perimental results. The solid and dashed lines in Figure 1 have been calculated using the following values for the pertinent rate constants in the mechanism of Chart I: $k_3 = 7.1k_7$, $k_4 = 16k_{15} - 8.1k_9$, $k_5 = 4.0k_{15}$, $k_6 = 5.1k_{16}$, $k_8 < 0.3\sqrt{k_{13}k_{14}}$, $k_{10} = 7.5\sqrt{k_{13}k_{14}}$, $k_{11} < 0.2k_{16}$, and $k_{12} = 2.5\sqrt{k_{13}k_{14}}$ (the overall rate constants of all of the steps in the mechanism except 1, 2, 15, and 16 have the form: $k_n' = k_n/\eta$).

The rearrangement of N-nitro-N-methylaniline has also been studied in a series of water–glycerol mixtures with similar results.

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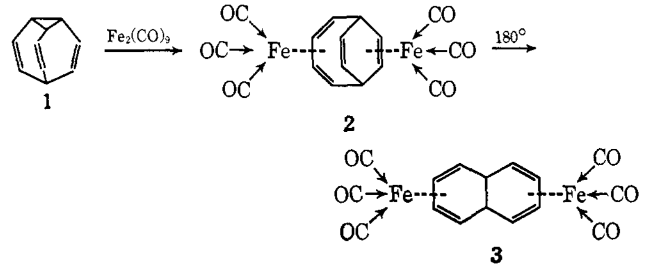
*Octahapto*bicyclo[4.2.2]deca-2,4,7,9-tetraenediiron Hexacarbonyl. The Structure of the Reaction Product of $Fe_2(CO)_9$ with Bullvalene

Sir:

The reaction of tricyclo[3.3.2.0^{4,6}]deca-2,7,9-triene (bullvalene) (**1**) with $Fe_2(CO)_9$ in boiling benzene yields a complex $C_{10}H_{10}Fe_2(CO)_6$ (**2**), mp 120°, which on heating to 180° in an autoclave was transformed into the known *octahapto*-9,10-dihydronaphthalenediiron hexacarbonyl (**3**).[1]



The nmr spectrum (Figure 1) of **2** as well as the facile conversion of **2** into **3** led to the postulate[1] of structure **2** for the complex, which thus would be the first example of a π complex of bicyclo[4.2.2]deca-2,4,7,9-tetraene (**4**), the remarkable $C_{10}H_{10}$ hydrocarbon first synthesized by Jones and Scott.[2] In the present communication we report the results of an X-ray structural analysis of **2** which confirms the previous structural assignments. The formation of **2** from bullvalene and $Fe_2(CO)_9$ is of particular interest in view of the demonstrated photorearrangement of **4** into **1**,[2] indicating that the reverse of a photochemical rearrangement process may be achieved thermally in the presence of iron carbonyl fragments.

The reddish-brown crystals of **2** belong to the orthorhombic system. Cell dimensions, as determined by a least-squares fit to the settings for 12 reflections on a Picker FACS-1 diffractometer (Mo Kα, λ 0.7107 Å), are a = 12.447 (6), b = 19.854 (9), and c = 12.443 (6) Å. The space group is Pbca and there are eight molecules of $C_{10}H_{10}\cdot Fe_2(CO)_6$ (mol wt = 409.9) in the unit cell. At the present stage of refinement,[3] the R factor on 1191 nonzero reflections collected on the diffractometer (Mo Kα) is 0.052. A view of the molecular structure is shown in Figure 2.

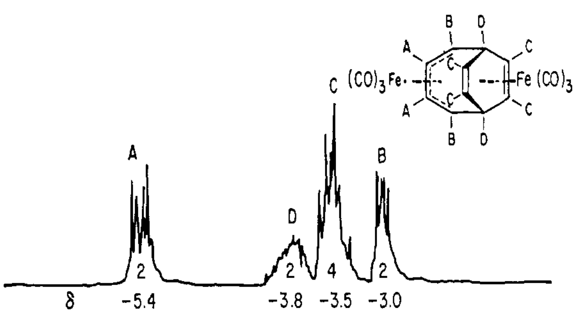


Figure 1. ^1H nmr spectrum of *octahapto*bicyclo[4.2.2]deca-2,4,7,9-tetraenediiron hexacarbonyl in $CDCl_3$ and suggested assignments.

