The compound, $H_2CH_3SO_3B_3N_3H_3$, is insoluble in nonpolar solvents.

The ^1H and ^{11}B data for $H_2(NC)B_3N_3H_3$ are confusing. If the cyanide group is acting normally as an electron-attracting substituent, the ortho and para NH protons should be shifted downfield relative to $H_3B_3N_3H_3$, and they are. The boron atom bound to the substituent should probably also be shifted downfield. There is one line in the ^{11}B spectrum at −35.9 ppm, which is downfield from $H_3B_3N_3H_3$ (−29.2 ppm). The relative chemical shift of this line does, however, correlate reasonably well with the relative NH proton shift in CH_3CN solution (see Figure 2). However, this leaves the lines at −26.9 and −22.9 ppm for the B–H doublet. This gives a coupling constant of 63 Hz from the ^{11}B spectrum, whereas the ^1H spectrum suggests 138 Hz, a confusing situation. The two lines at −35.9 and −26.9 ppm give a coupling constant of 143 Hz, but this leaves the line at −22.9 ppm for the boron bound to the cyanide. The line at −22.9 ppm is upfield from $H_3B_3N_3H_3$ (−29.2 ppm), which is apparently inconsistent with the properties of the cyanide group, an electron-attracting substituent.

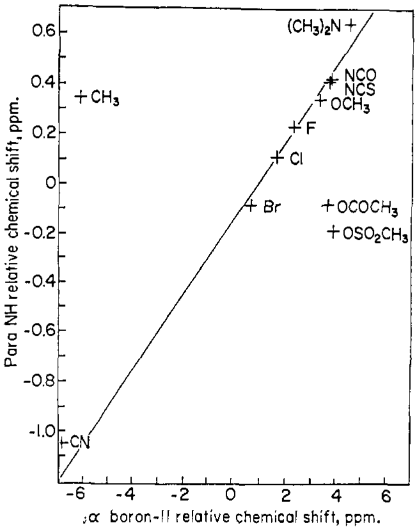

Figure 2.

Acknowledgments. We wish to thank the National Science Foundation, Grant No. GP-20200, for financial support of this research. We also wish to thank Dr. D. H. Marr, Hooker Chemical Co., Grand Island Research Center, for running the 100-MHz spectra and Dr. R. Kurland and Mr. J. Bernstein for running the ^{11}B spectra.

Stereochemically Nonrigid Organometallic Molecules. XXIX. Cycloheptatrienediiron Hexacarbonyl[1,2]

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Received January 6, 1971

Abstract: The crystal and molecular structures and other properties of cycloheptatrienediiron hexacarbonyl have been investigated. The molecule in the crystal has approximate mirror symmetry with the iron atoms lying on opposite sides of the mirror plane; the nmr spectrum strongly suggests, though it cannot prove, that the same structure persists in solution. A systematic name which refers to this structure explicity is (1,2,3-*trihapto*-4,5,6-*trihapto*cycloheptatri-1,3,5-ene)diiron(Fe-Fe) hexacarbonyl. A simple formalism which, however, should not be taken as a precise and literal description of the electronic structure, considers the π-electron system of the C_7H_8 ring to be divided into two adjacent allyl groups, each of which forms a π complex with one of the iron atoms. The C–C bonds in the allyl groups have an average length of 1.401 ± 0.008 Å and the Fe–C(allyl) distances have average values of 2.15 ± 0.03 Å to the outer atoms and 2.042 ± 0.003 Å to the center atoms. The Fe–Fe distance is 2.87 Å. This structure contrasts strikingly with the structures of $C_8H_8Ru_2(CO)_6$ and $C_8H_{10}Fe_2(CO)_6$, in which the M–M axes are turned nearly 90° toward the direction of a possible mirror plane analogous to the one found in $C_7H_8Fe_2(CO)_6$, but are nevertheless skew and quite unsymmetrically bonded. The significance of this structural difference on the interpretation of the fluxional behavior of the C_8H_8 and C_8H_{10} compounds is considered. $C_7H_8Fe_2(CO)_6$ crystallizes in the space group *Pbca* with unit cell dimensions $a = 24.269 \pm 0.006$, $b = 11.431 \pm 0.003$, and $c = 9.732 \pm 0.003$ Å, $Z = 8$; $D(\text{calcd}) = 1.83$ g cm^{-3}; $D(\text{obsd}) = 1.85 \pm 0.01$ g cm^{-3}. The structure was solved and refined using 3111 reflections collected on a counter diffractometer with Mo Kα radiation. Corrections were made for absorption, secondary extinction, and anomalous effects of the Zr filter on background estimates of low-angle reflections. All atoms other than hydrogen were refined anisotropically; hydrogen atoms all refined well isotropically. Final conventional and weighted residuals were 6.1 and 4.2%, respectively.

According to simple but generally reliable rules concerning valence in olefin–metal carbonyl molecules, each of the metal atoms in groups such as $(OC)_3Fe$–$Fe(CO)_3$ and $(OC)_3Ru$–$Ru(CO)_3$ would be considered to lack three electrons of a closed-shell (noble

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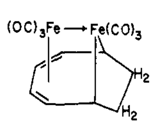
(1) Previous paper in this series: J. L. Calderon, F. A. Cotton, B. G. DeBoer, and J. Takats, *J. Amer. Chem. Soc.*, **93**, 3592 (1971).

(2) Supported by the National Science Foundation under Grant No. 7034X.

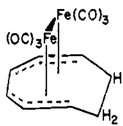
(3) NSF Predoctoral Fellow, 1966–1970.

gas) configuration. Therefore, such $M_2(CO)_6$ moieties would normally be expected to interact with olefinic systems capable of supplying a total of six electrons, or with portions of more extensive olefinic systems, so as to leave any π electrons beyond the requirement of six not engaged in metal–carbon bonding. Naturally, the olefin must also meet certain steric requirements. Aside from the somewhat anomalous substance $[C_3H_5Fe(CO)_3]_x$, in which the three electrons per metal atom are supplied by separate *trihapto*allyl groups,[4] most olefin complexes of the type (polyolefin)$M_2(CO)_6$ contain cyclic trienes or tetraenes, such as cycloheptatriene, cyclooctatriene, and cyclooctatetraene.

