Table VII. Stokes' Radii (Å) for Protic and Dipolar Aprotic Solvents at 25°

Solvent	Me_4N^+	Et_4N^+	Pr_4N^+	Bu_4N^+	Am_4N^+	Ref
[a]	3.47	4.00	4.52	4.94	5.29	41[b]
Water	2.07	2.86	3.97	4.77	5.27	[c]
Formamide	1.99	2.48	...	3.66	...	[d]
Methanol	2.19	2.49	3.27	3.87	4.33	21
Nitromethane	2.40	2.74	3.33	3.83	...	[e]
Acetonitrile	2.50	2.80	3.35	3.79	4.21	[f]
Nitrobenzene	2.64	2.78	3.39	3.87	...	[f]
Acetone	2.76	2.96	3.47	4.02	4.61	[f]
DMF	2.67	2.93	3.58	4.06	...	27
DMA	...	2.72	3.41	3.90	...	28

[a] Radii estimated from molecular volumes or models. [b] Page 125 of this reference. [c] D. F. Evans and R. L. Kay, *J. Phys. Chem.*, **70**, 366 (1966). [d] J. M. Notley and M. Spiro, *ibid.*, **70**, 1502 (1966). [e] R. L. Kay, S. C. Blum, and H. I. Schiff, *ibid.*, **67**, 1223 (1963). [f] D. F. Evans, C. Zawoyski, and R. L. Kay, *ibid.*, **69**, 387 (1965).

4.5 Å, necessitates caution. However, it seems certain that correction factors will account for a 10–15% increase in the Stokes' radius for all of the cations considered. If the tetramethylammonium ion is taken as anomalous, an extrapolation of the parabolic section of the curves suggests that corrections of 50–60% to the Stokes' radii of chloride and bromide are not unreasonable.

It is clear that the complex cations have solvent molecules associated with them in the transport process and, contrary to Prue and Sherrington,[37] who made no correction to Stokes' radii, that both chloride and bromide ions carry DMSO, DMF, and DMA solvent molecules with them.

Since all three solvents have electronegative groups in accessible positions, it is logical to assume that the solvation of the cation, like the interaction in the formation of an ion pair, involves the nitrogen protons of the ethylenediamine ligands. In the parlance of Parker,[10] the cations through the nitrogen protons act as hydrogen-bond donors and the solvents as hydrogen-bond acceptors.

Acknowledgment. The authors wish to acknowledge the cooperation of Professor R. M. Fuoss and Dr. J. F. Skinner who kindly supplied the program for the application of the Fuoss–Onsager–Skinner equation and Dr. A. J. Parker for his helpful discussion.

Studies of Iron Tricarbonyl Cyclooctatetraene Complexes

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Abstract: Two new 1,2-disubstituted cyclooctatetraene (COT) iron tricarbonyl complexes have been prepared and structurally characterized both in solution and in the solid state. Using proton nmr spectroscopy, we have established that the substituted COT ligands are bonded to the $Fe(CO)_3$ fragment in the manner of a 1,3-diene. Unlike the parent compound, $COTFe(CO)_3$, the new complexes do not undergo rapid intramolecular rearrangements in solution. A reexamination of previous work on the parent compound in the light of the present results on the substituted complexes strongly suggests that $COTFe(CO)_3$ has the analogous 1,3-diene type structure at low temperatures in solution. The results of Mössbauer spectroscopic investigations are reported which further corroborate this conclusion. In addition, some comments concerning the possible mechanism of rearrangement of $COTFe(CO)_3$ in solution are presented.

In 1959, the compound $C_8H_8Fe(CO)_3$ (I) was reported.[3–5] From its nmr spectrum,[3,4] which consists of a single, sharp proton resonance at room temperature, it was concluded[3,4,6] that the complex was an open-faced sandwich, with the C_8H_8 group being approximately planar and symmetrically bound to the iron atom. An X-ray crystallographic investigation showed,[7] however, that in the solid state at least, the cyclooctatetraene (COT) molecule is bound to the iron atom through only four of its carbon atoms, in the manner of a 1,3-diene (structure Ia, Figure 1). This result led to the further speculation[7] that perhaps, in solution, the molecule was stereochemically dynamic, with the COT moiety rotating eccentrically with respect to the remaining $Fe(CO)_3$ fragment. If such a rotation were sufficiently rapid, all eight COT protons could become equivalent on the nmr time scale.

That $COTFe(CO)_3$ is stereochemically dynamic was firmly established last year when its proton nmr spectrum as a function of temperature was investigated.[8–10] As the temperature is lowered, the sharp singlet is broadened until, at −155°, two well-separated resonances result. These are due to (1) protons on carbon atoms involved in π bonding to the iron atom, and (2) olefinic protons attached to the remaining four

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(1) Columbia University, New York, N. Y. 10027.

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(3) T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959); *J. Am. Chem. Soc.*, **82**, 336 (1960).

(4) M. D. Rausch and G. N. Schrauzer, *Chem. Ind.* (London), 957 (1959).

(5) A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, 32, 880 (1959).

(6) F. A. Cotton, *J. Chem. Soc.*, 400 (1960).

(7) B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 489 (1961).

(8) C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *ibid.*, **88**, 3444 (1966).

(9) F. A. Cotton, A. Davison, and J. W. Faller, *ibid.*, **88**, 4507 (1966).

