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.[5]

(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-
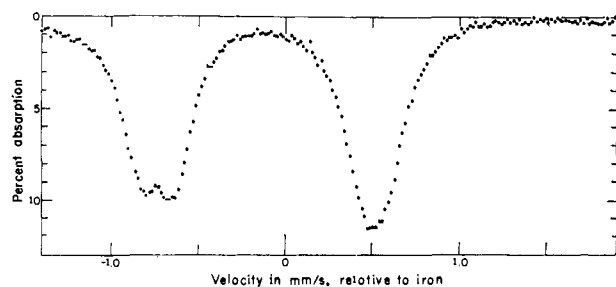

Fig. 1.—Mössbauer absorption spectrum of complex I.

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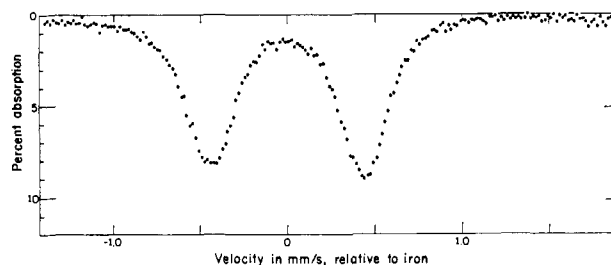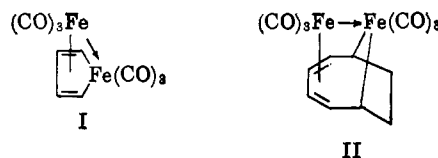
Fig. 2.—Mössbauer absorption spectrum of C_8H_{10}–$Fe_2(CO)_6$.

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-

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 cycloheptatriene–$Fe_2(CO)_6$ (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 cycloheptatriene–$Fe_2(CO)_6$ 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.

(CO)₃Fe—Fe(CO)₃

H R
III
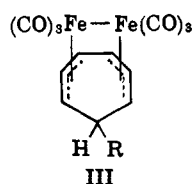
and the fluoroborate salt of a $C_7H_7Fe_2(CO)_6$ cation.[6] This same salt is also obtained from the methoxy complex (III, R = OCH_3) upon reaction with HBF_4. The complex salt reacts with $NaBH_4$ to regenerate cycloheptatriene-$Fe_2(CO)_6$ (III, R = H); the pK_{R^+} value of 8.0 indicates that it is considerably more stable than the $C_7H_7Fe(CO)_3$ cation reported in the preceding paper, but the most interesting feature of this complex cation is that it displays only one sharp single n.m.r. absorption which occurs at 5.2 τ.

We suggest that the structure of this complex cation is as shown in IVa where it is implied that the C_7H_7 ring is bonded to one iron atom as in a diene-$Fe(CO)_3$ complex[7] and to the other iron atom through the remaining three carbons as in the known π-allyl-Fe-$(CO)_3$ cations.[8] An Fe→Fe dative bond preserves the inert gas structure of each iron.

(CO)₃Fe→Fe(CO)₃   (CO)₃Fe—Fe(CO)₃   → etc.
IVa   **IVb**
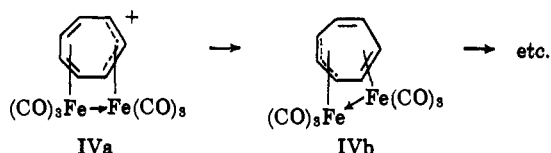
In order to account for the single n.m.r. absorption it is proposed that in solution rapid valence tautomerism to the equivalent structure (IVb) occurs with interchange of the roles of the two iron atoms. Such valence tautomerism would involve a rotation of $\pi/7$ of the Fe–Fe bond about the center of the ring. Seven such rapid interchanges would then result in equivalence of the seven protons in the n.m.r. spectrum.[9]

Acknowledgment.—We thank the National Science Foundation and the Robert A. Welch Foundation for financial assistance. We also thank Antara Chemicals for a gift of iron carbonyl.

(6) This salt crystallizes in orange needles from nitromethane; m.p. 170° dec.

