Synthesis, crystal and molecular structure of the first indium trihydride complex, $[InH_3\{\overline{CN(Pr^i)C_2Me_2N}(Pr^i)\}]$

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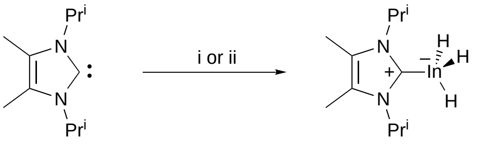
The reaction of either $[InH_3(NMe_3)]$ or $LiInH_4$ with an excess of the imidazol-2-ylidene carbene, $:\overline{CN(Pr^i)C_2Me_2N}(Pr^i)$, affords the first example of an indium trihydride complex, $[InH_3\{\overline{CN(Pr^i)C_2Me_2N}(Pr^i)\}]$, the X-ray crystal structure of which is described.

The chemistry of the binary hydrides of aluminium and gallium, $[(MH_3)_n]$ (M = Al, Ga), and their Lewis base adducts is now a well established field that derives its current importance from the application such compounds have in areas ranging from organic synthesis to chemical vapour deposition.[1] Despite early claims,[2] it seems unlikely that the corresponding indium trihydride $[(InH_3)_n]$ has yet been synthesised although monomeric InH_3 has been isolated and studied in a solid argon matrix.[3] In fact, the weakness of the In–H bond has meant that to date only five indium hydride compounds have been structurally characterised (*viz.* $[Li(thf)_2][\{(Me_3Si)_3C\}_2In_2H_5]$ **1**,[4] $K[H\{In(CH_2CMe_3)_3\}_2]$ **2**,[5] $K_3[K(Me_2SiO)_7]$ $[InH(CH_2CMe_3)_3]_4$ **3**,[6] $[InH\{2\text{-}Me_2NCH_2(C_6H_4)\}_2]$ **4**[7] and $[Me_2InB_3H_8]$ **5**[8]). In our laboratory we have become interested in extending this field to the stabilisation of indium trihydride complexes, which are as yet unknown. With this goal in mind we saw imidazol-2-ylidene carbenes as potentially useful ligands, primarily because their AlH_3 complexes (*e.g.* $[AlH_3\{\overline{CN(Mes)C_2H_2N}(Mes)\}]$ **6**, Mes = $C_6H_2Me_3$-2,4,6, mp 246 °C[9]) are known to be considerably more stable than normal AlH_3 adducts (*e.g.* $[AlH_3(NMe_3)]$ decomp. at 100 °C[10]). This stability stems from the high nucleophilicity of such carbenes which we have previously exploited in the preparation of a series of complexes between $:\overline{CN(Pr^i)C_2Me_2N}(Pr^i)$ **7** and indium trihalides, *viz.* $[InX_3\{\overline{CN(Pr^i)C_2Me_2N}(Pr^i)\}_n]$ (*n* = 1, **8**; 2, **9**) and $[HCN(Pr^i)C_2Me_2N(Pr^i)]^+[InX_4\{\overline{CN(Pr^i)C_2Me_2N}(Pr^i)\}]^-$ **10** (X = Cl, Br).[11] We now wish to report the use of **7** in the synthesis of the first structurally authenticated indium trihydride complex.

Treatment of an ethereal solution of $[InH_3(NMe_3)]$[12] (generated *in situ* from $LiInH_4$[2] and $NMe_3{\cdot}HCl$ at −30 °C) with 2 equiv. of **7** at −40 °C led to a moderate yield (42%) of $[InH_3\{\overline{CN(Pr^i)C_2Me_2N}(Pr^i)\}]$ **11** after recrystallisation from diethyl ether (Scheme 1). Complex **11** is an extremely air sensitive, colourless material that decomposes, depositing indium metal and generating hydrogen gas, at temperatures greater than −20 °C in solution and −5 °C in the solid state. Interestingly, treatment of $LiInH_4$ with 2 equiv. of **7** also gave **11** in a moderate yield (38%). This is not surprising and has a precedent in aluminium chemistry with the reaction of $LiAlH_4$ with tertiary amines which can yield alane adducts, $[AlH_3(NR_3)]$, and Li_3AlH_6.[13] It seems likely that in the present reaction a related complex indium hydride is being generated as a by-product in the formation of **11**. Unfortunately attempts to characterise this by-product have so far proved fruitless owing to its thermal instability. It is noteworthy that the aluminium analogue of **11**, *viz.* $[AlH_3\{\overline{CN(Pr^i)C_2Me_2N}(Pr^i)\}]$ **12**, can also be prepared in high yield by the reaction of **7** with either $[AlH_3(NMe_3)]$ or $LiAlH_4$.[12]



7 **11**

Scheme 1 *Reagents and conditions*: i, $[InH_3(NMe_3)]$, Et_2O, −30 °C, 2 h; ii, $LiInH_4$, Et_2O, −30 °C, 5 h

It is interesting that only a 1 : 1 complex is formed in the reaction of an excess of **7** with $[InH_3(NMe_3)]$ despite the fact that 2 : 1 complexes of the same carbene with indium halides, *e.g.* **9**, are readily formed.[11] This is presumably because the InH_3 unit is less Lewis acidic than InX_3 (X = Cl, Br), and therefore more easily electronically satisfied. Indeed, treatment of **11** with tertiary amines did not lead to the formation of five-coordinate complexes and no other reaction occurred.

