $\mu = 2.185$ mm^{-1}, $F(000) = 6136$. Data collection: 2θ from 2.98 to 49.42°, $-21 \leq h \leq 19$, $-37 \leq k \leq 37$, $-26 \leq l \leq 25$; of 64586 reflections, 18449 were independent and 11876 were observed ($F > 4\sigma(F)$), semiempirical absorption correction with SADABS (max./min. transmission 1.000/0.684), $R_1 = 0.0622$, $wR_2 = 0.1033$ ($F > 4\sigma(F)$), GOF(F^2) = 1.076; maximum residual electron density 1.098 e Å^{-3}. The weighting factor was $w^{-1} = \sigma^2 F_o^2 + (0.0279\,P)^2 + 53.5075\,P$ with $P = (F_o^2 + 2\,F_c^2)/3$. The structure was solved by direct methods (SHELXTL, version 5). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined using fixed isotropic U_i values and a riding model. Crystallographic date (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112178. 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).

[8] Holleman-Wiberg, *Lehrbuch der Anorganischen Chemie*, 101. ed., DeGruyter, Berlin, **1995**.

[9] J. Donohue, *The Structures of the Elements*, Wiley, New York **1974**, 244.

[10] If the four R*In groups each donate two electrons, and the two In atoms each donate three electrons or—more probably—each only one electron (inert s electron pair!) to the In_6 framework of **2**, $14 = 2n+2$ or $8 = 2n-2$ framework electrons (n = number of framework atoms) can be calculated. According to the framework electron counting rules of Wade and Mingos[8] in the first case $R^*_4In_6$ should be classified as a *closo* compound (In_6 octahedron), in the latter case as a double-capped *closo* compound ("*hypoprecloso*" compound; double-capped In_4 tetrahedron).[11] $R^*_4In_6$ can be described as the supersilyl derivative of the *closo*-hexahydridohexaindate $In_6H_6^{2-}$, which has two hydride ions less and is a homologue of the known *closo*-hexahydridohexaborate $B_6H_6^{2-}$.[8]

[11] By employing $R^*_6In_8$ we recently isolated an indane, which in terms of its framework electron number[10] is related to $R^*_4In_6$. According to the X-ray structural analysis in the structure of the present In_8 cluster (double-capped In_6 octahedron) the octaindane is rather classified as a *hypoprecloso* compound in accordance with the discussion in ref. [10]: N. Wiberg, T. Blank, H. Schnöckel, A. Purath, unpublished results.

[12] W. Uhl, M. Layh, W. Hiller, *J. Organomet. Chem.* **1989**, *368*, 139.

[13] P. J. Brothers, K. Hübler, U. Hübler, B. C. Noll, M. M. Olmstead, P. P. Power, *Angew. Chem.* **1996**, *108*, 2528; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2355.