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Synthesis and Crystal Structure of a *closo*-Indacarborane Dimer

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Summary: Interaction of the $Na^+(THF)Li^+[2,3\text{-}(SiMe_3)_2C_2B_4H_4]^{2-}$ double salt with $(Me)_2CHInI_2$ in a molar ratio of 1:1 in dry THF produced the *closo*-indacarborane 1-[$(Me)_2CH$]-1-In^{III}-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (**1**) as a white, air-sensitive, and low-melting crystalline solid in 39% yield. Complex **1** was characterized by ^1H, ^{11}B, and ^{13}C NMR spectra, by mass and IR spectra, and also by X-ray crystallography. The crystal structure of **1** reveals that the indacarborane is a dimeric cluster with intercluster indium–boron distances in the range 2.847 (5)–3.248 (6) Å and an indium–indium contact of 3.696 (1) Å. The indium metal in each cage occupies an apical vertex of a pentagonal bipyramid and is slipped significantly toward the unique boron above the C_2B_3 face in an η^3 fashion. The angles of tilt in the In-bound isopropyl group from the axis that bisects the C_2B_3 centroid and the apical indium and from the axis that bisects the apical boron and the apical indium are in the range of 36.7–45.1°.

Compounds with weak indium–indium interactions have attracted recent theoretical[1] and experimental[2-4] attention. Relatively short In(I)–In(I) contacts have been observed in the polymers $[In(C_5H_5)]_\infty$ and $[In(C_5H_4Me)]_\infty$ (3.986 (1) Å),[2] the hexamer $[In(C_5Me_5)]_6$ (3.942 (1)–3.963 (1) Å),[3] and the dimer $[In\{C_5(CH_2Ph)_5\}]_2$ (3.631 (2) Å).[4] However, we are not aware of any In(III) derivatives with short metal–metal contacts. Herein we report the synthesis and X-ray crystal structure of 1-isopropyl-2,3-bis(trimethylsilyl)-2,3-dicarba-1-inda-*closo*-heptaborane(7), 1-[$(Me)_2CH$]-1-In^{III}-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (1). Compound 1 exists as an unusual dimer in the solid state. To the best of our knowledge, this constitutes the first structural report on an indium–boron compound.[5]

Treatment of the double salt $Na^+(THF)Li^+[2,3\text{-}(SiMe_3)_2C_2B_4H_4]^{2-}$ with *i*-$PrInI_2$ in a 1:1 mole ratio in dry THF solution resulted in the isolation of colorless, air-sensitive, and low-melting crystals of 1 in 39% yield.[6] The ^1H and ^{13}C NMR spectra of 1 were consistent with the presence of two equivalent $SiMe_3$ groups and one isopropyl substituent. The ^{11}B NMR spectrum showed broad, ill-defined singlet resonances at 16.33 and 9.63 ppm and a broad doublet at −41.77 ppm ($^1J(^{11}B\text{–}^1H) = 125$ Hz).[7] The relative intensity of the 16.33 ppm resonance is twice that of the other two resonances. Unfortunately, the foregoing spectral data do not permit a distinction to be made between an η^5 or η^3 (borallyl) attachment of the *i*-PrIn moiety to the C_2B_3 face. It was therefore necessary to undertake an X-ray crystallographic study.[8]

The solid-state structure of 1 consists of indacarborane dimers (Figure 1). The monomeric units are crystallographically independent, but pairs of dimers are related by a center of inversion. The most interesting structural features are the short, intercage indium–indium and indium–boron contacts. The indium–indium distance in 1 (3.696 (1) Å) is very similar to that in the In(I) dimer $[In\{C_5(CH_2Ph)_5\}]_2$ (3.631 (2) Å).[4] As pointed out by Janiak and Hoffman,[1] a modicum of metal-metal bonding is possible in unbridged Tl(I) or In(I) dimers of the type $(RM)_2$. As noted above, there is no literature precedent for indium–boron bond distances. However, there are clearly two categories of In–B distances in 1, namely six

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(3) Beachley, O. T., Jr.; Blom, R.; Churchill, M. R.; Faegri, K., Jr.; Fettinger, J. C.; Pazik, J. C.; Victoriano, L. *Organometallics* **1989**, *8*, 346. Beachley, O. T., Jr.; Churchill, M. R.; Fettinger, J. C.; Pazik, J. C.; Victoriano, L. *J. Am. Chem. Soc.* **1986**, *108*, 4666.

(4) Schumann, H.; Janiak, C.; Gorlitz, F; Loebel, J.; Dietrich, A. *J. Organomet. Chem.* **1989**, *363*, 243.

(5) The synthesis and spectroscopic data of 1,2,3-$MeInC_2B_4H_6$ have been reported by Grimes et al., and Greenwood et al. have investigated the reaction of Me_3In with $B_{10}H_{14}$. However, no structural data are available for these compounds. See: Grimes, R. N.; Rademaker, W. J.; Denniston, M. L.; Bryan, R. F; Greene, P. T. *J. Am. Chem. Soc.* **1972**, *94*, 1865. Greenwood, N. N.; Thomas, B. S.; Waite, D. W. *J. Chem. Soc., Dalton Trans.* **1975**, 299.