(10) C. E. Keller, B. A. Shoulders, and R. Pettit, *ibid.*, **88**, 4760 (1966).

carbons. Three quite different structural interpretations of the low-temperature spectrum were suggested,[8-10] however; these are shown in Figure 1. Of the three suggested configurations, structure Ia was by far the most consistent with the bulk of other chemical and physical data accumulated for COTFe(CO)$_3$ (see Discussion). Nevertheless, structures Ib and Ic could not be completely eliminated as possibilities.

In an attempt to resolve the controversy, and in order to provide some insight into the details of the stereochemically dynamic process or processes responsible for the equivalence of all eight proton resonances in a solution of COTFe(CO)$_3$ at temperatures above −110°,[8] the present study was initiated. Since the completion of this work further evidence has appeared from one of the groups working on this problem.[11,11a] As will be shown, our conclusions are in complete accord with theirs.

Experimental Section

Chemicals. The iron pentacarbonyl and triiron dodecacarbonyl used in the preparations were obtained from Alfa Inorganics. Cyclooctatetraene was a gift of BASF, and was redistilled before use. Cycloocta-1,5-dieneiron tricarbonyl (V) and trimethylenemethaneiron tricarbonyl were generously made available to us by Professor G. Emerson. The 1,2-disubstituted cyclooctatetraenes were already available in our laboratories.[12] All other chemicals were of reagent grade purity.

Preparation of Compounds. **Cyclooctatetraeneiron tricarbonyl** (I) was prepared in 87% yield by the method of Manuel and Stone.[3] Long red-black needles, mp 90–92° (lit. 92°), were obtained after sublimation at 80–90° (0.5 mm) and recrystallized from petroleum ether (bp 30–60°); proton nmr ($CHCl_3$, room temperature): τ 4.61; infrared (CCl_4): 2180, 2030 (doublet), 1550 (br, w), and 1100 (br) cm^{-1}.

Norbornadieneiron tricarbonyl (II) was obtained from iron pentacarbonyl and norbornadiene as reported by Pettit[13] and characterized by infrared spectroscopy (neat): 3000, 2900, 2850, 2040, 1950, 1300, and 1175 cm^{-1}.

1,8-Dicarbomethoxycyclooctatetraeneiron tricarbonyl (III) was prepared by refluxing triiron dodecacarbonyl (6.35 g, 12.5 mmoles) under nitrogen with 1,8-dicarbomethoxycyclooctatetraene (2.2 g, 10.0 mmoles) in 30 ml of benzene for 48 hr. Filtration of the reaction mixture gave 0.8 g of a solid (complex infrared spectrum in the CH and CO stretching frequency regions) and a red filtrate which was *ca.* 85% starting material judging from its nmr spectrum. Chromatography over 70 g of silica gel gave a red band containing *ca.* 30% new product (nmr). A second chromatography over 50 g of Merck acid-washed alumina gave 1.6 g of yellow starting material when eluted with benzene and a red band when eluted with diethyl ether–benzene (1:4). The red band yielded 0.422 g of a red solid (12%) which was purified by recrystallization from petroleum ether–diethyl ether and sublimed twice at 80° (0.5 mm). The final product of orange crystalline material melted at 114–115° and showed only one spot on a thin layer chromatogram.

Anal. Calcd for $C_{15}H_{12}O_7Fe$: C, 50.05; H, 3.34. Found: C, 49.85; H, 3.48.

The spectral analyses showed proton nmr ($CDCl_3$): τ 2.72, 4.91, 5.91, and 6.29 (2:2:2:6); infrared (KBr): 2065 (s), 2000 (s), 1730, 1600 (br, w), 1250 (s), 1065, and 1055(w) cm^{-1}; (CCl_4): 2065 (s), 2000 (doublet, s), 1730, 1250, 1065, and 1055 cm^{-1}; mass spectrum: 360 (parent ion), 332 (−CO), 304 (−2CO), 276 (−3CO) amu.

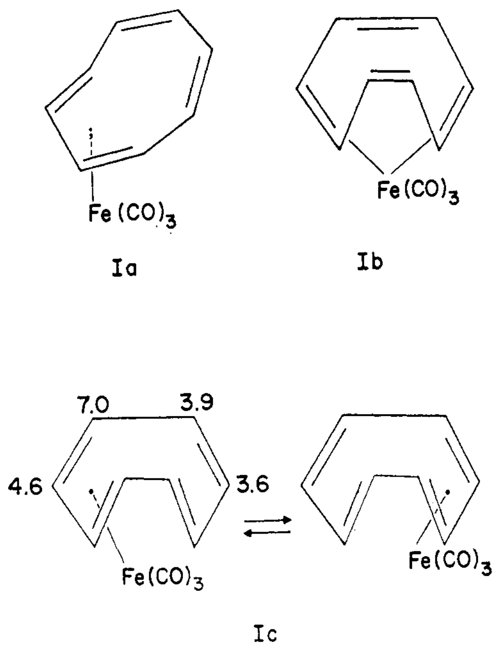

Figure 1. Possible structural configurations of COTFe(CO)$_3$ in solution.[8-11] The numbers associated with structure Ic are chemical shift values proposed[10] to explain the observed nmr spectrum on the basis of a dynamic model.

