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Key indicators

Single-crystal X-ray study

T = 173 K

Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$

R factor = 0.041

wR factor = 0.104

Data-to-parameter ratio = 40.1

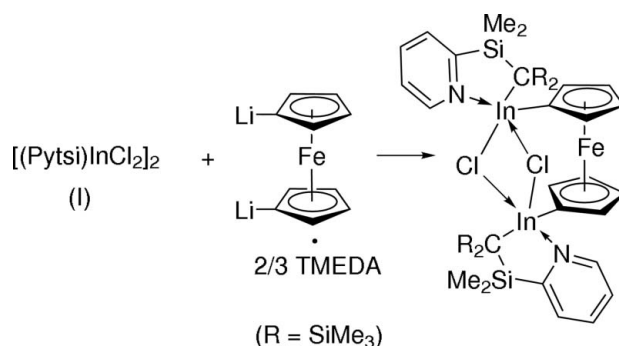
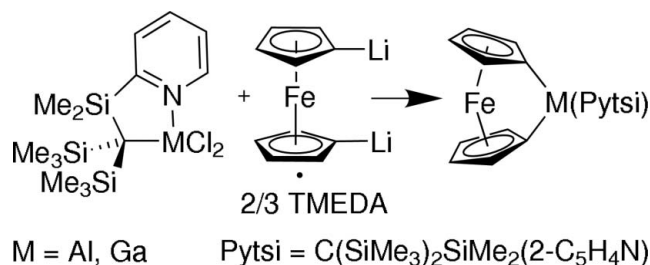
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A monomeric fourfold-coordinated indium dihalide with an unusual coordination geometry

The single-crystal X-ray analysis of the title compound, $\{[\text{dimethyl}(2\text{-pyridyl})\text{silyl}]\text{bis}(\text{trimethylsilyl})\text{methyl}\}\text{diiodoindium(III)}$, $[\text{In}(\text{C}_{14}\text{H}_{28}\text{NSi}_3)_2\text{I}_2]$, revealed monomeric molecules containing tetracoordinated In with an unusual trigonal–pyramidal geometry.

Comment

We recently synthesized the first [1]alumina- and [1]gallaferrocenophanes (scheme 1) (Schachner *et al.*, 2005*a,b*). We intended to use a similar procedure to prepare a hitherto unknown [1]indiaferrocenophane and synthesized the starting material, $(\text{Pytsi})\text{InCl}_2$, (I) [Pytsi = $\text{C}(\text{SiMe}_3)_2\text{SiMe}_2(\text{C}_5\text{H}_4\text{N}-2)$; Schachner *et al.*, 2005*b*]. In contrast with the respective dichlorides of aluminium and gallium (scheme 1), indane (I) is a chloro-bridged dimer in the solid state (scheme 2). Compound (I) reacted with dilithioferrocene, but did not give the targeted [1]ferrocenophane. Instead, an unusual ferrocene derivative could be isolated, in which the two Cp ligands were bridged by an $\text{In}(\mu\text{-Cl})_2\text{In}$ group (scheme 2). This result might suggest that a monomeric indium dihalide is needed for the synthesis of the target [1]indiaferrocenophane.



Reaction of InI_3 with $\text{Li}(\text{THF})(\text{Pytsi})$ (THF is tetrahydrofuran) in a 1:1 ratio resulted in $(\text{Pytsi})\text{InI}_2$, (II), in a moderate isolated yield of 56%. In contrast with the dichloride, (I), the title compound, (II), crystallizes as a monomer (Fig. 1).

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The In atom in compound (II) is fourfold-coordinated by atoms I1, I2, C7 and N1. The In1/I1/I2/C7 subset can be described as a trigonal pyramid, with atom In1 at the centre of the trigonal base and atom N1 at the apex. The sum of the three angles I1–In1–I2, C7–In1–I1 and C7–In1–I2 is 356.4°, which is only a few degrees away from an idealized planar coordination. At first glance, the coordination of the In centre looks like that of a trigonal-bipyramid with one apical position unoccupied. A close inspection of the packing of the molecules shows an I atom at a distance of 4.3421 (4) Å, approximately along the axis of the trigonal pyramid, with the N1–In1–I1 angle being 165.79 (11)° [symmetry code: (i) $-x, 1-y, -z$]. The In1–I1 distance is ~ 0.4 Å greater than the sum of the usually accepted van der Waals radii, which are 1.93 and 1.96 Å, respectively (Bondi, 1964).



