available chemicals and utilized directly for the reduction of ketone without isolation. Furthermore, the product is often sufficiently pure to be used directly without further purification.

---

[10] Postdoctoral Research Associate on Grant No. DA 31-124 ARO(D) 453 supported by the U. S. Army Research Office (Durham).

Herbert C. Brown,* S. Krishnamurthy[10]
Richard B. Wetherill Laboratory
Purdue University, Lafayette, Indiana 47907

Received July 5, 1972

Novel Iron Carborane μ and π Complexes Derived from *nido*-$C_2B_4H_8$. A Paramagnetic Small Carborane Sandwich Compound

Sir:

Several transition metal–small carborane π complexes obtained from $C_2B_3H_7$[1] or $C_2B_4H_8$[2] in the gas phase and from $2\text{-}CH_3C_3B_3H_6$[3,4] or its monoanion derivative[4] 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,[5,6] which yields the first known small carborane sandwich species as well as two stable and structurally novel metallocarborane intermediates. The reaction of sodium dicarbahexaborate(1−) with π-cyclopentadienyliron dicarbonyl iodide in tetrahydrofuran at 25° generates a moderately air-stable yellow solid, $\mu\text{-}[(\pi\text{-}C_5H_5)Fe(CO)_2]C_2B_4H_7$ (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, $(\pi\text{-}C_5H_5)Fe^{II}(\pi\text{-}C_2B_4H_7)$ (II), and a brown crystalline paramagnetic species, $(\pi\text{-}C_5H_5)Fe^{III}(\pi\text{-}C_2B_4H_6)$ (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%.

$$2,3\text{-}C_2B_4H_8 + NaH \longrightarrow Na^+C_2B_4H_7^- + H_2$$

$$Na^+C_2B_4H_7^- + (\pi\text{-}C_5H_5)Fe(CO)_2I \xrightarrow[-NaI]{25^\circ} \mu\text{-}[(\pi\text{-}C_5H_5)Fe(CO)_2]C_2B_4H_7$$

$$\mu\text{-}[(\pi\text{-}C_5H_5)Fe(CO)_2]C_2B_4H_7 \xrightarrow[-2CO]{uv} (\pi\text{-}C_5H_5)Fe^{II}(\pi\text{-}C_2B_4H_7) + (\pi\text{-}C_5H_5)Fe^{III}(\pi\text{-}C_2B_4H_6)$$

The proposed structures of the three complexes (Figure 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 (calcd for $^{56}Fe^{12}C_7{}^{11}B_4{}^1H_{11}$, 195.058; found, 195.060).

The 32.1-MHz ^{11}B nmr spectrum of I in CCl_4 solution contains doublets of approximately equal areas at δ −16.4 ppm relative to external $BF_3 \cdot O(C_2H_5)_2$ (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 $Fe(C_5H_5)^+$ and Fe^+.

The 100-MHz proton nmr spectrum of I contains a sharp C_5H_5 singlet at δ −4.83 relative to external $(CH_3)_4Si$; a cage C–H peak at −6.52; H–B quartets centered at −3.27 (J = 147 Hz) and +0.98 (J = 169 Hz); and a broad B–H–B resonance at +0.91. The characteristic infrared absorptions (CCl_4 solution *vs.* 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) cm^{-1}.

The ^{11}B nmr spectrum of II in CCl_4 consists of two well-resolved doublets in a 3:1 area ratio, the larger centered at δ +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 II contains sharp singlets at δ −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}B and ^1H nmr spectra, which indicate, respectively, the pseudo-equivalence[7] of the basal B–H groups in the carborane ligand and of the five cyclopentadienyl protons in a rapidly rotating C_5H_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}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[8] such as $HFe(\pi\text{-}C_5H_5)_2^+$,[9] an isoelectronic analog of II.[10] An intermediate possibility,

---

[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.*, **11**, 1925 (1972).

[6] A. Tabereaux and R. N. Grimes, *J. Amer. Chem. Soc.*, **94**, 4768 (1972).

[7] This effect, in which the ^{11}B resonances of structurally nonequivalent borons are effectively superimposed, has also been observed in the spectra[2] of $(\pi\text{-}C_2B_4H_6)Fe(CO)_3$ and $(\pi\text{-}C_2B_3H_7)Fe(CO)_3$ (the structure of the latter compound has been confirmed by an X-ray study; see ref 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, *Advan. 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] Protonation of the $[(C_2B_9H_{11})_2Fe]^{2-}$ ion gives a $[(C_2B_9H_{11})_2FeH]^-$ species which may contain an Fe–H bond: M. F. Hawthorne, L. F. Warren, Jr., K. P. Callahan, and N. F. Travers, *ibid.*, **93**, 2407 (1971).

