

Reaction of $[\text{In}(\text{NEt}_2)_3]_2$ with $\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3\text{H})_3$: Synthesis and Characterization of New Azaindatranes and Azaindocane

Pavel L. Shutov,^[a] Sergey S. Karlov,^{*[b]} Klaus Harms,^[a] Andrei V. Churakov,^[c]
Jörg Lorberth,^[a] and Galina S. Zaitseva^[b]

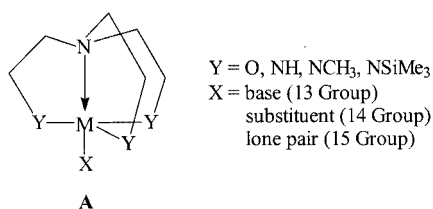
Keywords: N ligands / Indium / Tripodal ligands / Amides

$[\text{In}(\text{NEt}_2)_3]_2$ and $\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3\text{H})_3$ react to yield monomeric azaindatrane **1**, $\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3\text{In}$, which is unstable without additional donor (e.g. pyridine), turning into dimeric azaindatrane **2**, $[\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_2(\text{CH}_2\text{CH}_2\text{NH})\text{In}]_2$. An intermediate product of this transformation is oligomeric azaindocane **3**, $[\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_2\text{In}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)]_3$. The composition and structures of new compounds have been established by ^1H and ^{13}C NMR spectroscopy. The crystal structures of **1**·Py, *trans*-**2**, and **3** have been determined by X-ray diffraction studies.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

The chemistry of indium amido compounds continues to be of interest due to their importance in preparing nitride ceramic materials and semiconductors.^[1–3] During our studies of groups 13–15 metallatranes (**A**, Scheme 1, Y = O) and azametallatranes (**A**, Scheme 1, Y = NR)^[4–8] we have reported the synthesis and X-ray investigation of the first azaindatrane – $[\text{N}(\text{CH}_2\text{CH}_2\text{NMe})_3\text{In}]_2$.^[8] This compound is dimeric both in the solid phase and in solution due to the formation of an (In–N)₂ core with a very unusual set of In–N distances.^[8]



Scheme 1

Monomeric tris-amides of group 13 elements are a promising class of precursors of technologically important group 13 nitride semiconductors.^[1–3] Bulky substituents R in the parent tetramine $\text{N}[\text{CH}_2\text{CH}_2\text{NRH}]_3$ are expected to stabilize the monomeric structure of azaindatranes. We re-

port here the reactions of $[\text{In}(\text{NEt}_2)_3]_2$ and InCl_3 with $\text{N}[\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)\text{H}]_3$ ($\text{Me}_3\text{Si-tren}$) and the lithium salt of $\text{Me}_3\text{Si-tren}$ $\{\text{N}[\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)\text{Li}]\}_3$, respectively. We aimed to prepare Me_3Si -containing azaindatranes and to estimate the influence of bulky Me_3Si groups on structure and stability of monomeric species.

We therefore synthesized four new indium tris-amides containing $[\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3]^{3-}$ or $[\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_2(\text{CH}_2\text{CH}_2\text{NH})]^{3-}$ moieties: $\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3\text{In}$ (**1**), $\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3\text{In}\cdot\text{C}_5\text{H}_5\text{N}$ (**1**·Py), dimeric derivative **2**, and oligomeric compound **3** (Scheme 2). The structures of compounds **1**·Py, *trans*-**2**, and **3** have been confirmed by X-ray diffraction studies.

Results and Discussion

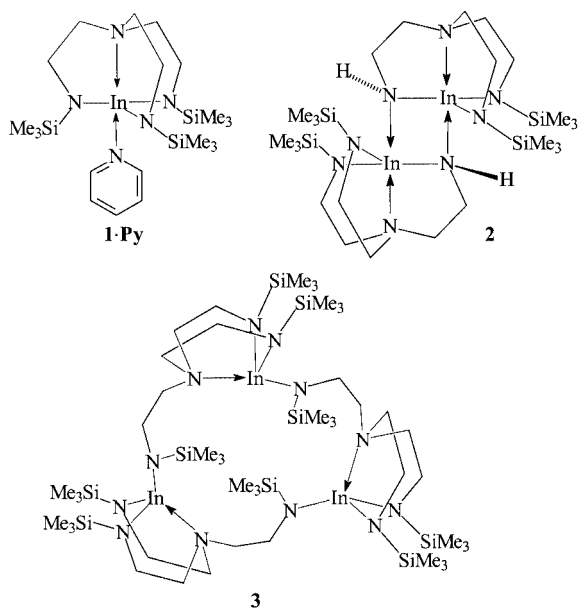
Verkade et al. have carried out syntheses, NMR spectroscopy investigations and X-ray diffraction studies of closely related tris(*N,N',N''*-trimethylsilyl)azaatranes of boron (**4**), aluminium (**5**), and gallium (**6**) (Scheme 3).^[9–11] The reaction of $\text{B}(\text{NMe}_2)_3$ with $\text{Me}_3\text{Si-tren}$ afforded **4** in low yield (6%),^[9] which was explained by the preferred formation of polymeric products. However, the structure of these polymeric products was not established. Compounds of the type $\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3\text{M}$ [M = Al (**5**), yield 18%;^[9] Ga (**6**), yield 88%^[11]] were synthesized also, via transamination of $\text{M}(\text{NMe}_2)_3$ with $\text{Me}_3\text{Si-tren}$. Dimeric aluminium azaatrane **7**, the structure of which is analogous to azaindatrane **2**, was obtained during attempts to grow single crystals of **5** from pentane solution.^[10]