The molecular structure of **11** is depicted in Fig. 1. During the course of refinement it was found that the methyl groups attached to C(6) were disordered over two sites, each having a 50% occupancy (only one disordered set is depicted in Fig. 1). The molecule is monomeric, sits on a mirror plane and does not display any intermolecular interactions. Unfortunately the hydride ligands attached to In could not be located from difference maps but their presence can be assumed from spectroscopic evidence (*vide infra*). By contrast the hydride ligands were located in the crystal structure of the isostructural

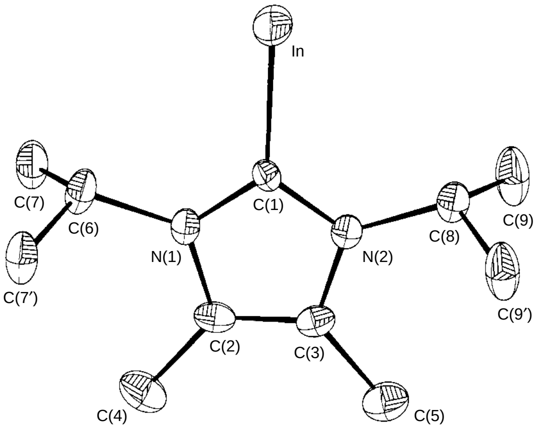


Fig. 1 Molecular structure of $[InH_3\{\overline{CN(Pr^i)C_2Me_2N}(Pr^i)\}]$ **11**. Selected bond lengths (Å) and angles (°): In–C(1) 2.260(6), N(1)–C(1) 1.354(9), N(1)–C(2) 1.402(8), N(2)–C(1) 1.331(9), N(2)–C(3) 1.413(9), C(2)–C(3) 1.340(11); N(2)–C(1)–N(1) 105.8(6), N(2)–C(1)–In 125.6(5), N(1)–C(1)–In 128.6(5), C(1)–N(1)–C(2) 110.2(6), C(1)–N(2)–C(3) 110.9(6), C(3)–C(2)–N(1) 106.9(7), C(2)–C(3)–N(2) 106.2(6).

compound **12**, the aluminium centre of which was found to have a distorted tetrahedral environment.[12] The In–C(1) distance in **11** is longer than is normally seen for In–C bonds [*e.g.* 2.174 Å av. in trimethyl(quinuclidine)indium].[14] Similar trends in M–C (carbene) bond lengths have been observed in other group 13–carbene complexes.[9,11] In addition, the bond lengths and angles within the carbene heterocycle are close to those in **8** and suggest a degree of delocalisation within the ring. Of particular note is the N–C(carbene)–N angle of 105.8(6)° which lies between the normal value for free imadazolylidene carbenes (*ca.* 102°) and imadazolium cations (*ca.* 108°).[9]

The solution NMR data for **11** support its proposed structure. Its ^{1}H NMR spectrum is similar to that of **8** but also displays a very broad resonance at δ 5.58 which integrates for three hydrogens and has been assigned as the hydride resonance. The broadness of this peak is due to the high quadrupole moment of the indium centre (^{115}In 95%, $I = 9/2$, ^{113}In 5%, $I = 9/2$) to which the hydrides are attached. This also accounts for the fact that no resonance was observed for the indium coordinated carbene centre, C(1), in the ^{13}C NMR spectrum of **11**, as was the case in the ^{13}C NMR spectrum of **8**.[11] Additionally, no signal was seen in its ^{115}In NMR spectrum which is not surprising considering the lack of spherical symmetry about In. The IR spectrum of **11** (Nujol mull) displays a strong, broad absorbance centred at 1640 cm^{-1} which has been attributed to its In–H stretching modes. This is at a significantly lower frequency than in free InH_3 (1754.5 cm^{-1}),[3] presumably because the nucleophilic carbene donor is weakening the In–H bonds in **11** relative to those in InH_3. Moreover, the In–H stretching absorbance for **11** is at a lower wavenumber than the corresponding Al–H stretching regions for its aluminium counterparts **6** (1743 cm^{-1})[9] and **11** (1730 cm^{-1}).[12] A similar trend is seen for the uncoordinated, monomeric hydrides, InH_3 (1754.5 cm^{-1}) and AlH_3 (1882.9 cm^{-1}).[3]

The indium trihydride complex **11** represents the first example of a new class of compound, the chemistry of which should prove fruitful. To establish this we are currently examining its further reactivity and the preparation of a series of related indium trihydride complexes. The results of these studies will be presented in a later publication.

