Dimethylindium octahydrotriborate, $Me_2InB_3H_8$: synthesis, crystal structure and spectroscopic properties of a volatile indium hydride

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Reaction between trimethylindium and tetraborane(10) at room temperature yields the volatile, viscous liquid dimethylindium octahydrotriborate, the first reported example of a volatile indium hydride; spectroscopic properties of the vapour indicate a molecular structure akin to that of $Me_2AlB_3H_8$, although the crystal structure implies a more ionic formulation, $[Me_2In]^+[B_3H_8]^-$, with the coordination at each indium centre being augmented *via* secondary intermolecular interactions with terminal hydrogen atoms.

The comparative weakness of the In–H bond[1] has meant that relatively few indium hydride derivatives have been convincingly characterized. Although the molecules InH,[2] InH_2[3] and InH_3[4] have been identified in the gas phase or a low-temperature matrix environment, the dimer In_2H_6 has not yet been observed. As for complex hydrides, the IR spectrum of matrix-isolated Me_2InBH_4 vapour implies the presence of $Me_2In(\mu\text{-}H)_2BH_2$ molecules,[5] but only $K\{H[In(CH_2CMe_3)_3]_2\}$[6] and $[(tsi)In(H)(\mu\text{-}H)Li(thf)_2(\mu\text{-}H)In(\mu\text{-}H)(H)(tsi)]$ [tsi = $C(SiMe_3)_3$][7] have been investigated by X-ray diffraction. Here we report the synthesis of the first volatile indium hydride, $[Me_2InB_3H_8]$, and an investigation of its structure in the solid, vapour and solution phases.

Trimethylindium (0.138 g, 0.86 mmol) reacted with tetraborane(10) (0.069 g, 1.129 mmol) at room temperature in all-glass apparatus over a period of 12 h to yield a colourless, viscous, slightly volatile liquid,† subsequently shown to be $[Me_2InB_3H_8]$. Fractionation *in vacuo* caused the product to condense as a white solid at −15 °C. The compound was extremely air- and moisture-sensitive and decomposed *in vacuo* over a period of 3–4 days at room temperature to indium metal and a mixture of BMe_3 and $[MeBH_2]_2$. Identification of dimethyldiborane, $[MeBH_2]_2$, as the only more volatile co-product and chemical analysis‡ confirming the empirical formula $C_2H_{14}InB_3$ imply that the primary reaction is according to eqn. (1)

$$Me_3In + B_4H_{10} \longrightarrow Me_2InB_3H_8 + 1/2[MeBH_2]_2 \quad (1)$$

which represents the first example of synthesis of a B_3H_8 derivative by direct insertion of a methylmetal fragment into one of the apical vertices of tetraborane(10). Yields based on this reaction and the amount of trimethylindium taken were typically 63–69%. Samples of $[Me_2InB_3H_8]$ were loaded in preconditioned Pyrex capillaries for the purpose of crystal growth. Further characterization was achieved by measuring (i) the ^{11}B and ^1H NMR spectra of solutions in $[^2H_8]$toluene at temperatures in the range −90 to 40 °C and (ii) the IR spectrum of the solid at 77 K and of the vapour isolated in a nitrogen matrix at 14 K.

