Communications to the Editor

Synthesis and Characterization of $HFe_4(CO)_{12}CBH_2$. A Cluster-Substituted Tricoordinate Monoborane

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Monoborane, BH_3, is the prototype of an unsaturated molecule possessing an empty valence orbital and can only be studied under rigorously controlled conditions.[1] Replacement of H with other monovalent radicals or coordination with Lewis bases yields more tractable monoboranes with extremely valuable reaction properties.[2] That is, substituents that donate electron density to the empty 2p orbital of boron reduce the Lewis acidity of borane and modify the activity of the B–H bonds. Herein we report the serendipitous preparation of a carbido cluster substituted monoborane in which the cluster substituent apparently fully satisfies the empty orbital of the borane. The novel monoborane has unprecedented structural features as well as unusual chemical properties.

The new compound arose during a search for better routes to metal-rich metallaboranes.[3] Dissolving $Fe_2(CO)_9$ in THF at 50 °C followed by addition of $BH_3{\cdot}THF$ and reaction for 3 h leads to a mixture of products which are separated by low-temperature chromatography. Fractional crystallization of the tail of the band containing $HFe_3(CO)_9BH_4$ gave deep brown crystals in very low yield. The spectroscopic data[4] allow the new compound to be formulated as $HFe_4(CO)_{12}CBH_2$ (I), and the electron-counting rules suggest a 62-electron (closo) octahedral cluster.[5] However, two of the spectroscopic data are inconsistent with a simple closed structure having a Fe_4CB octahedral cluster core; i.e., the IR spectrum shows the presence of a BH_2 group, and the ^{11}B NMR resonance is at relatively high field.[4,6] A variety of other structural possibilities exist, but the solution data do not establish a unique structure.

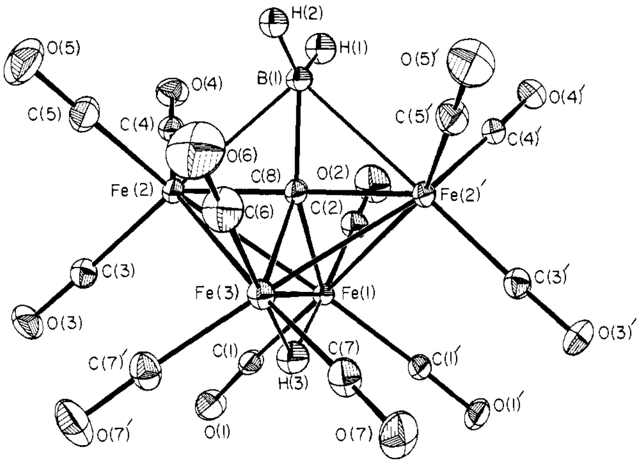

Figure 1. Structure of $HFe_4(CO)_{12}CBH_2$. Selected bond distances: Fe(1)–Fe(2), 2.660 (1); Fe(1)–Fe(3), 2.586 (1); Fe(2)–Fe(3); 2.673 (1); Fe(3)–H(3), 1.59 (6); Fe(1)–H(3), 1.56 (5); Fe(1)–C(8), 1.941 (4); Fe(2)–C(8), 1.844 (1); C(8)–B(1), 1.574 (6); B(1)– H(1), 1.04 (5); B(1)–H(2), 1.25 (5); B(1)–Fe(2), 2.427 (3) Å.

Hence, a crystallographic investigation was undertaken, and the solid-state structure of the new compound is shown in Figure 1.[7] In essence, the molecule consists of a known butterfly carbido cluster fragment $[HFe_4(CO)_{12}C]^-$ bound via the carbido carbon to a $[BH_2]^+$ fragment.[8] The BH_2 fragment, carbido carbon, "hinge" iron atoms and two attached axial CO's, and bridging H of the butterfly fragment are coplanar by virtue of being on a crystallographic mirror plane. The boron–carbido carbon distance is normal for a single bond (1.574 (6) Å) as are the B–H terminal distances (1.04 (5) and 1.25 (5) Å).[9,10] The planar geometry and the C–B–H and H–B–H angles (121.8 (30)°, 120.1 (22)°, and 118.0 (37)°) define an sp^2 hybridized boron atom. The Fe(2)–B (and by symmetry the Fe(2′)–B) distance is 2.427 (3) Å which, although longer than the normal Fe–B bonding distance (2.1 Å), is substantially shorter than the sum of van der Waals radii.[11] It is important to note that the carbido cluster fragment has the geometry of a 62- rather than 60-electron butterfly; i.e., the dihedral angle between the "wings" is 105° and the Fe(2)–C–Fe(2′) angle is 178° compared to 102 ± 2° and 176 ± 2° for the 62-electron and 129 ± 1° and 148 ± 1° for the 60-electron systems, respectively.[12] The pattern of Fe–Fe and Fe–C distances is likewise characteristic of the 62- rather than 60-electron cluster geometry.[13]

