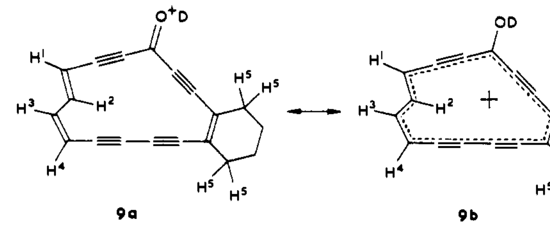

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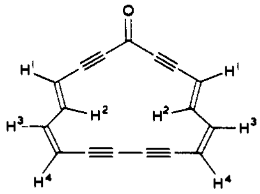

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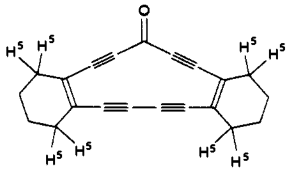

11

It is also of interest to compare the nmr spectrum of the tetradehydro[17]annulenone **10**[3] with that of the model **7**. It can be seen (Table I, entries D and H) that now the outer protons are shifted *upfield* by $\tau \sim 0.6$, and the inner protons *downfield* by $\tau \sim 3.3$, clearly confirming the existence of a paramagnetic ring current in **10**.

Finally, the nmr data show that the allylic H-5 protons are also affected by the ring currents. Thus, in the aromatic **8** and **9** they are shifted *downfield* by τ 0.35 and 0.55, respectively, as compared with **7** (Table I, entries F and G), while in the nonaromatic tetradehydro[13]annulenone **11**[4] they are shifted *upfield* by τ 0.35 (Table I, entries E and I).[15]

Acknowledgments. We are indebted to the Science Research Council for financial support (to G. P. C. and G. H. M.), and to New Hall, Cambridge, for the award of a Junior Fellowship (to G. M. P.).

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(15) The small upfield shift of the allylic protons in the nmr spectrum of **11** had already tentatively been ascribed to the presence of a paramagnetic ring current,[4] but this evidence was not conclusive in the absence of the observation of an opposite shift in compounds possessing a diamagnetic ring current.

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Small Carborane Metallocene Analogs. Iron π Complexes Containing the Formal *nido*-$C_2B_4H_6^{2-}$ and *cyclo*-$C_2B_3H_7^{2-}$ Ligands

Sir:

The recent synthesis[1] of $(\pi\text{-}2\text{-}CH_3C_3B_3H_5)Mn(CO)_3$ in the vapor-phase reaction of $2\text{-}CH_3C_3B_3H_6$ with $Mn_2(CO)_{10}$, and also in the reaction[2] of the $2\text{-}CH_3C_3B_3H_5^-$ ion with $BrMn(CO)_5$, has suggested the probable existence of other small carborane–transition metal complexes. Attention was directed to 2,3-dicarbahexaborane(8), $C_2B_4H_8$, which in contrast to the $C_3B_3H_7$ derivatives is a readily obtainable carborane.[3] In theory, removal of the two bridge protons from $2,3\text{-}C_2B_4H_8$ should generate a pyramidal $C_2B_4H_6^{2-}$ anion whose five-membered basal ring contains six delocalized electrons, analogous to $C_5H_5^-$. Although this ion apparently has not been prepared as such,[4] its formal existence in the known polyhedral $1\text{-}CH_3GaC_2B_4H_6$[5] and $1\text{-}CH_3InC_2B_4H_6$[6] species suggested that π complexes of formal $C_2B_4H_6^{2-}$ might be prepared directly from $2,3\text{-}C_2B_4H_8$ and appropriate transition metal carbonyls. Accordingly, a mixture of $C_2B_4H_8$ and excess $Fe(CO)_5$ was heated to 240° in a Pyrex tube, the lower end of which was maintained at 25°. Removal of excess $Fe(CO)_5$ and $C_2B_4H_8$ by distillation at −45° yielded two products which were nonvolatile at that temperature, but which could be separated from each other by repeated fractionation through a trap at −23°.