Cyclooctatetraene[*c*]furan-1(3H)oneiron tricarbonyl (IV) was obtained by refluxing the organic ligand (0.5 g, 3.12 mmoles) for 48 hr under nitrogen with a solution of iron pentacarbonyl (0.78 g, 4.0 mmoles) in 15 ml of ethylcyclohexane. Filtration yielded a pyrophoric solid and a bright red filtrate. The latter was chromatographed on 50 g of Merck acid-washed alumina to yield, on elution with ethyl ether–benzene (1:4) 0.104 g (11%) of red solid, mp 135–137°.

Anal. Calcd for $C_{13}H_8O_5Fe$: C, 52.04; H, 2.69. Found: C, 51.80; H, 2.88.

The spectral analyses showed proton nmr ($CDCl_3$): τ 4.05, 4.4, 4.9, 5.18, 5.4 (1:2:1:2:2); infrared (KBr): 2065, 1960, 1750, 1160, 1060, and 1050 cm^{-1}; (CCl_4): 2890, 2800, 2065, 1998 (br), 1760, 1175, 1060, and 1050 cm^{-1}; mass spectrum: 300 (parent ion), 272 (−CO), 244 (−2CO), 216 (−3CO) amu. This compound was also prepared by treating iron pentacarbonyl (2.75 g, 14 mmoles) at reflux temperature in methylcyclohexane with 1.6 g (10.0 mmoles) of 1,8-diformylcyclooctatetraene for 4 days. Filtration and chromatography over alumina gave 0.25 g of crystalline product (IV) which had physical properties identical with those of the material obtained directly from the lactone.

Physical Measurements. Mössbauer Studies. Solid samples were mounted as thin (10–50 mg/cm^2) wafers between strips of 1-mil aluminum foil clamped in a copper sample holder which could, in turn, be mounted on the cold finger of a liquid nitrogen dewar. Solution spectra were obtained with the use of a liquid sample cell having 3-mil thickness aluminum windows and an inlet–outlet system constructed from No. 22 hypodermic needle tubing. The thickness of the liquid layer was *ca.* 40 mil. Solutions were first prepared by dissolving ~50 mg of the solid in 2.0 ml of solvent and then injected into the sample cell by means of a hypodermic syringe mated to the cell inlet tube. Immediately after filling, the cell was plunged into liquid nitrogen and held at 78°K until mounted in the dewar for measurement. Solvents used in this phase of the work included EPA (16% v/v ethanol and 42% v/v each of 2-propanol and diethyl ether), nitrobenzene, *n*-octane, and methyltetrahydrofuran (MTF).

The Mössbauer spectrometer used in this work employs a constant acceleration drive in conjunction with a 400-channel analyzer operated in the time mode, as has been described in the literature.[14] Velocity calibrations were based on natural iron foil data,[15] while

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(11) F. A. L. Anet, H. D. Kaesz, A. Maasbol, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 2489 (1967); F. A. L. Anet, *ibid.*, **89**, 2491 (1967).

(11a) NOTE ADDED IN PROOF. Further work by another group has also recently been published (W. K. Bratton, F. A. Cotton, A. Davison, A. Musco, and J. W. Faller, *Proc. Natl. Acad. Sci. U. S.*, **58**, 1324 (1967)) which offers definitive proof of mechanisn for the corresponding ruthenium complex, COTRu(CO)$_3$. Our temperature-dependent spectra show the same trends as predicted by their calculations for a cyclooctatetraene complex undergoing 1,2 shifts.

(12) R. Breslow, W. Horspool, H. Sugiyama, and W. Vitale, *J. Am. Chem. Soc.*, **88**, 3677 (1966).

(13) R. Pettit, *ibid.*, **81**, 1266 (1959).

(14) G. K. Wertheim, "Mössbauer Effect: Principles and Applications," Academic Press Inc., New York, N. Y., 1964, Chapter 2.

(15) H. Shechter, H. Ron, S. Niedwiedz, and R. H. Herber, *Nucl. Instr. Methods*, **44**, 268 (1966), and references contained therein.

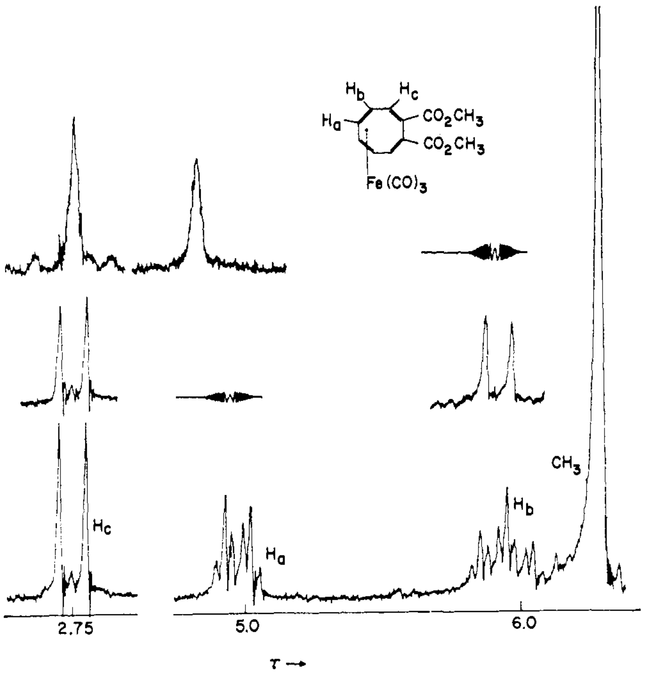

Figure 2. Proton nmr spectrum of III in chloroform solution showing the results (top two spectra) of spin decoupling experiments.

drift and reference point standardizations were carried out for each spectral measurement using an NBS standard sodium nitroprusside absorber.

