Synthesis and Molecular Structure of Hexacarbonyl(tropone)diiron

Noboru Morita, Chizuko Kabuto,† and Toyonobu Asao*
Department of Chemistry, College of General Education, Tohoku University, Kawauchi, Sendai 980
†Instrumental Analysis for Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980

(Received December 5, 1988)

Synopsis. Molecular structure of hexacarbonyl(tropone)diiron has been investigated by X-ray diffraction studies.

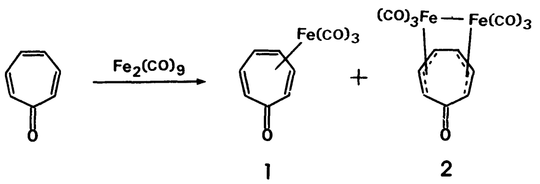
Previously, tricarbonyl(tropone)iron has been obtained by the reaction of acetylene with $Fe_2(CO)_9$,[1)] or of tropone with $Fe(CO)_5$,[2)] $Fe_2(CO)_9$,[3,4)] or $Fe_3(CO)_{12}$,[5)] and the complexes of tropone derivatives have also been obtained by the reaction of substituted tropones with $Fe_2(CO)_9$.[4)]

Dodge reported in 1964[6)] the X-ray analysis of the complex to clarify the structure of tricarbonyl[(2,3,4,5-η)-2,4,6-cycloheptatrienone]iron. Furthermore, many interesting chemical properties have been explored for the complexes.[7)] Recently we have succeeded in optical resolution of the complex,[8)] although partial resolution has been reported,[9)] and kinetic data of 1,3-haptotropic rearrangement,[8)] absolute configuration[10)] of the complex and the related complexes have been reported.

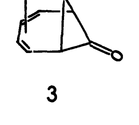
In the course of our studies on synthesis and properties of tricarbonyl iron complex of tropone and its derivatives, we have isolated new hexacarbonyl diiron complexes along with tricarbonyl iron complexes. We have tentatively proposed a structure of hexacarbonyl-[μ-[(2,3,4-η:5,6,7-η)-2,4,6-cycloheptatrienone]]diiron for the new complex of tropone based on the spectroscopic data.[11)]

Recently, we have investigated a molecular structure of the new complex by X-ray diffraction and we have found our proposed structure is correct, the results of which will be reported herein.

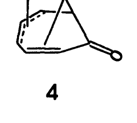
In the synthetic study of tricarbonyl(tropone)iron **1** by the reaction of tropone with excess of $Fe_2(CO)_9$ in refluxing ether, we isolated a new complex **2** as dark reddish crystals in 14% yield besides known complex **1** in 56% yeild.[11)] Some substituted tropones also afforded mixtures of type **1** and type **2** complexes.[12)] The complex **2** was also obtained from **1** by the reaction with $Fe_2(CO)_9$ in 25—30% yeild, and it was also found that **2** gradually decomposed by heating in benzene to give **1** and tropone itself.



1 2



3



4

Mass spectrum of the new complex **2** by FD method showed a molecular ion peak at m/z 386 corresponding to $C_7H_6OFe_2(CO)_6$, coincided with the results of elemental analysis, and the abundant fragment ions by electron impact mode were observed at m/z 274 (1), 246 (1), 218 (5), 106 (58), and 78 (100). The infrared spectrum of **2** in KBr disk showed absorptions at 2060, 2025, 2010, 1995, 1980, 1960, 1955, and 1599 cm^{-1}, the ultraviolet absorption spectrum in ethanol showed maxima at 224 nm (log ε 4.26), 341 (3.94), and 432 (3.49), and ^{1}H NMR in $CDCl_3$ at 90 MHz showed signals at δ=3.33 (d, J=7.15 Hz, H-2,7), 4.40—4.67 (m, H-3,6), and 4.67—4.99 (m, H-4,5), ^{13}C NMR in $CDCl_3$ at 22.5 MHz showed signals at δ=209.50 (s, C-1), 191.96 (s, Fe-CO), 74.10 (d, J=161.6 Hz, C-3,6), 63.69 (d, J=156.2 Hz, C-2,7), and 62.49 (d, J=161.9 Hz, C-4,5).

From these sepctroscopic data we assigned a structure of hexacarbonyl[μ-[(2,3,4-η:5,6,7-η)-2,4,6-cycloheptatrienone]]diiron for the complex **2**, similar to hexacarbonyl(cycloheptatriene)diiron.[13)] However, we could not exclude other structures such as **3** and **4**. Therefore, we carried out an X-ray crystallographic analysis of **2**. The molecular structure and atom labeling scheme for the complex **2** are presented in Fig. 1.

