

An Electron-deficient Indium Hydride. Crystal Structure and N.M.R. Spectrum of $(\text{Me}_3\text{Si})_3\text{C}\overline{\text{In}}(\text{H})(\mu\text{-H})\text{Li}(\text{thf})_2(\mu\text{-H})\overline{\text{In}}(\mu\text{-H})(\text{H})\text{C}(\text{SiMe}_3)_3$ (thf = tetrahydrofuran)

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The hydride $(\text{Me}_3\text{Si})_3\text{C}\overline{\text{In}}(\text{H})(\mu\text{-H})\text{Li}(\text{thf})_2(\mu\text{-H})\overline{\text{In}}(\mu\text{-H})(\text{H})\text{C}(\text{SiMe}_3)_3$ (**1**) (thf = tetrahydrofuran) has been structurally characterised; there are probably single hydrogen bridges between In and Li and between In and In in the crystal, and the structure is probably preserved in solution in toluene or thf.

The only previously known indium hydrides which are stable above 20 °C appear to be a solid $(\text{InH})_x$ of unknown structure,¹ the trialkylindates $\text{M}[\text{InR}_3\text{H}]$ (M = Na or K; R = Me, Et,² or Me_3SiCH_2 ³), and sodium diethylindate $\text{Na}[\text{InEt}_2\text{H}_2]$.² Alkyltriindates and tetrahydroindates are reported to be too unstable for isolation and characterisation.¹ We have now shown that by attaching the large tris(trimethylsilyl)methyl (Tsi) group to indium it is possible to obtain an alkyltriindate which is sufficiently stable for a crystal structure determination and for investigation of its properties in solution.

The reaction between $[\text{Li}(\text{thf})_3(\mu\text{-Cl})\text{In}(\text{Tsi})\text{Cl}_2]$ ⁴ and an excess of LiAlH_4 in tetrahydrofuran (thf) at -40 °C gave a grey residue from which a white solid (**1**) was obtained by extraction with toluene. Extremely moisture-sensitive colourless trapezoidal plates were obtained from toluene at -20 °C.†

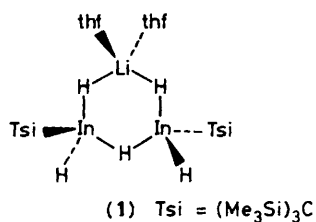
No hydrogen atoms were found in the crystal structure determination, but the presence of In-H bonds may be inferred from i.r. and n.m.r. spectra. There are four strong peaks at 1635, 1660, 1695, and 1725 cm^{-1} , reasonably assigned as $\nu(\text{In-H})$, in a region of the i.r. spectrum where most Tsi derivatives do not absorb. The ¹H n.m.r. spectrum showed easily assigned signals at δ 0.55 (27H, s, Me_3Si), 1.38 (4H, m, thf), and 3.55 (4H, m, thf), but quadrupolar interactions with ¹¹⁵In (I 9/2) or possible intramolecular exchange made signals from In-H protons weak, broad, and difficult to observe. However, a broad signal at δ 4.7 (w_1 900 Hz) from In-H-Li protons in (**1**) was detected by the ⁶Li{¹H} nuclear Overhauser effect,⁵ which suggests that hydrogen bridges between

lithium and indium persist in toluene or thf. Although it is not possible to establish with certainty that the species in solution are identical with those in the crystal (since the number of hydrogen atoms in each bridge cannot be deduced from our n.m.r. experiments), the structure (**1**) fits both the crystallographic and spectroscopic data, and is consistent with the Li content found by atomic absorption (the compound was too unstable for satisfactory C and H analysis).

The In-C bonds (Figure 1) are inclined at *ca.* 34° on either side of the plane defined by the lithium and indium atoms, so that if each indium bears a terminal hydrogen, leaving three for the bridging positions, co-ordination of both indium and lithium is roughly tetrahedral. The LiO_2 plane is twisted though *ca.* 24° from the perpendicular to the In_2Li plane by the steric constraints of the Tsi groups.

The molecule (**1**) may be regarded as electron deficient with electron density from In-H bonds delocalised on to lithium. Alternatively, it may be viewed as a tightly interlocked ion pair $[\text{Li}(\text{thf})_2][\text{Tsi}_2\text{In}_2\text{H}_5]$ in which the di-indate anion has displaced thf from the co-ordination sphere of the lithium with a gain in electrostatic energy as cation and anion come closer together. It is probable that both descriptions are required for a full account of the bonding.

