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Structural and Dynamical Properties of Dicyclopentadienyltetracarbonyldiiron Derivatives with Linked Rings

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Previous studies of the fluxional processes (cis-trans isomerization and CO scrambling) in the cis and trans isomers of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ (**1**, **2**) and various substitution products thereof, which lead to detailed mechanistic conclusions, have been extended to systems in which the $\eta^5\text{-C}_5\text{H}_5$ rings are linked. The systems now described are $(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{CMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4)\text{Fe}_2(\text{CO})_4$ (**6**), a derivative of **6** with $(\text{PhO})_3\text{P}$ replacing a terminal CO (**7**), the azulenyl complex $(\text{C}_{10}\text{H}_8\text{-C}_{10}\text{H}_8)_2\text{Fe}_2(\text{CO})_4$ (**8**), and a derivative of **8** with an $\text{Fe}(\text{CO})_3$ group attached to the 1,3-butadiene portion of the seven-membered ring of each azulenyl group (**9**). The crystal structure of **8** has been determined. Bridge-terminal CO exchange occurs in **6** about as rapidly as in **1**, much more slowly in **8** and **9**, and not at all in **7**. These results are all in accord with the previously proposed mechanism which (1) requires bridged species to pass directly to staggered configurations of the nonbridged intermediates and (2) assumes the necessity of internal rotation in order for bridge-terminal exchange to be consummated. Crystallographic data for **8**: space group $C2/c$; $a = 8.971$ (2) Å, $b = 15.267$ (3) Å, $c = 14.316$ (2) Å, $\beta = 93.56$ (1)°, $Z = 4$. The structure was refined anisotropically to $R_1 = 0.029$ and $R_2 = 0.037$. The structure is derived from that of the cis isomer of **1** in an obvious way; it retains a C_2 symmetry axis and has $\text{Fe-Fe} = 2.500$ (2) Å. A comparison of the infrared spectrum of (**7**) with that of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ indicated that the cis-bridged isomer of the latter compound is predominant in solutions in nonpolar solvents in contrast with $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ where the populations of cis- and trans-bridged isomers are almost equal at room temperature. A steric argument is proposed to account for this difference.

Introduction

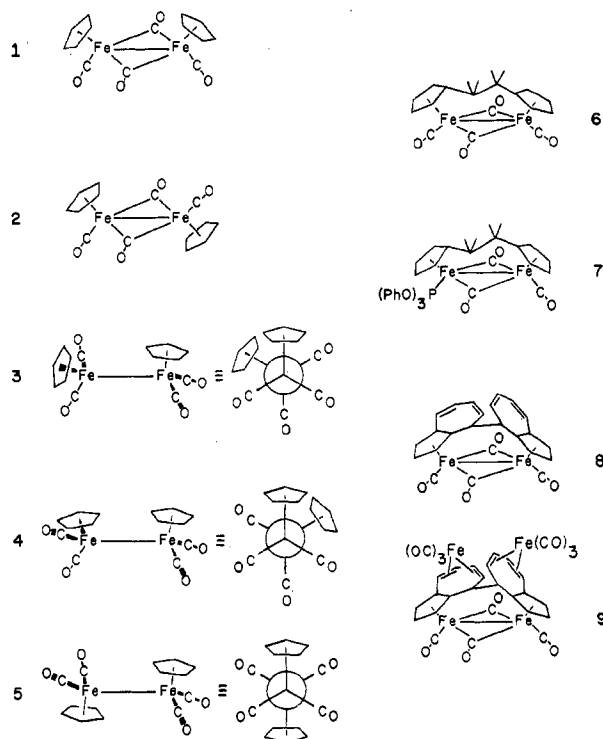
It has been known since 1970 that the cis and trans isomers of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ (**1**, **2**) undergo rapid interconversion,¹ with an activation energy, as determined by proton NMR line shape analysis, of about 12 kcal mol⁻¹. The mechanism originally proposed involved passage through nonbridged intermediates (of which there are three, the enantiomorphous gauche rotamers, **3** and **4**, and the anti rotamer, **5**) and thus, as explicitly suggested,¹ the interchange of bridging and terminal carbonyl ligands should also occur rapidly. Within a very short time, Gansow, Burke, and Vernon² had confirmed this prediction by a ¹³C NMR study of the same molecule. From the ¹³C NMR data of Gansow et al., Adams and Cotton inferred a very detailed mechanistic hypothesis³⁻⁶ to account for the relative rates of cis-trans interconversion, CO scrambling in the trans isomer, and CO scrambling in the cis isomer. A good deal of evidence has since been published to show that this mechanism, and no other, is correct.^{4,7-9} More recently ¹³C spectra of superior quality have been reported and used in a complete line shape analysis to evaluate the activation energy for bridge-terminal CO exchange, with the result $E_a = 11.7 \pm 1.0$ kcal/mol.¹⁰