The molecular structure of $Me_2InB_3H_8$ **1**, as deduced from the structure of a single crystal at 150K,§ is shown in Fig.1 and consists of a B_3H_8 ligand linked to a dimethylindium centre *via* two bridging hydrogen atoms. As such, it represents a rare example of a structurally authenticated compound containing an In–H bond. The In–H bond lengths [2.18(4) Å av.] are significantly longer than those in $[R_3In\text{–}H\text{–}InR_3]^-$ (R = CH_2CMe_3) [1.950(23) and 1.933(15) Å],[6] although viewed in the context of the corresponding parameters for gaseous $[Me_2AlB_3H_8]$ and $[Me_2GaB_3H_8]$ (1.989 and 1.906 Å, respectively)[8] and of a structure for solid $[H_2GaBH_4]$[9] which features Ga–H contact distances in the range 1.87–2.41 Å they are not unduly long. Although the bidentate ligation of the B_3H_8 moiety resembles that found in both $Me_2AlB_3H_8$ and $Me_2GaB_3H_8$, closer comparison of the three structures points to a more ionic formulation, $[Me_2In]^+[B_3H_8]^-$, for the indium compound, coordination at each In centre being augmented *via* secondary interactions with the terminal hydrogen atoms H(2) and H(4) attached to the basal boron atoms [B(1) and B(2)] (see Fig. 2). Hence (i) intermolecular In···H distances are as short as 2.53 Å; (ii) M···B distances [2.735(6), 2.754(6) Å] are much longer than the values for $[Me_2AlB_3H_8]$ and $[Me_2GaB_3H_8]$

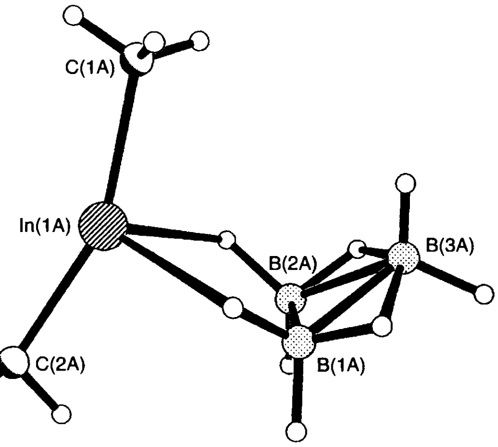

Fig. 1 The molecular structure of **1**. Relevant bond lengths (Å) and angles (°) are: In(1A)–C(1A) 2.105(5), In(1A)–B(1A) 2.735(6), In(1A)–B(2A) 2.754(6), In(1A)–H(1A) 2.22(4), In(1A)–H(3A) 2.16(4), B(1A)–B(2A) 1.779(7), B(1A)–B(3A) 1.790(8), B(2A)–B(3A) 1.809(8), B(1A)–H(1A) 1.11(4), B(1A)–H(13A) 1.11(6), B(3A)–H(13A) 1.49(6), C(1A)–In(1A)–C(2A) 158.6(2), H(1A)–In(1A)–H(3A) 81(2).

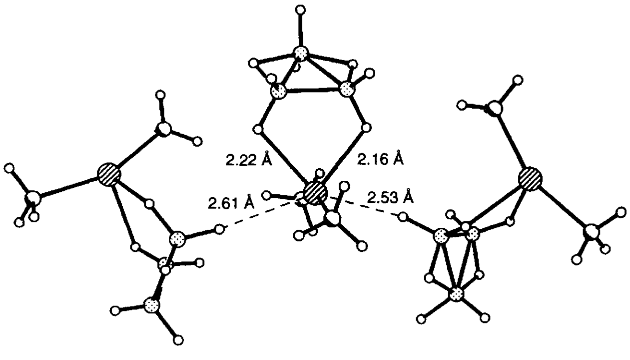

Fig. 2 Intermolecular interactions in solid **1**

would lead us to expect [2.307(8) and 2.344(9) Å, respectively];[10] (iii) the hydrogen-bridged B(1)–B(3) units differ but little in length from the 'direct' B(1)–B(2) linkage [B(1)–B(3) is somewhat longer than B(1)–B(2) in the molecular species $Me_2MB_3H_8$ (M = Al or Ga),[8] whereas the reverse is true in the $B_3H_8^-$ anion[10]]; and (iv) the C–In–C angle [158.6(2)°] is significantly wider than that found in either of the gaseous aluminium or gallium compounds (126.8 and 130.3°, respectively),[8] being very similar to that featured by [Me_2InO_2CMe] [152.2(6)°][11] in which the In centre effectively increases its coordination number from four to six by interaction with oxygen atoms of other O_2CMe units. The angle between the In centre and the two bridging hydrogen atoms [H(1)–In–H(3), 81(2)°] is also substantially tighter than the corresponding values in typical molecular B_3H_8 derivatives {*e.g.* [$Be(B_3H_8)_2$], 125.1(11)°},[12] reflecting the increased crowding of the In coordination sphere.

