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Novel Iron-Carborane  $\mu$ - and  $\pi$ -Complexes  
Derived From Nido- $C_2B_4H_8$ . A Paramagnetic  
Small Carborane Sandwich Compound

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13. ABSTRACT The reaction of $NaC_2B_4H_7$ with $(\eta-C_5H_5)Fe(CO)_2I$ gives $\mu-[(\eta-C_5H_5)Fe(CO)_2]C_2B_4H_7$ (I) in which the metal atom is bound to the cage via a B-Fe-B three-center bond. Ultraviolet irradiation of I yields $(\eta-C_5H_5)Fe^{II}(\eta-C_2B_4H_7)$ (II), a diamagnetic sandwich complex containing a non-terminal hydrogen which may be at least partially bonded to the iron atom, and $(\eta-C_5H_5)Fe^{III}(\eta-C_2B_4H_7)$ (III), a paramagnetic sandwich species which is isoelectronic with ferricinium ion. The conversion of II to III also occurs during thick-layer chromatography on silica gel. The structural characterization of I, II, and III is based on $^{11}B$ and $^1H$ nmr, mass spectra, infrared spectra, and the epr spectrum of III. The three complexes are moderately to highly air-stable and are obtained in yields of >50% for I and >90% for the mixture of II and III.	

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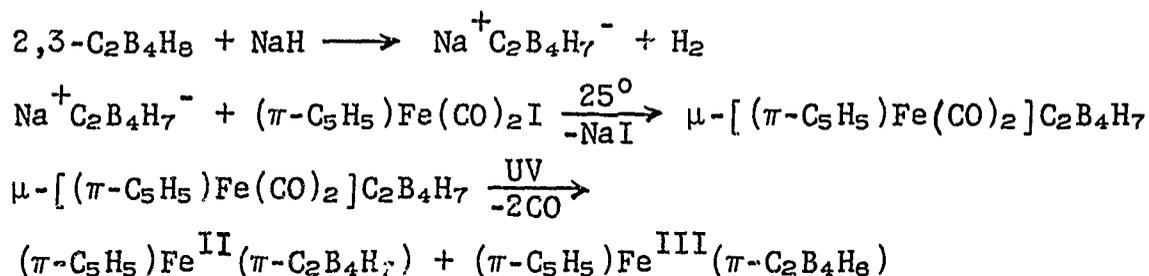
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Dicarb-a-nido-hexaborane(8) sandwich complex metallo-carboranes carboranes iron complexes paramagnetic complexes						

Sir:

Several transition metal-small carborane  $\pi$ -complexes obtained from  $C_2B_3H_7$ <sup>1</sup> or  $C_2B_4H_8$ <sup>2</sup> in the gas phase and from 2- $CH_3C_3B_3H_6$ <sup>3,4</sup> or its mono-anion derivative<sup>4</sup> have been described recently. We now report a new approach to the preparation of such complexes, based on the readiness of the  $C_2B_4H_7^-$  anion to undergo heteroatom insertion,<sup>5,6</sup> which yields the first known small carborane sandwich species as well as two stable and structurally novel metallocarborane intermediates. The reaction of sodium dicarbaheptaborate (1-) with  $\pi$ -cyclopentadienyliron dicarbonyl iodide in tetrahydrofuran at 25° generates a moderately air-stable yellow solid,  $\mu$ -[( $\pi$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>]C<sub>2</sub>B<sub>4</sub>H<sub>7</sub> (I), in which the iron atom is evidently bound to the cage by a three-center two-electron B-Fe-B bond. Under ultraviolet irradiation in vacuo, I loses 2 mol equiv of CO and rearranges to a sublimable orange solid, ( $\pi$ -C<sub>5</sub>H<sub>5</sub>)Fe<sup>II</sup>( $\pi$ -C<sub>2</sub>B<sub>4</sub>H<sub>7</sub>) (II), and a brown crystalline paramagnetic species, ( $\pi$ -C<sub>5</sub>H<sub>5</sub>)Fe<sup>III</sup>( $\pi$ -C<sub>2</sub>B<sub>4</sub>H<sub>8</sub>) (III). The conversion of II to III also occurs during thick-layer chromatography of II on silica gel. Complex I is obtained in >50% yield, while the total yield of II and III, which form in approximately equal amounts from I, is >90%.



The proposed structures of the three complexes (Fig. 1) are based on mass spectroscopic, nmr, and infrared evidence. Complexes I, II, and III exhibit mass spectroscopic parent peaks at  $m/e$  252, 196, and 195 respectively, and in each case the profile is consistent with the indicated formulas (since both iron and boron are polyisotopic, the profile in the parent region is highly characteristic for a given composition). The empirical formulas are further supported by an exact mass determination of III (calculated for  $^{56}\text{Fe}^{12}\text{C}_7^{11}\text{B}_4^1\text{H}_{11}$ , 195.058, found 195.060).