Nmr Studies. Most of the proton nmr spectra were recorded on Varian A-60A and HA-100 spectrometers, both equipped with a variable-temperature probe and spin decoupler. Tetramethylsilane was used as an internal standard. The very low temperature ($-155° < T < -60°$) study of COTFe(CO)$_3$ was carried out at the JEOLCO Instruments and Applications Center, Medford, Mass., on their 100-MHz, high-resolution nmr instrument with the assistance of Dr. J. Konaka and Mr. Y. Ogowa.

Other Measurements. Ultraviolet spectra were taken on a Cary 15 recording spectrometer. Infrared spectral studies were carried out with a Perkin-Elmer 421 instrument using polystyrene as the calibrant.

Results

Nuclear Magnetic Resonance Studies. The proton nmr spectra at 35° of chloroform solutions of the two new disubstituted complexes, III and IV, are shown in Figures 2 and 3, respectively. The formulation of these two compounds as 1,3-diene bonded complexes on the basis of these spectra is relatively straightforward. Compound III, the diester, has three sets of chemically nonequivalent, equally intense ring proton resonances centered around τ 2.72, 4.91, and 5.91 (Figure 2). The low-field doublet may be assigned to the olefinic protons (H_c) which are coupled to protons H_b ($J_{H_b-H_c}$ = 10 cps). When the H_b resonance is saturated, H_c is decoupled and becomes a singlet (Figure 2). The so-called "inner" and "outer" protons of the 1,3-diene system occur as complex multiplets at τ 5.91 (H_b) and 4.91 (H_a), respectively. Saturation of H_a transforms H_b into a doublet, and saturation of H_b transforms H_a into a singlet (Figure 2). The spectrum of compound IV, the lactone, is somewhat more complex (Figure 3), but again may be readily assigned on the basis of a 1,3-diene formulation. The two protons in the lactone ring, which are in fact chemically nonequivalent, occur as barely resolved resonances at τ 5.175 and 5.185; of equal intensity is a complex pattern which occurs in the τ 5.45 region. By analogy to the spectrum of the diester compound, we assign these to the outer proton (H_b, H_b') resonances. The inner protons, H_a and H_a', appear at τ 4.45 and have the expected relative intensity for two protons. The sharp doublet centering on τ 4.9 is assigned to proton H_d, from which we obtain $J_{H_c-H_d}$ = 10.5 cps. We attribute the high-field chemical shift of this "olefinic" proton to its proximity to the magnetic shielding cone of the lactone ring carbonyl group. Finally, in the normal olefinic region (τ 4.05) is proton H_c, which occurs as a complex multiplet of intensity 1. Irradiation of H_c collapses H_d to a singlet, whereas saturation of the H_a, H_a' resonances greatly simplifies the H_b, H_b' multiplet (Figure 3). Saturation of the H_b, H_b' multiplet converts H_c into a clean doublet from which we obtain, as before, $J_{H_c-H_d}$ = 10.5 cps. These decoupling experiments thus support our structural assignment. In addition to the spectra shown in Figures 2 and 3, the spectra of III and IV were recorded over the temperature range −60° to +120° without any appreciable change in appearance.

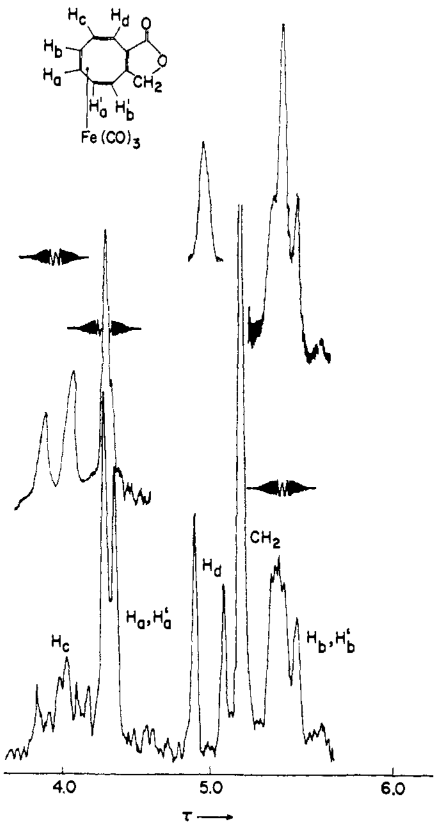

Figure 3. Proton nmr spectrum of IV in chloroform solution showing the results (top three spectra) of spin decoupling experiments.

The proton nmr spectrum of the parent compound, I, is shown in Figure 4 for several temperatures. As may be seen from the figure, these spectra display considerably more structure than reported previously.[8–10] In particular, at −155°, four discrete resonances result. These resonances may be assigned to the four stereochemically different protons of the COT ring bonded to the Fe(CO)$_3$ moiety in the manner of a 1,3-diene (structure Ia, Figure 1). The two upfield resonances at τ 5.22 and 5.45 are the "inner" and "outer" protons of the 1,3-diene system, and the resonances at lower