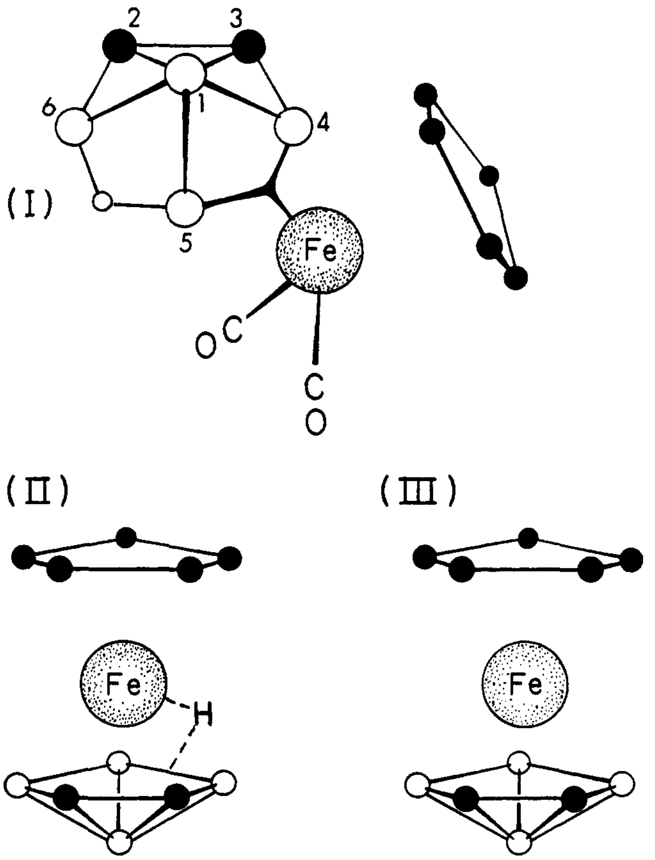

Figure 1. Proposed structures of μ-[(π-C_5H_5)Fe$(CO)_2$]$C_2B_4H_7$ (I), (π-C_5H_5)Fe^{II}(π-$C_2B_4H_7$) (II), and (π-C_5H_5)Fe^{III}(π-$C_2B_4H_6$) (III). The solid circles represent CH groups and the open circles BH groups. A possible location for the anomalous hydrogen atom in II, involving partial bonding to iron and to the carborane cage, is indicated schematically. If an Fe–H bonding interaction exists in II, the C_5H_5 and carborane rings are likely to be skewed relative to each other.

which we suggest schematically in Figure 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}B and ^1H nmr resonances and by the paramagnetic resonance spectrum (to be described in a subsequent paper). The only peaks observed in the ^{11}B nmr spectrum are humps at δ +154 and +281 with half-widths of ~375 and 900 Hz, respectively. For comparison, the ^{11}B nmr spectra of paramagnetic iron(III) dicarbollyl complexes (*e.g.*, (π-C_5H_5)Fe(π-$C_2B_9H_{11}$)) exhibit broad singlets over a range of several hundred parts per million.[11] However, unlike the spectrum of III, those of the dicarbollyls are sufficiently well resolved to permit some correlation with structure.[11] We attribute the contrast to the presumably lesser average effect of the paramagnetic metal atom on the boron atoms of the large C_2B_9 cage, as compared to the effect on the C_2B_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 δ −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 Hz) 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.[11]

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

Acknowledgment. We are grateful for the assistance of Professor Arthur Brill and Dr. Nick Hill in obtaining epr spectra. This work was supported by the Office of Naval Research.

Larry G. Sneddon, Russell N. Grimes*
Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

Received May 30, 1972

---

[11] 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, *J. Amer. Chem. Soc.*, **90**, 879 (1968).

Medium Effects on the Lifetime and Reactivity of Triplet Exciplexes

Sir:

Phenomena involving formation and reaction of exciplexes have been the subject of much recent investigation and some controversy.[1-11] It is generally agreed that transfer of charge contributes to the binding energy of a wide variety of exciplexes,[1-3,6-8] but whether charge transfer is generally the driving force behind exciplex formation or if other factors such as excitation–resonance are also important is a major area of controversy.[3-7] The same confusion exists to some degree as to whether an exciplex is best described as a delocalized excited species or as more nearly an activated ion pair. There has also been disagreement as to whether exciplexes decay to ions in polar solvents or whether observed ions are formed directly *via* different processes.[8-12] While useful information regarding exciplex structure has been obtained from studies of exciplex emission and chemical reactions proceeding *via* exciplexes,[1,2,4,13-16] the short lifetimes of most exciplexes have necessitated a reliance on quenching data for solvent and structure–reactivity correlations.[5-9]

Recently we found that exciplexes formed by reaction of excited metalloporphyrin triplets and nitroaromatics have sufficient half-lives for observation by flash spectroscopy.[17] This direct observation technique has now been extended to investigate several

---

(1) B. Stevens, *Advan. Photochem.*, **8**, 161 (1971).

(2) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).

(3) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).

(4) M. T. McCall, G. S. Hammond, O. Yonemitsu, and B. Witkop, *J. Amer. Chem. Soc.*, **92**, 6991 (1970).

(5) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *ibid.*, **94**, 3679 (1972); G. N. Taylor and G. S. Hammond, *ibid.*, **94**, 3684, 3687 (1972).

(6) T. R. Evans, *ibid.*, **93**, 2081 (1971).

(7) J. B. Guttenplan and S. G. Cohen, *ibid.*, **94**, 4040 (1972).

(8) H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1968).

(9) D. Rehm and A. Weller, *ibid.*, **73**, 834 (1969); H. Knibbe, D. Rehm, and A. Weller, *ibid.*, **73**, 839 (1969).

(10) N. Mataga, T. Okada, and N. Yamamoto, *Chem. Phys. Lett.*, **1**, 119 (1967).

(11) T. Okada, H. Matsui, H. Oohora, H. Matsumoto, and N. Mataga, *J. Chem. Phys.*, **49**, 4717 (1968).

(12) Y. Taniguchi and N. Mataga, *Chem. Phys. Lett.*, **13**, 596 (1972).

(13) G. N. Taylor, *ibid.*, **10**, 355 (1971).

(14) E. A. Chandross and H. T. Thomas, *ibid.*, **9**, 393 (1971).

(15) E. A. Chandross and H. T. Thomas, *ibid.*, **9**, 397 (1971).

(16) I. G. Lopp, R. W. Hendren, P. D. Wildes, and D. G. Whitten, *J. Amer. Chem. Soc.*, **92**, 6440 (1970).

(17) J. K. Roy and D. G. Whitten, *ibid.*, **93**, 7093 (1971).