Compound (II) is an example of a structurally characterized indium dihalide species with only fourfold-coordinated In atoms in monomeric molecules. A search of the Cambridge Structural Database (Version 5.26; Allen, 2002) for indium dihalides with at least one In–C or one In–N bond revealed that several species with fourfold coordination (Veith & Recktenwald, 1984; Veith *et al.*, 1991; Annan *et al.*, 1991; de Souza *et al.*, 1993; Cowley *et al.*, 1995; Fischer *et al.*, 1996; Jutzi *et al.*, 1996; Black *et al.*, 1997; Delpech *et al.*, 2002; Kuhner *et al.*, 1998; Abernethy *et al.*, 2000; Felix *et al.*, 2000; Stender *et al.*, 2001; Peppe *et al.*, 2001; Cheng *et al.*, 2002; Baker *et al.*, 2002; Schulte & Gabbai, 2002; Bock *et al.*, 2004) and one species with threefold coordination are known (Schulz *et al.*, 1993; Petrie *et al.*, 1993). However, all known species with tetra-coordination exhibit In in a tetrahedral environment. From the study of Lewis acid–base adducts, it is known that the pyramidalization of the Lewis acid moiety becomes more pronounced with increasing donor bond strength (see, for example, Jiao *et al.*, 1994; Jonas *et al.*, 1994). If this effect were to be of importance in species (II), then the nearly planar I₂InC group would suggest a very weak In–N donor interaction. The weakness of the bond should be evident in an unusually long In–N bond. However, the known indium dichloride (η^1 -Me₄C₅CH₂CH₂NMe₂)InCl₂, in which the In atom shows a similar set of coordinated atoms to those in compound (II), exhibits tetrahedrally surrounded In atoms, with an In–N bond length of 2.265 (5) Å (Jutzi *et al.*, 1996). Within the standard uncertainty, the In–N distance in compound (II) is the same (Table 1).

We can only speculate that the unusual coordination geometry of In in compound (II) results mainly from steric crowding in the vicinity of In. It may be that the large I atoms and two bulky SiMe₃ groups do not allow for a pyramidalization of the Lewis acid moiety. To the best of our knowledge,

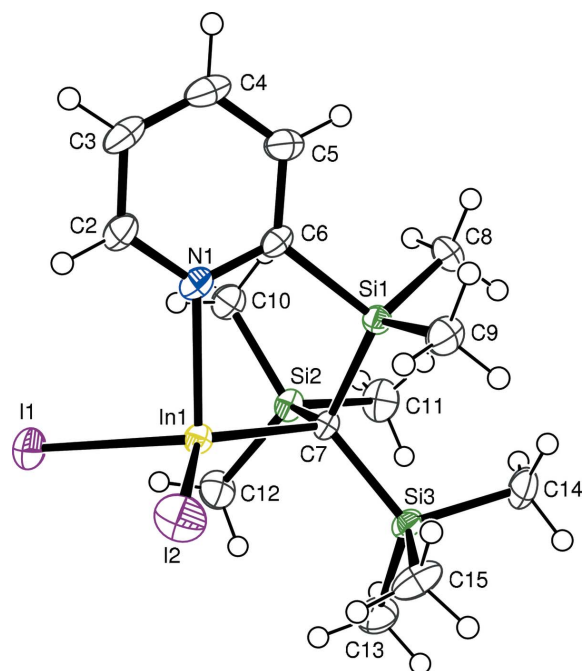


Figure 1
A view of the molecule of (II), with displacement ellipsoids drawn at the 50% probability level.

compound (II) is the first indium dihalide with such an unusual coordination polyhedron (Fig. 1).