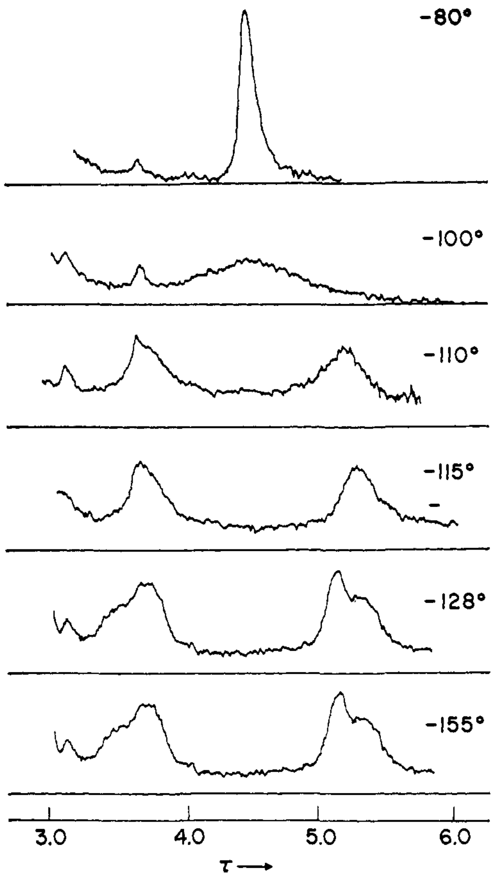

Figure 4. Temperature dependence of the proton nmr spectrum of I in mixed Freon solvents. A better −155° spectrum is shown in Figure 5.

fields, τ 3.55 and 3.81, result from the two sets of olefinic protons. This assignment was verified by a spin-decoupling experiment, in which it was found that the two upfield resonances did not collapse to a single resonance upon strong irradiation of the downfield resonance (Figure 5). Further proof that the two sets of resonances do not result from spin–spin coupling is also set forth in Figure 5. Here we have overlaid the upfield and downfield portions of the −155° spectrum, from which it is evident that the two sets of peaks cannot be spin–spin coupled. In addition we note that, if coupling were responsible for the observed spectrum, the coupling constant would have to be 20–25 cps, which is impossibly high.

By analogy to the spectra of the disubstituted cyclooctatetraeneiron tricarbonyl complexes reported above, we identify the resonances at τ 5.22 and 5.45 with H_a and H_b, respectively (protons are labeled H_a, H_b, H_c, H_d with increasing distance from the iron atom). The greater breadth of H_b may be attributed, at least in part, to the fact that it is coupled to both H_a and H_c, whereas H_a is coupled only to one nearest neighbor, H_b. A similar argument may be used to assign the resonances at τ 3.55 and 3.81 to H_c and H_d, respectively. Further evidence for these assignments was sought by a decoupling experiment, in which strong irradiation of the H_c resonance caused the upfield doublet to become more nearly, although not completely, symmetric (Figure 5). One possible reason for the failure of this upfield doublet to become completely symmetric is that, even at −155°, some dynamic behavior may still be occurring. The

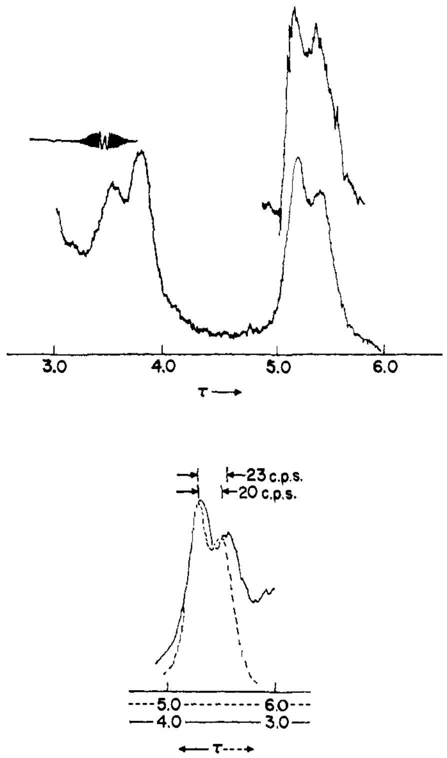

Figure 5. Spin decoupling experiment (top) and visual comparison of the upfield and downfield portions (bottom) of the −155° proton nmr spectrum of I in mixed Freon solvents.

temperature dependence of the spectrum will be discussed later.

Mössbauer Spectral Studies. The results of the Mössbauer studies of I, II, III, IV, and related compounds are summarized in Table I. The spectra of the neat solid absorbers consist of well-separated doublets and were analyzed using the computational methods described previously.[16] The frozen solution spectra of I and IV contain an asymmetric absorption

Table I. Mössbauer Parameters for $RFe(CO)_3$ Compounds at 78°K

R	Solvent[a]	Isomer shift,[b,c] mm/sec	Quadrupole splitting,[c] mm/sec
Cyclooctatetraene (I)	...	+0.31	1.24
	EPA	+0.34	1.16
	$C_6H_5NO_2$	+0.36	1.21
	n-C_8H_{18}	+0.36	1.23
	MTF	+0.35	1.20
1,8-Dicarbomethoxy-COT, $C_8H_6(CO_2CH_3)_2$ (III)	...	+0.33	1.27
COT lactone (IV)	...	+0.33	1.25
	MTF	+0.33	1.17
Norbornadiene (II)	...	+0.29	2.15
Cycloocta-1,5-diene (V)	...	+0.23	1.83
$C_8H_8[Fe(CO)_3]_2$	...	+0.24	1.32
Cyclobutadiene	...	+0.28	1.54
	EPA	+0.26	1.55

[a] EPA = 16:42:42, v/v, ethanol-1-propanol-diethyl ether; MTF = methyltrihydrofuran. [b] From $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ at 294 ± 1°K. [c] All values reported to ±0.03 mm/sec.

