Finally, the ultraviolet spectrum of the triafulvene III in cyclohexane shows an essentially symmetric single maximum at 246 mμ (log ϵ 4.30); in methanol the maximum is at 245 mμ (log ϵ 4.33). There is evidence neither for absorption above 300 mμ nor for a solvent effect as is found for other triafulvenes, and the position of the maximum suggests qualitative agreement with Julg's prediction[12] that the longest wave length (V $\leftarrow$ N) absorption for methylenecyclopropene will fall near 200 mμ.

(12) A. Julg. *J. chim. phys.*, **50**, 652 (1953).

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The Tropylium–Iron Tricarbonyl Cation

Sir:

Organometallic cationic complexes of the type LM(CO)$_3^+$ in which L is a tropylium ring π-bonded to a metal (M) are known for the group VI-B metals chromium,[1] molybdenum,[2] and tungsten.[3] The presumed structure of these complexes is indicated in formula I. The seven carbon atoms of the ring are symmetrically bonded to the metal by means of the six π-electrons, and the metal attains the effective atomic number of the next inert gas.[4]

I
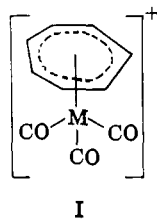
The analogous cationic complex containing iron is of some theoretical interest for, if the bonding in such a complex were to be similar, the effective atomic number of iron would exceed that of krypton by two.

Previous attempts to prepare salts of the tropylium–iron tricarbonyl cation have been unsuccessful.[5] Whereas the triphenylmethyl cation abstracts hydride ion from cycloheptatriene–M(CO)$_3$ complexes (M = Cr, Mo, and W) to give tropylium–M(CO)$_3$ complexes, in the case of cycloheptatriene–iron tricarbonyl addition occurs to give a substituted cycloheptadienyl–iron tricarbonyl cation.[6]

We now wish to report the synthesis of the tropylium–tricarbonyl cation by the following route.

II
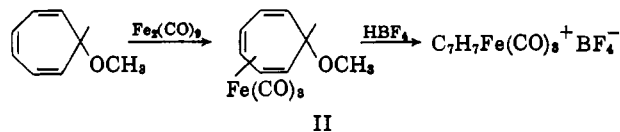
Treatment of methyl tropyl ether with iron enneacarbonyl gave the corresponding iron tricarbonyl complex (II) which reacted with fluoroboric acid to give the fluoroborate salt of the tropylium–iron tricarbonyl cation. The salt crystallizes in yellow needles from nitromethane, m.p. 112° dec. (*Anal.* Calcd. for C$_7$H$_7$-Fe(CO)$_3$BF$_4$: C, 37.78; H, 2.22; B, 3.18. Found: C, 37.44; 2.03; B, 3.32). It is stable in inert atmosphere but hydrolyzes rapidly in water to give tropyl alcohol–iron tricarbonyl from which the cation can be regenerated by treatment with fluoroboric acid.

As with the chromium, molybdenum, and tungsten complexes, the n.m.r. spectrum of the tropylium–iron tricarbonyl cation shows a single sharp absorption, but further comparison of these complexes reveals several significant differences. The pK_{R^+} values listed in Table I indicate that the tropylium–iron tricarbonyl cation is slightly less stable than the tropylium cation, whereas the group VI-B metal complex cations are considerably more stable.
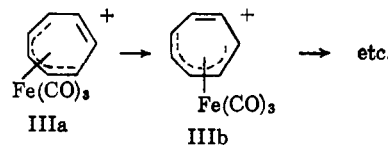
TABLE I

Complex	τ^a	p$K_{R^+}{}^b$
C$_7$H$_7^+$BF$_4^-$	0.72	4.7
C$_7$H$_7^+$Fe(CO)$_3$BF$_4^-$	4.20	4.5
C$_7$H$_9^+$Fe(CO)$_3$BF$_4^-$	. . .	4.7
C$_7$H$_7^+$Cr(CO)$_3$BF$_4^-$	3.42	6.3
C$_7$H$_7^+$Mo(CO)$_3$BF$_4^-$	3.82	6.2
C$_7$H$_7^+$W(CO)$_3$BF$_4^-$	3.83	$\sim$6^c

^{a} Position of single n.m.r. peak measured in liquid SO$_2$. ^{b} Measured in H$_2$O at 30.0°. ^{c} Approximate value only because of secondary decomposition.

