

A remarkably stable indium trihydride complex: synthesis and characterisation of $[\text{InH}_3\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$

David E. Hibbs, Cameron Jones* and Neil A. Smithies

Department of Chemistry, University of Wales, Cardiff, PO Box 912, Park Place, Cardiff, UK CF1 3TB.
E-mail: jonesca6@cardiff.ac.uk

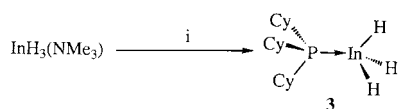
Received (in Cambridge, UK) 27th November 1998, Accepted 15th December 1998

The reaction of $[\text{InH}_3(\text{NMe}_3)]$ with $\text{P}(\text{C}_6\text{H}_{11})_3$ affords the first example of a phosphine–indium trihydride complex, $[\text{InH}_3\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$, which exhibits remarkable thermal stability; the X-ray crystal structure of the complex is described.

The utility of Lewis base adducts of AlH_3 and GaH_3 as chemical vapour deposition precursors to thin films of the group 13 metal¹ or semiconducting materials² has led to their chemistry being extensively studied over the last decade.³ Until very recently no corresponding InH_3 complexes were known, presumably because of thermal instability that arises from the weakness of the In–H bond. We have reversed this situation with the syntheses of $[\text{InH}_3\{\text{CNPR}^i\text{C}_2\text{Me}_2\text{NPr}^i\}]$ **1** and $[\text{InH}_3(\text{NMe}_3)]$ **2**,^{4,5} the former being stabilised by coordination to a highly nucleophilic ‘Arduengo’ carbene. Despite this, **1** is not stable in the solid state above -5°C (decomp. $> -20^\circ\text{C}$ in solution) and **2** is only stable in dilute solutions below -30°C . It seems likely that if InH_3 complexes are to find similar applications to their aluminium and gallium counterparts, then examples will need to be found that are stable at room temperature. Herein we report the synthesis and structural characterisation of such a compound, $[\text{InH}_3(\text{PCy}_3)]$ **3** (Cy = cyclohexyl), which represents the first example of a phosphine adduct of InH_3 , and the first InH_3 complex to have had its hydride ligands located by X-ray crystallography.

Treatment of an ethereal solution of $[\text{InH}_3(\text{NMe}_3)]$ ⁵ with 1 equiv. of PCy_3 at -40°C led to the high yield formation (71%) of **3** after recrystallisation from toluene (Scheme 1). Interestingly, **3** could not be formed from the direct reaction of PCy_3 with LiInH_4 (LiH elimination) which is in contrast to the high yield preparation of $[\text{GaH}_3(\text{PCy}_3)]$ **4** from the reaction of LiGaH_4 and PCy_3 in diethyl ether.⁶ In addition, there was no evidence for the formation of **3** from the reaction of a 1 : 1 mixture of PCy_3 and anhydrous HCl with LiInH_4 in diethyl ether at -40°C {cf. the formation of $[\text{AlH}_3(\text{PCy}_3)]$ **5** by a similar route⁷}.

Compound **3** is remarkably thermally stable and decomposes in the solid state only at temperatures in excess of 50°C to indium metal, hydrogen gas and PCy_3 (cf. **4**, decomp. $> 130^\circ\text{C}$; **5**, decomp. $> 160^\circ\text{C}$). At room temperature (25°C) crystalline samples of **3** showed only minimal decomposition over a period of 7 days under an argon atmosphere, as determined from the ^1H NMR of the sample after that period. Surprisingly, **3** also displays considerable stability to oxygen and moisture in the solid state as it shows no decomposition in air over 24 h at room temperature. In benzene solutions samples of **3** are less stable but still take ca. 1 h to decompose at 25°C . As has been suggested for **4** and **5**, the unusual stability of **3** can probably be attributed to the steric properties of the phosphine ligand.



Scheme 1 Reagents and conditions: i, PCy_3 , $-\text{NMe}_3$, Et_2O , -40°C , 2 h.