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(16) H. Brafman, M. Greenshpan, and R. H. Herber, *Nucl. Instr. Methods*, **42**, 245 (1966).

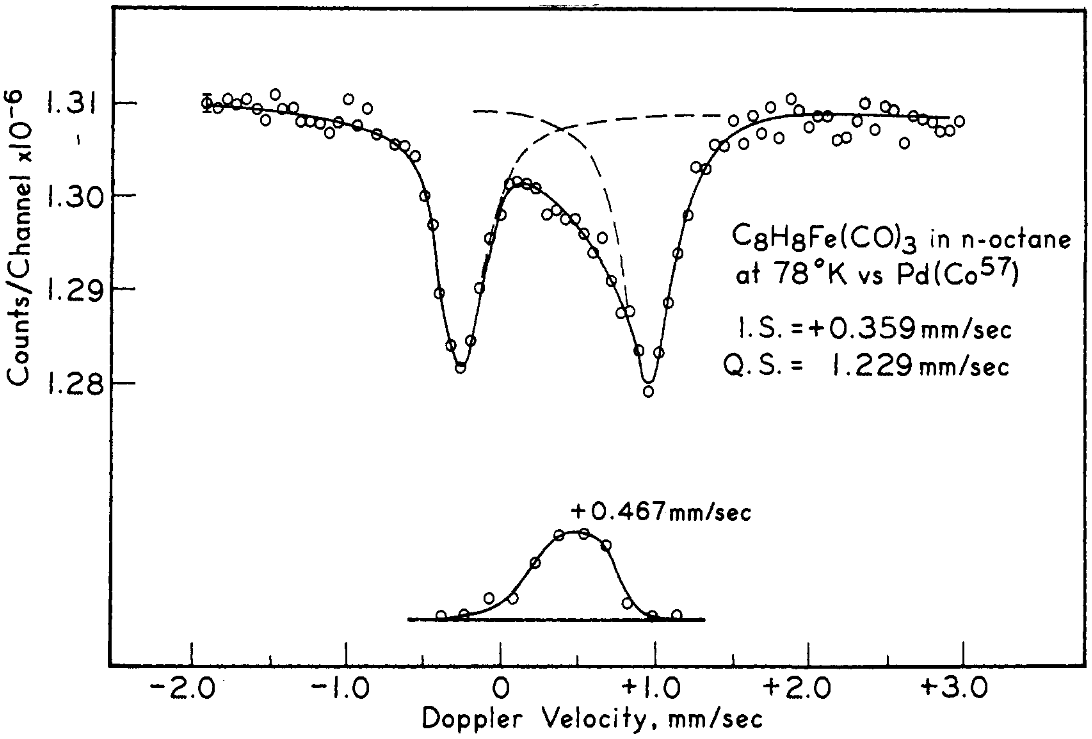

Figure 6. Mössbauer spectrum of I in *n*-octane.

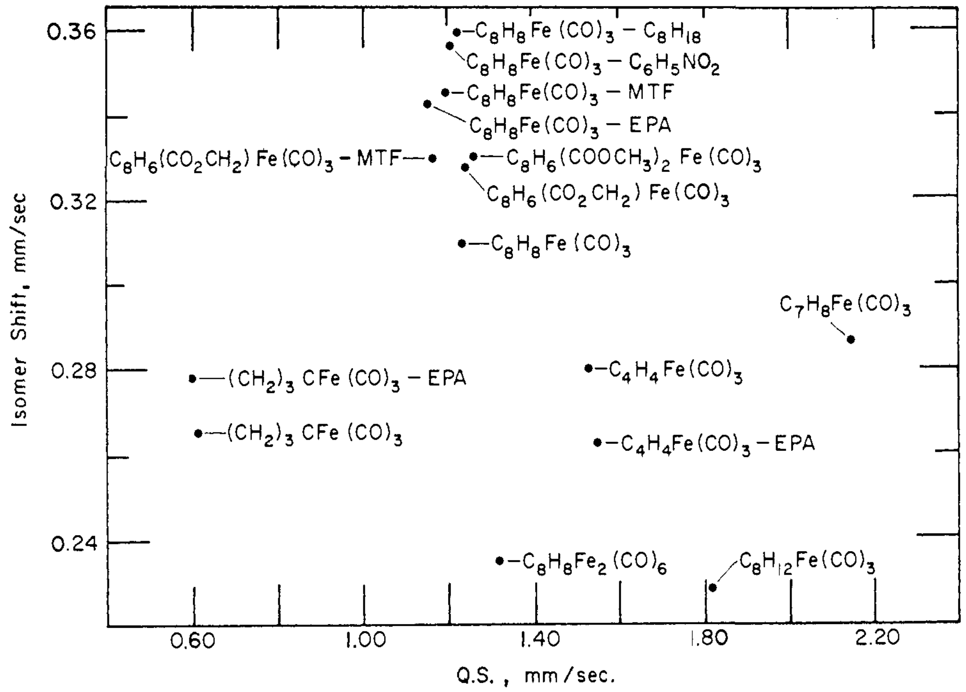

Figure 7. Correlation diagram showing Mössbauer parameters for a variety of organometallic iron carbonyl complexes.

