Isolation of a Transition-metal Complex of Hexaborane(10); μ-$Fe(CO)_4$–B_6H_{10}

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Summary The reaction of hexaborane(10) with ennea-carbonyldi-iron gives the novel complex μ-$Fe(CO)_4$–B_6H_{10}, in which the iron centre is shown to be co-ordinated to the unique basal boron–boron bond of B_6H_{10}.

Hexaborane(10) is thought to possess a two-centre two-electron bond along a basal edge of its pentagonal pyramidal structure.[1] Protonation of this bond has been suggested to occur in the exchange of bridging hydrogen atoms with D_2O[2] and DCl;[3] indeed, Lipscomb[4] has predicted $B_6H_{11}^+$ to be stable. To the extent that this site is appreciably basic, B_6H_{10} might be expected to form complexes with transition-metal Lewis acids.

Accordingly, the reaction of $Fe_2(CO)_9$ with B_6H_{10}[5] yielded a volatile, yellow, crystalline solid (m.p. 37—38° decomp.). On the basis of i.r., ^{11}B F.t. n.m.r., and mass spectra we have formulated the yellow solid as μ-$Fe(CO)_4$–B_6H_{10}.

The mass spectrum shows a parent ion multiplet (*m/e* 243 for $^{10}B\,^{11}B_5\,^{56}Fe\,^{12}C_4\,^{16}O_4$) with an isotope pattern which fits very closely with that calculated for an ion containing a B_6FeC_4 fragment. The presence of four carbonyl groups is demonstrated by four isotope clusters centred at 28, 56, 84, and 112 mass units below the parent ion multiplet. The i.r. spectrum shows four carbonyl stretching frequencies (2078vs, 2018vs, 1986vs, and 1981sh cm^{-1} in methylcyclohexane), which are consistent with both local C_{2v} symmetry, and an $Fe(CO)_4$ unit. Further, terminal B–H stretching and B–H–B modes are present (2578s, 2555sh, 2495m, 1935sh, and 1850w cm^{-1} Kel-F mull), but no feature attributable to an Fe–H–B unit is observed.

The ^{11}B F.t. n.m.r. spectrum (28·877 MHz, wide band proton decoupled; C_6H_{12}; $BF_3 \cdot Et_2O$ external; a positive chemical shift represents a ^{11}B nucleus more shielded than that in the reference) is consistent with the C_s symmetry expected for a 4,5-bridged hexaborane unit. In view of the similar chemical shifts for B_6H_{10}[6] the assignments for the apical boron B^1 (δ + 54·4, J_{BH} 183 Hz, 1B) and the unique basal boron B^2 (δ − 11·4, 1B) are unequivocal. However, an ambiguity exists in assignments for B^3, B^6 and B^4, B^5 to signals at δ − 0·2 p.p.m., 2B and δ − 4·9 p.p.m., 2B.

The complex may be handled for brief periods in air but is thermally and photolytically unstable. Thermal decomposition yields metallic iron, CO, $Fe(CO)_5$, and hexaborane(10) (as determined by mass spectrometry), which is further evidence for the proposed structure.

We wish to thank Professor W. N. Lipscomb for a gift of the B_5H_9 from which the B_6H_{10} was prepared, and Ms. Norma J. Maraschin for assistance with the mass spectrum.

(*Received*, 14*th August* 1972; *Com.* 1420.)

Added in proof: After the submission of this manuscript the isolation and characterization of $[B_6H_{11}][BCl_4]$ was reported by H. D. Johnson, II, V. T. Brice, G. L. Brubaker, and S. G. Shore, *J. Amer. Chem. Soc.*, 1972, **94**, 6711.

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