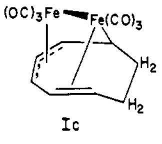
The specific compounds of the three ligands just mentioned, to which we shall restrict our attention here, are: $C_8H_{10}Fe_2(CO)_6$ (I); $C_7H_8Fe_2(CO)_6$ (II); $C_8H_8Fe_2(CO)_6$ (III), and $C_8H_8Ru_2(CO)_6$ (IV). The first of these four compounds to be prepared was $C_8H_{10}Fe_2(CO)_6$ (I), reported in 1963 by King[5] who suggested the structure Ia for it. This structure has a plane of symmetry and environmentally nonequivalent iron atoms. A little later Emerson, Mahler, Pettit, and Collins[6] reported the isolation of $C_7H_8Fe_2(CO)_6$ (II). The Mössbauer spectra (Fe) of both I and II were studied and the conclusion was drawn that the two iron atoms are chemically equivalent in each of these complexes. Since King-type structures, Ia and IIa, place the metal atoms in different environments, Pettit and his coworkers proposed structures Ib and IIb. The two compounds I and II were reported to have similar infrared and nmr absorption patterns, though these have never been described in detail. Later, Keller, Emerson, and Pettit[7] reported the preparation of compound III, to which they assigned structure IIIb on the basis of its Mössbauer, infrared, and nmr (here reported in detail) spectra. The nmr spectrum was complex but consistent with the ring protons being divided into two sets of four by a plane of symmetry.



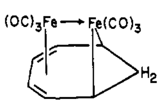
Ia



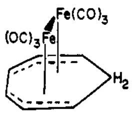
Ib



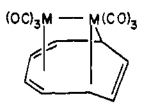
Ic



IIa

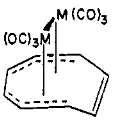


IIb



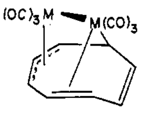
IIIa, M=Fe

IVa, M=Ru



IIIb, M=Fe

IVb, M=Ru



IIIc, M=Fe

IVc, M=Ru

Several years ago work was begun in this laboratory on cyclooctatetraene complexes of ruthenium carbonyl moieties,[8] and this has led to a detailed reinvestigation of compounds I, II, and III. Questions about the true nature of these three molecules were engendered by the results of an X-ray crystallographic investigation[9] of IV, which was found to have neither a King-type, IVa, nor a Pettit-type, IVb, structure, but rather structure IVc (or its enantiomorph). This structure has nonequivalent metal atoms and lacks a plane of symmetry; all eight protons are in different environments. Its nmr spectrum at 25° is similar to that of III and it has been shown that such a spectrum, which entails nmr equivalence of the protons by pairs, is due to a rapid intramolecular rearrangement which interconverts the two enantiomorphs of IVc, possibly by way of IVa as a transition state or short-lived intermediate. From the temperature range over which the limiting low-temperature spectrum collapses to the simpler room-temperature one, the activation energy can be estimated to be in the range of 8–12 kcal/mol. Thus it is probable that the symmetrical, King-type structure IVa is only about 10 ± 2 kcal/mol less stable than the skew structure IVc.

In view of the results on compound IV, it seemed worthwhile to carry out a crystallographic study of the structures of one or more of the compounds, I, II, and III. A sample of the original batch of I was available from Professor King, and an X-ray study[10] showed it to have the skew structure Ic. A study of the temperature dependence of the nmr spectrum of I then revealed that it too is a fluxional molecule, the two enantiomorphs of Ic undergoing rapid interconversion at room temperature.[11]

At this point, it might have seemed safe to conclude that structures of type b were *generally* incorrect and that molecules I–IV would all have the skew, c, type structures which could give rise to an apparent plane of symmetry in the nmr spectra at room temperature by interconversion of the enantiomorphs *via* structures of type a. However, we were unwilling to accept this as a *general* conclusion and wondered whether it would apply to compound II in particular, since the methylene bridge instead of a $-CH_2CH_2-$ or $-CH{=}CH-$ bridging group might alter the conformation of the hexatriene unit so as to change significantly its preferred steric relationship when bonding to an $M_2(CO)_6$ moiety. Compound II, which has never been fully described in the literature, was therefore prepared and thoroughly characterized spectroscopically and crystallographically. The results of that investigation are reported here.

Experimental Section

Preparation. To 1.50 g (16.3 mmol) of cycloheptatriene in 100 ml of degassed pentane was added 12.0 g (33.0 mmol) of diiron enneacarbonyl. The mixture was refluxed under nitrogen, with stirring, for 18 hr. Using a vacuum line the solvent was removed and the residue dried for 2 hr. A small amount of $C_7H_8Fe(CO)_3$ which distilled out was discarded.[12] The dry residue was then

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(4) H. D. Murdoch and E. A. Lucken, *Helv. Chim. Acta*, **47**, 1517 (1964).

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

(6) G. F. Emerson, J. E. Mahler, R. Pettit, and R. Collins, *J. Amer. Chem. Soc.*, **86**, 3590 (1964).

(7) C. E. Keller, G. F. Emerson, and R. Pettit, *ibid.*, **87**, 1388 (1965).

(8) (a) F. A. Cotton, A. Davison, and A. Musco, *ibid.*, **89**, 6796 (1967); (b) F. A. Cotton, A. Davison, T. J. Marks, and A. Musco, *ibid.*, **91**, 6598 (1969).

(9) F. A. Cotton and W. T. Edwards, *ibid.*, **90**, 5412 (1968).

(10) F. A. Cotton and W. T. Edwards, *ibid.*, **91**, 843 (1969).

(11) F. A. Cotton and T. J. Marks, *J. Organometal. Chem.*, **19**, 237 (1969).

(12) This material may be collected, if desired. The reaction of cyclo-

extracted with three 10-ml portions of deoxygenated benzene, and the extracts were transferred under nitrogen to a chromatography column (4.5 × 50 cm) packed with deactivated alumina (Merck, acid washed). The column was eluted under nitrogen with a 1/4 (v/v) mixture of benzene and petroleum ether (37–49°). The large orange band was collected and the solvent removed under vacuum. The resulting red-orange crystalline product was extracted with 50 ml of anhydrous ether, the ether extract filtered, and the filtrate then diluted with 50 ml of pentane. This solution was cooled slowly to −78° and maintained at that temperature for 12 hr while crystals formed. The supernatant liquid was removed with a syringe and the crystals were washed with two 10-ml portions of pentane, yielding 0.51 g (8.5% based on cycloheptatriene) of(1,2,3-*trihapto*-4,5,6-*trihapto*cycloheptatri-1,3,5-ene)diiron(Fe–Fe) hexacarbonyl as air-stable, lustrous, red-orange platelets. The melting behavior (under nitrogen) is not sharply defined; decomposition and softening begin around 120° and are essentially complete by 140°.