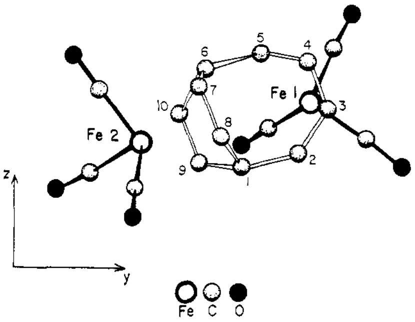


Figure 2. View of the complex along the x direction. The C–C bond lengths (Å, esd ± 0.02) are C_1–C_2 1.60, C_2–C_3 1.41, C_3–C_4 1.36, C_4–C_5 1.42, C_5–C_6 1.59, C_6–C_7 1.53, C_7–C_8 1.40, C_1–C_8 1.51, C_1–C_9 1.49, C_9–C_{10} 1.39, and C_6–C_{10} 1.51. The angles (deg) are $C_2C_1C_8$ 113, $C_2C_1C_9$ 118, $C_8C_1C_9$ 102, $C_1C_2C_3$ 125, $C_2C_3C_4$ 121, $C_3C_4C_5$ 121, $C_4C_5C_6$ 124, $C_5C_6C_7$ 115, $C_5C_6C_{10}$ 119, $C_7C_6C_{10}$ 101, $C_6C_7C_8$ 117, $C_1C_6C_7$ 117, $C_1C_9C_{10}$ 118, and $C_6C_{10}C_9$ 116.

The standard deviations in the Fe–C lengths are 0.012–0.016 Å, while those of the C–C lengths are 0.02 Å, and those of the C–C–C angles are 0.6–0.7°. The agreement in the molecular dimensions related by a noncrystallographic mirror plane perpendicular to the C_3–C_4, C_7–C_8, and C_9–C_{10} bonds is well within these deviations. The mode of interaction of the $Fe(CO)_3$ group with the "butadiene" moiety of **4** (*i.e.*, C_2, C_3, C_4, C_5) is similar to that found in other π complexes of $Fe(CO)_3$ with 1,3-dienes.[4,5] The two $Fe_1\cdots C$ (outer) distances (2.100 (14) and 2.097 (14) Å) are slightly longer than the two $Fe_1\cdots C$ (inner) distances (2.038 (16) and 2.041 (15) Å). An unusual feature of the molecular geometry is the exceptional length (1.60 (2) and 1.59 (2) Å) of the C_1–C_2 and C_5–C_6 bonds. In view of the geometrical features of the π-complexed butadiene moiety (the distances C_2–C_3 and C_4–C_5 being somewhat longer than C_3–C_4) and the large $-\delta$ value of the A protons (attached to C_3 and C_4) in the nmr spectrum (Figure 1), the bonding

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[1] G. N. Schrauzer, P. Glockner, and R. Merényi, *Angew. Chem.*, **76**, 498 (1964); *Angew. Chem., Int. Ed. Engl.*, **3**, 509 (1964).

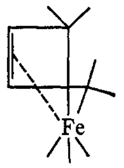
[2] M. Jones, Jr., and L. T. Scott, *J. Amer. Chem. Soc.*, **89**, 150 (1967); M. Jones, Jr., S. D. Reich, and L. T. Scott, *ibid.*, **92**, 3118 (1970).

[3] The temperature factors of all nonhydrogen atoms in the structure have been refined anisotropically.

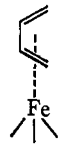
[4] O. S. Mills and G. Robinson, *Acta. Cryst.*, **16**, 758 (1963).

[5] R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 1 (1964).

could with some justification be described in terms of σ–π structure **5** rather than the "classical" π-complex interaction **6**. However, it must be emphasized



5



6

that structure **5** expresses the bonding in terms of the valence-bond approximation, overly emphasizing the presence of Fe–C σ bonds. The structure actually results from the bonding and back-bonding interactions between the butadiene and $Fe(CO)_3$ moieties which must give rise to changes in the bond lengths in the four-carbon chain.[6] Accordingly, the bonding of all carbon atoms to Fe is of an intermediate type which cannot be expressed by one localized VB structure alone. Recognizing the difficulties in formulating a complicated bonding situation, we prefer the less committal structure **6**.[7]

The interaction of the second $Fe(CO)_3$ group with atoms C_7, C_8, C_9, and C_{10} appears to be the first reported X-ray structural information on an iron tricarbonyl complex of a 1,4-diene system. The $Fe_2 \cdots C_9$ and $Fe_2 \cdots C_{10}$ distances (2.122 (13) and 2.131 (13) Å) are slightly shorter than the $Fe_2 \cdots C_7$ and $Fe_2 \cdots C_8$ lengths (2.172 (13) and 2.175 (13) Å), although all the $Fe_2 \cdots C$ (olefin) distances are longer than their $Fe_1 \cdots C$ counterparts. These longer distances are consistent with a somewhat weaker bonding of an $Fe(CO)_3$ group to a nonconjugated diene than to a 1,3-diene as is suggested by simple Hückel theory.[5,7] In $Fe(CO)_3$ complexes with 1,3-dienes, the projection of one of the carbonyl groups onto the best plane defined by the four carbon atoms of the diene group is almost perpendicular to the central C–C bond. When the $Fe(CO)_3$ group complexes with the 1,4-diene portion of the present structure, the projection of one of the carbonyl groups onto the best plane defined by the C_7, C_8, C_9, and C_{10} atoms is almost perpendicular to the C_7–C_8 bond.

