

Preliminary communication

PREPARATION OF  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-B}_2\text{H}_5)$ : A NEUTRAL METALLO-DIBORANE(6) ANALOGUE OF A METAL-OLEFIN COMPLEX

JEFFREY S. PLOTKIN and SHELDON G. SHORE\*

Department of Chemistry, The Ohio State University,  
 Columbus, Ohio 43210

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Summary

The reaction of  $\text{B}_2\text{H}_6$  with  $\text{K}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$  in dimethyl ether at  $-78^\circ\text{C}$  gives  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-B}_2\text{H}_5)$ . This compound may be viewed as a direct electronic and structural analogue of the metal-olefin complex  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-C}_2\text{H}_4)]^+$ .

We have prepared  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-B}_2\text{H}_5)$ , the first example of a neutral volatile metallo-diborane(6) complex in which the metal atom occupies a bridging site (Figure 1).

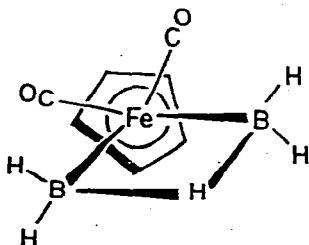
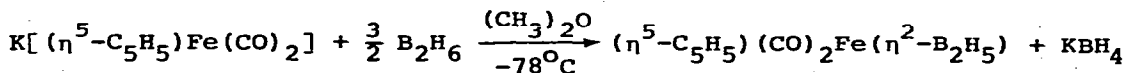


Figure 1. The proposed structure of  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-B}_2\text{H}_5)$



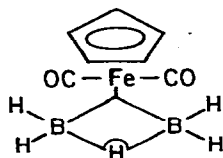
Addition of  $\frac{3}{2}$  equivalents of  $\text{B}_2\text{H}_6$  to a dimethyl ether slurry of  $\text{K}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$  at  $-78^\circ\text{C}$  results in a dark brown solution and a fine white precipitate. After removal of the solvent at  $-78^\circ\text{C}$  the yellow crystalline  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-B}_2\text{H}_5)$  can be readily sublimed from the crude reaction mixture under vacuum at room temperature. This compound may be handled in air for short periods of time, although extended air exposure results in decomposition of the ferri-diborane complex to  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ . In vacuum  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-B}_2\text{H}_5)$  shows no evidence of decomposition after several hours at room temperature. The mass spectrum reveals a mass cut-off at  $m/e = 204$ . Elemental composition was confirmed by high resolution mass measurement. Calculated for  $^1\text{H}_{10} \text{ }^{11}\text{B}_2 \text{ }^{12}\text{C}_7 \text{ }^{16}\text{O}_2 \text{ }^{56}\text{Fe}$ : 204.02158; Found: 204.02206.

Boron-11 and proton NMR spectra are in agreement with the proposed structure shown in Figure 1. The 28.9 MHz  $^{11}\text{B}$  NMR spectrum consists of a triplet of doublets which upon proton decoupling collapses to a sharp singlet at  $\delta = -6.5$  (a negative sign indicates an upfield shift in ppm from  $\text{BF}_3 \cdot \text{O}(\text{Et})_2 = 0$ ). This triplet arises from the coupling of two equivalent terminal hydrogen atoms with each boron atom,  $J_{\text{BH}_t} = 117$  Hz. Each component of the triplet is further split into a doublet owing to coupling of the boron atoms with the unique bridging hydrogen atom,  $J_{\text{BH}_\mu} = 26$  Hz. The 90 MHz  $^{11}\text{B}$ -decoupled proton NMR spectrum consists of a sharp resonance at 5.09 $\delta$ , due to the cyclopentadienyl ring, and two broader resonances at 2.73 $\delta$  and -5.33 $\delta$  with relative intensities 4:1, assignable to the terminal and bridge hydrogens, respectively.

The infrared spectrum ( $\text{CH}_2\text{Cl}_2$  soln;  $\text{cm}^{-1}$ ) of  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-B}_2\text{H}_5)$  is also consistent with the proposed structure. For example, as is often the case for the  $\text{BH}_2$  groups,

the terminal B-H stretching region contains two bands at 2492(m) and 2435(m), while the expected bridging B-H bands occur at 1892(w) and 1698(w) [1]. Two sharp carbonyl bands are present at 2045(vs) and 1990(vs). These bands fall in the same region as the carbonyl bands of other neutral cyclopentadienyl iron dicarbonyl derivatives such as  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{CH}_3)$  [2].

This compound is of special interest, not only because it is the first example of a neutral metallo-diborane(6) complex, but also because it relates the bonding mode of metal-olefin complexes and the 3-center, 2-electron bond concept. As a first approximation it is helpful to consider  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-B}_2\text{H}_5)$  as a derivative of diborane(6) in which a cyclopentadienyl iron dicarbonyl fragment has replaced a bridging hydrogen. Thus, a reasonable valence bond structure for this molecule is that shown below (I).

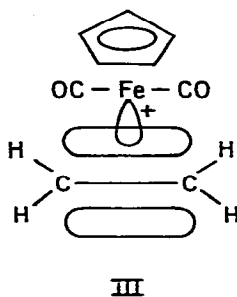
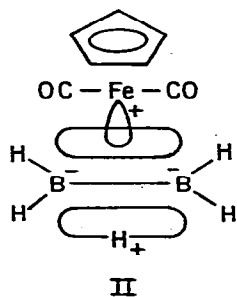


I

This 3-center, 2-electron bond representation allows the iron to have six bonding electron pairs. Any other valence bond structures in which the iron is bound to the  $\text{B}_2\text{H}_5$  system via two 2-center, 2-electron iron-boron bonds are clearly less favorable since this would require the iron to have seven bonding electron pairs. It should be pointed out, however, that for the previously reported anionic complex  $[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5]^-$  we have noted that both types of valence bond structures must be given consideration in the absence of experimental evidence [3].

An alternate, but equivalent, view of the bonding description clearly illustrates the concept that  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-B}_2\text{H}_5)$

can be viewed as a direct electronic and structural analogue of the cationic metal-olefin complex  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-C}_2\text{H}_4)]^+$  [4]. Consideration of the diborane(6) species in terms of the protonated double bond model of Pitzer [5] (II) allows the iron-boron bonding mode to be likened, at least qualitatively, to the familiar Dewar-Chatt-Duncanson model [6,7] of metal-olefin bonding (III). In both instances, as pictured below, a metal orbital of the  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}^+$  fragment can be thought of as overlapping with the  $\pi$  electron density of each of the iso-electronic  $\text{B}_2\text{H}_5^-$  and  $\text{C}_2\text{H}_4$  species.



The validity of this analogy is currently the subject of further study. It is anticipated that by use of such physical techniques as X-ray crystallography, photoelectron and Mössbauer spectroscopy, together with an investigation of the chemistry of  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-B}_2\text{H}_5)$  a more complete understanding of the iron-boron bonding interaction will emerge.

#### Acknowledgement

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