Anal. Calcd for $C_{13}H_8Fe_2O_6$: C, 41.98; H, 2.17. Found: C, 41.7; H, 2.30.

The infrared spectrum in cyclohexane solution (Perkin-Elmer 521) has bands at 2058 (s), 2015 (vs), 1992 (s), 1978 (s), 1960 (m), and 1935 (vs) cm^{-1}.

Nuclear magnetic resonance spectra were recorded on a Varian Associates HA-100 spectrometer and were calibrated by measuring the distance in hertz from the lock signal with a Varian V-4315 electronic counter. Temperature measurements were made with a Digitec digital thermometer connected to a calibrated copper–constantan thermocouple which was inserted in the nitrogen stream just below the sample in the probe. The calibration of this system was checked frequently.

Pmr samples were prepared by freeze–thaw degassing of solvents and tetramethylsilane and vacuum distilling these directly onto the solid samples. The sample tubes were then sealed off under high vacuum. Since $C_7H_8Fe_2(CO)_6$ is not particularly soluble in most organic solvents, some difficulty was encountered in obtaining low-temperature spectra. The best solvent mixture was found to be 3/1 (v/v) toluene-d_8–$CHFCl_2$, which permitted spectra to be recorded down to about −100°. Down to this temperature no collapse of any signals was seen and no broadening was observed which could not be attributed to loss of resolution.

Spin-decoupling experiments were performed on Varian Associates T-60 or HA-100 spectrometers, using frequency-sweep double-resonance techniques. Because of solubility problems, signal-to-noise ratios were poor and decoupling experiments were not unambiguous. In acetone-d_6 solutions it was possible to observe that irradiation of the multiplet at τ 5.8 caused the multiplet at τ 4.9 to collapse to a broadened singlet. Also, irradiation of the multiplet at τ 7.3 caused the fine structure of the multiplet at τ 5.8 to collapse and the resonance to narrow somewhat; this irradiation also seemed to perturb the multiplet at τ 7.8. Thus, these results appear to indicate the same order of chemical shifts as found for protons belonging to the coordinated π systems of $C_8H_8Ru_2(CO)_6$ (IV) and $C_8H_{10}Fe_2(CO)_6$ (I).

X-Ray Data Collection. A thick but otherwise typical elongated crystal plate was selected, cut to a more suitable length, and glued to the end of a glass fiber. The crystal was bounded by {100} and {010} side faces, separated by 0.162 (5) and 0.107 (5) mm, respectively.[13] The slightly irregular cut ends are well approximated by $(0\bar{2}5)$ and (023) at distances of 0.099 and 0.102 mm from an origin centered with respect to the side faces. The maximum length of the crystal was 0.273 (5) mm. Oscillation and Weissenberg photographs of this crystal revealed *mmm* Laue symmetry and the following systematic absences: $0kl, k \neq 2n$; $h0l, l \neq 2n$; $hk0, h \neq 2n$. These uniquely indicate space group *Pbca* (D_{2h}^{15}, 61).[14] The crystal was transferred to a General Electric XRD-5 diffractometer equipped with a manually operated goniostat, scintillation detector, molybdenum X-ray tube, and pulse-height discriminator set to pass ~95% of the Mo Kα peak. For intensity measurements, this instrument was operated at a nominal 2° takeoff angle to the X-ray tube anode, and a zirconium filter was placed between crystal and detector. The crystal was oriented so that its long dimension and the *c* axis were coincident with the φ axis, and 2θ values for the *h*00, 0*k*0, and 00*l* sets of reflections (18, 19 and 12 values, respectively) were accurately measured. For each axis, the cell dimension and the true zero of 2θ (the latter to account for small orientation or centering errors) were hand fitted to these values assuming λ(Mo Kα_1, Kα_2, Kβ) 0.70926, 0.71354, 0.63225 Å. The resulting cell dimensions are a = 24.269 (6), b = 11.431 (3), c = 9.732 (3) Å and the three "true zero" values differed by at most 0.05°. The unit cell volume of 2700 (1) Å^3 and formula weight of 371.90, assuming $Z = 8$, give a calculated density of 1.829 g cm^{-3}, in agreement with the value of 1.85 (1) g cm^{-3} observed by flotation in aqueous zinc iodide.

The intensities of 3111 reflections within one octant of the sphere bounded by $2\theta = 55°$ ($\lambda^{-1} \sin \theta = 0.650$) were measured by a coupled θ–2θ scan technique. Each reflection was measured by performing a 1.33° (2θ) scan, centered on the peak, at a rate of 2°/min, accumulating P counts in 40 sec. Stationary background counts, B_1 and B_2, were taken for 20 sec each at the low and high 2θ limits of the scan, respectively. All 427 systematically absent reflections in the region of the data set were also measured and found to conform to the stated extinction rules. The crystal orientation was checked at least twice a day and three strong, nearly orthogonal reflections were remeasured at least once every 3 hr. These standard reflections exhibited small random fluctuations (±2%) superimposed upon a slow decline to 95.0% of their initial values. In two separate episodes, intensities dropped by 10.3 and 15.4%, remained stable, and then returned to normal.[15] However, the number of measurements of the standard reflections within each episode was more than adequate to provide accurate scaling, as verified by an after-the-fact comparison of final F_o and F_c values for the 318 affected data. The three most intense reflections were measured at a reduced X-ray tube current and placed on the common scale by means of the standard reflections. All other reflections gave peak counting rates of 14,000 cps or less, for which errors due to coincidences were found to be less than those which would be introduced by scaling up from a lower current.

Assuming a linear background over the scan range (see below), the net integrated intensity, I, and its standard deviation, $\sigma(I)$, were calculated[16] as $I = P - B_1 - B_2$ and $\sigma(I) = [P + B_1 + B_2 + (pI)^2]^{1/2}$, where the "ignorance factor", p, was set to 0.04, except for the three most intense reflections where it was increased to 0.065 to account for the additional uncertainty in their scaling. Any I less than $0.5(P + B_1 + B_2)^{1/2}$ was set equal to $0.5(P + B_1 + B_2)^{1/2}$. The observed magnitudes of the structure factors, F_o, and their standard deviations, $\sigma(F_o)$, were taken to be $F_o = (I/Lp)^{1/2}$ and $\sigma(F_o) = F_o - (F_o^2 - \sigma(I)/Lp)^{1/2}$ for $I \geq \sigma(I)$ and $\sigma(F_o) = (\sigma(I)/Lp)^{1/2}$ for $I \leq \sigma(I)$, where Lp is the Lorentz-polarization factor.