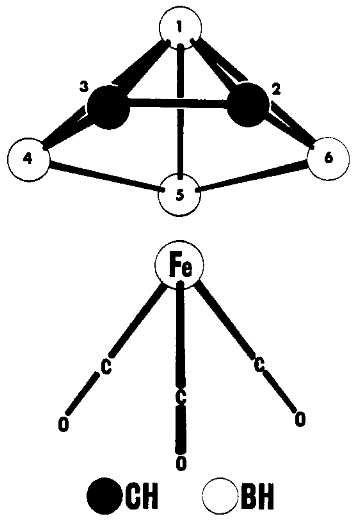

Figure 1. Proposed structure of $(\pi\text{-}C_2B_4H_6)Fe(CO)_3$.

The less volatile material, a deep orange liquid, was characterized as $(\pi\text{-}C_2B_4H_6)Fe(CO)_3$ (I), shown in Figure 1. The mass spectrum contains a sharp cutoff at *m/e* 214, corresponding to the parent ion, and the profile in the parent region corresponds virtually exactly with the calculated intensities based on natural isotopic distributions.[7] The presence of three carbonyl groups is clearly indicated by strong groupings at *m/e* 186, 158, and 130, corresponding to the loss of one, two, and three CO units, respectively. The 32.2-MHz ^{11}B nmr spectrum of I in CCl_4 solution exhibits three broad, well-separated doublets in a 1:2:1 area ratio, at δ −18.9 ppm relative to $BF_3 \cdot O(C_2H_5)_2$, $J = 160$ cps; δ −5.16, $J = 150$; and δ +17.7, $J = 160$, assigned to B(5)-H, B(4,6)-H, and B(1)-H, respectively.[8] The

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(1) J. W. Howard and R. N. Grimes, *J. Amer. Chem. Soc.*, **91**, 6499 (1969).

(2) J. W. Howard, Ph.D. Dissertation, University of Virginia, 1970.

(3) T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964).

(4) Treatment of $2,3\text{-}C_2B_4H_8$ with excess NaH removes only one bridge proton, forming the $C_2B_4H_7^-$ ion: T. Onak and G. B. Dunks, *ibid.*, **5**, 439 (1966).

(5) R. N. Grimes and W. J. Rademaker, *J. Amer. Chem. Soc.*, **91**, 6498 (1969).

(6) R. N. Grimes and W. J. Rademaker, manuscript in preparation.

(7) Hydrogen loss in the parent region is negligible owing to the much more facile cleavage of CO groups from the molecule.

(8) Assignments of the B(5)-H and B(1)-H resonances, which conceivably could be interchanged, are based on the observation that apex B-H resonances of related carboranes and metallocarboranes (*e.g.*, $2,3\text{-}C_2B_4H_8$,[3] $2,4\text{-}C_2B_5H_7$,[9,10] $2\text{-}CH_3C_3B_3H_5Mn(CO)_3$,[1] $1\text{-}CH_3GaC_2B_4H_6$[5]) are found at high field.

(9) T. Onak, G. B. Dunks, R. A. Beaudet, and R. L. Poynter, *J. Amer. Chem. Soc.*, **88**, 4622 (1966).

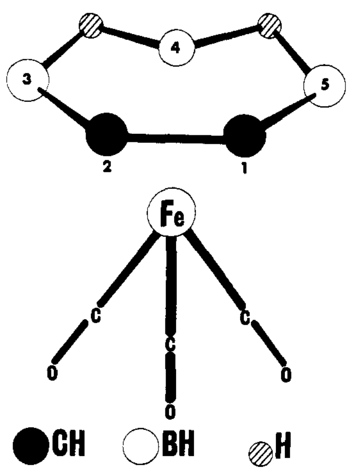

Figure 2. Proposed structure of (π-$C_2B_3H_7$)$Fe(CO)_3$.

100-MHz proton nmr spectrum of I in CCl_4 contains a sharp C–H singlet of area 2 at δ -5.58 ppm relative to $(CH_3)_4Si$, as well as partially overlapped quartets at δ -6.30, $J = 152$, area 2; δ -4.87, $J = 152$, area 1; and δ -0.24, $J = 160$, area 1, assigned to H–B(4,6), H–B(5), and H–B(1), respectively.

The ir spectrum of I (CCl_4 solution *vs.* CCl_4) contains two very strong CO stretching bands at 2076 and 2017 cm^{-1}, in agreement with the proposed structure; the only other well-defined absorptions are at 3090 (m), 2960 (w), 2590 (vvs, BH stretch), 1270 (vs), and 1188 (s) cm^{-1}. No significant bands are present in the B–H–B stretching region.