The most significant differences are seen in the infrared absorption spectra. The group VI-B metal complexes each show a single strong absorption band in the C–H stretching region,[7] but the corresponding iron complex shows three strong bands which presumably reflect a lower symmetry of the C$_7$H$_7$ ligand in the iron complex.[8] Furthermore, the group VI-B metal complexes are transparent in the 650–800 cm.$^{-1}$ region while the iron complex shows an intense absorption band at 731 cm.$^{-1}$ suggestive of the presence of a *cis* double bond.

On the basis of this evidence, we propose that the structure of the tropylium–iron tricarbonyl cation is as shown in IIIa. The iron atom is bonded to five carbons of the ring, leaving one double bond not involved in coordination to the metal. The ligand–metal bonding is then analogous to that found in other pentadienyl–iron tricarbonyl cationic complexes.[9] The pK_{R^+} value of the C$_7$H$_7$–Fe(CO)$_3$ cation is very similar to that of the cycloheptadienyl–iron tricarbonyl cation (see Table I). The salt displays carbonyl absorption typical of dienyl–iron tricarbonyl cations (strong absorption peaks at 2070 and 2120 cm.$^{-1}$).[9]

IIIa   IIIb

(1) J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 3475 (1961).
(2) H. J. Dauben, Jr., and L. R. Honnen, *J. Am. Chem. Soc.*, **80**, 5570 (1958).
(3) H. J. Dauben, Jr., L. R. Honnen and D. J. Bertelli, Abstracts, 15th Southwest Regional Meeting, American Chemical Society, Baton Rouge, La., Dec. 3, 1959, p. 89.
(4) D. A. Brown, *J. Inorg. Nucl. Chem.*, **10**, 39 (1959).
(5) An account of these is given in ref. 6.
(6) H. J. Dauben. Jr., and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 497 (1961).

(7) H. P. Fritz. "Advances in Organometallic Chemistry," Vol. 1. Academic Press, Inc., New York, N. Y., 1964, p. 240.
(8) ν_{C-H} 3086, 3076, and 3086 cm.$^{-1}$ for the Cr, Mo, and W complexes, respectively, and 3093, 3070, and 3056 cm.$^{-1}$ for the Fe complex measured as hexachlorobutadiene mulls using a Beckman IR-7 spectrometer.
(9) R. Pettit and G. F. Emerson, ref. 7, p. 1.

In order to account for the single absorption in the n.m.r. spectrum at 4.2 τ it is proposed that in solution the system undergoes rapid valence tautomerism to produce the equivalent structure IIIb. Extension of this rearrangement would eventually lead to rotation of the iron tricarbonyl group around the C_7H_7 ring, and this would result in equivalence of the ring protons. The position of the single n.m.r. absorption is also consistent with this. If five of the protons in III are assumed to have the same chemical shifts as the corresponding protons in the cycloheptadienyl–iron tricarbonyl cation,[10] then the very reasonable value of 3.8 τ must be employed for the two protons of the noncoordinated olefinic bond in order that the average value of the seven protons be 4.2 τ.[11]

Acknowledgment.—We thank the National Science Foundation and the Robert A. Welch Foundation for financial assistance, and the Antara Chemical Company for a gift of iron pentacarbonyl.

(10) Data from Dauben and Bertelli.[6]

(11) The situation for the $C_7H_7Fe(CO)_3$ cation is analogous to that already seen in cyclooctatetraene–iron tricarbonyl for which a dynamic effect has also been postulated.[12] In this case an average value of 3.9 τ is required for the four olefinic protons of the two double bonds not coordinated to iron in order that the total average be equal to 4.8 τ as observed, assuming that the other four protons have the same chemical shift as those in cycloheptatriene–iron tricarbonyl.

(12) B. Dickens and W. N. Lipscomb, J. Chem. Phys., 37, 2084 (1962).

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Organometallic Complexes of the Type Triene–Fe₂(CO)₆

Sir:

We wish to report the isolation of a series of related organometallic complexes of the general type triene–$Fe_2(CO)_6$ and to present data pertaining to their structure. Reaction of cycloheptatriene, 7-methoxy-1,3,5-cycloheptatriene, 1,3,5-cyclooctatriene, and cyclooctatetraene with iron enneacarbonyl produced, in each case, an orange-red crystalline complex giving satis-
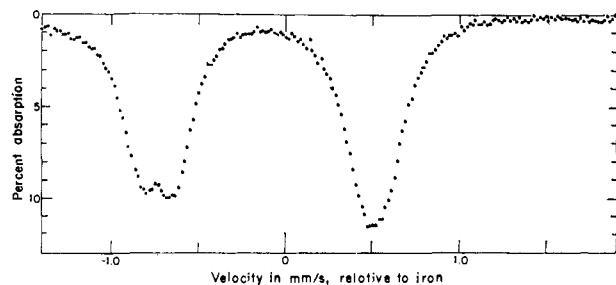