Solution and Refinement.[17] The positions of the two iron atoms were readily obtained from a three-dimensional Patterson function. A difference Fourier synthesis phased by these two iron atoms revealed the positions of all other nonhydrogen atoms. Least-squares refinement of all nonhydrogen atoms gave R_1 = 10.3%, R_2 = 9.0% with isotropic temperature factors and R_1 = 7.4%, R_2 = 5.9% with anisotropic temperature factors, using absorption-corrected data. The absorption corrections were calculated from

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heptatriene with triiron dodecacarbonyl in refluxing benzene yields almost exclusively $C_7H_8Fe(CO)_3$: F. A. Cotton and C. R. Reich, unpublished observation.

(13) Here and throughout this paper, the number enclosed in parentheses is the standard deviation in the least significant digit listed, *i.e.*, 123.4 (12) = 123.4 ± 1.2.

(14) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1969.

(15) The cause of these decreases was never directly determined, but is presumed to be electronic, since a subsequent general renovation of the circuitry seems to have eliminated the problem. The phenomenon has not reappeared in several subsequent data sets.

(16) Very small additional terms, which were included in both formulas to account for the hidden lowest order decade of the scaler, are not shown.

(17) Local versions of the following programs were employed: (1) MIXG2A, D. P. Shoemaker, diffractometer settings; (2) DRAB70, B. G. DeBoer, data reduction, absorption corrections, and secondary extinction coefficients; (3) FORDAP, A. Zalkin, Fourier syntheses; (4) SFLS5, C. T. Prewitt, full-matrix least-squares refinement; (5) DTEMP, M. D. LaPrade, distance and angles; (6) ORTEP, C. K. Johnson, thermal ellipsoid drawings.

The conventional R factor is defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, where F_o and F_c are the *magnitudes* of the observed and calculated structure factors. The least-squares program minimizes $R_2 = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$, where the weight $w = \sigma^{-2}(F_o)$. Scattering factors for neutral iron, carbon, and oxygen were taken from D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965), the iron values being modified by the real and imaginary anomalous dispersion corrections given in D. T. Cromer, *ibid.*, **18**, 17 (1965). Hydrogen scattering factors were those of R. Mason and C. B. Robertson, *Advan. Struct. Res. Diffr. Methods*, **2**, 57 (1966).

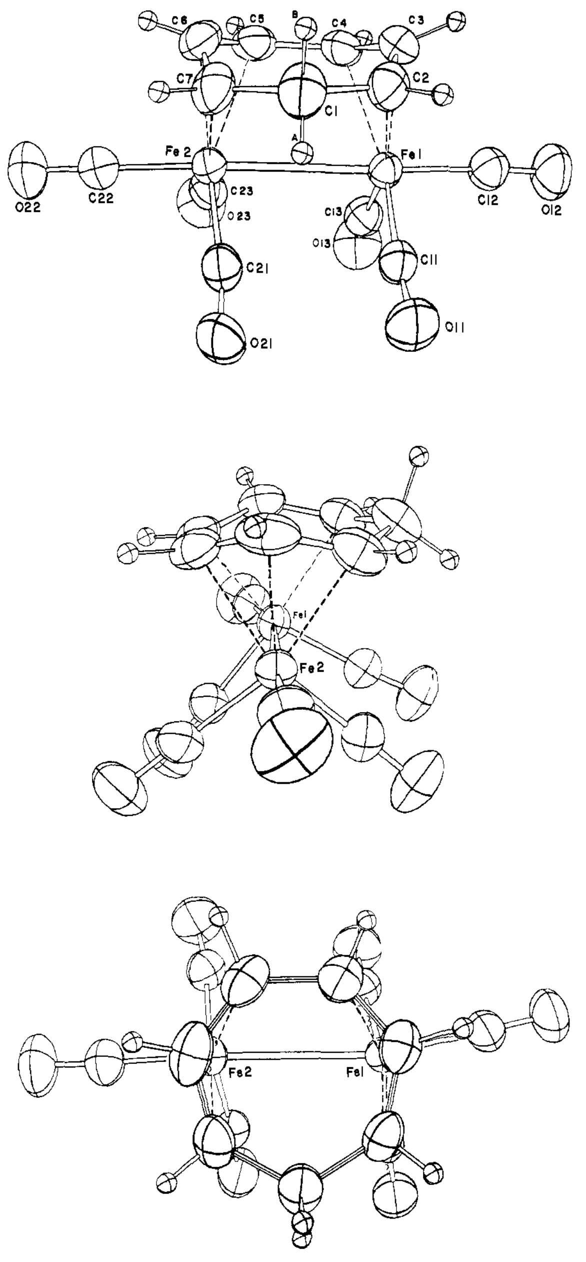

Figure 1. Three perspective views of the $C_7H_8Fe_2(CO)_6$ molecule. The one at the top defines the numbering scheme. Atoms other than hydrogen are represented as 50% probability contours in the thermal vibration ellipsoids, while hydrogen atoms are arbitrarily described as spheres of radius 0.1 Å.

Table I. Final Positional and Isotropic Thermal Parameters[a]

Atom	x	y	z	B, Å^2 [b]
Fe1	0.10919 (2)	−0.00392 (4)	0.08916 (4)	2.82
Fe2	0.15892 (2)	0.06312 (4)	0.34443 (4)	2.95
C1	0.0415 (1)	−0.0454 (4)	0.3510 (4)	4.4
C2	0.0481 (1)	−0.0928 (3)	0.2089 (4)	4.0
C3	0.0888 (1)	−0.1672 (3)	0.1580 (4)	4.0
C4	0.1450 (1)	−0.1566 (3)	0.1889 (4)	3.9
C5	0.1687 (1)	−0.1243 (3)	0.3213 (4)	4.3
C6	0.1402 (2)	−0.0909 (3)	0.4397 (4)	4.6
C7	0.0915 (2)	−0.0233 (3)	0.4379 (3)	4.3
C11	0.0625 (1)	0.1168 (2)	0.0847 (3)	3.6
O11	0.0310 (1)	0.1891 (2)	0.0754 (3)	5.9
C12	0.0937 (1)	−0.0530 (3)	−0.0812 (3)	4.0
O12	0.0848 (1)	−0.0779 (3)	−0.1922 (3)	6.0
C13	0.1701 (1)	0.0598 (3)	0.0205 (3)	3.8
O13	0.2074 (1)	0.0992 (3)	−0.0327 (3)	6.0
C21	0.1212 (1)	0.1939 (3)	0.3088 (3)	3.9
O21	0.0993 (1)	0.2814 (2)	0.2971 (3)	6.3
C22	0.1867 (1)	0.1130 (3)	0.5035 (4)	4.2
O22	0.2055 (1)	0.1472 (3)	0.6032 (3)	6.6
C23	0.2255 (1)	0.0916 (3)	0.2698 (4)	3.9
O23	0.2686 (1)	0.1104 (2)	0.2346 (3)	6.0
H1A	0.019 (1)	0.032 (3)	0.349 (4)	6.0 (8)
H1B	0.018 (2)	−0.107 (3)	0.400 (4)	7.1 (9)
H2	0.014 (1)	−0.095 (3)	0.162 (3)	5.6 (8)
H3	0.079 (1)	−0.224 (3)	0.083 (4)	6.4 (9)
H4	0.170 (1)	−0.192 (3)	0.124 (3)	4.5 (7)
H5	0.209 (1)	−0.153 (3)	0.329 (3)	5.3 (7)
H6	0.158 (1)	−0.096 (3)	0.520 (4)	4.6 (7)
H7	0.081 (1)	0.007 (3)	0.526 (4)	5.9 (8)