The crystallographic result shows that the structure **2** is indeed correct for this complex. Two independent

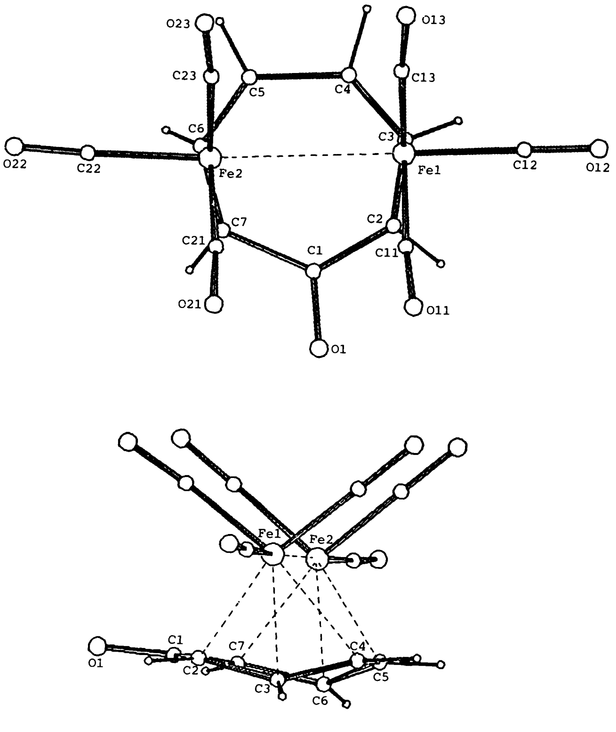


Fig. 1. Two perspective views of the $C_7H_6OFe_2(CO)_6$ molecule.

Table 1. Interatomic Bond Distances (Å) and Angles (deg) for Selected Bond in $C_7H_6OF_2(CO)_6$[a)]

Fe1-Fe2	2.894
Fe1-C2, Fe2-C7	2.123
Fe1-C3, Fe2-C6	2.040
Fe1-C4, Fe2-C5	2.177
C1-O1	1.230
C1-C2, C1-C7	1.456
C2-C3, C6-C7	1.414
C3-C4, C5-C6	1.394
C4-C5	1.447
C11-C21	2.821
C13-C23	2.830
O11-O21	2.973
O13-O23	3.023
C2-C1-O1, C7-C1-O1	118.6
C2-C1-C7	122.8
C1-C2-C3, C1-C7-C6	129.3
C2-C3-C4, C5-C6-C7	124.3
C3-C4-C5, C4-C5-C6	126.1
Fe2-Fe1-C2, Fe1-Fe2-C7	85.4
Fe2-Fe1-C3, Fe1-Fe2-C6	92.7
Fe2-Fe1-C4, Fe1-Fe2-C5	70.6
Fe2-Fe1-C11, Fe1-Fe2-C21	84.4
Fe2-Fe1-C12, Fe1-Fe2-C22	174.9
Fe2-Fe1-C13, Fe1-Fe2-C23	92.9
C11-Fe1-C12, C21-Fe2-C22	93.1
C12-Fe1-C13, C22-Fe2-C23	89.6
C11-Fe1-C13, C21-Fe2-C23	101.6

a) The values are averaged over the equivalent bonds for mirror symmetry of the structure between two independent molecules. The e.s.d.'s are 0.003, 0.017, 0.023 Å for Fe-Fe, Fe-C, C-C bonds and 0.5, 0.8, 1.6° for Fe-Fe-C, C-Fe-C, C-C-C angles.

complexes of **2** exist in the crystalline state; however there is no essential difference in the structure of tropone ligand as well as in the way of coordination. As shown in perspective views of complex **2** (Fig. 1), the structure has an approximate mirror plane within the experimental errors. Table 1 lists the average values over the geometrically equivalent bond distances and angles for the two molecules. Tropone ligand is bent in a similar way to the case of cycloheptatriene complex, though the planarity is more retained. Somewhat longer distance of Fe_1-Fe_2 (2.894 Å) in **2** compared to that in the latter (2.866 Å) may be due to the difference of the planarity.

Experimental

Reaction of Tropone and $Fe_2(CO)_9$. A slurry of tropone (0.9 g, 8.5 mmol) and $Fe_2(CO)_9$ (8 g, 22 mmol) in 60 ml of anhydrous ether was heated at reflux under argon atmosphere for ca. 7 h. The reaction mixture was chromatographed on silica gel. The first eluent with a mixture of ether and benzene (1:9) gave green-colored $Fe_3(CO)_{12}$. From the next orange colored band eluted with a mixture of benzene and CH_2Cl_2 (1:9), complex **1** (1.18 g, 56%) was obtained as orange solid. From the successive reddish colored band eluted with ethyl acetate, complex **2** (466 mg, 14%) was obtained as dark reddish crystals. Recrystallization of **2** from benzene afforded an analytical sample, mp 118—120 °C as dark reddish prisms. Found: C, 39.92; H, 1.44%. Calcd for $C_7H_6OFe_2(CO)_6$; C, 40.45; H, 1.57%.