Our synthetic results are summarized in Scheme 4. Treatment of $[\text{In}(\text{NEt}_2)_3]_2$ with $\text{Me}_3\text{Si-tren}$ in the presence of an

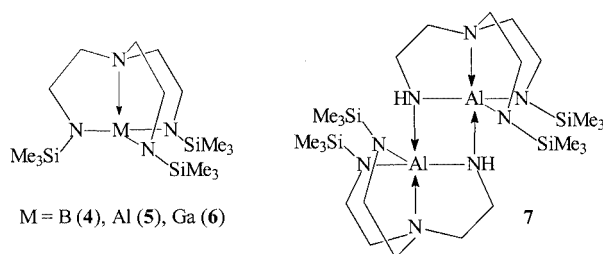
^[a] Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, 35032 Marburg/Lahn, Germany

^[b] Chemistry Department, Moscow State University, Leninskie Gory 1, str. 3, 119899 Moscow, Russia
E-mail: sergej@org.chem.msu.su

^[c] Institute of General and Inorganic Chemistry, RAS, Leninsky Prospect 31, 119991 Moscow, Russia

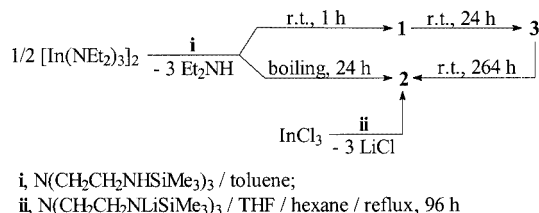


Scheme 2



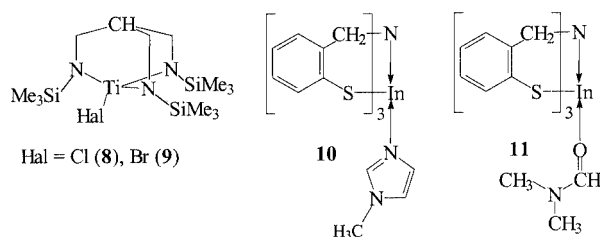
Scheme 3

excess of C_5H_5N led, after standard workup, to **1**·Py in good yield. Notably, carrying-out this reaction without pyridine led to complex **1** (NMR spectroscopic data). Unfortunately, **1** could not be obtained as a pure solid. According to NMR spectroscopic data this compound is an adduct of **1** with one molecule of $HNEt_2$ formed during transamination. However, no additional evidence of this transure was obtained by other methods. Compound **1** is unstable in toluene and in C_6D_6 and turns over 24 h into the oligomeric compound azaindocane **3**, which was obtained after recrystallization from pentane ($-30\text{ }^\circ\text{C}$). This transformation might be explained by the lesser steric hindrances in **3** compared with monomeric complex **1**. To the best of our knowledge no similar reactions have been found in “atrane” chemistry.



Scheme 4

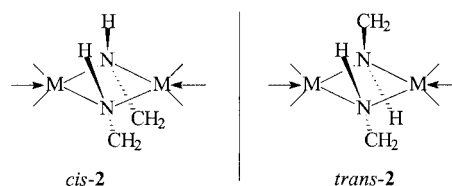
Further standing of solutions of **3** at room temperature afforded dimeric azaindatrane **2**. The conversion ($\approx 70\%$, 1H NMR data) of the oligomeric ocane **3** into the dimer **2** was observed after 11 days. Formally, the bulky Me_3Si group is substituted by hydrogen during this reaction. However, the true nature of this transformation is unclear. An analogous dimerization passing through desilylation processes has been found for $(Me_3Si)_3$ -azaalumatrane **6**^[10] and related titanium derivatives (compounds **8** and **9**, Scheme 5).^[12] A hydrolytic pathway in the first case, and the reaction of titanium complexes with solvent protons (THF), have been proposed as possible explanations for the formation of desilylated dimers. However, all attempts to prepare **7** by controlled hydrolysis of monomeric **6** failed.^[10] The authors did not report the formation of any oligomeric products during both dimerization reactions.^[10,12]



Scheme 5

Complex **1**·Py also turns into **2** at room temperature (40 days, 100%). However, the formation of **3** was undoubtedly detected by NMR spectroscopy in this reaction. Azaatrane **2** was obtained in moderate yield from the reaction of $[In(NEt_2)_3]_2$ with Me_3Si -tren at $95\text{ }^\circ\text{C}$ (24 h) – no traces of **1** and **3** being detected in reaction mixture after heating. Compound **2** was the only product that contains an atrane framework in the reaction between $InCl_3$ and the Li_3 -salt of Me_3Si -tren. The lithium salt was prepared in situ by treatment of tetramine (Me_3Si -tren) with three equivalents of $nBuLi$.