[a] Standard deviations[13] are those derived from the inverse of the final least-squares matrix. [b] For nonhydrogen atoms, the "equivalent isotropic temperature parameters" are listed. They correspond to a mean-square displacement which is the average of the mean-square displacements along the three principal axes of the ellipsoid of anisotropic motion and are equal to one-third of the trace of the anisotropic thermal tensor, expressed in an orthogonal coordinate system.

the measured crystal dimensions given above and an absorption coefficient of 22.24 cm^{-1}. Transmission factors ranged from 0.831 to 0.693 and the 12% variation in intensity observed for 004 as a function of φ at $\chi = 90°$ was completely removed. Introducing the eight hydrogens in calculated positions and including their positional and isotropic thermal parameters in further refinement gave $R_1 = 6.5\%$ and $R_2 = 4.5\%$.

At this point, inspection of a list of F_o and F_c revealed that, with the exception of the very strongest reflections, F_o was consistently greater than F_c in the region of small $(\lambda^{-1} \sin \theta)$. This was found to be due to the effect of the zirconium filter upon the low 2θ background measurements, B_1. Because the spectral dispersion is smaller at small 2θ angles, the constant offset of $-0.67°$ from the Kα peak put the detector in a region of the Bragg-scattered white radiation which is on the short-wavelength side of the zirconium K absorption edge, where the absorptivity of the filter is much greater. This results in an underestimation of B_1 and a failure of the linear background assumption.[18] This was verified by plotting $q = (B_2 - B_1)/(P - 2B_2)$ as a function of $(\lambda^{-1} \sin \theta)$ for all reflections for which $(P - 2B_2)$ was greater than 1000 counts and observing that the points clustered strongly about a single smooth curve. This curve was approximated by taking q equal to a constant 0.12 up to $(\lambda^{-1} \sin \theta) = 0.140$ $(2\theta = 11.4°)$ and thereafter allowing it to decline linearly to zero at $(\lambda^{-1} \sin \theta) = 0.320$ $(2\theta = 26.3°)$. All of the data in this region were corrected by multiplying F_o by $(1 - q)^{1/2}$ and I by $(1 - q)$; the standard deviations $\sigma(F_o)$ were left unchanged. Of the 372 data so corrected, 31 fell in the region of constant, maximum q. A secondary extinction correction of the form[19] $F_{c,\mathrm{corr}} = (1 - c\beta I/T)F_c$, where β is proportional to $[(1 + \cos^4 2\theta)(1 + \cos^2 2\theta)^{-2}(-dT^{-1}/d\mu)]$, T is the transmission factor, and c was included among the refined parameters, was introduced into the final cycles of least-squares refinement which gave the final values for R_1 and R_2 of 6.09 and 4.17%. Secondary extinction effects were quite small ($\leq 12\%$ reduction of I), but significant (2.75σ). Shifts in positional parameters caused by the combined secondary extinction and K-edge corrections were $\sim 1\sigma$ or less, but thermal parameters decreased by $\sim 5\sigma$ for iron and up to 2σ for other atoms.

In the final cycle of refinement, the secondary extinction parameter shifted by 0.35 of its standard deviation, but no other parameter shifted by more than 0.13σ. The magnitudes of correlation coefficients obtained from the inverse of the final least-squares matrix were never greater than 0.44, and, among positional parameters for nonhydrogen atoms, only that for the x coordinates of C23 and O23 (+0.30) exceeded 0.20.

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(18) If B_1 were always measured under these conditions, presumably a correct data set would result. It is the decline of this effect with increasing 2θ which causes the error. Neglecting the effects of mosaic spread and finite source width, the effect should extend to a θ value given by $\tan \theta \approx \lambda_\alpha \sin (\Delta\theta)(\lambda_\alpha - \lambda_{K\,\mathrm{edge}}^{-1})$, for a small offset $\Delta\theta$. This gives $2\theta = 21.4°$ for the present case, 8.2° if a niobium filter is substituted, and 18.9° for nickel-filtered copper radiation (all with $\Delta\theta = 0.33°$). We have recently acquired niobium filters so as to obviate this problem in the future.

(19) W. H. Zachariasen, *Acta Crystallogr.*, 16, 1139 (1963); 23, 558 (1967).