The more volatile complex is a pale yellow liquid, identified as (π-$C_2B_3H_7$)$Fe(CO)_3$ (II), for which the structure in Figure 2 is proposed. The mass spectrum exhibits a sharp cutoff at *m/e* 204, corresponding to the parent ion, and the observed relative intensities in the parent region are in very close agreement with those calculated for the indicated composition.[7] Most importantly, the presence of three boron atoms is unequivocally established. As with complex I, the presence of three CO groups in the mass spectrum is shown by intense peak groupings at *m/e* 176, 148, and 120.

The ^{11}B nmr spectrum of a CCl_4 solution of II consists of one broad, slightly asymmetric doublet at δ -4.90, $J \approx 135$, indicating that all three boron atoms are in similar electronic environments. Significantly, no other peaks were found, in agreement with a structure having no apex boron atoms. The 100-MHz proton nmr of II in CCl_4 contains a sharp C–H resonance of area 2 at δ -5.38, as well as quartets at δ -7.42, $J = 126$, area 1, and δ -3.70, $J = 135$, area 2, assigned to H–B(4) and H–B(3,5) respectively. In addition, a broad hump of area 2 centered at δ $+3.7$ is attributed to the bridge proton resonance. The ir spectrum of II (CCl_4 solution *vs.* CCl_4) exhibits very strong CO stretching bands at 2068 and 2007 cm^{-1} and other principal absorptions at 3008 (m), 2569 (vvs, BH stretch), 1888 (ms, B–H–B stretch), 1700 (m), 1600 (m), 1350 (m), and 1050 (m) cm^{-1}.

Somewhat surprisingly, complex I is less thermally stable than II, the former decomposing at 230° while II is unchanged at that temperature. Solutions of the complexes in CCl_4 appear to be unaffected by exposure to air for several hours, as monitored by ir spectra. Investigations of these compounds and related species are continuing.

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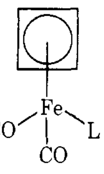
(10) R. N. Grimes, *J. Amer. Chem. Soc.*, **88**, 1895 (1966).

Cycloaddition Reactions between Cyclobutadiene and Unsaturated Molecules Coordinated to Iron

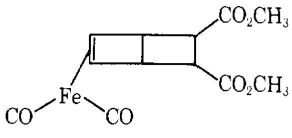
Sir:

We wish to report on some novel cycloaddition reactions between cyclobutadiene and other olefinic systems while both components are coordinated to a transition metal and to demonstrate the potential of these reactions in organic synthesis.

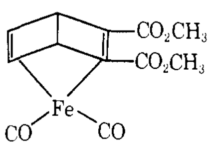
We had previously shown[1] that cyclobutadieneiron tricarbonyl, upon irradiation in the presence of dimethyl maleate, afforded cyclobutadiene(dimethyl maleate)iron dicarbonyl (I, L = dimethyl maleate). An analogous compound (I, L = dimethyl fumarate) was obtained when the irradiation was conducted in the presence of dimethyl fumarate.[1] Both complexes were of normal stability. In particular, they displayed no tendency to undergo cycloaddition reactions leading to the complex II; this is in strong contrast to the very facile addition which occurs between cyclobutadiene and dimethyl maleate and dimethyl fumarate when neither of the reagents is coordinated to a metal.[2] However, irradiation of cyclobutadieneiron tricarbonyl in the presence of dimethyl acetylenedicarboxylate affords only dimethyl phthalate and no intermediate complex analogous to I can be isolated.



I



II



III

A rational explanation for the difference in behavior of the acetylenic and olefinic dienophiles is that in both instances the light acts on the iron–carbonyl complex to eject a molecule of carbon monoxide; the resultant cyclobutadieneiron dicarbonyl then reacts with both the acetylene and olefin derivatives to form complexes of the type I. In the case where L is the acetylenic ligand, the molecule undergoes intramolecular cycloaddition to generate the Dewar benzene complex III which suffers further degradation to dimethyl phthalate. The formation of such a Dewar benzene complex would involve loss of only one of the five coordinate bonds about the iron atom in I whereas a similar cycloaddition reaction with the maleate ligand, leading to the complex II, would require loss of two coordinating bonds and would be energetically less favorable.

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(1) P. Reeves, J. Henery, and R. Pettit, *J. Amer. Chem. Soc.*, **91**, 5888 (1969).

(2) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **88**, 623 (1966).