doublet of the type shown for COTFe(CO)$_3$ in *n*-octane in Figure 6. This resonance pattern could be decomposed into a symmetric doublet and a broad single absorption. The latter accounts for about 15–20% of the total area under the resonance curve and has an isomer shift with respect to the standard of +0.48 ± 0.03 mm/sec. The intensity of the singlet absorption peak was insensitive to the nature of the solvent. Similar results were obtained in the frozen solution Mössbauer spectra of $C_4H_4Fe(CO)_3$. Frozen EPA solutions of $(CH_2)_3CFe(CO)_3$ showed only the doublet observed with the neat solid, however. Evaporation of the EPA solvent from the solution prepared for the C_4H_4-Fe(CO)$_3$–EPA determination left a solid residue, the Mossbauer spectrum of which was identical with that of the $C_4H_4Fe(CO)_3$ solid. Compounds of Table I for which no solution spectra are reported were not sufficiently soluble in the solvents used to permit spectroscopic study.

The data given in Table I are also shown *inter alia* in the correlation diagram, Figure 7, in which the coordinate axes are the isomer shift (IS) from sodium nitroprusside and the quadrupole splitting (QS). All data refer to T_s = 295°K and T_a = 78°K. From this figure it is immediately apparent that the QS and, to a lesser extent, the IS of the neat solid and/or frozen solvent matrices of I, III, and IV are all very similar. On the other hand, the QS and IS of II and V, both of which have established 1,5-diene structures,[13] are significantly different. Intermediate between these two sets of compounds are the spectral values for C_4H_4-$Fe(CO)_3$ and $C_8H_8Fe_2(CO)_6$, both of which have been previously taken as model 1,3-diene complexes for alternative interpretations[9,10] of the nmr spectrum of I.

Ultraviolet Absorption Spectra. The ultraviolet spectra of several compounds used in this study are reported in Table II. A strong band at 33,300 cm^{-1} appears in the spectrum of all complexes thought to contain an iron atom bound to a 1,3-diene group in the organic ligand molecule. The absence of such a band in the spectrum of norbornadieneiron tricarbonyl, II, is therefore not unexpected, although one cannot rule out the possibility that a weaker band at 33,300 cm^{-1} is hidden under the intense tail absorption.

Table II. Ultraviolet Spectra of $RFe(CO)_3$ Complexes

R	Solvent	Max, cm^{-1}	ϵ_{max}[a]
C_8H_8 (I)	...	33,000	...
	Mull	33,300	...
	Cyclohexane	33,300	15,000
	Ethanol	33,300	...
$C_8H_6(CO_2CH_3)_2$ (III)	Ethanol	33,300 27,000[b]	13,000 16,000
$C_8H_6(COOCH_2)$ (IV)	Ethanol	33,300	13,100
C_7H_8 (II)	Ethanol	...	...

[a] All compounds showed, in addition to the peaks listed, large tail absorption which generally extended into the visible region of the spectrum, which makes the values reported for the extinction coefficients somewhat uncertain. [b] Also present in the free ligand.

Discussion

As indicated previously, the present work was carried out in order to establish the low-temperature solution structure of $COTFe(CO)_3$. We also hoped for evidence on the nature of its stereochemically dynamic[17] behavior at higher temperatures.

Prior to the low-temperature nuclear magnetic resonance studies reported last year,[8-10] there was general agreement[18] that, as in the crystals, solutions of $COTFe(CO)_3$ contained the $Fe(CO)_3$ group bound to four coplanar adjacent carbon atoms (structure Ia, Figure 1). The conjugated nature of the remainder of the ring was shown by the formation of an adduct with tetracyanoethylene and by reversible protonation and hydride addition reactions.[19] The Diels–Alder reactions of the complex and other[3,4] studies further support the 1,3-diene formulation on chemical grounds alone.[20] With the publication of the low-temperature nmr spectrum of $COTFe(CO)_3$ by three different groups,[8-10] each proposing a different structure (Figure 1), came the first serious challenge to the accepted structure. The present study and the work of Anet[11] have in our opinion established the correct structure (see also ref 11a).

The structural characterization of two new disubstituted cyclooctatetraeneiron tricarbonyl complexes, as well as the parent $COTFe(CO)_3$ molecule at low temperatures in solution, has been achieved by the complementary use of nmr, Mössbauer, and ultraviolet spectroscopic techniques. From their proton nmr spectra (Figures 2 and 3) and appropriate decoupling experiments described above, we conclude that both III and IV have the 1,3-diene type structure. The chemical shift values obtained for these two complexes are incompatible with the previously suggested[10] dynamic structure for compound I, in which grossly different chemical shifts were assigned (Ic, Figure 1) so that their time averaged values would agree with the experimental observations. As indicated above, the nmr spectrum of $COTFe(CO)_3$ at −155° (Figure 4) can readily be assigned on the basis of structure Ia (Figure 1). In order to assign the spectrum on the basis of structure Ib, one would have to assume that the $Fe(CO)_3$ moiety will induce enough asymmetry in a tub form of the COT ring to cause the two sets of proton resonances to split further by 20–25 cps. We have found no such splitting for the olefinic protons in the nmr spectrum of tub-bonded cycloocta-1,5-dieneiron tricarbonyl. Furthermore, as pointed out by other workers,[11] the tub structure cannot satisfactorily explain the observed proton chemical shifts, for it is known[21] that the olefinic protons for norbornadiene and COT (tub form) bonded to $Mo(CO)_4$ commonly occur at $\tau > 7$. The chemical shifts observed for $COTFe(CO)_3$ (Figure 4) can satisfactorily be explained by the 1,3-diene structural formulation, however, using either the mono-[11] or disubstituted (Figures 2 and 3) cyclooctatetraene complexes as models. Here, the olefinic protons on carbon atoms bonded to the $Fe(CO)_3$ moiety occur in the region $4.5 < \tau < 6.0$, which is where the $COTFe(CO)_3$ proton resonances are found. In a similar manner, it should be possible in the future to distinguish between the tub and 1,3-diene attachments of cyclooctatetraene to metal atoms on the basis of their proton nmr spectra. Corroborative nmr spectral proof for structure Ia is obtained from the results shown in Figure 5, which cannot be interpreted on the basis of either alternative (Figure 1) structural formulation.