Table II. Anisotropic Thermal Parameters[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe1	2.93 (2)	2.87 (2)	2.64 (2)	0.18 (2)	−0.08 (2)	−0.20 (2)
Fe2	3.13 (2)	2.94 (2)	2.77 (2)	−0.27 (2)	−0.26 (2)	−0.10 (2)
C1	3.9 (1)	5.8 (2)	3.6 (1)	−1.4 (2)	0.4 (1)	0.4 (2)
C2	3.4 (1)	4.6 (2)	3.9 (2)	−1.1 (1)	−0.6 (1)	0.5 (1)
C3	4.6 (2)	2.9 (1)	4.3 (2)	−0.8 (1)	−0.8 (1)	0.1 (1)
C4	4.4 (2)	2.6 (1)	4.8 (2)	0.1 (1)	−0.8 (1)	−0.1 (1)
C5	4.3 (2)	2.8 (1)	5.7 (2)	0.0 (1)	−1.5 (1)	0.8 (1)
C6	5.6 (2)	4.2 (2)	3.9 (2)	−1.6 (1)	−1.5 (2)	1.6 (1)
C7	4.7 (2)	5.5 (2)	2.8 (1)	−1.3 (1)	0.3 (1)	0.5 (1)
C11	3.9 (1)	3.7 (1)	3.0 (1)	0.2 (1)	−0.4 (1)	−0.3 (1)
O11	6.0 (1)	5.4 (1)	6.4 (1)	2.6 (1)	−1.5 (1)	−1.0 (1)
C12	4.5 (2)	4.1 (2)	3.5 (2)	0.3 (1)	−0.1 (1)	−0.4 (1)
O12	7.5 (2)	6.9 (2)	3.6 (2)	0.4 (1)	−1.0 (1)	−1.5 (1)
C13	3.9 (2)	4.0 (2)	3.4 (1)	0.0 (1)	0.2 (1)	0.0 (1)
O13	4.9 (1)	7.9 (2)	5.3 (1)	−1.3 (1)	1.7 (1)	0.5 (1)
C21	3.7 (1)	4.3 (2)	3.8 (2)	0.3 (1)	−0.4 (1)	−0.7 (1)
O21	7.2 (2)	4.9 (1)	6.7 (2)	2.3 (1)	−2.2 (1)	−2.0 (1)
C22	4.9 (2)	3.9 (2)	3.9 (2)	−0.2 (1)	−0.6 (1)	−0.2 (1)
O22	8.8 (2)	6.4 (2)	4.7 (1)	0.0 (1)	−2.5 (1)	−1.4 (1)
C23	3.8 (2)	3.6 (1)	4.2 (2)	−0.6 (1)	−0.1 (1)	−0.2 (1)
O23	4.0 (1)	7.0 (2)	7.0 (2)	−1.4 (1)	0.9 (1)	0.0 (1)

[a] In units of Å^2 and for anisotropic temperature factors of the form $\exp(-0.25\Sigma_i\Sigma_j h_i h_j a_i a_j B_{ij})$ for $i, j = 1, 2, 3$, where h_i and a_i are the ith reflection index and reciprocal cell edge, respectively. Standard deviations[13] were derived from the inverse of the final least-squares matrix.

The standard deviation of an observation of unit weight, $[\Sigma w(F_o - F_c)^2/(m - n)]^{1/2}$, where $m = 3111$ (the number of data) and $n = 223$ (the number of parameters refined), was 0.872. Average values of $w(F_o - F_c)^2$ were essentially constant with F_o and $(\lambda^{-1} \sin \theta)$, the greatest deviation indicating that the very weakest reflections were weighted too lightly. The peaks and holes of a final difference Fourier synthesis were apparently scattered at random and did not exceed ±0.48 e/Å^3. A table of the final F_o and F_c values has been deposited with the ASIS National Auxiliary Publications Service.[20]

Results

The Crystal Structure. The final atomic positional parameters are reported in Table I along with the isotropic temperature parameters for the hydrogen atoms and equivalent isotropic temperature parameters for the other atoms. The components of the anisotropic thermal parameter tensors for atoms other than hydrogen are given in Table II. Interatomic distances are collected in Table III and bond angles in Table IV. Figure 1 gives perspective views of the molecule from three approximately perpendicular directions and defines the atom labeling scheme.

In the crystal, the $C_7H_8Fe_2(CO)_6$ molecule occupies a general position and thus has no rigorous symmetry elements. There is an approximate plane of symmetry passing through C1 and bisecting the Fe1–Fe2 and C4–C5 bonds, but deviations from such mirror symmetry are quite noticeable, as may be appreciated from the middle view in Figure 1. The two ends of the $Fe_2(CO)_6$ "sawhorse" are twisted about 9° about the Fe1–Fe2 axis and by about 8° around axes normal to the Fe1–Fe2 bond and the mean plane of the ring. Other deviations are too small to merit attention. The twisting of the sawhorse may perhaps be rationalized as a means of lessening repulsion between carbonyl groups, with the amount of twist being limited by the bonding requirements of the C_7H_8 group.

Table III. Interatomic Distances[a] (Å) in $C_7H_8Fe_2(CO)_6$

Fe1–Fe2	2.866 (1)	Fe1–C11	1.785 (3)
		Fe1–C12	1.791 (3)
Fe1–C2	2.141 (4)	Fe1–C13	1.779 (3)
Fe1–C3	2.043 (3)	Fe2–C21	1.788 (4)
Fe1–C4	2.178 (3)	Fe2–C22	1.782 (4)
		Fe2–C23	1.802 (3)
Fe2–C5	2.168 (3)		
Fe2–C6	2.041 (4)	C11–O11	1.130 (4)
Fe2–C7	2.116 (4)	C12–O12	1.137 (4)
		C13–O13	1.136 (4)
Fe1–C1	3.069 (4)	C21–O21	1.138 (4)
Fe2–C1	3.109 (4)	C22–O22	1.142 (5)
		C23–O23	1.121 (4)
Fe1–C5	3.014 (4)		
Fe2–C4	2.951 (3)	C1–H1A	1.04 (4)
		C1–H1B	1.03 (4)
C1–C2	1.495 (5)	C2–H2	0.94 (4)
C1–C7	1.501 (5)	C3–H3	1.00 (4)
C2–C3	1.394 (5)	C4–H4	0.97 (3)
C6–C7	1.412 (5)	C5–H5	1.04 (3)
C3–C4	1.402 (5)	C6–H6	0.90 (3)
C5–C6	1.397 (5)	C7–H7	0.96 (4)
C4–C5	1.458 (5)		
		Fe1–H1A	3.37 (4)
C2–C7	2.590 (5)	Fe1–H2	2.62 (4)
C3–C6	3.135 (5)	Fe1–H3	2.61 (4)
		Fe1–H4	2.63 (3)
C11–C21	2.750 (5)		
C13–C23	2.797 (5)	Fe2–H1A	3.42 (4)
		Fe2–H5	2.76 (3)
O11–O21	2.918 (4)	Fe2–H6	2.50 (3)
O13–O23	2.999 (4)	Fe2–H7	2.66 (4)

[a] These distances are uncorrected for thermal motion. Their standard deviations[13] were derived from the standard deviations of the atomic coordinates and cell dimensions.

The shapes and orientations of the thermal ellipsoids seem reasonable. Those of the ring carbon atoms suggest that vibrational motion of the C_7H_8 group about the Fe1–Fe2 axis makes a contribution to the overall thermal motion of the ring atoms. All intermolecular contacts appear to be normal. The minimum intermolecular distances are hydrogen-to-oxygen contacts (2.51 Å) and hydrogen-to-hydrogen contacts (2.63 Å), while all others exceeded 2.73 Å.

