Apparent Oxidative Coupling of the Ferraborane Dianion $[B_2H_4Fe_2(CO)_6][Li]_2$. Preparation and Structural Characterization of *conjuncto*-$B_4H_8Fe_4(CO)_{12}$

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It is now well recognized that direct bonding to transition-metal centers greatly perturbs the structural and chemical properties of boranes.[1] For example, the Brönsted acidity of bridging hydrogens is sometimes enhanced to such an extent that multiply charged anionic clusters are accessible via repeated deprotonation.[2-4] In such anionic species one expects the B–H terminal hydrogen to become more negative with a corresponding increase in chelating ability. Hence, on the basis of the work of Kodama, Shimoi, and co-workers with $B_2H_4(PMe_3)_2$,[5] we speculated that the reaction of $[B_2H_4Fe_2(CO)_6]^{2-}$ with $Fe(CO)_4Br_2$ might lead to $(CO)_4FeB_2H_4Fe_2(CO)_6$ which would be isoelectronic with an early metallaborane of unknown origin, $(CO)_4MnB_2H_6Mn_2(H)(CO)_6$.[6] In the event, one product of this reaction produced in modest yield results from an apparent oxidative coupling of two $[B_2H_4Fe_2(CO)_6]^{2-}$ anions. Coupled cages are well-known in general, and the known linkages between borane cages range from one unsupported B–B bond[7] to one three-center two-electron bond[8] to two three-center two-electron bonds[9] all the way up to complex cage fusions.[10] However, the linkage between the B_2Fe_2 units observed here is unprecedented in metal cluster chemistry. The synthesis and properties of *conjuncto*-$B_4H_8Fe_4(CO)_{12}$, described below, suggest, in the more general case, that main group–transition element clusters with multiple hydride bridges could often be useful as potential monomers for the synthesis of larger coupled cluster products.

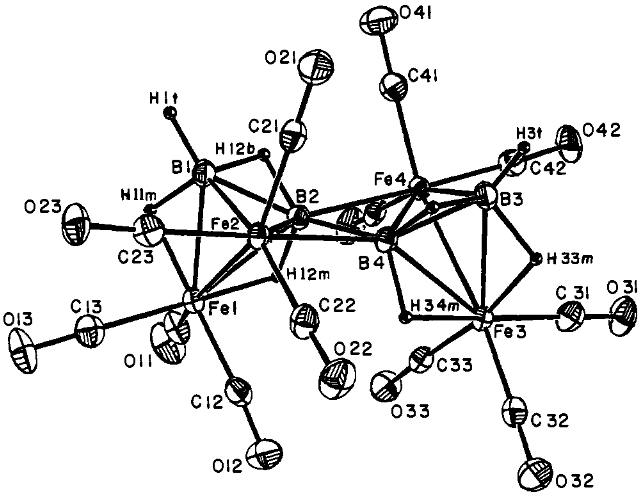
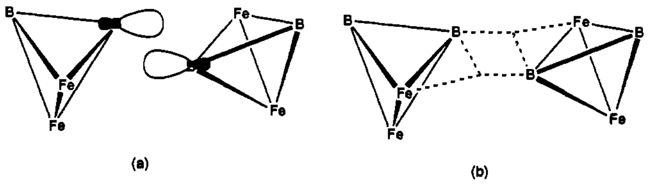


Figure 1. The structure and labeling scheme of $[B_2H_4Fe_2(CO)_6]_2$. Atoms are shown as 50% thermal ellipsoids except for hydrogen atoms, which are drawn at a fixed radius. Selected distances (Å) are as follows: Fe(1)–Fe(2) = 2.591 (1), Fe(1)–B(1) = 2.183 (2), Fe(1)–B(2) = 2.205 (2), Fe(2)–B(1) = 2.086 (2), Fe(2)–B(2) = 2.082 (2), B(1)–B(2) = 1.733 (3), Fe(2)–B(4) = 2.218 (2), B(2)–B(4) = 1.727 (3), Fe(1)–H(11m) = 1.69 (3), Fe(1)–H(12m) = 1.53 (3), B(1)–H(11m) = 1.29 (3), B(2)–H(12m) = 1.29 (3), B(1)–H(12b) = 1.25 (3), B(2)–H(12b) = 1.26 (3), B(1)–H(1t) = 1.13 (3).