We showed previously that the trihydroborates $[\text{Li}(\text{thf})_3(\mu\text{-H})_3\text{BR}]$ [R = Tsi or $(\text{Me}_2\text{PhSi})_3\text{C}$] probably have $(\mu\text{-H})_3$ bridges between B and Li,⁶ and it is of interest that the indium compound prepared similarly has a different structure. The Al-H bond in $\text{Na}[\text{Me}_3\text{Al-H-AlMe}_3]$, which has a linear Al-H-Al system,⁷ is the same length as that in $[(\text{Me}_2\text{AlH})_2]$, in which the Al-H-Al angle is 103°,⁸ and it has been



† Crystal Data: $\text{C}_{28}\text{H}_{75}\text{In}_2\text{LiO}_2\text{Si}_6$, $M = 849.0$, monoclinic, space group $P2_1/n$, $a = 12.921(3)$, $b = 14.466(2)$, $c = 25.400(5)$ Å, $\beta = 95.73(2)^\circ$, $U = 4723$ Å³, $D_c = 1.19$ g cm^{-3} , $Z = 4$. Monochromated Mo-K α radiation, $\lambda = 0.71069$ Å, $\mu = 11.3$ cm^{-1} . $R = 0.062$, $R' = 0.071$ for 1269 reflections with $2 < \theta < 18^\circ$ and with $|F^2| > \sigma(F^2)$ measured on an Enraf-Nonius CAD4 diffractometer. The intensity was too weak to measure for $\theta > 18^\circ$. Reflections from a roughly spherical crystal fragment, *ca.* 0.25 mm diameter sealed in a capillary under argon, decreased in intensity by *ca.* 15% during data collection, and a correction was made for this. The structure was solved by routine heavy atom methods. As in many other crystals containing the Tsi group each silicon atom was disordered over two possible sites, and in (**1**) the occupancies were in a 70 : 30 ratio. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors. Issue No. 1, 1986.

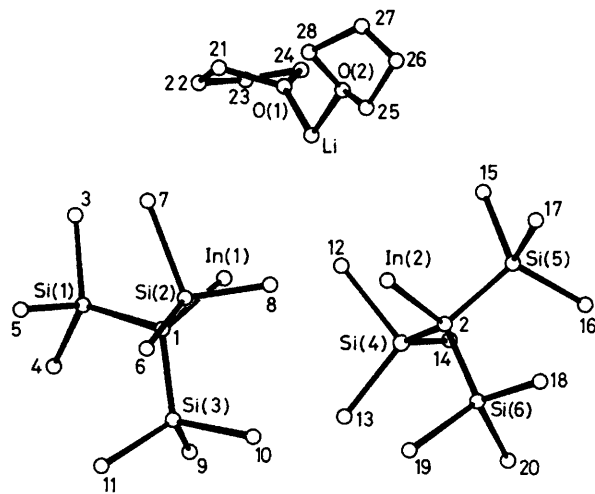


Figure 1. The molecular structure of (**1**). Mean bond lengths and angles are: In-C 2.20(3), Li-O 1.82(9), Si-C 1.87(4), Si-Me 1.94(9), In ··· In 3.482(3), In ··· Li 3.38(9) Å; In-C-Si 106(1), Si-C-Si 113(2), C-Si-C 108(4), O-Li-O 116(5)°. Only the silicon sites with higher occupancy are shown. Carbon atoms are designated by numerals only.

suggested⁷ that the strength of the electron deficient hydrogen bridge is little affected by the angle at hydrogen. It is not perhaps surprising that in $[\text{Li}(\text{thf})_2][\text{Tsi}_2\text{In}_2\text{H}_5]$ the ability of the small lithium to bond to hydrogens on two different indium atoms leads to the cyclic structure. Similar hydrogen bridges have been postulated in $[(\text{R}_2\text{AlH})_3]$ ($\text{R} = \text{Me}$ or Et)⁹ and $\text{Me}_3\text{PBeB}_2\text{H}_8$ ¹⁰ and substantiated by diffraction studies on polymeric AlH_3 ¹¹ and $[\text{Et}_2\text{AlH}_3\text{Ti}_2(\text{C}_5\text{H}_5)_2(\text{C}_{10}\text{H}_8)]$.¹²

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