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(6) For compilations of the dimensions in the complexed "butadiene" moiety, see M. R. Churchill and P. H. Bird, *Inorg. Chem.*, **8**, 1941 (1969); S. M. Johnson and I. C. Paul, *J. Chem. Soc. B*, in press.

(7) For a recent review and discussion of the bonding in these complexes, see M. R. Churchill and R. Mason, *Advan. Organometal. Chem.*, **5**, 93 (1967).

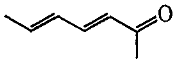
(8) Alfred P. Sloan Research Fellow.

Mechanistic Aspects of 3,5-Heptadien-2-one Photoisomerization

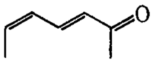
Sir:

Recent reports of the photoisomerization of 2,4-hexadiene have demonstrated the occurrence of a two-bond isomerization in which both double bonds of a hexadiene molecule are isomerized as the result of absorption of one photon.[1,2] The quantum yield data show that a common triplet state or rapidly equilibrating isomeric triplet states are intermediates in the isomerization.[2] We wish to report preliminary results of our closely related study, the photoisomerization of 3,5-heptadien-2-one, which does not proceed *via* one common excited state.

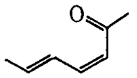
Irradiation of any of the three known geometric isomers of 3,5-heptadien-2-one (tt, tc, and ct)[3,4] as a 10^{-3} *M* solution in ethyl ether results in rapid formation of the same photostationary state of these three isomers. No other products were detected. Glpc analysis of isomer mixtures were carried out using a 20 ft × 1/4 in. 5% FFAP on 60–80 mesh Anakrom AB column at 100°. The photoenol, 6-hydroxy-1,3,5-heptatriene, is not a likely intermediate because its formation would require hydrogen transfer *via* an eight-membered ring and because no conjugated dienones were detected.[5]



tt



tc



ct

Quantum yields (Table I) were determined by irradiation of pure[6] samples of tt, tc, and ct for short periods to ensure low conversion (2–8%) and glpc analysis of the products. A check of the accuracy of the quantum yields was made by using them along with measured

Table I. Quantum Yields for Photoisomerization of 3,5-Heptadien-2-one[a,b]

Wavelength, nm	$\Phi_{tt \to ct}$	$\Phi_{tt \to tc}$	$\Phi_{tc \to tt}$	$\Phi_{tc \to ct}$	$\Phi_{ct \to tt}$	$\Phi_{ct \to tc}$
254	0.28	0.14	0.17	0.25	0.36	0.12
313	0.24	0.15	0.28	0.17	0.23	0.13

[a] Determined for *ca.* 2×10^{-2} *M* solutions at room temperature.
[b] Average uncertainty is ±8% at the 90% confidence level.

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(1) H. L. Hyndman, B. M. Monroe, and G. S. Hammond, *J. Amer. Chem. Soc.*, **91**, 2852 (1969).

(2) J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **91**, 5684 (1969).

(3) An earlier study of tt as a *ca.* 0.3 *M* solution in ethanol was complicated by polymerization, and only one photoisomer was detected. G. Büchi and N. C. Yang, *Chem. Ind.* (*London*), 357 (1955); *J. Amer. Chem. Soc.*, **79**, 2318 (1957). Our irradiation of a 10^{-2} *M* ether solution of tt led to 88% recovery of heptadienone isomers after the photostationary state had been reached.

(4) The absence of the *cis,cis* isomer in the photoproduct mixtures may be caused by its rapid disappearance *via* a pyran intermediate in a dark reaction. Details of dienone photoisomerizations including this work will be covered in a forthcoming paper.

(5) Unconjugated isomers result from photoenolization of conjugated aliphatic enones; *cf.* N. C. Yang and M. J. Jorgenson, *Tetrahedron Lett.*, 1203 (1964).

(6) Final conversion values were corrected for small amounts of contaminating isomers. Monochromatic 254- and 313-nm light was isolated by the method described by Calvert and Pitts[7] and potassium ferrioxalate actinometry was used.

(7) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, pp 728–747, 783–786.