Compound **2** has a *trans* structure for the central $(In-NH)_2$ core, as confirmed by X-ray data (vide infra). However, the ^{13}C NMR spectra of all the reaction mixtures that lead to **2** contain signals (trace amounts) that may be assigned to *cis*-**2** (Scheme 6), but the *cis*-isomer was not isolated as a pure solid. Conversely, only the *cis*-isomer of **7** was formed in the dimerization of $N(CH_2CH_2NSiMe_3)_3Al$ (**6**).^[10] Analogously, we recently found that only the *cis*-isomer of $[N(CH_2CH_2NMe)_3In]_2$ was formed in the reaction of $[In(NEt_2)_3]_2$ with Me -tren $[N(CH_2CH_2NMeH)_3]$, with no traces of *trans*-isomer.^[8]



Scheme 6

Thus, we conclude that the dimeric azaatrane **2** is the most thermodynamically stable product of the transamination reaction of $[\text{In}(\text{NEt}_2)_3]_2$ with $\text{Me}_3\text{Si-tren}$. Donor ligands (e.g. pyridine) partially stabilize the monomeric structure of azaindatrane (compound **1**·Py).

Both ^1H and ^{13}C NMR data agree with the suggested structures for **1**, **1**·Py, **2**, and **3**. In the ^1H NMR spectra of **1** and **1**·Py, signals of methylene protons of the azaindatrane skeleton appear as a set of two pseudo-triplets, forming an AA'MM' spin system ($J = 4.9\text{--}5.1$ Hz). This pattern is a general feature of the "azaatrane" framework for various azametallatranes.^[13] The δ_{C} signals of the azaatrane skeleton lie within the range typical of those in closely related monomeric derivatives of group 13 elements.^[9–11] Thus, **1** and **1**·Py are monomeric in C_6D_6 solution.

In contrast, the ^1H and ^{13}C NMR spectra of **2** and **3** are more complicated. For **2** the data are consistent with a dimer. After purification, **2** was found in solution as one of two geometrical isomers (according to X-ray data – *trans*-**2**) of the In_2N_2 core (Scheme 6). This is documented by two singlets of the Me_3Si groups and twelve partially overlapping multiplets of six CH_2 groups in the ^1H NMR spectrum of **2**. Eight signals of the atrane skeleton carbon atoms appear in the ^{13}C NMR spectrum of **2**. The hydrogen atoms of six methylene groups and methylene carbon atoms as well as each Me_3Si group of one monomeric unit in **3** are also non-equivalent.

Notably, no molecular ions $[\text{M}^+]$ or heavy ions that contain at least one In atom were found in mass-spectra (EI, 70 eV) of studied compounds (**1**·Py, **2** and **3**).

Herein we report the crystal structures of azaindatranes **1**·Py and **2** and also of **3** [Figure 1 (one independent molecule), Figure 2 and Figure 3, respectively]. Important bond lengths and angles for **1–3** are summarized in Table 1.

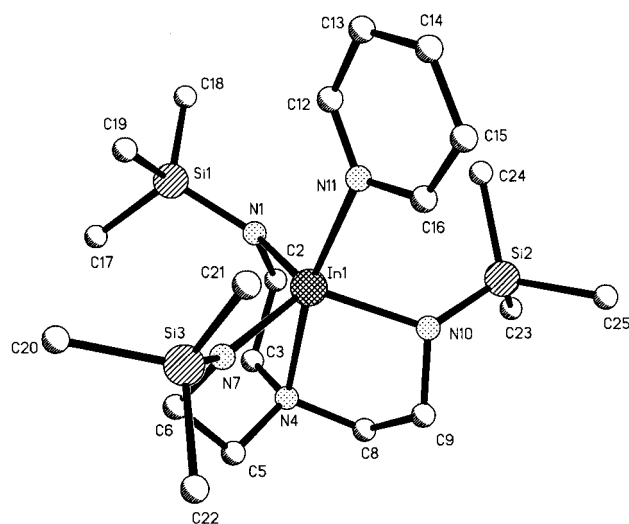


Figure 1. Molecular structure of **1**·Py (one independent molecule); hydrogen atoms omitted for clarity

The coordination polyhedron of the In atom in complex **1**·Py represents a distorted trigonal bipyramid (TBP) with N(4) (N_{ax}) and N(11) (N_{ax}^b) (Scheme 7) occupying the axial

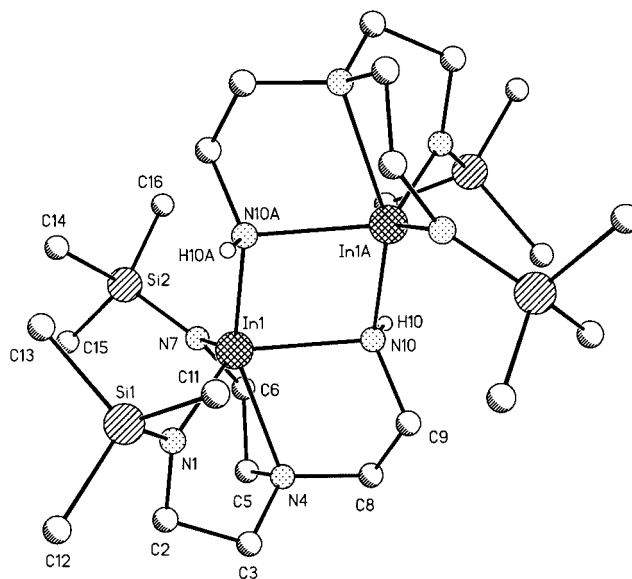


Figure 2. Molecular structure of **2**; hydrogen atoms (except H10 and H10A) omitted for clarity