The coordination geometry of the boron atom suggests that I might be described as cluster substituted monoborane with the $HFe_4(CO)_{12}C$ fragment contributing one electron to the B–C bond. This creates a problem as the carbido butterfly fragment in I would then be expected to have the same cluster geometry as $[Fe_4(CO)_{12}CC(O)Me]^-$, i.e., a structure corresponding to 60 cluster electrons.[14] On the other hand, viewing I as $[HFe_4(CO)_{12}C]^-$, $[BH_2]^+$ is not very informative, and we propose the following explanation for the observed structure. The $[HFe_4(CO)_{12}C]^-$ anion has a high lying filled MO with π symmetry with respect to the mirror plane of I.[12] This filled MO with combined metal and carbon character can interact strongly with the empty B2p orbital.[12,15] As schematically shown in Chart Ia, the pπ

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[1] Fehlner, T. P. In *Boron Hydride Chemistry*; Muetterties, E. L.; Ed.; Academic: New York, 1975; p 175.

[2] Brown, H. C. *Hydroboration*; Benjamin: New York, 1962.

[3] Fehlner, T. P. *New. J. Chem.* **1988**, *12*, 307.

[4] MS(EI), $P^+ = 586$ (−12 CO); $^{56}Fe_4{}^{12}C_{12}{}^{16}O_{11}{}^{11}B^1H_3{}^+$, 557.714 obsd, 557.717 calcd; NMR ^{11}B (hexane, 20 °C), δ 9.57 (br t, FWHM 360 Hz, {^1H} 170 Hz; $J_{BH} \simeq 90$ Hz); ^1H (C_6D_6, 20 °C), δ 4.0 (br, s, 2 H), −26.1 (s, 1 H); IR (hexane, cm^{-1}), 2525 w, 2470 w (BH_2); 2050 vs, 2032 s, 2020 s, 2001 m (CO).

[5] Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.

[6] Rath, N. P.; Fehlner, T. P. *J. Am. Chem. Soc.* **1988**, *110*, 5345.

[7] Crystal data: $C_{13}H_3BO_{12}Fe_4$, monoclinic, $P2_1/m$, $a = 7.651$ (2) Å, $b = 15.723$ (5) Å, $c = 8.890$ (2) Å, $\beta = 110.50$ (2)°, $V = 1001.7$ Å^3, $Z = 2$, μ(Mo Kα) = 2.897 mm^{-1}, D(calcd) = 1.941 g cm^{-3}, $T = 298$ K, brown specimen, 0.4 × 0.3 × 0.2 mm. Of 3395 data collected (Syntex P1 bar, $4° \leq 2\theta \leq 60°$) with no absorption correction, 2570 were observed ($3\sigma F_o$). Non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically: $R_1 = 0.039$, $R_2 = 0.046$, GOF = 2.11.

[8] Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4541. Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4544.

[9] Olmsted, M. M.; Power, P. P.; Weese, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 2541.

[10] Shore, S. G. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975; p 79.

[11] Wong, K. S.; Scheidt, W. R.; Fehlner, T. P. *J. Am. Chem. Soc.* **1982**, *104*, 1111. Housecroft, C. E.; Fehlner, T. P.; Buhl, M. L.; Long, G. J. *J. Am. Chem. Soc.* **1987**, *109*, 3323.

[12] Bradley, J. S.; Harris, S.; Newsam, J. M.; Hill, E. W.; Leta, S.; Modrick, M. A. *Organometallics* **1987**, *6*, 2060.

[13] The molecular formula of I can be construed as having the same formal electron count as clusters such as $Ru_4(CO)_{12}C_2Ph_2$, $Co_4(CO)_{10}C_2Et_2$, or $H_2Cp_4Co_4B_2H_2$. However, the latter exhibit well behaved octahedral structures (62-electron tetrametal butterflies), whereas I does not. The reason why a CBH_2 rather than a CHBH fragment is found in I is not obvious.

[14] Bradley, J. S.; Ansell, G. B.; Leonowicz, M. E.; Hill, E. W. *J. Am. Chem. Soc.* **1981**, *103*, 4968.

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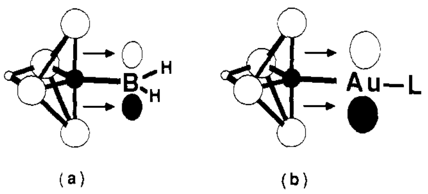
Chart I



interaction is maximized for the observed cluster structure. The strength of this interaction must be sufficient to prevent the adoption of the presumably preferred 60-electron $[Fe_4(CO)_{12}CC(O)Me]^-$ structure. Clearly the B2p orbital is substantially occupied as even though I was prepared in the presence of THF, no THF is found in the solid state. This, plus the very slow reaction with Lewis bases, shows that the formal acid site on I is sterically and/or electronically inaccessible.