The 32.1-MHz  $^{11}\text{B}$  nmr spectrum of I in  $\text{CCl}_4$  solution contains doublets of approximately equal areas at  $\delta$ -16.4 ppm rel to external  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  ( $J=139$  Hz); -3.2 (165); -1.6 (178); and + 52.0 (181). The high-field resonance is attributed to the apex B-H group, but specific assignment of the low-field peaks is ambiguous at present. The location of the iron substituent at a bridging, rather than terminal, position is indicated by the fact that all of the boron resonances are doublets arising from terminal B-H groups. The presence of two CO groups is evidenced by mass spectral peak groupings having local cutoffs at  $m/e$  224 and 196, corresponding to the loss of one and two CO units, respectively; in addition, strong peaks are observed at  $m/e$  121 and 56, arising from  $\text{Fe}(\text{C}_5\text{H}_5)^+$  and  $\text{Fe}^+$ .

The 100-MHz proton nmr spectrum of I contains a sharp  $\text{C}_5\text{H}_5$  singlet at  $\delta$ -4.83 rel to external  $(\text{CH}_3)_4\text{Si}$ ; a cage C-H peak at -6.52; H-B quartets centered at -3.27 ( $J=147$ ) and +0.98 (169); and a broad B-H-B resonance at +0.91. The characteristic infrared absorptions ( $\text{CCl}_4$  solution vs.  $\text{CCl}_4$ ) are at 3030 (m, cyclopentadienyl C-H), 3115 (w, carboranyl C-H), 2580

(s, B-H), 2010 (vs, CO), and 1965 (vs, CO)  $\text{cm}^{-1}$ .

The  $^{11}\text{B}$  nmr spectrum of II in  $\text{CCl}_4$  consists of two well-resolved doublets in a 3:1 area ratio, the larger centered at  $\delta + 8.49$  (167), assigned to the basal B-H groups, and the smaller at  $+ 20.0$  (153), assigned to the apex B-H. The 100-MHz proton nmr spectrum of III contains sharp singlets at  $\delta -4.82$  and  $-4.10$ , assigned to the cage C-H and cyclopentadienyl groups, respectively, and a moderately broad band at  $+ 14.40$  assigned to the unique hydrogen, discussed below. The H-B quartets are not well resolved and are partly obscured by the H-C resonances.

The gross "sandwich" structure of II is strongly supported by the  $^{11}\text{B}$  and  $^1\text{H}$  nmr spectra, which indicate, respectively, the pseudo-equivalence<sup>7</sup> of the basal B-H groups in the carborane ligand and of the five cyclopentadienyl protons in a rapidly rotating  $\text{C}_5\text{H}_5$  ring. However, the location of the seventh, or anomalous, carboranyl hydrogen presents an intriguing problem which cannot be completely resolved from the spectral data. The total absence in the  $^{11}\text{B}$  nmr spectrum of the secondary splitting normally associated with B-H-B bridging groups indicates that such a feature is probably not present in a fixed sense, although hydrogen tautomerism between two equivalent bridging positions is conceivable. However, the singlet resonance at high field in the proton nmr spectrum is strongly reminiscent of Fe-H bonding as is found in metal hydride complexes<sup>8</sup> such as  $\text{HFe}(\pi\text{-C}_5\text{H}_5)_2^+$ <sup>9</sup>, an isoelectronic analog of II. An intermediate possibility, which we suggest schematically in Fig. 1 (II), is that of a hydrogen which is partially bonded both to the iron atom and to the carborane cage.

The expected paramagnetism of III is confirmed by the broad, widely separated  $^{11}\text{B}$  and  $^1\text{H}$  nmr resonances and by the paramagnetic resonance spectrum (to be described in a subsequent paper). The only peak observed in the  $^{11}\text{B}$  nmr spectrum is a hump at  $\delta + 106$  with a half-width of  $\sim 700$  Hz. For comparison, the  $^{11}\text{B}$  nmr spectra of paramagnetic iron(III) dicarbollyl complexes (e.g.,  $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\pi\text{-C}_2\text{B}_9\text{H}_{11})$ ) exhibit broad singlets over a range of several hundred ppm.<sup>10</sup> However, unlike the spectrum of III, those of the dicarbollyls are sufficiently well resolved to permit some correlation with structure. We attribute the contrast to the presumably lesser average effect of the paramagnetic metal atom on the boron atoms of the large  $\text{C}_2\text{B}_9$  cage, as compared to the effect on the  $\text{C}_2\text{B}_4$  ligand in III, in which three of the four borons are directly bonded to iron.

The proton nmr spectrum of III contains a peak at  $\delta -12.35$  ( $w_{1/2} = 300$  Hz, area 5) assigned to the cyclopentadienyl ring, a resonance of area 2 at  $+ 7.35$  ( $w_{1/2} = 235$ ), attributed to the carboranyl C-H groups, and broad, largely overlapped humps at  $-3.35$ ,  $-5.5$ , and  $+ 10.6$  which are presumably H-(B)resonances appearing as singlets in the absence of BH coupling<sup>1C</sup>

The structures, chemistry and spectroscopic properties of these new complexes are under further investigation and will be discussed in detail at a later date.