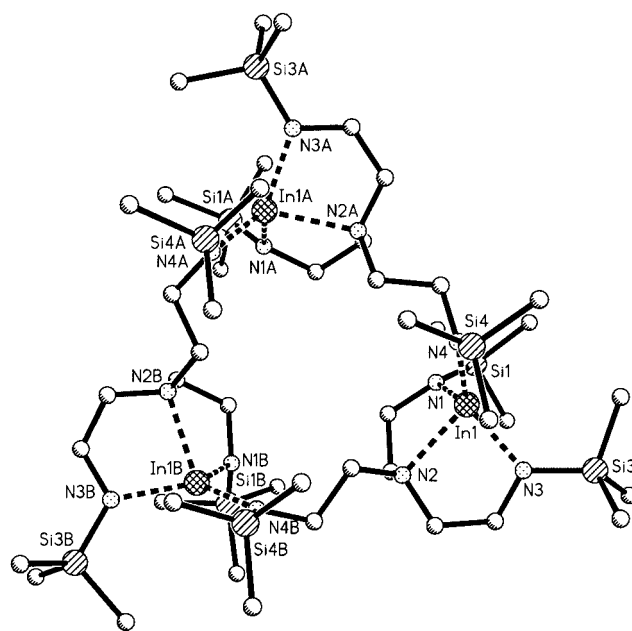


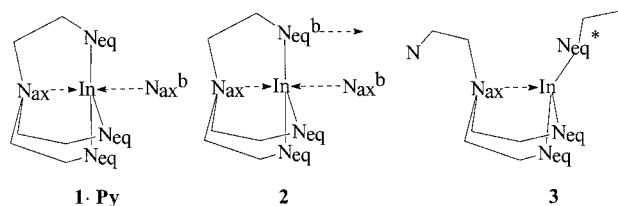
Figure 3. Molecular structure of **3**; hydrogen atoms and solvate cyclohexane molecule omitted for clarity

positions. Three other nitrogen atoms [N(1), N(7), and N(10)] lie in equatorial sites (N_{eq}); $N_{\text{eq}}\text{--In--}N_{\text{eq}}$ angles range between $112.3(1)^\circ$ and $121.5(1)^\circ$, $N_{\text{ax}}\text{--In--}N_{\text{eq}}$ angles range between $78.4(1)^\circ$ and $80.9(1)^\circ$, and $N_{\text{ax}}^b\text{--In--}N_{\text{eq}}$ angles range between $90.8(1)^\circ$ and $107.3(1)^\circ$ for **1**·Py. The N(4)–In–N(11) fragment is close to linear for both independent molecules of **1**·Py [$169.3(1)^\circ$, $169.2(1)^\circ$]. These angles are smaller than those of closely related structures: $179.1(2)^\circ$ for **10** and $178.4(4)^\circ$ for **11** (Scheme 5).^[14] However, they are greater than those in the dimer $[\text{N}(\text{CH}_2\text{CH}_2\text{NMe}_3)\text{In}]_2$: $150.3(1)\text{--}157.77(9)^\circ$ for two independent molecules.^[8] The latter proves that there is less

Table 1. Selected bond lengths (Å) and angles (°) for **1**·Py (two independent molecules), **2**, and **3** (^a: Displacement of In atom from the plane defined by the three N_{eq} atoms towards the N_{ax} atom; ^b: displacement of N_{ax} atom from the plane defined by the three carbon atoms towards the indium atom)

	1 ·Py	2	3
N _{ax} →In	2.412(3)	2.427(1)	2.398(3)
N _{ax} →In ^b	2.340(3)	2.206(1)	2.326(3)
In–N _{eq}	2.091(3)	2.076(1)	2.096(3)
	2.100(3)	2.098(1)	2.107(3)
	2.120(3)	2.123(3)	
In–N _{eq} [*] (2) or In–N _{eq} ^b (3)	—	2.249(1)	—
ΔIn (to N _{ax}) ^a	0.38	0.44	0.38
ΔN _{ax} ^b (to In)	0.36	0.39	0.37
N _{ax} –In–N _{ax} ^b	169.3(1)	153.89(5)	169.2(1)
N _{eq} –In–N _{eq} (or N _{eq} ^b , or N _{eq} [*])	112.3(1)	119.43(6)	113.7(1)
	121.5(1)	108.64(6)	116.5(1)
	116.6(1)	119.19(5)	120.4(1)
N _{eq} –M–N _{ax} ^b	103.9(1)	119.59(6)	104.0(1)
	107.3(1)	102.87(5)	106.4(1)
	90.6(1)	81.51(5)	90.8(1)
N _{eq} –M–N _{ax}	80.1(1)	79.86(5)	80.9(1)
	79.7(1)	78.70(5)	79.8(1)
	79.0(1)	75.33(5)	78.4(1)
C–N _{ax} –C	114.7(3)	112.7(1)	114.8(3)
	114.2(3)	114.0(1)	112.4(3)
	113.5(3)	113.4(1)	114.9(3)

steric hindrance in **1**·Py than in dimeric [N(CH₂CH₂NMe)₃In]₂. Analogously to **1**·Py, the coordination environment at the In atom in **2** is formed by three covalently linked nitrogen atoms [N_{eq}: N(1), N(7); N_{eq}^b: N(10)] and two-coordinated nitrogen atoms – N_{ax}: N(4) and N_{ax}^b: N(10A) and may be regarded as TBP, which is more distorted than that in **1**·Py due to the steric influence of second azaatrane framework. For compound **2**, the central (In–N)₂ unit is planar, differing from that of closely related [N(CH₂CH₂NMe)₃In]₂ and **7** where central arrays form a puckered rectangle.^[8,10]