Experimental

InI₃ (1.642 g, 3.31 mmol) in tetrahydrofuran (THF; 25 ml) at 195 K was added to Li(THF)(Pytsi) (Al-Juaid *et al.*, 2000; 1.236 g, 3.31 mmol) in THF (10 ml) at 195 K, resulting in a green solution. The solution was stirred for 1 h at 195 K before being allowed to warm to room temperature. After the mixture had been stirred for an additional 16 h, all volatiles were removed *in vacuo* and a green solid was left behind. This crude product was washed with diethyl ether (3 × 15 ml) and the washings were combined and filtered. Subsequently, the solvent was removed *in vacuo* and the remaining solid was heated to 373 K under vacuum to remove unreacted starting materials by a flask-to-flask condensation. Diethyl ether (10 ml) was added to the remaining solid, and the resulting solution was filtered and finally kept at 248 K to afford (II) (1.237 g, 56%). Spectroscopic analysis: ¹H NMR (500 MHz, C₆D₆, 298 K, δ , p.p.m.): 0.26 (18H, s, SiMe₃), 0.36 (6H, s, SiMe₂), 6.32 (1H, *pst*, 5-H), 6.72 (1H, *pst*, 4-H), 6.79 (1H, *d*, $J = 7.6$ Hz, 3-H), 8.46 (1H, *d*, $J = 5.4$ Hz, 6-H); ¹³C NMR: 3.97 (SiMe₂), 6.55 (SiMe₃), 125.50 (5-C), 129.48 (3-C), 138.83 (4-C), 147.81 (6-C), 169.32 (*ipso*-C); MS: $m/z = 536$ (100) [C₁₄H₂₈IInNSi₃]⁺, 264 (85) [C₁₂H₂₂NSi₃]⁺. Anal. Calcd for C₁₄H₂₈NSi₃InI₂ (663.272): C, 25.35; H, 4.26; N, 2.11. Found: C, 25.19; H, 4.51; N, 2.06.

Crystal data

[In(C₁₄H₂₈NSi₃)I₂]
M_r = 663.26
 Monoclinic, *P*2₁/*c*
a = 9.9492 (1) Å
b = 13.6254 (2) Å
c = 18.9012 (3) Å
 β = 116.972 (1)°
V = 2283.58 (6) Å³
Z = 4

D_x = 1.929 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 8085 reflections
 $\theta = 1.0$ –32.0°
 $\mu = 3.89$ mm⁻¹
T = 173 (2) K
 Block, colourless
 0.10 × 0.10 × 0.08 mm

Data collection

Nonius KappaCCD area-detector diffractometer	6166 reflections with $I > 2\sigma(I)$
φ scans, and ω scans with κ offsets	$R_{\text{int}} = 0.031$
Absorption correction: none	$\theta_{\text{max}} = 32.0^\circ$
14706 measured reflections	$h = -14 \rightarrow 14$
7936 independent reflections	$k = -18 \rightarrow 20$
	$l = -28 \rightarrow 28$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 7.7352P]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.104$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 1.75 \text{ e } \text{\AA}^{-3}$
7936 reflections	$\Delta\rho_{\text{min}} = -2.16 \text{ e } \text{\AA}^{-3}$
198 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$).

In1–I1	2.7172 (4)	In1–C7	2.207 (3)
In1–I2	2.6891 (4)	In1–I1 ⁱ	4.3421 (4)
In1–N1	2.270 (3)		
N1–In1–C7	91.00 (12)	I1–In1–I2	103.958 (14)
N1–In1–I2	102.26 (8)	C7–In1–I1	127.91 (9)
N1–In1–I1	96.56 (9)	C7–In1–I2	124.57 (9)
N1–In1–I1 ⁱ	165.79 (11)		

Symmetry code: (i) $-x, -y + 1, -z$.

H atoms were placed in calculated positions, with C–H distances in the range 0.95–0.99 \AA , and included in the refinement in the riding-model approximation, with $U_{\text{iso}}(\text{H})$ constrained to be $1.2U_{\text{eq}}(\text{C})$ for all aromatic H atoms and $1.5U_{\text{eq}}(\text{C})$ for all methyl H atoms. The highest peak was located 0.40 \AA from In1 and the deepest hole 0.57 \AA from Iⁱⁱ.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

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