Preparation of a Stable Small Ferraborane, $B_4H_8Fe(CO)_3$

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Summary The orange liquid $B_4H_8Fe(CO)_3$ has been prepared by direct reaction of pentaborane(9) with iron pentacarbonyl and also by the reaction of tetraborane(10) with enneacarbonyldi-iron; spectroscopic evidence shows that the $Fe(CO)_3$ group has replaced the apex BH group in B_5H_9 and that the compound has structural and bonding affinities with $C_4H_4Fe(CO)_3$ and $C[Fe(CO)_3]_5$.

THE recent growth of metalloborane chemistry has emphasized that the higher boranes can frequently behave as *polyhapto*-ligands rather than as electron-deficient species.[1] However, few examples are yet known in which the metal atom forms part of a small borane cluster, though two isomers of $B_4H_8Co(\pi\text{-}C_5H_5)$ and $B_4H_6Co_2(\pi\text{-}C_5H_5)_2$ were reported last year.[2] Recently we became aware that our three groups had independently synthesized the ferraborane, $B_4H_8Fe(CO)_3$; this is the first example of a small polyhedral metalloborane to be prepared by direct reaction of a borane and a metal complex.

Reaction of pentaborane(9) and iron pentacarbonyl in a hot–cold reactor maintained at 493–293 K for 72 h yielded an orange liquid (m.p. *ca.* 278 K) which was purified by vacuum fractionation and identified as $B_4H_8Fe(CO)_3$, η^4-tetraborane(8)-tricarbonyliron. The yield of $B_4H_8Fe(CO)_3$ depends critically upon the temperature of the reaction; below 473 K or above 503 K only trace amounts are formed. The optimum temperature is *ca.* 493 K, when the yield is 10—20%. The compound is readily soluble in a wide range of organic solvents. The ^{11}B n.m.r. spectrum (in CD_2Cl_2) exhibits a doublet at δ +4·69 p.p.m. (J 162 Hz) (rel. to BF_3–Et_2O), which upon irradiation (^1H) collapses to a singlet at δ +4·71 p.p.m. The ^1H spectrum shows a quartet at τ 7·56 (H_t) (J 158 Hz) and a broad multiplet at τ 13·65 (H_μ) in the ratio *ca.* 1 : 1. On irradiation (^{11}B) the quartet collapses to a singlet and the multiplet sharpens. The mass spectrum shows a sharp cut off at m/e 192 and successive loss of 3CO groups can be observed. An accurate mass measurement on the parent ion shows it to be $^{11}B_4{}^1H_8{}^{12}C_3{}^{16}O_3{}^{56}Fe$ (192·0194 a.m.u.). The gas-phase i.r. spectrum exhibits absorptions at 2568m (ν_{BH}), 2078s (ν_{CO}), 2018vs (ν_{CO}), and 1856w (ν_{BHB}) cm^{-1}. These results identify the compound as $B_4H_8Fe(CO)_3$ and indicate that the iron atom occupies the apical position in the FeB_4 square-based pyramid (Figure). The other isomer with the iron atom in the base has not been observed, possibly owing to the high temperature used,[2] although a second product, tentatively identified as $B_7H_9Fe(CO)_3$, has been found in trace amounts.

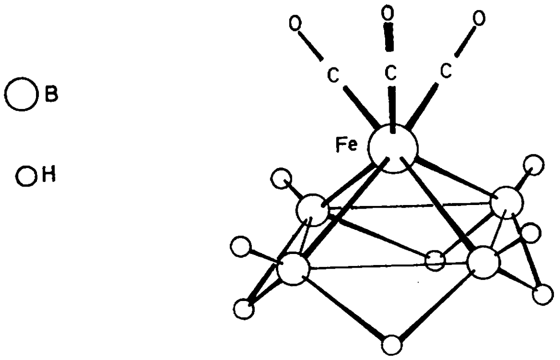

FIGURE. Proposed structure of $B_4H_8Fe(CO)_3$

An alternative route to $B_4H_8Fe(CO)_3$ is by the reaction of tetraborane(10) with $Fe_2(CO)_9$ at 198 K during 16 h; this produces the ferraborane in 2—3% yield, a second product of the reaction being μ-$Fe(CO)_4$-B_6H_{10}.[3]

It will be noted that $B_4H_8Fe(CO)_3$ obeys the electron-count rules formulated by several workers[4] and is a new member of the series which includes the end members B_5H_9, $C_4H_4Fe(CO)_3$, and $Fe_5(CO)_{15}C$. It is also noteworthy that B_5H_9 reacts with $Fe(CO)_5$ by loss of a BH group, whereas *nido*-$C_2B_4H_8$ reacts by loss of two bridge hydrogen atoms to give *closo*-$C_2B_4H_6Fe(CO)_3$,[5] and B_6H_{10} forms the simple η^2-adduct $B_6H_{10}Fe(CO)_4$.[3]

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