Scheme 7

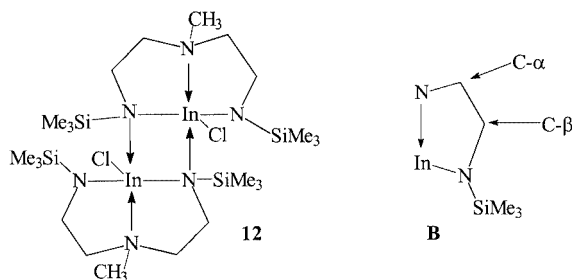
For both **1**·Py and **2**, the indium atoms are displaced by 0.38 Å (**1**·Py, both independent molecules) and 0.44 Å (**2**) from the plane defined by the three equatorial nitrogen atoms toward pyridine ring (**1**·Py) or N(10A) (**2**). These values characterize the extent of TBP distortion (this displacement should be zero in an ideal TBP).

The transannular bond lengths N_{ax}→In [2.412(3), 2.398(3) Å for **1**·Py; 2.427(1) for **2**] and N_{ax}^b→In [2.340(3), 2.326(3) Å for **1**·Py; 2.206(1) Å for **2**] in both compounds lie within the typical range for similar indium–nitrogen interactions [2.099(2)–2.62 Å]. Interestingly, the considerable

contraction of N_{ax}^b→In in **2**, compared with that in **1**·Py, does not noticeably influence the N_{ax}→In contact. To the best of our knowledge, the structures of only two tris(amido) indium species containing pyridine as additional ligand [(C₆H₅)₂N]₃In·Py, (2,6-*i*Pr₂C₆H₃NH)₃In·2Py] have previously been studied by X-ray diffractometry.^[2,3] Notably, N_{ax}^b→In (Py→In) in **1**·Py [2.340(3), 2.206(1) Å, two independent molecules] are shorter than those in (2,6-*i*Pr₂C₆H₃NH)₃In·2Py [2.460(4), 2.421(4) Å] with a pentacoordinate In atom,^[3] but similar to that in the complex [(C₆H₅)₂N]₃In·Py [2.264(4) Å] with a tetracoordinate indium atom.^[2]

Compound **3** appears to be only the second "azaindo-cane", the first being the structurally characterized dimeric **12** (Scheme 8)^[15]. In contrast to the type of In atom coordination environment found in **1**·Py and **2**, the coordination polyhedron of In atoms in trimeric compound **3** represents a strongly distorted trigonal monopyrmaid. Each indium atom in **3** is displaced by 0.22 Å from the plane defined by the two N_{eq} and one N_{eq}^{*} atoms towards the N_{ax} atom (Scheme 7). The angles formed by the three equatorial nitrogen atoms and indium atom deviate by less than 7° from the ideal value of 120°, and both N_{ax}–In–N_{eq} angles are close to 90°. However, the N_{ax}–In–N_{eq}^{*} angle is noticeably greater than 90°. The lower In coordination number in **3** (CN = 4) compared with **1**·Py and **2** (CN = 5) leads to considerable shortening of N_{ax}→In in **2** [2.294(4) Å] as against those in **1**·Py [2.412(3), 2.427(1) Å] and **2** [2.398(3) Å].

All five-membered rings of the atrane skeleton in **1**·Py and **2** as well as the ocane framework of **3** adopt an "envelope"-like conformation (Scheme 8, **B**). All carbon atoms in β-positions to the N_{ax} atom in **1**·Py and **2** occupy "flap" sites, while C-α atoms form the base of the envelope plane.



Scheme 8

This is contrary to conformations of ocane rings in **3** and those previously found for "usual" metallatranes (without C- β substituents).^[16] However, as observed for azametallatranes, C- β as well as C- α atoms may occupy "flap" sites of the "envelope".^[6,17]

Conclusion

Transamination of $[\text{In}(\text{NEt}_2)_3]_2$ and $\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3\text{H})_3$ affords the monomeric azaindatrane **1**, which is converted into the dimeric azaindatrane **2** via the unexpected azaindocane **3**. The desilylated dimer **2** has also been obtained from the reaction of InCl_3 with $\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3\text{Li})_3$. The structures of **2** and **3** as well as of the adduct **1**·Py have been confirmed by X-ray diffraction analyses.

Experimental Section

General Remarks: All manipulations were performed under dry, oxygen-free argon using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. InCl_3 (Aldrich) was used as supplied. The starting materials $\text{Me}_3\text{Si-tren}$ ^[18] and $[\text{In}(\text{NEt}_2)_3]_2$ ^[19] were prepared according to the literature. C_6D_6 was obtained from Deutero GmbH and dried with sodium. ^1H and ^{13}C NMR spectra were recorded with Bruker AC200, AC300, AC500 spectrometers at 300 K. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. Elemental analyses were carried out by the Microanalytical Laboratory of the Fachbereich Chemie of the Philipps-University of Marburg (Heraeus Rapid Analyser). Mass spectra (EI-MS) were recorded with a Varian CH-7a device using electron impact ionization at 70 eV; mass spectra (FD-MS) were recorded with a HP-5989B device; all assignments were made with reference to the most abundant isotopes.