(6) An 8.48-mmol sample of $Na^+(THF)Li^+[2,3\text{-}(SiMe_3)_2C_2B_4H_4]^{2-}$ double salt[10] was allowed to react with 8.49 mmol of anhydrous (*i*-Pr)-InI_2[11] (3.493 g) in dry THF (20 mL) at 0 °C for 2 h and then 1 h at room temperature, during which time the solution became turbid and its color turned to off-white. After removal of THF from the heterogeneous solution in vacuo, the residue was heated to 160 °C, and the products were sublimed and/or distilled from the reactor into a detachable U-trap that was held at 0 °C. The contents of this U-trap were warmed to 10 °C and pumped overnight through another detachable U-trap, held at −23 °C, to collect the *nido*-carborane precursor 2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ (0.95 g, 4.32 mmol). An air-sensitive white solid, identified as 1-[$(Me)_2CH$]-1-In-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (1), remained in the first U-trap (1.25 g, 3.32 mmol, 39% yield; soluble in both polar and nonpolar organic solvents; mp 25 °C). The residue that remained in the reactor after sublimation was insoluble in organic solvents and was therefore discarded.

(7) Spectroscopic Data for 1: ^1H NMR (C_6D_6, relative to external Me_4Si) δ 4.9–3.2 [v br, ill-defined peak, 3 H, basal H_t, $^1J(^1H\text{–}^{11}B)$ unresolved], 1.41 [m, 1 H, *i*-Pr CH, $^3J(^1H\text{–}^1H) = 5.75$ Hz], 1.28 [d, 6 H, *i*-Pr Me, $^3J(^1H\text{–}^1H) = 5.75$ Hz], 0.91 [q (br), 1 H, apical H_t, $^1J(^1H\text{–}^{11}B) = 126$ Hz], 0.35 [s, 18 H, $SiMe_3$]; ^{11}B NMR (C_6D_6, relative to external $BF_3{\cdot}OEt_2$) δ 16.33 [v br, ill-defined peak, 2 B, basal BH, $^1J(^{11}B\text{–}^1H)$ unresolved], 9.63 [v br, ill-defined peak, 1 B, basal BH, $^1J(^{11}B\text{–}^1H)$ unresolved], −41.77 [d (br), 1 B, apical BH, $^1J(^{11}B\text{–}^1H) = 125$ Hz]; ^{13}C NMR ($CDCl_3$, relative to external Me_4Si) δ 124.43 [s (br), cage carbons (SiCB)], 31.23 [d (br), 1 C, *i*-Pr CH, $^1J(^{13}C\text{–}^1H) = 127.7$ Hz], 22.68 [q (br), 2 C, *i*-Pr Me, $^1J(^{13}C\text{–}^1H) = 126.0$ Hz], 2.57 [q, 6 C, $SiMe_3$, $^1J(^{13}C\text{–}^1H) = 118.6$ Hz]; IR (cm^{-1}; $CDCl_3$ vs $CDCl_3$) 2952 (vs), 2907 (vs), 2852 (vs), 2720 (sh) [ν(C–H)], 2576 (vvs), 2433 (s, sh) [ν(B–H)], 1935 (vw, br), 1875 (vw, br), 1456 (m, s), 1406 (m, s) [$\delta(CH)_{asym}$], 1368 (m, s), 1318 (m, br), 1252 (vs) [$\delta(CH)_{sym}$], 1180 (vs), 1142 (m, s), 1114 (m, s), 1065 (m, br), 982 (m, s), 833 (vvs, br) [ρ(CH)], 728 (w, s), 690 (m, s), 651 (vs), 624 (m, s), 530 (w, s), 491 (w, br); mass spectral analysis (HREI peak match) theoretical mass for $^{12}C_{11}{}^1H_{29}{}^{10}B^{11}B_3{}^{28}Si_2{}^{115}In$ and $^{12}C_{11}{}^1H_{29}{}^{11}B_4{}^{28}Si_2{}^{115}In$ 375.1255 and 376.1219, measured mass 375.1259 and 376.1229.

(8) A data set was collected at 230 K on a colorless plate-shaped crystal (mounted in a 0.7-mm glass capillary in a drybox) of triclinic space group $P\bar{1}$ with the following unit cell parameters: $a = 11.018$ (3) Å, $b = 12.394$ (3) Å, $c = 14.485$ (4) Å, $\alpha = 73.01$ (2)°, $\beta = 87.67$ (2)°, $\gamma = 89.90$ (2)°, $V = 1890.0$ (9) Å^3, $Z = 4$, and $D_{calcd} = 1.32$ g/cm^3. Full-matrix least-squares refinements of 1 converged at $R = 0.027$ and $R_w = 0.037$ for 3444 observed ($I > 3.0\sigma(I)$) reflections. The structure was solved by the heavy-atom methods stored in the program package SHELXTL-PLUS (Sheldrick, G. M. Structure Determination Software Programs; Nicolet Instrument Corp.: Madison, WI, 1988).