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Notes and References

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‡ *Spectroscopic data* for **11**: ^{1}H NMR (250 MHz, $C_6D_5CD_3$, $SiMe_4$, 243 K) δ 1.04 [d, 12 H, CH(C*H*$_3$)$_2$, $^3J_{HH}$ 6 Hz], 1.54 (s, 6 H, Me), 5.05 [br, 2 H, C*H*(CH$_3$)$_2$], 5.58 (br s, 3 H, In–H), ^{13}C NMR (100.6 MHz, $C_6D_5CD_3$, 243 K) δ 10.0 (Me), 20.7 [CH(*C*H$_3$)$_2$], 46.3 [*C*H(CH$_3$)$_2$], 121.0 (C=C); IR ν 1640 cm^{-1} (s, br, In–H str.).

§ *Crystal data* for **11**: $C_{11}H_{23}InN_2$, M = 298.13, orthorhombic, space group *Pnma*, a = 15.1920(10), b = 9.5780(9), c = 9.7010(9) Å, U = 1411.6(2) Å^3, Z = 4, D_c = 1.403 g cm^{-3}, $F(000)$ = 608, μ = 16.46 cm^{-1}, crystal 0.15 × 0.25 × 0.20 mm, Mo-Kα radiation (λ = 0.710 69 Å), 150(2) K.

All crystallographic measurements were made using a FAST area detector diffractometer following previously described procedures.[15] The structure was solved by direct methods (SHELXS86)[16] and refined on F^2 by full matrix least squares (SHELX93)[17] using all unique data. All non-hydrogen atoms are anisotropic with H-atoms [except those attached to In] included in calculated positions (riding model). Neutral-atom complex scattering factors were employed.[18] Empirical absorption corrections were carried out by the DIFABS method.[19] Final R (on F) and wR (on F^2) were 0.0425 and 0.1004 for $I > 2\sigma(I)$, and 0.0752 and 0.1074 for all data. CCDC 182/799.

1 *Chemistry of Aluminium, Gallium, Indium and Thallium*, ed. A. J. Downs, Blackie, Glasgow, 1993; C. Jones, G. A. Koutsantonis and C. L. Raston, *Polyhedron*, 1993, **12**, 1829; A. J. Downs and C. R. Pulham, *Chem. Soc. Rev.*, 1994, 175 and references therein.

2 E. Wiberg and M. Schmidt, *Z. Naturforsch., Teil B*, 1957, **12**, 54.

3 P. Pullumbi, Y. Bouteiller, L. Manceron and C. Mijoule, *Chem. Phys.*, 1994, **185**, 25.

4 A. G. Avent, C. Eaborn, P. B. Hitchcock, J. D. Smith and A. C. Sullivan, *J. Chem. Soc., Chem. Commun.*, 1986, 988.

5 O. T. Beachley, S. L. Chao, M. R. Churchill and R. F. See, *Organometallics*, 1992, **11**, 1486.

6 M. R. Churchill, C. H. Lake, S. L. Chao and O. T. Beachley, *J. Chem. Soc., Chem. Commun.*, 1993, 1577.

7 C. Kümmel, A. Meller and M. Noltemeyer, *Z. Naturforsch., Teil B*, 1996, **51**, 209.

8 S. Aldridge, A. J. Downs and S. Parsons, *Chem. Commun.*, 1996, 2055.

9 A. J. Arduengo, H. V. R. Dias, J. C. Calabrese and F. Davidson, *J. Am. Chem. Soc.*, 1992, **114**, 9724.

10 J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1960, **82**, 2141.

11 S. J. Black, D. E. Hibbs, M. B. Hursthouse, C. Jones, K. M. A. Malik and N. A. Smithies, *J. Chem. Soc., Dalton Trans.*, 1997, 4313.

12 C. Jones and N. A. Smithies, unpublished work.

13 E. M. Marlett and W. S. Park, *J. Org. Chem.*, 1990, **55**, 2968.

14 D. C. Bradley, H. Dawes, D. Frigo, M. B. Hursthouse and B. Hussain, *J. Organomet. Chem.*, 1987, **325**, 55.

15 J. A. Darr, S. A. Drake, M. B. Hursthouse and K. M. A. Malik, *Inorg. Chem.*, 1993, **32**, 5704.

16 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

17 G. M. Sheldrick, SHELXL-93 Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993.

18 *International Tables for X-ray Crystallography*, ed. J. A. Ibers and W. C. Hamilton, Kynnoch Press, Birmingham, England, 1974, vol. 4.

19 N. P. C. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158, adapted for FAST geometry by A. I. Karavlov, University of Wales, Cardiff, 1991.

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