Azaindocane 3 (Reaction of $[\text{In}(\text{NEt}_2)_3]_2$ with $\text{Me}_3\text{Si-tren}$): A solution of $\text{Me}_3\text{Si-tren}$ (0.85 g, 2.35 mmol) in toluene (15 mL) was added at room temperature to a solution of $[\text{In}(\text{NEt}_2)_3]_2$ (0.78 g, 1.18 mmol) in toluene (10 mL). The NMR spectrum of reaction mixture revealed the presence of **1**^[20] after 1 h. The reaction mixture was then stirred for a further 24 h, and all volatiles were subsequently removed under reduced pressure. The resultant solid residue was recrystallized from *n*-pentane (10 mL) to give colorless crystals **3** (yield 0.95 g, 85%). All attempts to obtain an analytically pure sample failed, probably due to the presence of traces of dimeric **2** (analytical data below) as well as variable amounts of solvent, which could not completely be removed. Single crystals of **3**

suitable for X-ray analysis were collected by recrystallization from cyclohexane.

Data for 1: ^1H NMR (C_6D_6 , 300.130 MHz): δ = -0.26 (s, 27 H, 3SiMe_3), 2.04 (t, $^3J_{\text{H,H}}$ = -5 Hz, 6 H, $\text{N}(\text{CH}_2)_3$), 3.02 (t, $^3J_{\text{H,H}}$ = -5 Hz, 6 H, 3SiNCH_2) ppm. ^{13}C NMR (C_6D_6 , 75.47 MHz): δ = -2.21 (SiCH_3), 45.61 (SiNCH_2), 58.06 [$\text{N}(\text{CH}_2)_3$] ppm.^[21]

Data for 3: ^1H NMR (C_6D_6 , 500.130 MHz): δ = -0.19 (s, 27 H, 3SiMe_3), 0.32 , 0.33 (2s, 54 H, 6SiMe_3), 2.10 – 2.15 (m, 3 H), 2.30 – 2.32 (m, 6 H), 2.55 – 2.61 (m, 3 H), 2.83 – 2.89 (m, 3 H), 2.91 – 2.98 (m, 6 H), 3.15 – 3.17 (m, 3 H), 3.20 (br. s, 6 H), 3.27 – 3.33 (m, 3 H), 3.42 – 3.48 (m, 3 H) (18CH_2 groups) ppm. ^{13}C NMR (C_6D_6 , 50.32 MHz): δ = -1.72 (SiCH_3), 1.77 (SiCH_3), 3.05 (SiCH_3), 40.79 , 42.75 , 44.82 , 54.61 , 57.28 , 58.20 (CH_2 groups) ppm. EI-MS and FD-MS: $[\text{M}^+]$ was not found. $\text{C}_{45}\text{H}_{117}\text{In}_3\text{N}_{12}\text{Si}_9$ (1423.73): calcd. C 37.96, H 8.28, N 11.81; found C 36.82, H 8.68, N 10.93.

Conversion of 3 into 2: After standing for 11 days at room temperature, a toluene solution of **3** was converted into dimeric **2** (70%), as detected by NMR spectroscopy.

trans-N,N'-Bis(trimethylsilyl)azaindatrane Dimer 2.^[22] **Method A (Reaction of $[\text{In}(\text{NEt}_2)_3]_2$ with $\text{Me}_3\text{Si-tren}$):** A solution of $\text{Me}_3\text{Si-tren}$ (1.67 g, 4.62 mmol) in toluene (25 mL) at room temperature was added to a solution of $[\text{In}(\text{NEt}_2)_3]_2$ (1.53 g, 2.31 mmol) in toluene (15 mL). The reaction mixture was then boiled under reflux for 24 h, and then all volatiles were removed under reduced pressure. The so-obtained solid residue was recrystallized from *n*-pentane (10 mL) to give colorless crystals **2** (yield 1.45 g, 66%) after standing at -30°C .

Method B (Reaction of InCl_3 with Li_3 -Salt of $\text{Me}_3\text{Si-tren}$): A solution of trilithium salt, freshly prepared from $\text{Me}_3\text{Si-tren}$ (3.8 g, 10.5 mmol) and *n*-butyllithium (1.6 M in *n*-hexane, 19.7 mL, 9.8 mmol), in THF (15 mL) at room temperature, with stirring, was added dropwise to a suspension of InCl_3 (2.32 g, 10.5 mmol) in THF (20 mL). The reaction mixture was then boiled under reflux for 96 h, and all volatiles were subsequently removed under reduced pressure. *n*-Pentane (40 mL) was then added to the residue, and insoluble substances were removed by filtration. The solution was then reduced in volume to 10 mL and stored at -30°C for 3 days to obtain colorless crystals, which were separated by rapid decantation of the cold mother liquor to give **2** (yield 2.41 g, 57%). An analytically pure sample was obtained by recrystallization from pentane. ^1H NMR (C_6D_6 , 500.130 MHz): δ = -0.28 (br. s, 36 H, 4SiMe_3), 1.72 – 1.98 (m, 4 H), 2.08 – 2.29 (m, 8 H), 2.49 – 2.67 (m, 4 H), 2.80 – 3.11 (m, 8 H) (12CH_2 groups) ppm; the NH proton signals could not be located, probably due to overlap with CH_2 multiplets. ^{13}C NMR (C_6D_6 , 75.47 MHz): δ = -2.24 (SiCH_3), 3.21 (SiCH_3), 42.62 , 43.31 , 43.82 , 59.29 , 60.55 , 60.93 (CH_2 groups) ppm. EI-MS and FD-MS: $[\text{M}^+]$ was not found. $\text{C}_{24}\text{H}_{62}\text{In}_2\text{N}_8\text{Si}_4$ (804.79): calcd. C 35.82, H 7.77, N 13.92; found C 35.05, H 8.04, N 13.09.