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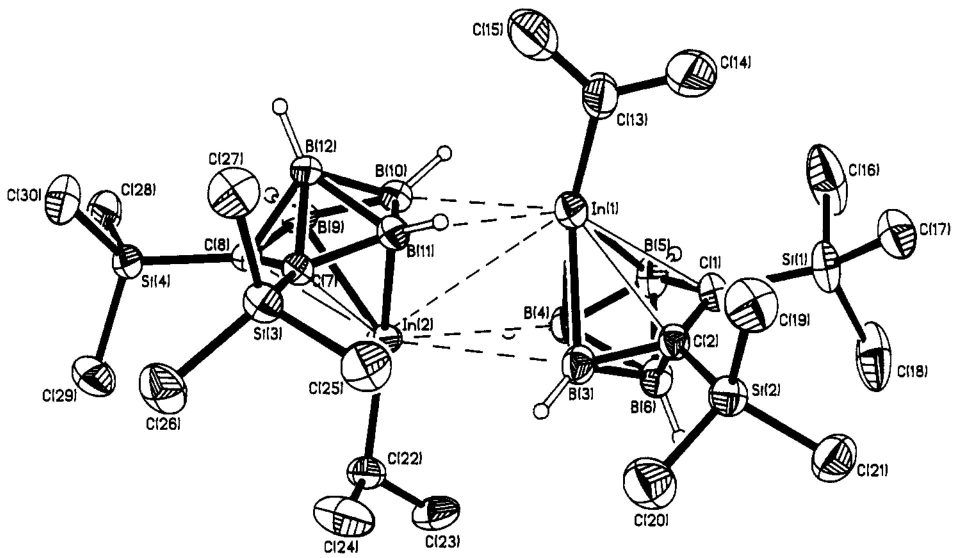

Figure 1. Perspective view of 1 with thermal ellipsoids drawn at the 40% probability level, showing the atom-numbering scheme. The hydrogen atoms on $SiMe_3$ and $(Me)_2CH$ groups are omitted for clarity. The thinner lines and the broken lines represent weaker interactions within and between the indacarborane cages, respectively. Pertinent parameters include the following: In(1)-C(1) = 2.676 (5), In(1)-C(2) = 2.660 (4), In(1)-B(3) = 2.425 (6), In(1)-B(4) = 2.297 (5), In(1)-B(5) = 2.431 (6), In(1)-B(10) = 2.847 (5), In(1)-B(11) = 3.014 (6), In(1)-C(13) = 2.143, In(1)-(C_2B_3 centroid 1) = 2.100, In(2)-C(7) = 2.624 (4), In(2)-C(8) = 2.639 (4), In(2)-B(9) = 2.416 (5), In(2)-B(10) = 2.302 (5), In(2)-B(11) = 2.446 (5), In(2)-C(22) = 2.156 (5), In(2)-B(3) = 3.248 (6), In(2)-B(4) = 3.045 (6), In(2)-In(1) = 3.696 (1), In(2)-(C_2B_3 centroid 2) = 2.083 Å; (centroid 1)-In(1)-C(13) = 134.9, (centroid 2)-In(2)-C(22) = 139.1°.

intracage distances, which average 2.386 (6) Å, and four intercage distances, which average 3.038 (6) Å. For comparison, the sum of the covalent radii for In and B is 2.26 Å.

The indium atom of each monomeric unit is η^5-bonded to a C_2B_3 carborane face and thus occupies one of the apical vertices of an overall pentagonal-bipyramidal array. However, it should be noted that, in each monomeric unit, the indium atom is slipped significantly toward an η^3-bonding (borallyl) posture. Thus, each indium-boron$_{\text{unique}}$ distance (In(1)-B(4) and In(2)-B(10)) is shorter than the other two by over 0.1 Å and the average intracage In-B distance (2.386 (6) Å) is considerably shorter than the average In-C distance (2.650 (5) Å). Finally, the In-$C_{i\text{-Pr}}$ bond makes angles of 45.1 and 40.5° in molecule 1 and 40.9 and 36.7° in molecule 2 to the axis that bisects the C_2B_3 centroid and the apical indium atom and the axis that bisects the apical boron and the apical indium, respectively. A similar arrangement of alkyl groups has been observed in C_2H_5-Al- and CH_3-Ga-substituted heterocarboranes.[5,9]

The development of the chemistry of indacarborane, particularly the coordination chemistry, is currently underway in our laboratories.

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Supplementary Material Available: Tables of positional and thermal parameters and selected bond distances, bond angles, and torsion angles (6 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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