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(20) For this table, order NAPS Document No. NAPS-01395 from the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022, remitting $2.00 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: CCMIC–NAPS.

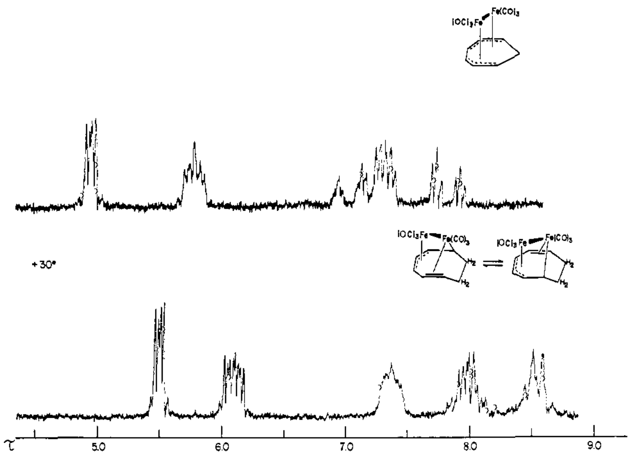

Figure 2. Proton magnetic resonance spectra of $C_7H_8Fe_2(CO)_6$ and $C_8H_{10}Fe_2(CO)_6$ both recorded at 100 MHz, 30°, in CS_2. Frequency scale is in τ units (TMS τ 10).

The Structure in Solution. The pattern of CO stretching bands in the infrared is consistent with the structure (IIb) which the molecule has in the crystal, but does not discriminate between this and structures of type a or c. It is the pmr spectrum which provides strong evidence that structure IIb persists in solution. This spectrum is shown in Figure 2, where it is also compared directly with that of $C_8H_{10}Fe_2(CO)_6$, which is a fluxional molecule having a c-type instantaneous structure. It should be stressed before undertaking to assign and interpret the pmr spectrum of $C_7H_8Fe_2(CO)_6$ that this spectrum is independent of temperature down to $-100°$, in marked contrast to the spectra of $C_8H_{10}Fe_2(CO)_6$ and $C_8H_8Ru_2(CO)_6$ which undergo drastic changes[8,11] in the range 0 to $-100°$. Thus it seems reasonable to conclude that $C_7H_8Fe_2(CO)_6$ is not a fluxional molecule like the others just mentioned and to seek an interpretation of its spectrum in terms of a plausible static structure.

Table IV. Angles[a] (Deg) in $C_7H_8Fe_2(CO)_6$

C7-C1-C2	119.7 (3)	H1A-C1-H1B	107 (4)
C1-C2-C3	128.8 (3)	C2-C1-H1A	110 (2)
C1-C7-C6	126.3 (3)	C2-C1-H1B	104 (2)
C2-C3-C4	124.1 (3)	C7-C1-H1A	107 (2)
C7-C6-C5	123.6 (3)	C7-C1-H1B	108 (2)
C3-C4-C5	126.5 (3)	H2-C2-C1	111 (2)
C6-C5-C4	127.1 (3)	H2-C2-C3	116 (2)
		H3-C3-C2	119 (2)
Fe2-Fe1-C2	86.9 (1)	H3-C3-C4	116 (2)
Fe2-Fe1-C3	93.6 (1)	H4-C4-C3	116 (2)
Fe2-Fe1-C4	70.1 (1)	H4-C4-C5	116 (2)
Fe1-Fe2-C7	85.5 (1)	H5-C5-C4	111 (2)
Fe1-Fe2-C6	94.0 (1)	H5-C5-C6	119 (2)
Fe1-Fe2-C5	72.0 (1)	H6-C6-C5	117 (2)
		H6-C6-C7	117 (2)
Fe2-Fe1-C11	94.7 (1)	H7-C7-C6	114 (2)
Fe2-Fe1-C12	167.2 (1)	H7-C7-C1	111 (2)
Fe2-Fe1-C13	82.3 (1)		
Fe1-Fe2-C21	80.8 (1)	Fe1-C11-O11	175.3 (2)
Fe1-Fe2-C22	176.1 (1)	Fe1-C12-O12	175.9 (2)
Fe1-Fe2-C23	94.4 (1)	Fe1-C13-O13	174.9 (2)
		Fe2-C21-O21	173.5 (2)
C12-Fe1-C11	95.0 (2)	Fe2-C22-O22	177.9 (2)
C12-Fe1-C13	87.5 (2)	Fe2-C23-O23	174.0 (2)
C11-Fe1-C13	101.6 (2)		
C22-Fe2-C21	95.5 (2)	C12-Fe1-C3	88.1 (2)
C22-Fe2-C23	87.3 (2)	C22-Fe2-C6	88.0 (2)
C21-Fe2-C23	103.3 (2)		

[a] Standard deviations[13] were calculated from the standard deviations of atomic coordinates.

The following assignment of the $C_7H_8Fe_2(CO)_5$ pmr spectrum seems reasonably certain on the basis of the decoupling results described in the Experimental Section, the characteristic appearance of the multiplet at lowest field, and the seemingly characteristic upfield position for the protons at the ends of the hexatriene unit: multiplet at τ 4.9, protons 4 and 5; multiplet at τ 5.8, protons 3 and 6; multiplet at τ 7.3, protons 2 and 7; multiplets at τ 7.0 and 7.8, protons 1A and 1B. The individual assignments for protons 1A and 1B remain uncertain. The marked difference in their chemical shifts, some 80 Hz, is not surprising in view of their very different spatial relationships to the rest of the molecule. It is not certain why the splittings in the triplets belonging to one of the methylene protons is less well resolved than the splittings in the triplets of the other, but this may be due to different degrees of long-range coupling.

Discussion

The crystallographic work shows that the type of structure, IIb, proposed by Emerson, *et al.*,[6] for $C_7H_8Fe_2(CO)_6$ is indeed correct for this compound, even though the analogous structures of type b also proposed for compounds with eight-membered rings are not.[21]

It can be seen in Figure 2 that while the pmr spectra of $C_7H_8Fe_2(CO)_6$ and $C_8H_{10}Fe_2(CO)_6$ do have broad, overall similarities, there are also pronounced differences in the chemical shifts of protons in the hexatriene units. We believe that these differences are so large as to justify the conclusion that the two molecules have their hexatriene moieties bonded in different ways to the $Fe_2(CO)_6$ groups. If this be correct, it seems an eminently reasonable, though not an absolute mandatory, conclusion that $C_7H_8Fe_2(CO)_6$ retains in solution the structure which it has in the crystal.