Adduct of N,N',N''-Tris(trimethylsilyl)azaindatrane with Pyridine, 1·Py (Reaction of $[\text{In}(\text{NEt}_2)_3]_2$ with $\text{Me}_3\text{Si-tren}$ in the Presence of Pyridine): Pyridine (5 mL) and then a solution of $\text{Me}_3\text{Si-tren}$ (2.99 g, 8.25 mmol) in toluene (20 mL) were added at room temperature to a solution of $[\text{In}(\text{NEt}_2)_3]_2$ (2.73 g, 4.12 mmol) in toluene (10 mL). The reaction mixture was then stirred for 12 h, and all volatiles were subsequently removed under reduced pressure. The resultant solid residue was recrystallized from *n*-pentane (10 mL) to give colorless crystals **1**·Py (yield 3.59 g, 79%). Single crystals of **1**·Py suitable for X-ray analysis were collected by recrystallization from *n*-pentane (-30°C , saturated solution). ^1H NMR (C_6D_6 ,

Table 2. Crystal data, data collection, structure solution and refinement parameters for **1**·Py, **2**, and **3**

Compound	1 ·Py	2	3
Empirical formula	C ₂₀ H ₄₄ In ₁ N ₅ Si ₃	C ₂₄ H ₆₂ In ₂ N ₈ Si ₄	C ₄₈ H ₁₂₃ In ₃ N ₁₂ Si ₉
Molecular mass	553.69	804.82	1465.85
Colour, habit	colourless prism	colourless prism	colourless plate
Crystal size (mm)	0.35 × 0.31 × 0.30	0.45 × 0.24 × 0.21	0.39 × 0.15 × 0.05
Crystal system	monoclinic	monoclinic	trigonal
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>R</i> -3
Unit cell dimensions, <i>a</i> (Å)	19.426(1)	10.364(1)	22.485(1)
<i>b</i> (Å)	12.0030(4)	16.309(1)	
<i>c</i> (Å)	24.639(1)	11.797(1)	22.485(1)
β (°)	90.080(4)	107.886(7)	26.544(2)
Volume (Å ³)	5745.0(4)	1897.6(3)	11622(1)
<i>Z</i>	8	2	6
Density (calculated) [g·cm ⁻³]	1.280	1.409	1.257
Absorption coefficient [mm ⁻¹]	0.963	1.367	1.061
<i>F</i> (000)	2320	832	4608
θ range (°)	1.34–25.89	2.20–26.18	1.30–24.98
Index ranges	–23 ≤ <i>h</i> ≤ 23 –13 ≤ <i>k</i> ≤ 14 –30 ≤ <i>l</i> ≤ 30	–12 ≤ <i>h</i> ≤ 12 –20 ≤ <i>k</i> ≤ 20 –14 ≤ <i>l</i> ≤ 14	–26 ≤ <i>h</i> ≤ 26 –24 ≤ <i>k</i> ≤ 26 –31 ≤ <i>l</i> ≤ 31
Reflections collected	55794	17852	20441
Independent reflections	11076 [<i>R</i> _{int} = 0.0394]	3754 [<i>R</i> _{int} = 0.0308]	4520 [<i>R</i> _{int} = 0.0764]
Data/restraints/parameters	11076/0/542	3754/0/183	4520/0/226
Goodness-of-fit on <i>F</i> ²	1.031	1.054	0.954
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0280, <i>wR</i> ₂ = 0.0718	<i>R</i> ₁ = 0.0172, <i>wR</i> ₂ = 0.0422	<i>R</i> ₁ = 0.0490, <i>wR</i> ₂ = 0.1287
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0332, <i>wR</i> ₂ = 0.0733	<i>R</i> ₁ = 0.0205, <i>wR</i> ₂ = 0.0431	<i>R</i> ₁ = 0.0727, <i>wR</i> ₂ = 0.1374
Extinction coefficient	—	0.0003(4)	—
Largest diff. peak/hole [e·Å ⁻³]	0.521/–0.708	0.285/–0.263	0.938/–0.624

300.130 MHz): δ = –0.14 (s, 27 H, 3SiMe₃), 2.30 [t, ³*J*_{H,H} = –5 Hz, 6 H, N(CH₂)₃], 3.14 (t, ³*J*_{H,H} = –5 Hz, 6 H, 3SiNCH₂), 6.55–6.59 (m, 2 H, Py hydrogen atoms), 6.81–6.86 (m, 1 H, Py hydrogen), 8.80–8.83 (m, 2 H, Py hydrogen atoms) ppm. ¹³C NMR (C₆D₆, 75.47 MHz): δ = –2.82 (SiCH₃), 44.51 (SiNCH₂), 61.76 [N(CH₂)₃], 124.24, 138.11, 150.12 (Py carbon atoms) ppm.^[21] EI-MS: [M⁺] not found. C₂₀H₄₄InN₅Si₃ (553.676): calcd. C 43.39, H 8.01, N 12.65; found C 42.99, H 7.70, N 11.92.

Conversion of **1·Py into **2**:** After standing at room temperature for 40 days, a toluene solution of **1**·Py was converted into dimer **2** (100%), as detected by NMR spectroscopy. According to ¹H NMR data the reaction mixture contained **1**·Py, **2**, and **3** (ratio 5:3:2) after 18 days.