The occupation of the B2p orbital can be estimated from the ^{11}B NMR chemical shift.[16] Considering the boron in I as three coordinate, one expects the ^{11}B shift to lie in the range δ 87 to 7. The low field limit corresponds to compounds with little back donation into the B 2p orbital, e.g., BMe_3, and the high field limit to compounds with large back donation, e.g., BI_3. Hence, the shift of δ 9 observed for I is consistent with strong back donation from the carbido cluster to the boron atom. In addition, the ^{11}B–H coupling constant is typical of that observed for related boranes, e.g., BH_3·THF.

One might also view I as being derived from a hypothetical square-pyramidal carbido cluster cation $[HFe_4(CO)_{12}CBH]^+$ which has opened up into the observed structure on the addition of the base H^- to boron. This reaction has been observed for the all-transition-metal system, $Os_5(CO)_{15}C$, which opens into structure *I* on the addition of another ligand, e.g., CO.[17] If the osmium cluster is viewed as a $[Os_4(CO)_{12}C]^-$ carbido fragment bound to a $[Os(CO)_4]^+$ fragment, then the latter plays the role of the BH_2 fragment in *I*, i.e., I is a borane mimic of the "bridged-butterfly" pentaosmium carbido cluster. Note, however, if the boron atom actually occupied a cluster vertex, one would expect a tetrahedral disposition of nearest neighbors rather than the trigonal one observed.

Further, I is structurally very similar to $HFe_4(CO)_{12}CAu(PPh_3)$ with the $[Au(PPh_3)]^+$ fragment replacing the $[BH_2]^+$ fragment.[18] The carbido framework of the gold derivative is that of the 62-electron butterfly despite the fact that the $AuPPh_3$ fragment is formally an exo-ligand to the carbido carbon. As noted by the authors, the structural parameters suggest that a p orbital of the gold atom is interacting with the wing-tip iron atoms, and the bonding situation is analogous to that of I (Chart Ib). If the $[AuPPh_3]^+$ had behaved like $[H]^+$,[19] one would have expected it to bridge a C–Fe edge to yield a structure analogous to that of $HFe_4(CO)_{12}CH$.[8] Hence, one might well view the $[Au(PPh_3)]^+$ as isolobal to the $[BH_2]^+$ fragment. Considering, in addition, the tendency of gold fragments to form Au–Au bonds, this may be a better representation of the bonding capabilities of this fragment.

A more detailed analysis of the properties of the electronic structure of I is required, but it is clear from the information presented here that the use of metal clusters as ligands has the potential for the stabilization of unusual bonding modes particularly where p backbonding as well as steric bulk is advantageous.

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Registry No. $Fe_2(CO)_9$, 15321-51-4; BH_3·THF, 14044-65-6; $HFe_4(CO)_{12}CBH_2$, 119850-57-6.

Supplementary Material Available: Tables of atom coordinates, bond distances and angles, and anisotropic temperature factors (4 pages); tables of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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The First High Resolution Direct NMR Observation of an f-Block Element

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The last decade has seen a dramatic increase in the importance of the organometallic chemistry of the lanthanide elements.[1-4] In particular, iodides, cyclopentadienyls, and bis(trimethylsilyl)amides of Sm(II), Eu(II), or Yb(II), due to their unique reactivity (e.g., as selective reducing agents[4-7]), have attracted much attention. Yet high resolution, solution-state NMR, one of the organometallic chemists' most informative tools, has not previously been applied to the direct observation of an f-block element, excluding complexes of the f^0 La(III). The reason for this neglect is probably because the majority of complexes [except those of La(III), Yb(II), and Lu(III)] are paramagnetic, and many of the NMR-active f-block nuclei have large quadrupole moments. Yet for certain of these elements spin-1/2 isotopes exist, and the range of diamagnetic compounds is rapidly increasing. As a case in point, ^{171}Yb is a spin-1/2 nucleus, with a natural abundance of 14.27% and a moderately sized, positive gyromagnetic ratio (4.712×10^7 rad T^{-1} s^{-1}); these features combine to give a receptivity four times greater than that of ^{13}C. Three solid-state, wide-line studies of this nucleus have appeared.[8-10] We now report ^{171}Yb chemical shift solution NMR data for the series of Yb(II) complexes **1–7**, Table I.

NMR experiments were performed on a Bruker WM360 spectrometer. We originally chose $[Yb(\eta\text{-}C_5Me_5)_2(OEt_2)]$ (**1**)[11] as the ^{171}Yb chemical shift standard, due to its good solubility, thermal stability, and low-frequency resonance. {Subsequently a referee has suggested a lower frequency standard having similar characteristics, $[Yb(\eta\text{-}C_5Me_5)_2(THF)_2]$ (**7**), see Table I.} The

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