Reaction of 1 and $Fe_2(CO)_9$. A slurry of **1** (500 mg, 2.0 mmol) and $Fe_2(CO)_9$ (1.25 g, 3.4 mmol) in 60 ml of anhydrous ether was heated at reflux for 2 h. The reaction mixture was separated by chromatography on silica gel to afford **1** (186 mg, 37%) and **2** (247 mg, 29%).

Crystal Measurements, Data Collection, and X-Ray Structure Refinement for 2. A redish crystal with the sizes of 0.2×0.2×0.23 mm was used for data collection on a Rigaku automated four-circle diffractometer with a rotating anode (40 kV, 150 mA) using graphite monochromated Cu $K\alpha$ radiation (1.5418 Å). Crystal data are as follows: M.F.=$C_7H_6OFe_2(CO)_6$, M.W.=385.88, triclinic, space group $P\bar{1}$, a=14.660(3), b=12.919(3), c=9.086(3) Å, α=92.50(2), β=115.20(2), γ=112.00(2)°, V=1400.7(9) Å^3, Z=4, $D_{\mathrm{calcd.}}$=1.83 g cm^{-3}. A total of 4250 reflections within 2θ=128° were collected by the θ-2θ scan mode. The structure determination was rather difficult, but finally succeeded by the direct method in consideration of pseudo-symmetrical location for eigth Fe atoms in the unit cell. The structure, thus obtained, were refined by the block diagonal least-squares method to prove the correct space group of $P\bar{1}$. After the Fe, C, and O atoms were refined anisotropically and the calculated H atoms were included, the final R value was 0.082 (R_w=0.093) for 3074 reflections with $F_o>3\sigma(F_o)$.

Tables of positional and anisotropic thermal parameters of heavy atoms, and observed and calculated structural factors are kept at the Chemical Society of Japan, Document No. 8872. The details of crystallographic data should be requested to the author.

The authors are grateful to Dr. Hideo Sotokawa, Research Institute of Non-aqueous Solutions, Tohoku University for the technical asistant in X-ray diffraction analysis.

References

1) E. Weiss and W. Hübel, *Chem. Ber.*, **95**, 1179 (1962).

2) M. Franck-Newmann, F. Brion, and D. Martina, *Tetrahedron Lett.*, **1978**, 5033.

3) D. F. Hunt, G. L. Farrant, and G. T. Rodeheaver, *J. Organomet. Chem.*, **38**, 349 (1972).

4) A. Eisenstadt, *J. Organomet. Chem.*, **97**, 443 (1975).

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

6) R. P. Dodge, *J. Am. Chem. Soc.*, **86**, 5429 (1964).

7) Z. Goldschmidt, H. E. Gottlieb, and D. Cohen, *J. Organomet. Chem.*, **294**, 219 (1985); Z. Goldschmidt, H. E. Gottlieb, and A. Almadhoun, *ibid.*, **326**, 405 (1987), and references cited therein.

8) A. Tajiri, N. Morita, T. Asao, and M. Hatano, *Angew. Chem., Int. Ed. Engl.*, **24**, 329 (1985).

9) S. Litman, A. Gedanken, Z. Goldschmidt, and Y. Bakal, *J. Chem. Soc., Chem. Commun.*, **1978**, 983.

10) H. Sotokawa, A. Tajiri, N. Morita, C. Kabuto, M. Hatano, and T. Asao, *Tetrahedron Lett.*, **28**, 5873 (1987); A. Tajiri, H. Sotokawa, N. Morita, C. Kabuto, M. Hatano, and T. Asao, *Tetrahedron Lett.*, **28**, 6465 (1987).

11) N. Morita and T. Asao, *Chem. Lett.*, **1982**, 1575.

12) N. Morita, T. Asao, A. Tajiri, H. Sotokawa, and M. Hatano, *Chem. Lett.*, **1985**, 1879.

13) F. A. Cotton, B. G. DeBoer, and T. J. Marks, *J. Am. Chem. Soc.*, **93**, 5069 (1971); W. P. Fehlhammer and H. Stolzenberg, "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel; Pergamon: Oxford, 1982; Vol. 4, p. 513.