X-ray Crystallographic Study: Crystal data, data collection, structure solution and refinement parameters for compounds **1**·Py, **2**, and **3** are presented in Table 2. Experimental intensities were measured with a Stoe IPDS diffractometer using graphite-monochromatized Mo-*K*_α radiation (λ = 0.71073 Å) at 193(2) K. The structures were solved by direct methods^[23] and refined by full-matrix least-squares on *F*²^[24] with anisotropic thermal parameters for all non-hydrogen atoms. All H atoms were placed in calculated positions and refined using a riding model.

CCDC-224379 (for **1**·Py), -224380 (for **2**), and -224381 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Philipps-University Marburg, Chemistry Department, with a grant for P. L. S.

- [1] A. P. Purdy, *Inorg. Chem.* **1994**, *33*, 282–286.
- [2] J. Kim, S. G. Bott, D. M. Hoffman, *Inorg. Chem.* **1998**, *37*, 3835–3841.
- [3] J. S. Silverman, C. J. Carmalt, A. H. Cowley, R. D. Culp, R. A. Jones, B. G. McBurnett, *Inorg. Chem.* **1999**, *38*, 296–300.
- [4] P. L. Shutov, S. S. Karlov, K. Harms, A. V. Churakov, J. A. K. Howard, J. Lorberth, G. S. Zaitseva, *Eur. J. Inorg. Chem.* **2002**, 2784–2788.
- [5] P. L. Shutov, S. S. Karlov, K. Harms, D. A. Tyurin, A. V. Churakov, J. Lorberth, G. S. Zaitseva, *Inorg. Chem.* **2002**, *41*, 6147–6152.
- [6] P. L. Shutov, D. A. Sorokin, S. S. Karlov, K. Harms, Yu. F. Oprunenko, A. V. Churakov, M. Yu. Antipin, G. S. Zaitseva, J. Lorberth, *Organometallics* **2003**, *22*, 516–522.
- [7] E. V. Gauchenova, S. S. Karlov, A. A. Selina, E. S. Chernyshova, A. V. Churakov, J. A. K. Howard, N. A. Troitsky, S. N. Tandura, J. Lorberth, G. S. Zaitseva, *J. Organomet. Chem.* **2003**, *676*, 8–21.
- [8] P. L. Shutov, S. S. Karlov, K. Harms, O. Kh. Poleshchuk, J. Lorberth, G. S. Zaitseva, *Eur. J. Inorg. Chem.* **2003**, 1507–1510.
- [9] J. Pinkas, B. Gaul, J. G. Verkade, *J. Am. Chem. Soc.* **1993**, *115*, 3925–3931.
- [10] J. Pinkas, T. Wang, R. A. Jacobson, J. G. Verkade, *Inorg. Chem.* **1994**, *33*, 4202–4210.

- [11] J. Pinkas, T. Wang, R. A. Jacobson, J. G. Verkade, *Inorg. Chem.* **1994**, 33, 5244–5253.
- [12] S. Friedrich, L. H. Gade, A. J. Edwards, M. McPartlin, *Chem. Ber.* **1993**, 126, 1797–1805.
- [13] J. G. Verkade, *Coord. Chem. Rev.* **1994**, 137, 233–295.
- [14] R. J. Motekaitis, A. E. Martell, S. A. Koch, J. Hwang, D. A. Quarless, M. J. Welch, *Inorg. Chem.* **1998**, 37, 5902–5911.
- [15] N. Emig, H. Nguyen, H. Krautscheid, R. Réau, J.-B. Cazaux, G. Bertrand, *Organometallics* **1998**, 17, 3599–3608.
- [16] G. S. Zaitseva, S. S. Karlov, B. A. Siggelkow, E. V. Avtomonov, A. V. Churakov, J. A. K. Howard, J. Lorberth, *Z. Naturforsch., Teil B* **1998**, 53, 1247–1254.
- [17] P. L. Shutov, S. S. Karlov, K. Harms, D. A. Tyurin, A. V. Churakov, J. A. K. Howard, J. Lorberth, G. S. Zaitseva, *J. Molec. Struct. J. Mol. Struct.* **2004**, 689 261–268.
- [18] G. S. Zaitseva, B. A. Siggelkow, S. S. Karlov, G. V. Pen'kovoy, J. Lorberth, *Z. Naturforsch., Teil B* **1998**, 53, 1255–1258.
- [19] G. Rossetto, N. Brianese, A. Camporese, M. Porchia, P. Zarella, R. Bertocello, *Main Group Met. Chem.* **1991**, 14, 113–122.
- [20] 4,6,11-Tris(trimethylsilyl)-1,4,6,11-tetraaza-5-indatricyclo-[3.3.3.0^{1,5}]undecane.
- [21] Assignments of CH_2 signals agree with the data of Verkade et al. for $\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3\text{M}$ ($\text{M} = \text{B}, \text{Al}$).^[9]
- [22] 4,6-Bis(trimethylsilyl)-1,4,6,11-tetraaza-5-indatricyclo-[3.3.3.0^{1,5}]undecane dimer.
- [23] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, 46, 467–473.
- [24] G. M. Sheldrick, *SHELXL-97*. Program for the Refinement of Crystal Structures. University of Göttingen, Germany, **1997**.

Received November 26, 2003

Early View Article

Published Online April 6, 2004