The ^1H NMR spectrum of a [$^2H_8$]toluene solution of [$Me_2InB_3H_8$] at room temperature shows a sharp singlet at δ_H −0.22 (relative intensity 6, CH_3) and a broad resonance centred at δ_H 0.85 (relative intensity 8, B_3H_8). The ^{11}B spectrum of such a solution at 40 °C consists of a nonet centred at δ_B −32.1 [$J(^{11}B–^1H)$ 33.4 Hz]. Cooling the sample to −90 °C merely results in broadening of the observed resonances. These properties indicate magnetic equivalence of both methyl groups, all eight boron-bound hydrogen atoms and all three boron atoms, so that, in contrast to the aluminium and gallium analogues,[13] the $Me_2InB_3H_8$ molecule is fluxional, even at temperatures down to −90 °C.

The gaseous $Me_2AlB_3H_8$ molecule is known to incorporate a bidentate B_3H_8 moiety,[8] and similarities in the patterns of IR bands associated with the matrix-isolated vapours of the aluminium and indium compounds argue strongly that the latter compound also vaporizes as a molecular species of the type $Me_2M(\mu\text{-}H)_2B_3H_6$. The existence of features characteristic (i) of the $\nu(B–H_t)$ and $\nu(B–H_b)$ modes of a bidentate B_3H_8 ligand,[8] (ii) of the deformation, rocking and twisting modes of a terminal BH_2 unit,[14] and (iii) of an Me_2In unit[6] reinforce this view.

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Footnotes

† The pure liquid was estimated to have a vapour pressure of the order of 0.5–1 Torr at room temperature on the basis of its distillation properties.

‡ Elemental analysis was performed by the Analytische Laboratorien, Gummersbach, Germany. Found: C, 12.20; H, 7.00; In 62.70; B, 16.70; calc. for $C_2H_{14}InB_3$: C, 12.96; H, 7.61; In 61.94; B, 17.49%.

§ *Crystal data* for $C_2H_{14}B_3In$, M = 185.38, monoclinic, $P2_1/c$, a = 11.718(4), b = 9.578(4), c = 14.994(5) Å, β = 105.31(4)°, U = 1623(1) Å^3 [from 2θ values for 38 reflections measured at ±ω (30 < 2θ < 32°), λ = 0.71073 Å], Z = 8, D_c = 1.517 g cm^{-3}, $F(000)$ = 720, T = 150 K, μ(Mo-Kα) = 2.80 mm^{-1}. Yellow needle, 0.5 × 0.1 × 0.1 mm. A sample of $Me_2InB_3H_8$ contained in a hand-drawn Pyrex capillary was mounted on a Stöe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.[15] A stable solid/liquid phase boundary was established at 286 K, and crystal growth was effected by cooling the sample at 5 K h^{-1}. Data were collected in the range $5 < 2\theta < 50°$ using ω–θ scans [ω scan-width (1.05 + 0.35 tanθ)°] at 150 K. The structure was solved by direct methods (SIR92[16]) and refined by full-matrix least squares (SHELXL93[17]). Hydrogen atoms were readily located in a difference map; the methyl hydrogens were then treated as rotating rigid bodies with $U_{iso}(H) = 1.5U_{eq}(C)$, while all other hydrogen atoms were refined freely. Anisotropic temperature parameters were refined for In, B and C atoms, and at convergence R_1 = 0.025 [based on F and all 2239 unique data with $F > 4\sigma(F)$], wR_2 = 0.0705 [based on F^2 and all 2481 unique data] for 178 parameters; ΔF maximum and minimum were 0.79 and −0.53 e Å^{-3}, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/189.

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