As is evident from Table I and Figure 7, Mössbauer spectroscopic studies strongly support the 1,3-diene structural assignment. From the figure, it is immediately apparent that both the frozen solution and solid Mössbauer spectra of I, III, and IV are all very similar and, as a group, quite different from the spectra of known 1,5-dienes. The variations in the quadrupole splitting parameters may be understood by referring to the description of the bonding of the iron atom to the C_8H_8 ring in solid $COTFe(CO)_3$ originally proposed by Dickens and Lipscomb.[7] These authors suggested that the bonding orbitals of the iron atom assume a quasi-

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(17) For a recent discussion and classification of stereochemically dynamic inorganic complexes, *cf.* S. J. Lippard, *Trans. N. Y. Acad. Sci.*, **29**, 917 (1967).

(18) See, for example, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1966, p 779.

(19) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962).

(20) R. T. Bailey, E. R. Lippincott, and D. Steele, *J. Am. Chem. Soc.*, **87**, 5346 (1965).

(21) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 1 (1965).

octahedral configuration, with two σ bonds to carbon atoms 1 and 4 of the 1,3-diene system, a μ bond to the ligand π system localized between carbon atoms 2 and 3, and σ bonds to the three carbonyl groups. Assuming a nearly equivalent bonding interaction between the metal and ligand atoms, this quasi-octahedral configuration is expected to give rise to a smaller quadrupole interaction than for the less symmetric ligand environments which occur in the 1,5-diene iron tricarbonyl complexes. Figure 7 verifies that this is indeed the case. A satisfactory explanation for the variations in isomer shift for the complexes shown in Figure 7 is not yet in hand.

Support for the structural assignment of $COTFe(CO)_3$ as a 1,3-diene has been further obtained from its ultraviolet spectrum. Reference to Table II indicates that a strong band at 33,300 cm^{-1} appears to be characteristic of complexes containing the $Fe(CO)_3$ group bonded to a conjugated 1,3-diene both in the solid state *and in solution.* Noteworthy is the absence of a corresponding band in the spectrum of $C_7H_8Fe(CO)_3$ where the $Fe(CO)_3$ group bonds to a nonconjugated diene. As with the nmr spectral information discussed above, this appears to be a potentially useful way of distinguishing possible modes of attachment of polyenes to transition metal atoms.

The mechanism by which the nmr spectrum of $COTFe(CO)_3$ becomes time averaged above $-110°$ is of considerable interest. A 1,5 shift as in Figure 1c will not average all the protons, except fortuitously; the chemical shifts would be averaged by either a series of 1,3 shifts in which the COT π bonds stay fixed, or a series of 1,2 shifts in which the π bonds move. Both of our disubstituted COT complexes, III and IV, are systems in which 1,2 shifts are relatively blocked: a π-electron shift in IV would lead to almost complete flattening of the COT ring because of the geometric demands of the ring fusion. However, the failure of III and IV to show any time-averaging phenomena is not rigorously connected to the mechanistic question. In III there is clearly one strongly preferred structure, a 1,3-diene complex in which the ester groups are skewed and the electron-deficient double bonds bearing these ester groups are not coordinated. In IV it is curious that the two possible 1,3-diene complexes involving unsubstituted double bonds are not in equilibrium. This may well indicate that such equilibration must proceed by a series of 1,2 shifts, blocked in IV. The weakness in this argument is that one isomer may for some reason be strongly preferred in IV as well; only one is isolated. To resolve this issue it will be necessary to examine *symmetric* bicyclic compounds related to IV.

The temperature dependence of the $COTFe(CO)_3$ spectrum was carefully examined in the hope that more detailed information concerning the mechanism of the averaging process might be obtained, as has been possible for other stereochemically dynamic complexes containing cyclic olefins.[22,23] An unambiguous interpretation was not possible, however. Two complicating factors are (1) the proximity of the two low-field resonances to the solvent peaks; and (2) the small separations between pairs of protons, H_a/H_b and H_c/H_d, which are averaging their environments (Figure 4). Also, one must consider the possibility that at the lowest temperature attainable with present instrumentation, $-155°$, some dynamic behavior may still be occurring. This might be the case in spite of the very similar appearance (Figure 4) of the spectra at -128 and $-155°$.

The stereochemically dynamic behavior of $COTFe(CO)_3$ probably consists of 1,2 shifts of the $Fe(CO)_3$ group with simultaneous motion of π electron density within the ring, as discussed above. However, unambiguous evidence for this mechanism will require further work (see ref 11a).

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(22) M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **88**, 4371 (1966).

(23) G. M. Whitesides and J. S. Fleming, *ibid.*, **89**, 2855 (1967).