Preparation of $[B_5H_3(CO)_2Fe(CO)_3]$. A Ferraborane Analogue of $B_6H_6^{2-}$

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Summary The isolation and characterization of a ferraborane analogue of a carbonyl derivative of $B_6H_6^{2-}$ produced in the direct reaction of B_5H_9 and $[Fe(CO)_5]$ is described.

IN the course of investigating the mechanism of the formation of $[B_4H_8Fe(CO)_3]$[1] from the reaction of $[Fe(CO)_5]$ with B_5H_9 we produced evidence supporting the existence of a number of unusual ferraboranes.[2] One of these, which is the first example of a carbonyl derivative of a *closo* ferraborane, has now been isolated and characterized.

The reaction of $[Fe(CO)_5]$ and B_5H_9 in a hot–cold reactor maintained at 280 °C–30 °C in daylight for *ca.* 1 h yielded, upon fractionation, substantial quantities of $[B_4H_8Fe(CO)_3]$ and a less volatile red liquid that freezes at *ca.* 5 °C to form an orange solid. Mass spectrometric measurements established the stoicheiometry of this material as $[B_5H_3Fe(CO)_5]$. The highest mass peak in the simple mass fragmentation pattern is at $m/e = 254$ with fragment ions corresponding to the successive loss of 5 CO molecules. The relative intensities of the peaks in the ion clusters beginning at m/e 254, 226, 198, 170, 142, and 114 are characteristic of ions containing 5 boron atoms and precise mass measurements on the parent ion yielded a composition $^{11}B_5{}^1H_3{}^{12}C_5{}^{16}O_5{}^{56}Fe$ (obs. 253·980 ± 0·002 a.m.u.; calc. 253·979 a.m.u.). The prominent doubly charged ion intensities and minor H and B fragmentation are indicative of a closed cage.[3,4]

Initial structural information from ^{11}B and ^1H n.m.r., i.r., and u.v. photoelectron spectra are consistent with a closed polyhedral structure which contains an $Fe(CO)_3$ group at one vertex, B–C–O groups at two vertices, and B–H groups at three vertices (Figure).

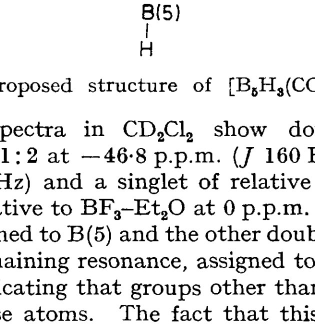

FIGURE. Proposed structure of $[B_5H_3(CO)_2Fe(CO)_3]$.

^{11}B-N.m.r. spectra in CD_2Cl_2 show doublets in the intensity ratio 1:2 at −46·8 p.p.m. (*J* 160 Hz) and −24·2 p.p.m. (*J* 150 Hz) and a singlet of relative intensity 2 at 12·8 p.p.m. relative to BF_3–Et_2O at 0 p.p.m. The low field doublet is assigned to B(5) and the other doublet to B(3) and B(4). The remaining resonance, assigned to B(1) and B(2) is a singlet indicating that groups other than hydrogen are bonded to these atoms. The fact that this singlet is the highest field peak in the spectrum is consistent with CO groups being bonded to the boron atoms. The 100 MHz ^1H n.m.r. spectrum (relative to Me_4Si) exhibits two quartets at τ 5·62 (*J* 165 Hz) and 6·82 (*J* 170 Hz), having relative intensities of *ca.* 1 : 2. On ^{11}B decoupling the quartets collapse to broad singlets. The higher field resonance is assigned to hydrogen atoms bonded to B(3) and B(4) near to the electron-rich metal atom. The i.r. spectrum in CH_2Cl_2 exhibits prominent absorptions at 2572s cm^{-1} (ν_{BH}), 2150s, 2110vs, 2020s, and 1980vs cm^{-1} (all ν_{CO}). The 2020 and 1980 bands are those expected for the $Fe(CO)_3$ group while the 2150 and 2110 ones are assigned to the CO units bound to the cage. These bands cannot be assigned to bridging CO groups but have frequencies similar to that observed for CO bound to a boron cage.[5] The u.v. photoelectron spectrum exhibits bands at 8·0 and 14·1 eV resulting from ionization of orbitals localized on iron and carbonyls respectively. The number and relative intensities of the individual bands at low ionization potential (8·6, 9·1, 9·8, 10·5, and 10·9 eV) are consistent with a substituted cage having the '*cis*' structure (shown in the Figure) as well as the '*trans*' structure.

As there are now several examples of the $Fe(CO)_3$ group acting as a formal BH group,[1,2,6] we formulate this compound as an analogue of a carbonyl derivative of $B_6H_6^{2-}$ and, as such, it obeys the formal electron counting rules for cages.[7] Considering that $B_{10}H_8(CO)_2$ and $B_{12}H_{10}(CO)_2$ were key intermediates in establishing the derivative chemistry of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$,[8] this compound should provide an entry into derivatives of polyhedral ferraboranes. Cluster bound carbonyl groups have also been observed in the cation $[\{Co(CO)_3\}_3CCO]^+$.[9] Finally, this compound is not unique as evidence has been produced for compounds formulated as $[B_5H_5(CO)Fe(CO)_3]$ and $[B_6H_4(CO)_2Fe(CO)_3]$.

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[1] N. N. Greenwood, C. G. Savory, R. N. Grimes, L. G. Sneddon, A. Davison, and S. S. Wreford, *J.C.S. Chem. Comm.*, 1974, 718.

[2] T. P. Fehlner, J. Ragaini, M. Mangion, and S. G. Shore, *J. Amer. Chem. Soc.*, in the press.

[3] R. E. Williams, 'Progress in Boron Chemistry,' eds. R. J. Brotherton and H. Steinberg, Pergamon Press, New York, 1970, **2**, 37.

[4] L. C. Ardini and T. P. Fehlner, *Internat. J. Mass Spectrometry Ion. Phys.*, 1972, **10**, 489.

[5] W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1964, **86**, 115.

[6] L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Amer. Chem. Soc.*, 1973, **95**, 6623.

[7] R. E. Williams, *Inorg. Chem.*, 1971, **10**, 210; K. Wade, *J.C.S. Chem. Comm.*, 1972, 792; *Inorg. Nuclear Chem. Letters*, 1972, **8**, 559; R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, 1972, **11**, 1974.

[8] W. H. Knoth, *J. Amer. Chem. Soc.*, 1966, **88**, 935.

[9] D. Seyferth, J. E. Hallgren, and C. S. Eschbach, *J. Amer. Chem. Soc.*, 1974, **96**, 1730.