In this paper we describe a number of additional confirmatory experiments, all centering around the concept of tying

together the two $\eta^5\text{-C}_5\text{H}_5$ rings with two-carbon bridges so as to eliminate any trans-bridged isomer and to restrict the nonbridged isomers to only the gauche ones. The molecules dealt with are **6-9**. Compound **6** has been reported previously,¹¹ while **7** is new. A substance with the same molecular formula as compound **8** has been mentioned once,¹² but it was not characterized in any other way. Compound **9** has been structurally characterized by Churchill and Bird,¹³ but its dynamical behavior has not been previously studied.

Experimental Section

Preparation of Compound 6. A modification of the literature procedure¹¹ was used. A mixture of 11.1 g (105 mmol) of ω,ω -dimethylfulvene,¹⁴ 29.0 g (148 mmol) of $\text{Fe}(\text{CO})_5$, and 45 ml of hexane was heated in a stainless steel bomb for 9 h at 170°. After removal of solvent at reduced pressure, the resulting oil was taken up in benzene and the solution was chromatographed on alumina. Of the four bands eluted with benzene, the first three yielded only oils which could not be induced to crystallize (in accord with the previous report¹¹). From the fourth band a solid was obtained on addition of petroleum ether (bp 60-110 °C) and recrystallized from benzene-petroleum ether to give 3.66 g (8% vs. the literature¹¹ report of 3.2%) of **6**, identified by its melting point [216-220 °C dec (lit. 200-220 °C)], its ir spectrum (CS₂ solution) [ν_{CO} 1995 (s), 1965 (m), 1787 (s) cm⁻¹ (lit. (KBr pellet) 2012 (w), 1988, 1938 (w), 1799 (w), 1767 cm⁻¹)], and its ¹H NMR spectrum (CDCl₃, previously unreported) [τ 4.80-4.92 (complex



multiplet, 8 H) and 8.56 (singlet, 12 H)].

A sample of **6** enriched in ^{13}C was prepared by placing 1.0 g (2.2 mmol) of **6**, prepared as above, and 120 ml of benzene in a Pyrex flask equipped with two gas inlets and having a total volume of 175 ml. The solution was frozen in liquid nitrogen and the flask was evacuated and then closed off until it had returned nearly to 25 °C. The 55-ml dead space was then filled with CO (1 atm, 25 °C) enriched to 90% with ^{13}C and the vessel was then sealed. The system was stirred at 25 °C for 12 h and then for a further 12 h while exposed to a 125-W Hanovia uv lamp placed 25 cm from the vessel. The compound was isolated by chromatography on alumina (benzene eluent) and the level of enrichment was monitored, approximately, by infrared spectroscopy. Enrichment of ca. 15%, as intended, was found.

Preparation of Compound 7. Compound **6** (0.15 g; 0.344 mmol), triphenyl phosphite (3.00 g, 9.7 mmol), and 75 ml of benzene in a Pyrex flask were irradiated for 12 h with a 125-W Hanovia ultraviolet lamp placed 1 cm from the flask. The reaction mixture was chromatographed on acid-washed alumina (Fisher, activity I, 80–200 mesh) using benzene as eluent. The solvent was evaporated at reduced pressure and the resulting red-violet powder was recrystallized from CS_2 -pentane to give 0.117 g (47%) of **7**, mp 195–196 °C dec. Anal. Calcd for $\text{C}_{37}\text{H}_{35}\text{Fe}_2\text{O}_6\text{P}$: C, 61.8; H, 4.9; P, 4.3. Found: C, 61.2; H, 4.6; P, 3.8.

The infrared spectrum of **7** has bands at 1996 (w), 1968 (s), 1789 (w), and 1755 (s) cm^{-1} . ^1H NMR spectrum (in CDCl_3): τ 2.6–3.0 (complex multiplet, 15 H), 4.82–4.96 (complex multiplet, 4 H), 5.32–5.40 (multiplet, 2 H), 6.04–6.12 (multiplet, 2 H), 8.62 (singlet, 12 H).

A sample of **7** enriched in ^{13}C was prepared by the above procedure using enriched **6** as starting material.