The solution NMR data† for **3** support its proposed structure. Its ^1H NMR spectrum exhibits the expected resonances for the phosphine ligand in addition to a broad hydride resonance that integrates for three hydrogens at $\delta 5.61$ (cf. $\delta 5.58$ in **1**^{4,5}) which is significantly downfield with respect to the related resonances in **4** ($\delta 4.32$ ⁶) and **5** ($\delta 4.25$ ⁷). The ^{31}P NMR spectrum of **3** displays a singlet at $\delta 7.43$ which can be compared to $\delta 11.1$ for the free ligand.⁷ A strong, broad In–H stretching absorbance was observed at 1661 cm^{-1} (cf. 1640 cm^{-1} for **1**⁵) in its IR spectrum (Nujol mull). This is at a lower frequency than the corresponding M–H stretches in **4** (1800 cm^{-1})⁶ and **5** (1750 cm^{-1})⁷ and reflects the relative weakness of the M–H bonds in **3**. No molecular ion was seen in the mass spectrum of **3** but a fragment corresponding to the free phosphine ligand was observed.

An X-ray crystal structure analysis‡ of **3** (Fig. 1) was carried out and it was found to be isomorphous to its aluminium and gallium counterparts, **5** and **4**, respectively. The quality of the X-ray data allowed the three hydride ligands to be located from difference maps and their positional and isotropic thermal parameters to be refined. The complex is monomeric and shows no evidence of intermolecular interactions through bridging hydrides. As in **4**, the metal centre has a slightly flattened tetrahedral geometry [P–In–H 101.4° (av.), H–In–H 116.2° (av.)] with an average In–H distance of 1.68 \AA . This distance compares well with the only other structurally characterised terminal In–H bond in a neutral complex, viz. $1.69(3)\text{ \AA}$ in $[\text{InH}\{2\text{-Me}_2\text{NCH}_2(\text{C}_6\text{H}_4)\}_2]$.⁸ Not surprisingly both these distances are shorter than bridging In–H distances, e.g. 1.87 \AA (av.)

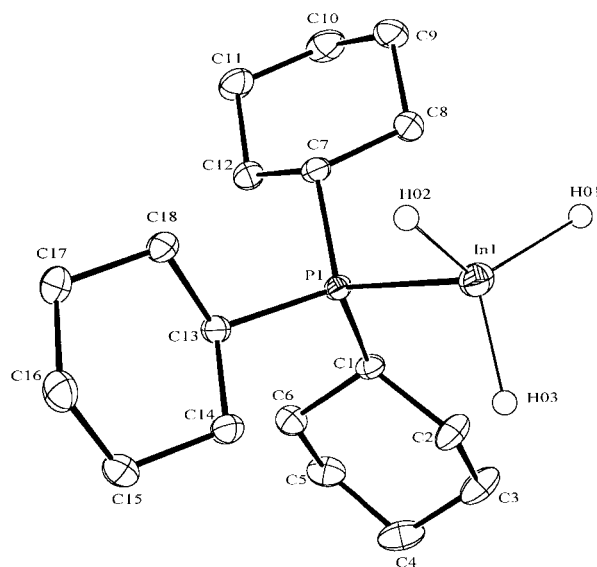


Fig. 1 Molecular structure of $[\text{InH}_3\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$ **3**. Selected bond lengths (Å) and angles ($^\circ$): In(1)–P(1) 2.6474(6), In(1)–H(01) 1.81(2), In(1)–H(02) 1.62(3), In(1)–H(03) 1.62(3), P(1)–C(13) 1.8433(17), P(1)–C(7) 1.8448(17), P(1)–C(1) 1.8632(17); P(1)–In(1)–H(01) 103.4(7), P(1)–In(1)–H(02) 97.3(11), P(1)–In(1)–H(03) 103.6(11), H(01)–In(1)–H(02) 121.3(13), H(01)–In(1)–H(03) 111.0(13), H(02)–In(1)–H(03) 116.4(16).

in $[\text{Li}(\text{tmeda})_2][\text{Me}_3\text{In-H-InMe}_3]$.⁹ The In–P distance in **3** [2.6474(6) Å] is in the normal region for such interactions though is slightly longer than In–P distances in four co-ordinate tertiary phosphine adducts of indium halides, e.g. 2.569 Å in $[\text{InI}_3(\text{PPri}_3)]$ ¹⁰ and 2.603 Å in $[\text{InI}_3(\text{PPh}_3)]$.¹¹

The remarkable thermal stability of **3** has prompted us to begin an investigation of its chemistry and the preparation of a range of related phosphine- and arsine-indium hydride complexes. The results of these investigations will form the basis of a later publication.

We gratefully acknowledge financial support from the EPSRC (studentship for N. A. S.).