Chart I



(a) (b)

The dianion $[B_2H_4Fe_2(CO)_6]^{2-}$ is prepared in good yield in situ as the lithium salt by the precise, slow addition of *n*-BuLi to $B_2H_6Fe_2(CO)_6$[11,12] in THF at low temperature with monitoring by IR spectroscopy.[13] Addition of an excess of $Fe(CO)_4Br_2$ followed by extraction of the reaction mixture with hexane and chromatography on silica gel yields an orange band (R_f = 0.7) eluted with hexane (yield ≈ 10% based on $B_2H_6Fe_2(CO)_6$). Crystallization from hexane in the freezer overnight led to well-formed, modestly air sensitive, red-orange crystals. Spectroscopic characterization[14] is consistent with a molecular formula of $B_4H_8Fe_4(CO)_{12}$, but the NMR data (two equivalent BH(terminal), two pairs of equivalent BHFe, two equivalent BHB, and two boron atoms without terminal hydrogens) and IR data (perturbed $Fe_2(CO)_6$ fragment) rule out a single-cage nido structure[15] even though the molecular formula suggests an isolobal analogy with B_8H_{12}.[16] Unambiguous structural characterization only resulted from a low-temperature X-ray diffraction study on a single crystal,[17] the results of which are given in Figure 1. The

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[13] IR (THF, cm^{-1}): 2443, 2416 w (BH); 1965 m, 1940 m (sh), 1904 vs, 1878 vs, 1869 vs, 1840 m (sh) (CO). ^{11}B NMR (THF, 20 °C, δ): −20.6 (br, fwhm, 309 Hz), {^1H} (fwhm, 234 Hz). ^1H NMR (THF-d_8, 20 °C, δ): 5.2 (br, s, 4 H); (THF-d_8, −60 °C, δ) 1.0 (calcd, 2 H), −11.5 (br s, 2 H).

[14] IR (hexane, cm^{-1}): 2524 vw (BH); 2088 w, 2067 m, 2034 vs, 2018 w, 2003 m, 1983 w (CO). ^{11}B NMR (hexane, 20 °C, δ): 0.8 (br, fwhm, 102 Hz, {^1H} 69 Hz), −2.55 (br, d, J_{BH} = 117 Hz). ^1H NMR (C_6D_6, 20 °C, δ): 3.1 (br, 2 H), −1.2 (br, 2 H), −13.0 (br, 2 H), −14.6 (br, 2 H). MS (EI) P^+ = 612 (−12CO); $^{56}Fe_4{}^{12}C_{12}{}^{16}O_{12}{}^{11}B_4{}^1H_8{}^+$, 611.7776 obsd, 611.7799 calcd.

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molecule consists of two distorted tetrahedral B_2Fe_2 cages related by a noncrystallographic C_2 axis joined along an Fe–B edge such that the two Fe and two B bridgehead atoms define a butterfly structure with a dihedral angle of 162.7 (1)°. The positions of the hydrogen atoms, located and refined, agree with the NMR data obtained in solution. All bond distances and angles are normal based on previously characterized metallaboranes. Although $[B_2H_5Fe_2(CO)_6]^{n-}$, n = 0–2, have not been crystallographically characterized, the structures of closely related Ta[18] ($Cp^*{}_2Ta_2(\mu\text{-}Br)_2(B_2H_6)$) and Nb[19] ($Cp^*Nb_2(B_2H_6)_2$) analogues have been reported.

The observation of a coupled cage structure rather than a single cage reflects the isomeric possibilities for a given cage electron count.[20] As $[B_2H_4Fe_2(CO)_6]_2$ is a mixed main group–transition element cluster and a rare example of a cluster containing equal numbers of boron and iron atoms, one wonders if it will behave more like a metal or main-group cluster. Application of the counting rules developed by Mingos and co-workers for metal cluster coupling and fusion provides a test.[21] Considering total cluster valence electrons, $[B_2H_4Fe_2(CO)_6]_2$ possesses 76 while the rules predict 74.[22] On the other hand, if one formulates the $B_2H_4Fe_2(CO)_6$ fragment as shown in Chart I, part a, then the coupling of two such fragments can be viewed as taking place with the formation of two three-center two-electron bonds, each generated by the interaction of an empty orbital on the bare boron of one fragment with the electron-rich Fe–B edge of the other fragment as shown in Chart I, part b. Thus, a coupling scheme that is predicated on the 8–18 electron rules and the elimination of two-electron edge bonds fails.[23,24]

