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Ferraborane $B_3H_7Fe_2(CO)_6$, a Diiron Analogue of Pentaborane(9)

Sir:

Recently we reported comparisons of the electronic structure¹ and photochemistry² of the five-atom, nido ferraborane, $B_4H_8Fe(CO)_3$,³ with that of the related compounds B_5H_9 and $C_4H_4Fe(CO)_3$. The aim of this work was to define more precisely the various roles of a metal atom in a cage environment. We now report the preparation and characterization of $B_3H_7Fe_2(CO)_6$,⁴ a compound that is also formally a five-atom, 14-electron (nido) cage. Structural characterization permits a test of the prediction that the geometrical structure of B_5H_9 should serve as an adequate model for the structure of the B_3Fe_2 cage.⁵ In addition this new compound provides an opportunity to examine the iron-iron interaction in a cage environment.⁶

The preparation of $B_3H_7Fe_2(CO)_6$ from B_5H_9 , $Fe(CO)_5$, and $LiAlH_4$ was carried out in a manner similar to the preparation of $B_2H_6Fe_2(CO)_6$.⁷ The major differences were that the solvent was changed to 1,2-dimethoxyethane and the temperature to 60–70 °C. Under these conditions an ~1% yield of $B_3H_7Fe_2(CO)_6$ is produced as the major ferraborane containing two iron atoms. The new compound is a volatile, orange, crystalline solid at room temperature that melts at 51 °C. It appears air sensitive but thermally stable in that several samples were kept at 45 °C for 2 months with no evidence of decomposition.

The new compound has the molecular formula $Fe_2B_3C_6O_6H_7$ ($^{56}Fe_2^{11}B_3^{12}C_6^{16}O_6^1H_7^+$, calcd 319.922 amu, obsd 319.921 amu). The parent ion in the mass spectrum fragments by the sequential loss of six CO molecules and the envelopes of the parent ion and first three fragment ions are consistent with a molecule containing three boron atoms. The Fe_2^+ ion is prominent in the fragmentation pattern. The infrared spectrum of a film exhibits bands at 2105 (w), 2060 (sh), 2035 (m), 1955 (m) cm^{-1} . There was no evidence for bridging carbonyls. The 100-MHz 1H FT NMR spectrum in CD_2Cl_2 exhibits two broad resonances (170 Hz, fwhm) at δ -2.6 and -16.6. On ^{11}B decoupling the two resonances sharpen considerably (30 Hz, fwhm) and a similarly sharp resonance appears at δ 3.0. The relative areas of the decoupled signals are 2 (δ 3.0) to 3 (δ -2.6) to 2 (δ -16.6). The 32.1-MHz ^{11}B FT NMR spectrum consists of four resonances that are analyzed as an overlapping doublet (160 Hz, area 2) and quartet (170 Hz, area 1) at 4.2 and 12.1 ppm, respectively.⁸ On 1H decoupling singlets appear at 4.2 and 12.1 ppm with relative areas of 2 and 1. These data show that the molecule contains the $Fe_2(CO)_6$ fragment, two Fe-H-B bridges, a pair of equivalent borons each coupled to one proton, one boron coupled to three magnetically equivalent protons, and two sets of two and one set of three equivalent protons. These data allow several structural possibilities; thus, a single-crystal X-ray diffraction study was carried out.

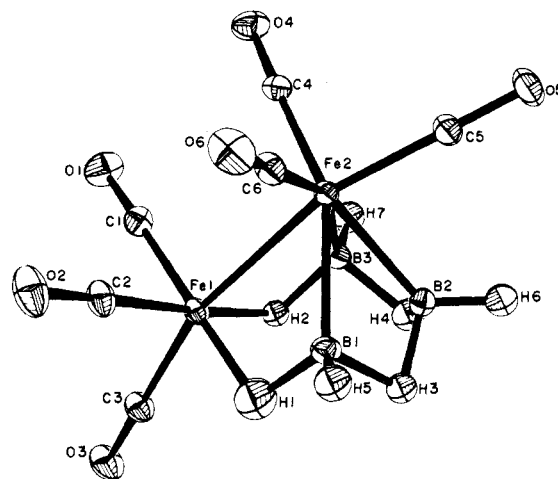
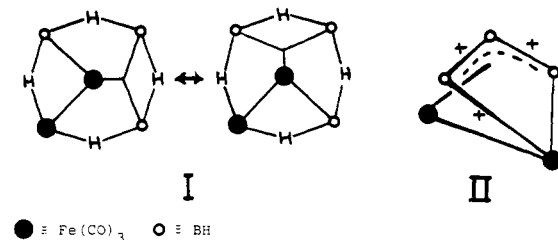


Figure 1. Structure of $B_3H_7Fe_2(CO)_6$.