Notes and references

† *Spectroscopic data* for **3**: ¹H NMR (400 MHz, C₆D₆, SiMe₄, 298 K) δ 0.92–1.75 (m, 33H, C₆H₁₁), 5.61 (br s, 3H, In–H); ¹³C NMR (100.6 MHz, C₆D₆, 298 K) δ 26.6 (s, CH₂), 27.7 (d, CH₂, ²J_{PC} 10.2 Hz), 30.5 (s, CH₂), 31.8 (d, CH, ¹J_{PC} 13.0 Hz); ³¹P NMR (36.3 MHz, C₆D₆, 85% H₃PO₄, 298 K) δ 7.43, IR ν 1661 cm⁻¹ (s, br, In–H str.); MS EI *m/z* (%): 280 (PCy₃⁺, 63), 197 (PCy₂⁺, 100), 114 (PCy⁺, 78).

‡ *Crystal data* for **3**: C₁₈H₃₆InP *M* = 398.26 triclinic, space group *P* $\bar{1}$, *a* = 8.1147(10), *b* = 10.897(2), *c* = 11.4273(10) Å, α = 74.940(9), β = 88.665(10), γ = 81.840(10)°, *V* = 965.8(2) Å³, *Z* = 2, *D*_c = 1.369 g cm⁻³, *F*(000) = 416, μ = 12.98 cm⁻¹, crystal 0.20 × 0.20 × 0.20 mm, radiation Mo–Kα (λ = 0.71073 Å), 150(2) K.

All crystallographic measurements were made using an Enraf-Nonius CAD4 diffractometer. The structure was solved by heavy atom methods (SHELXS86)¹² and refined on *F*² by full matrix least squares (SHELXL93)¹³ using all unique data. All non-hydrogen atoms are anisotropic with H-atoms [except those attached to In(1)] included in calculated positions (riding model). Neutral-atom complex scattering factors were employed.¹³ Empirical absorption corrections were carried out by the DIFABS method.¹⁴ Final *R* (on *F*) and *wR* (on *F*²) were 0.0199 and 0.0513 for *I* > 2σ(*I*), and 0.229

and 0.559 for all data. CCDC 182/121. See <http://www.rsc.org/suppdata/cc/1999/185> for crystallographic files in .cif format.

- 1 M. G. Simmonds and W. L. Gladfelter, in *The Chemistry of Metal CVD*, ed. T. Kodas and M. Hampden-Smith, VCH, Weinheim, 1994 and references therein.
- 2 J. N. Kidder, H. K. Yun, J. W. Rogers and T. P. Pearsall, *Chem. Mater.*, 1998, **10**, 777.
- 3 C. Jones, G. A. Koutsantonis and C. L. Raston, *Polyhedron*, 1993, **12**, 1829; M. G. Gardiner and C. L. Raston, *Coord. Chem. Rev.*, 1997, **166**, 1; *Chemistry of Aluminium, Gallium, Indium and Thallium*, ed. A. J. Downs, Blackie, Glasgow, 1993 and references therein.
- 4 D. E. Hibbs, M. B. Hursthouse, C. Jones and N. A. Smithies, *Chem. Commun.*, 1998, 869.
- 5 M. D. Francis, D. E. Hibbs, M. B. Hursthouse, C. Jones and N. A. Smithies, *J. Chem. Soc., Dalton Trans.*, 1998, 3249.
- 6 J. L. Atwood, K. D. Robinson, F. R. Bennett, F. M. Elms, G. A. Koutsantonis, C. L. Raston and D. J. Young, *Inorg. Chem.*, 1992, **31**, 2673.
- 7 F. R. Bennett, F. M. Elms, M. G. Gardiner, G. A. Koutsantonis, C. L. Raston and N. K. Roberts, *Organometallics*, 1992, **11**, 1457.
- 8 C. Kümmel, A. Meller and M. Noltemeyer, *Z. Naturforsch., Teil B*, 1996, **51**, 209.
- 9 D. E. Hibbs, M. B. Hursthouse, C. Jones and N. A. Smithies, *Organometallics*, 1998, **17**, 3108.
- 10 S. M. Godfrey, K. J. Kelly, P. Kramkowski, C. A. McAuliffe and R. G. Pritchard, *Chem. Commun.*, 1997, 1001.
- 11 M. A. Brown, D. G. Tuck and E. J. Wells, *Can. J. Chem.*, 1996, **74**, 1535.
- 12 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- 13 G. M. Sheldrick, SHELXL-93 Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993.
- 14 N. P. C. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

Communication 8/09279F