Although the oxidant remains to be identified, the apparent reaction

$$2[B_2H_4Fe_2(CO)_6]^{2-} + 4[ox] \rightarrow [B_2H_4Fe_2(CO)_6]_2 + 4[red] \qquad (1)$$

constitutes oxidative coupling not unlike that known for $[B_{10}H_{10}]^{2-}$, i.e.,[9,25]

$$2[B_{10}H_{10}]^{2-} + 4[ox] \rightarrow [B_{20}H_{18}]^{2-} + 4[red] + 2H^+ \qquad (2)$$

Indeed the cage–cage linkage in $[B_{20}H_{18}]^{2-}$ has been described as being composed of two three-center two-electron bonds as we now find in $[B_2H_4Fe_2(CO)_6]_2$. As each unit of $[B_2H_4Fe_2(CO)_6]_2$ has three bridging protons, two of which are FeHB bridges, deprotonation of the linked cluster product is possible, leading, in principle, to further condensation to higher linked species. Investigations along these lines are continuing.

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Supplementary Material Available: Tables of crystal data, atom coordinates, selected bond distances and angles, anisotropic thermal parameters, and H atom coordinates for $[B_2H_4Fe_2(CO)_6]_2$ (6 pages); tables of observed and calculated structure factors for $[B_2H_4Fe_2(CO)_6]_2$ (14 pages). Ordering information is given on any current masthead page.

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(17) Crystal data: $C_{12}H_8B_4O_{12}Fe_4$; orthorhombic, P_{bca}, a = 12.990 (4) Å, b = 12.279 (3) Å, c = 26.527 (10) Å, V = 4231.2 Å^3, Z = 8; D(calcd) = 3.30 g cm^{-3}; λ(Mo Kα) = 0.71073 Å; T = 123 ± 2 K; Enraf-Nonius CAD4 diffractometer. A total of 8410 reflections were collected in the $-h,-k,l$ and the $-h,-k,-l$ quadrants ($3.0° \leq 2\theta \leq 58.7°$), of which 5743 were unique and 4851 observed ($3\sigma(F_o)$). Lorentz, polarization and absorption corrections were applied. The structure was solved by direct methods, which revealed the positions of 24 non-hydrogen atoms. Subsequent difference electron density Fourier syntheses located the remaining atoms, including hydrogens. The structure was refined by a full-matrix least-squares process (anisotropic for non-hydrogen atoms with hydrogens at fixed isotropic displacement parameters); $R(F)$ = 3.4%, $R(wF)$ = 4.4%, GOF = 2.01, $\Delta(\rho)$ = 0.55 e Å^{-3}.

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o-Phenylenemagnesium Tetramer: The First Organomagnesium Cluster

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The chemistry of di- and polymetalated aromatic compounds has been dominated by organolithiums;[1] illustrative examples are 1,8-dilithionaphthalene,[2] 2,2′-dilithiobiphenyl,[3] and 1,2-dilithiobenzene (**1**).[4] The corresponding bifunctional organomagnesium compounds have received little attention.[5] Because of our interest in divalent organomagnesiums,[6] we investigated the synthesis and structure of *o*-phenylenemagnesium (**2**).

1,2-Bis(bromomagnesio)benzene, the di-Grignard reagent corresponding to **2**, has been obtained from (trimeric) *o*-phenylenemercury (**3**) by reaction with lithium metal to give **1**, followed by addition of magnesium bromide.[4a] In analogy with the transformation **3** → **1**, we prepared **2** by stirring **3** in THF with magnesium (Scheme I).

The progress of the reaction was monitored by the disappearance of the sparingly soluble **3**; after 2 weeks of stirring at room temperature, the resulting clear, slightly brownish solution was carefully decanted from the amalgam. In spite of some loss of material in this process, **2** was obtained in 90% yield (titration after hydrolysis[7]). Compound **2** was further characterized by ^1H and ^{13}C NMR spectroscopy[8] and by its conversion to **4**[9] with chlorotrimethylstannane.

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(8) **2**: ^1H NMR (toluene-d_8; 250 MHz) δ 8.12 (dd, ^3J = 5.0 Hz, ^4J = 3.3 Hz, 2 H, H(3,6)), 7.23 (dd, ^3J = 5.0 Hz, ^4J = 3.3 Hz, 2 H, H(4,5)); ^{13}C NMR (THF-d_8; 92.6 MHz) δ 189.1 (br m, C(1,2)), 140.6 (dd, ^1J = 150.0 Hz, ^3J = 4.9 Hz, C(3,6)), 124.3 (dm, ^1J = 155.7 Hz, C(4,5)). A $^{13}C\{^1H\}$ NMR spectrum showed sharp singlets for all carbons.

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