(7) R. Pettit and G. F. Emerson, "Advances in Organometallic Chemistry," F. G. A. Stone and R. West, Ed., Academic Press, New York, N. Y., 1964, pp. 1–46.

(8) G. F. Emerson and R. Pettit, J. Am. Chem. Soc., **84**, 4591 (1962); G. F. Emerson, J. E. Mahler, and R. Pettit, Chem. Ind. (London), 836 (1964).

(9) It is interesting that if one assumes values of 4.8 and 7.0 τ for the chemical shifts of the internal and terminal protons of a cyclic diene-Fe(CO)₃ species⁷ and values of 4.8 and 4.5 τ for the terminal and central protons of a π-allyl-Fe(CO)₃ fragment,⁸ then the average of these is 5.4 τ which is reasonable agreement with the observed value of 5.2 τ for 1V.

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On Variations in the Hyperfine Splitting of Benzene Negative Ion and on the Value of Q[1]

Sir:

A prime source of the value of Q in the equation $a = Q\rho$, proposed by McConnell[2] and describing the proton

(1) Supported in part by the U. S. Atomic Energy Commission.

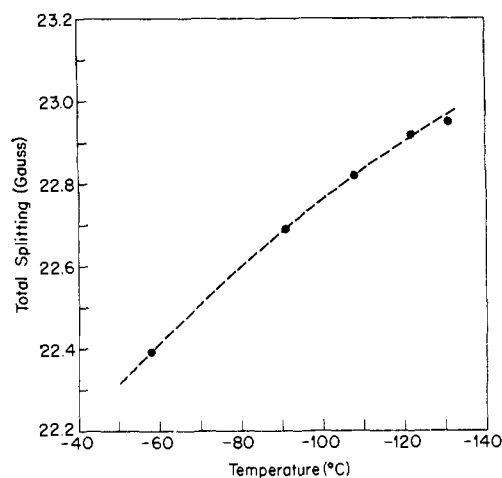(2) H. M. McConnell, J. Chem. Phys., **24**, 632 (1956); **24**, 764 (1956).

hyperfine splitting, a, by a proton bonded to a carbon atom with a π spin density, ρ, is the total spread of the e.s.r. spectrum of the benzene negative ion. This species is particularly important because, in contrast to other aromatic ion radicals, it has a hydrogen attached to each carbon of the π-electron system and therefore a probe of the spin density at each position. In addition, this radical has the trigonal 120° bond angles.[3] When the equation was first proposed,[2] the suggested value for $|Q|$ was the total spread of the spectrum of benzene negative ion. The value originally reported[4] seems also to have been found by later workers.[5] The purpose of this communication is to present some data which demonstrate a temperature dependence for the total spread of this spectrum and to try to relate this value to the value for Q from some other systems.

The benzene negative ion was produced by reduction of benzene by sodium–potassium alloy in a 2:1 mixture of 1,2-dimethoxyethane and tetrahydrofuran.[5] The sample was cooled by cold nitrogen flowing through a dewar tube surrounding the sample. A thermal junction wedged between the sample tube and the wall of the dewar tube was used to measure and control sample temperature. Measurements with a second thermocouple placed in a sample tube filled with pentane showed that the sample temperature was known to about 2°. The e.s.r. spectrometer was a Varian unit with 100 kc./sec. field modulation and used a Varian 12-in. magnet. The field and microwave frequency measuring equipment was described previously.[6]

The total spread of the spectrum as a function of temperature is shown in Fig. 1. These data are the results of several different runs. Experiments were also done with sodium alone and with a solvent mixture much richer in tetrahydrofuran. Points for these runs seemed to fall ≈ 0.05 gauss below the curve of Fig. 1, but it is not clear that a significant difference exists so these points are not shown. The line width was about 0.6–0.8 gauss and no attempt was made to narrow it

(3) Neglecting any instantaneous distortions arising from the Jahn-Teller effect.

(4) T. R. Tuttle and S. I. Weissman, J. Am. Chem. Soc., **80**, 5342 (1958).

(5) J. R. Bolton, Mol. Phys., **6**, 219 (1963).

(6) R. W. Fessenden and R. H. Schuler, J. Chem. Phys., **39**, 2147 (1963).