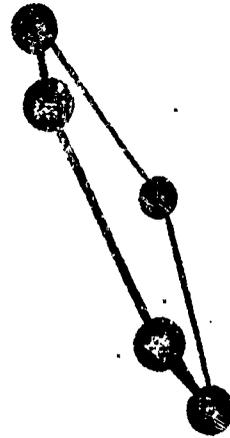
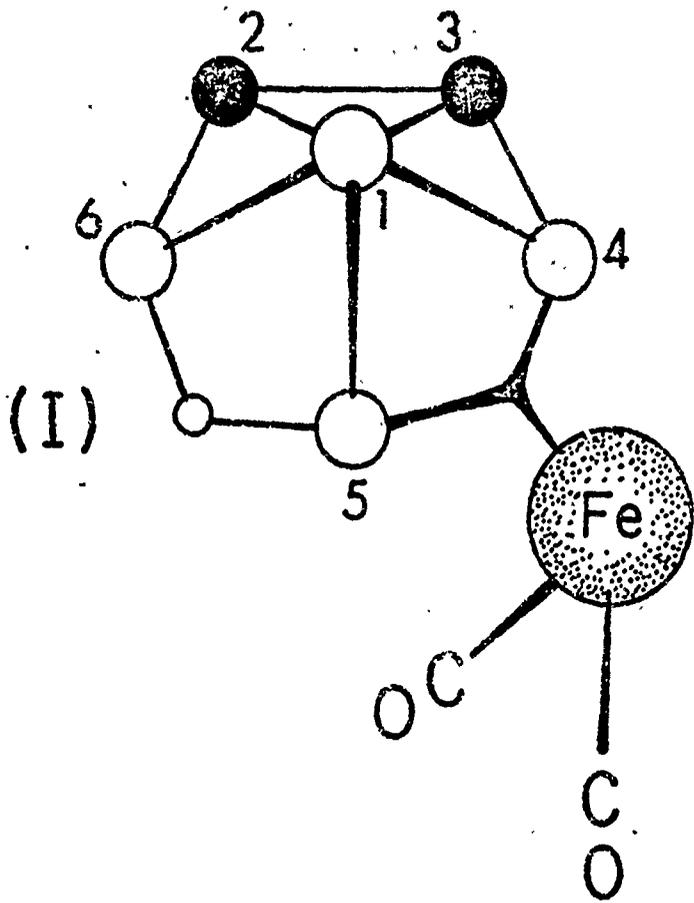
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References

- (1) D. A. Franz, V. R. Miller, and R. N. Grimes, J. Amer. Chem. Soc., 94, 412 (1972).
- (2) R. N. Grimes, ibid., 93, 261 (1971).
- (3) J. W. Howard and R. N. Grimes, ibid., 91, 6499 (1969).
- (4) J. W. Howard and R. N. Grimes, Inorg. Chem., 11, 263 (1972).
- (5) M. L. Thompson and R. N. Grimes, ibid., in press.
- (6) A. Tabereaux and R. N. Grimes, J. Amer. Chem. Soc., in press.
- (7) This effect, in which the  $^{11}\text{B}$  resonances of structurally nonequivalent borons are effectively superimposed, has also been observed in the spectra<sup>2</sup> of  $(\pi\text{-C}_2\text{B}_4\text{H}_6)\text{Fe}(\text{CO})_3$  and  $(\pi\text{-C}_2\text{B}_3\text{H}_7)\text{Fe}(\text{CO})_3$  (the structure of the latter compound has been confirmed by an X-ray study; see reference 1, footnote 11a). In all of these cases the boron atoms in question are those bonded directly to the metal atom.
- (8) For a review see M. L. H. Green and D. J. Jones, Adv. Inorg. Chem. Radiochem., 7, 115 (1965).
- (9) T. J. Curphey, J. O. Santer, M. Rosenbloom, and J. H. Richards, J. Amer. Chem. Soc., 82, 5249 (1960).
- (10) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, ibid., 90, 879 (1968).

Figure 1. Proposed structures of  $\mu$ - $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]\text{C}_2\text{B}_4\text{H}_7$  (I),  $(\eta\text{-C}_5\text{H}_5)\text{Fe}^{\text{II}}(\eta\text{-C}_2\text{B}_4\text{H}_7)$  (II), and  $(\eta\text{-C}_5\text{H}_5)\text{Fe}^{\text{III}}(\eta\text{-C}_2\text{B}_4\text{H}_6)$  (III). The solid circles represent CH groups and the open circles BH groups. A possible location for the anomalous hydrogen atom in II, involving partial bonding to iron and to the carborane cage, is indicated schematically. If an Fe-H bonding interaction exists in II, the  $\text{C}_5\text{H}_5$  and carborane rings are likely to be skewed relative to each other.



(II)



(III)