Fig. 1.—Mössbauer absorption spectrum of complex I.

factory C, H, and Fe analyses for the substance having an $Fe_2(CO)_6$ grouping attached to the corresponding triene.[1,2] The complexes are diamagnetic, they each show a similar infrared and n.m.r. absorption pattern,

(1) The melting points of these four complexes are 131–133, 92–94, 101–103, and 90–92°, respectively. The principal infrared bands for the CO stretching frequencies are 1960, 1975, 1995, 2015, and 2058 (±5 cm.⁻¹) for each complex and each shows an n.m.r. absorption corresponding to six protons in the region 4.8–5.5 (2H), 5.6–6.0 (2H), and 7.2–7.6 (2H) τ.

(2) Other organometallic compounds, especially diene–Fe(CO)₃ complexes, are also formed in the reaction. The reaction with cyclooctatetraene gives two other isomeric $Fe_2(CO)_6$ complexes, and this reaction will be discussed in more detail in a later paper.
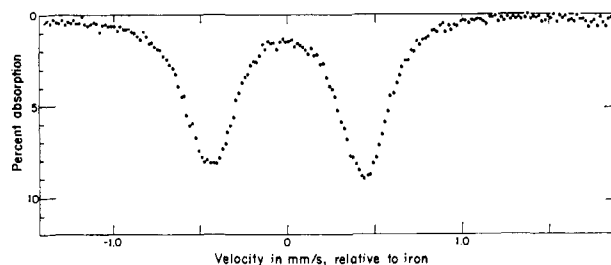

Fig. 2.—Mössbauer absorption spectrum of C_8H_{10}–$Fe_2(CO)_6$.

and they are therefore considered to have analogous structures.

The complex obtained from cyclooctatriene appears to be identical with the product derived from reaction of cyclooctatriene and $Fe_3(CO)_{12}$ reported by King.[3] By analogy with the ferrole derivative I, King proposed structure II for this cyclooctatriene complex. However, a comparison of the Mössbauer resonance spec-

I

II
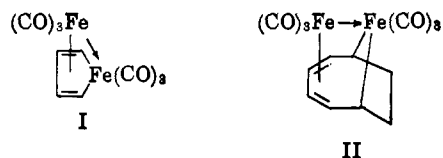
trum of I with each of the triene–$Fe_2(CO)_6$ complexes suggests that structure II is possibly incorrect. The Mössbauer spectrum of olefin–$Fe(CO)_3$ complexes invariably consists of two peaks resulting from an unsymmetrical electric field gradient at the Fe nucleus.[4] The spectrum of the ferrole (I) (Fig. 1) displays three maxima. The most reasonable interpretation is that these three peaks arise from the two Fe atoms in the ferrole complex being chemically nonequivalent, each of the two Fe atoms giving rise to a doublet of similar but not identical separation and chemical shift. On the other hand, the Mössbauer resonance spectra of C_8H_{10}–$Fe_2(CO)_6$ (Fig. 2) and the other three complexes listed above show only two peaks. We conclude therefore that the two iron atoms are chemically equivalent in these complexes.[5]

The n.m.r. spectrum of the cycloheptatriene–Fe_2-$(CO)_6$ complex shows the two CH_2 protons to be nonequivalent; therefore, the two equivalent iron atoms must lie on the same side of the ring. This conclusion is further substantiated by the high dipole moment of the material (4.8 D.).

On the basis of these data we propose that these compounds are essentially bis-π-allyl–iron carbonyl complexes as illustrated in formula III for cyclohepta-triene–$Fe_2(CO)_6$ (R = H) and its methoxy derivative (R = OCH_3). Each iron atom is bonded to three contiguous carbons of the triene in essentially the same manner as in other π-allyl–iron carbonyl complexes. An Fe–Fe bond is proposed in order to account for the diamagnetic properties and so that the two iron atoms attain the atomic number of krypton.

Triphenylmethyl fluoroborate reacts with cyclo-heptatriene–$Fe_2(CO)_6$ to produce triphenylmethane

(3) R. B. King, Inorg. Chem., 2, 807 (1963).

(4) R. Collins and R. Pettit, J. Am. Chem. Soc., 85, 2322 (1963).

(5) In each case, within experimental error, the two absorption peaks were symmetrical and of equal width at half-height. The possibility that the two peaks arise from two chemically different Fe atoms, each in a symmetrical electric field, is considered very remote.