A crystal $0.8 \times 0.3 \times 0.4$ mm was grown by annealing a polycrystalline sample at 45 °C. The crystal was monoclinic (space group $P2_1/c$, No. 14) with $a = 9.006$ (2), $b = 10.878$ (2), $c = 12.479$ (2) Å; $\beta = 99.54$ (1)°. Assuming $Z = 4$, $d_{calcd} = 1.77$ g/cm^3 . The iron atoms and 10 of the light atoms were located by direct methods using the MULTAN package.⁹ The rest of the nonhydrogen atoms were located by Fourier techniques and the model was refined to convergence assuming the atoms to vibrate anisotropically. The hydrogen atoms were located from a difference electron density map and included in the model as isotropic atoms. Two cycles of full-matrix least-squares refinement (based on the 2825 reflections with $F_o > 3\sigma F_o$ and $\sin \theta/\lambda \leq 0.69$) resulted in convergence with a conventional R value of 0.044 and a weighted R value of 0.059.

The structure of $B_3H_7Fe_2(CO)_6$ is shown in Figure 1. The atoms, including hydrogens, are represented as 50% thermal ellipsoids. The bond distances in the borane unit are normal:¹⁰ B-B, 1.773 (7) and 1.783 (7); B-H_{terminal}, 1.01 (5) to 1.09 (5); B-H_{bridge}, 1.19 (5) to 1.33 (4) Å. The Fe-Fe distance is 2.559 (2) which is in the range found for compounds considered to have an iron-iron single bond.¹¹ The three unbridged Fe(2)-B distances are nearly the same (2.050 (5), 2.062 (4), and 2.070 (5) Å) and are comparable with one unbridged Fe-B distance in $B_5H_8Fe(CO)_3$ ¹² and $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$ ¹³ (2.08, 2.08 Å) but smaller than the other (2.16, 2.15 Å). The two bridged Fe(1)-B distances (2.250 (4) and 2.273 (5) Å) are distinctly longer than the bridged Fe-B distance in the above two monoiron compounds (2.13, 2.12 Å). The Fe(1)-H_{bridge} distances (1.57 (4) and 1.58 (5) Å) are nearly equal to those in the two monoiron compounds (1.52, 1.56 Å), while the boron to Fe-H-B bridging hydrogen distances (1.33 (6) and 1.26 (4) Å) are within the range found for B-H-B bridges. Thus, except for the distortion¹⁴ caused by the size of the iron atoms, the cage structure is basically that of pentaborane(9) in which an apical and a basal BH fragment are replaced by $Fe(CO)_3$ fragments.

The bonding in $B_3H_7Fe_2(CO)_6$ can be viewed in two distinct fashions. The analogy to B_5H_9 stressed above would lead to the valence bond representation sketched in I below in which the



apical iron is bound to the three basal borons with a two-center and three-center bond. The total contribution of each $\text{Fe}(\text{CO})_3$ group and BH group to the cage bonding is two electrons and three orbitals.¹⁵ An alternate representation of the bonding results if the compound is viewed as being formed by the addition of $\text{B}_3\text{H}_7^{2-}$ (isoelectronic with the allyl ion, C_3H_5^-) to $\text{Fe}_2(\text{CO})_6^{2+}$. This formulation is sketched in II where it is suggested that the π system of the pseudo allyl ion donates four electrons to one iron and the two BH bonds donate four electrons to the other iron.¹⁶ With a single bond between the iron atoms, the 18-electron rule is satisfied. In this regard the new compound is related to ferracyclopentadiene complexes.^{11b}

A series of compounds containing the B_3H_7 fragment bound to a single metal atom have been described and the structure of one, $[(\text{CH}_3)_2\text{C}_6\text{H}_5\text{P}]_2\text{PtB}_3\text{H}_7$, has been determined.^{17,18} There are three striking differences between the B_3H_7 fragment in this compound and in $\text{B}_3\text{H}_7\text{Fe}_2(\text{CO})_6$. In the platinum compound the highest field ^1H resonance occurs at $\delta -4.9$ (assigned to B-H-B bridges) compared with $\delta -16.6$ in the iron compound for which Fe-H-B bridges are established by the static structure. Second, the B-B-B angle is 112.9° in the platinum compound (B(1)-B(3) distance of 3.15 Å), while this angle is 93.8° in the iron compound (B(1)-B(3) distance of 2.59 Å). Finally, the B_3 unit is asymmetrically coordinated to platinum in the solid state, while in the iron compound the coordination is very symmetrical. Thus, $\text{B}_3\text{H}_7^{2-}$, considered as a ligand, behaves rather differently in these two bonding situations.