The shape and dimensions of the $(C_7H_8)Fe_2$ moiety are consistent with a description of the bonding as a pair of (h^3-allyl)–metal interactions, with the ends of the two π-allyl fragments linked by a carbon–carbon single bond and a methylene bridge. The distances and angles found within the (h^3-allyl)–iron fragments are quite similar to those found in other molecules[10,22–26] where (h^3-allyl)–iron residues are considered to exist. It must be noted that the representation of the C_7H_8 group as two linked but independent allyl groups is doubtless an oversimplification, since there must be some degree of electronic coupling between them. The fact that the two terminal protons of each allyl group, *e.g.*, H2, H4 on the one hand and H7, H5 on the other, have considerably different chemical shifts demonstrates

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(21) To be strictly correct, direct disproof of b-type structures among the iron compounds has been provided only for $C_8H_{10}Fe_2(CO)_6$. However, we think it tolerably safe to assume that such a structure may also be ruled out for $C_8H_8Fe_2(CO)_6$ since it has been directly disproved for the ruthenium analog, $C_8H_8Ru_2(CO)_6$.

(22) M. R. Churchill, *Inorg. Chem.*, **6**, 190 (1967).

(23) M. R. Churchill and J. Wormald, *ibid.*, **9**, 2239 (1970).

(24) F. A. Cotton and J. Takats, *J. Amer. Chem. Soc.*, **90**, 2031 (1968).

(25) E. B. Fleischer, A. L. Stone, R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, *ibid.*, **88**, 3158 (1966).

(26) F. A. Cotton and M. D. LaPrade, *ibid.*, **90**, 2026 (1968).

that the end-for-end equivalence expected for an independent, symmetrical allyl group is absent. It is, of course, difficult to say how much of this magnetic nonequivalence may be attributed to electronic interactions between the two allyl fragments, but it is very likely that some such interaction does occur. Thus the chain of atoms C2, C3 $\cdots$ C6, C7 may also be considered, with some truth, as a hexatriene unit, though, as a zero-order approximation, the "two linked allyl groups" description seems preferable.

The iron–iron distance, 2.866 (1) Å, in this molecule is substantially greater than those found in other molecules with unbridged Fe–Fe units, *viz.*, 2.782 (4) Å in (azulene)$Fe_2(CO)_5$,[22] 2.769 (3) Å in (acenaphthylene)$Fe_2(CO)_5$,[23] 2.766 (1) Å in $[(CH_2)(CH_3)_3C_8H_4]Fe_2(CO)_5$,[24] and 2.764 (3) Å in $C_8H_8Fe_2(CO)_6$.[10] The only longer Fe–Fe bond (in comparable circumstances) of which we are aware is 2.88 Å (no uncertainty interval stated) reported[27] for $Fe_2(CO)_8^{2-}$. Since the carbon atoms of the opposed carbonyl "legs" of the $Fe_2(CO)_6$ sawhorse are actually closer together, 2.750 (5) and 2.797 (5) Å, than the iron atoms to which they are bound, it would appear that the (h^3-allyl)–Fe linkages are very strong and stretch the relatively weak Fe–Fe bond in order to maintain their own optimal geometry, or the closest feasible approach thereto. In this connection it is of interest to recall that $[C_3H_5Fe(CO)_3]_x$, in which x is most likely 2, readily dissociates, thus indicating that (h^3-allyl)$Fe(CO)_3$ groups are not intrinsically disposed to form strong Fe–Fe bonds.

Insofar as a bond can be described by the simple harmonic oscillator approximation, weakness should be manifested as well by easy compressibility as by easy extensibility. Thus the stretching of the Fe–Fe bond in $C_7H_8Fe_2(CO)_6$ from a "typical" value of $\sim$2.77 Å by the dimensions of the C_7H_8 group finds its opposite in the apparent compression of an Fe–Fe bond to lengths of 2.68 and 2.65 Å in the cases of $(C_5H_4{=}CH_2)Fe_2(CO)_6$ and $C(CH_2)_2(PPh_3)Fe_2(CO)_6$, where the π-olefin donor center and σ-carbon atom are relatively close together.[28,29]

When the structure of this molecule is compared with those of $C_8H_{10}Fe_2(CO)_6$ and $C_8H_8Ru_2(CO)_6$, two closely related lines of enquiry are suggested. One has to do with the factors responsible for the relative stabilities of the a-, b-, and c-type configurations and the other concerns the most probable pathway for interconversion of the enantiomorphous pairs of c structures of $C_8H_{10}Fe_2(CO)_6$ and $C_8H_8Ru_2(CO)_6$. On the first matter we are, regrettably, unable to make any comment beyond the rather obvious one that structures b and c must be quite competitive energetically, with small secondary structural features (ring size, restraints on conformation, intramolecular nonbonded repulsions, and the like) determining which type is actually adopted in each individual case.

With respect to rearrangement pathways for enantiomorphs of type c, the present results prompt some revision of views expressed in earlier papers[8b–11] from this laboratory. The actual observation of a b-type structure as the stable one in this case requires us to be more cautious than we previously have been in speculating about the rearrangement pathway. So long as the b-type structure remained purely hypothetical it seemed to us, and we so stated, that the a structure was definitely the most probable intermediate structure in the interconversion of the enantiomorphs. This was chiefly because the $c \rightleftarrows a \rightleftarrows c'$ process appears to involve only slight nuclear and electronic shifts. However, the fact that a b structure has now been observed in a molecule closely similar in type to I, III, and IV, whereas no a structure has yet been observed, obviously makes the $c \rightleftarrows b \rightleftarrows c'$ process a viable if not indeed a preferable alternative. In principle, there is some possibility of determining experimentally which process is operative, since one of them leads to site exchange and hence time-average equivalence of the two $Fe(CO)_3$ groups, whereas the other does not. Study of ^{13}C or ^{17}O nmr spectra at various temperatures might therefore resolve the question, but it remains to be seen whether practical difficulties such as relatively low solubilities combined with low abundances of the nuclei to be observed will frustrate such an experiment.

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(27) While a distance of 2.88 Å for $Fe_2(CO)_8^{2-}$ has appeared in the literature, the correct distance seems to be 2.75 Å. *Cf.* footnote 56 in L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7312 (1970).

(28) J. Meunier-Piret, P. Piret, and M. M. van Meerssche, *Acta Crystallogr.*, **19**, 85 (1965).

(29) R. E. Davis, *Chem. Commun.*, 248 (1968).