The B_3 unit is also of interest in terms of its NMR behavior as triborane compounds are known to display fluxional properties.¹⁹ The ^1H NMR of $\text{B}_3\text{H}_7\text{Fe}_2(\text{CO})_6$ exhibits only three types of hydrogen at temperatures as low as -70°C . Clearly, the resonance observed at high field is due to the two Fe-H-B bridging hydrogens. The resonance at lowest field is assigned to the terminal hydrogens on B(1) and B(3) based on the magnitude of the chemical shift and on a comparison of the coupled and decoupled spectra. This requires that the resonance in the bridging region (three protons) be assigned to the remaining terminal hydrogen on B(2) and the two B-H-B bridging hydrogens observed in the static structure. The fact that these three hydrogens are magnetically equivalent is most likely the result of some type of rapid (on the NMR time scale) intramolecular exchange. Compounds that exhibit similar behavior have been termed "selectively non-rigid".²⁰

Further studies of this diiron and analogue of B_5H_9 are in progress.

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Time-Resolved Resonance Raman Study of the Lowest ($d\pi^*$, ^3CT) Excited State of Tris(2,2'-bipyridine)ruthenium(II)

Sir:

We report the time-resolved resonance Raman (TR^3) spectrum of tris(2,2'-bipyridine)ruthenium(II) in its lowest electronically excited state, $^*\text{Ru}(\text{bpy})_3^{2+}$. This is the first report of the vibrational spectrum of an optically generated excited state in fluid solution. Because of intensive recent investigations of the photophysics¹ and photochemistry²⁻⁵ of $\text{Ru}(\text{bpy})_3^{2+}$, the potential of this complex in the conversion of light into chemical energy², and the fundamental significance of vibrational spectroscopy of the electronically excited state,⁶ our results and their attendant structural information content on $^*\text{Ru}(\text{bpy})_3^{2+}$ are of considerable interest.

TR^3 spectroscopy is now established as an important new technique for the study of the structures of transient chemical species with nanosecond,^{7a} ultimately picosecond,^{7b} time resolution. Quite recently, the first TR^3 studies of excited states, the optically forbidden triplets of β -carotene⁶ and *p*-terphenyl⁸, have been reported. Because the direct optical yield of these triplets is negligible, in both studies the excited states were produced by pulse radiolysis. The applicability of TR^3 to optically created excited states has not been demonstrated until now. In the present study, we use direct pulsed laser excitation to produce a near-saturation yield of $^*\text{Ru}(\text{bpy})_3^{2+}$ and to simultaneously observe the excited-state TR^3 spectrum.

Optical excitation of $\text{Ru}(\text{bpy})_3^{2+}$ at 265 nm or longer wavelength produces the emissive and photochemically active state (denoted $d\pi^*$, ^3CT , or $^*\text{Ru}(\text{bpy})_3^{2+}$ by various workers¹⁻⁴), with quantum yields approaching unity, in 10 ps or less.¹ The $^*\text{Ru}(\text{bpy})_3^{2+}$ is then relatively long lived (~ 665 ns) and has a strong ligand-centered $\pi^* \rightarrow \pi^*$ absorption maximum at 360 nm.³ We therefore used as our excitation source the third harmonic of a Nd:YAG laser (354.5 nm, 5-ns pulse width, ~ 5 mJ/pulse). The $^*\text{Ru}(\text{bpy})_3^{2+}$ is formed sufficiently rapidly, and the ground-state absorbance at 355 nm is sufficiently intense, that we can use a single 355-nm pulse both to excite the $\text{Ru}(\text{bpy})_3^{2+}$ and to probe the excited-state TR^3 spectrum. The Raman scattered radiation was detected using a Spex double monochromator, which provided ample rejection