Preparation of Compound 8. Iron dodecacarbonyl (1.15 g, 2.3 mmol) was dried under vacuum and added, along with azulene (0.4 g, 3.1 mmol), to 60 ml of heptane. The mixture was stirred for 48 h at 90 °C during which time some decomposition was evident. The resulting dark solution was evaporated almost to dryness and the residue was extracted with three 3-ml portions of CH_2Cl_2 . The extracts were placed on a chromatography column (1.5 × 30 cm) packed with 100–200 mesh Florisil and hexane. Some azulene was collected as a very fast, dark blue band, while simultaneously a small red band moved slowly at the top of the column. This band was eluted with a 1:1 mixture of hexane- CH_2Cl_2 and was identified as (azulene)- $\text{Fe}_2(\text{CO})_5^{15,16}$ by its ir spectrum in hexane (2038 (s), 1996 (s), 1978 (s) cm^{-1}).

The red band remaining at the top of the column was eluted with CH_2Cl_2 . The resulting dark red solution was diluted with an equal

Table I. Crystal Data for $\text{C}_{20}\text{H}_{16}\text{Fe}_2(\text{CO})_4$

FW 480.05	Monoclinic
$a = 8.971$ (2) Å	Space group $C2/c$
$b = 15.267$ (3) Å	Mo $K\alpha$ radiation
$c = 14.316$ (2) Å	$\mu = 15.53$ cm^{-1}
$\beta = 93.56$ (1)°	$d(\text{calcd}) = 1.63$ g cm^{-3} for $Z = 4$
$V = 1956.8$ (6) Å ³	

volume of hexane; the volume was then reduced to about half and the solution was then cooled to -78 °C. The dark red crystals which formed were separated by filtration and vacuum dried; yield 0.20 g (26% based on azulene). Compound **8** is fairly stable in air though the surface luster of the crystals was lost after several days' exposure to laboratory air. Ir (CS_2): 1998 (vs), 1958 (m), 1783 (s) cm^{-1} . The compound enriched in ^{13}C was prepared by the same procedure using enriched $\text{Fe}_3(\text{CO})_{12}$. The enriched substance has bands also at 1965, 1925, and 1750 cm^{-1} . The mass spectrum has a parent ion (M^+) peak at m/e 480 and prominent peaks at m/e 424 ($M - 2\text{CO}$) and 368 ($M - 4\text{CO}$), as well as many at lower masses.

X-Ray Crystallographic Study of Compound 8. X-ray data were collected using a red crystal, grown from hexane- CH_2Cl_2 solution at -5 °C, mounted on a glass fiber. This crystal had dimensions of 0.25 × 0.15 × 0.10 mm.

Preliminary x-ray examination of the crystal and data collection were performed on a Syntex PI computer-controlled diffractometer equipped with a graphite-crystal monochromator in the incident beam.

The crystal was found to be monoclinic. It was of good quality with an ω -scan peak width at half-height of 0.22–0.25° for several strong reflections. Fifteen reflections were carefully centered and their setting angles were refined by least squares to obtain unit cell dimensions and an orientation matrix for data collection. Unit cell dimensions and other crystal data are given in Table I. Data were collected at 22 °C using the θ - 2θ scan technique and a variable scan rate ranging from 4.0 to 24.0°/min depending on the intensity of the reflection. Four standard reflections, collected every 100 reflections, showed no evidence for crystal movement and no significant crystal decomposition. Unique data were collected up to $2\theta(\text{Mo } K\alpha)$ of 40° using a scan range from $2\theta(\text{Mo } K\alpha_1) - 0.5^\circ$ to $2\theta(\text{Mo } K\alpha_2) + 0.6^\circ$. No absorption correction was made in view of the small variation of transmission factors. Lorentz and polarization corrections were made; there was no evidence for secondary extinction. Of 1038 reflections collected, only those 656 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used for the refinement of the structure.

The iron atom was located using a three-dimensional Patterson function. The position of the iron atom was refined by least squares to give the agreement factors

$$R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o| = 0.378$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.461$$

$|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and w is the weighting factor given by $4|F_o|^2/\sigma^2$ where σ is the esd of $|F_o|^2$. Scattering factors and corrections for anomalous dispersion effects due to the iron atom were taken from the usual sources.¹⁷ Two successive difference Fourier maps, each followed by a cycle of full-matrix least-squares refinement of all atoms so far located, revealed the positions of all 15 nonhydrogen atoms. After two cycles of anisotropic refinement the last cycle converged with $R_1 = 0.046$ and $R_2 = 0.050$. Hydrogen atoms were then found in a difference map. Refinement was continued treating the hydrogen atoms isotropically and the others anisotropically. Three cycles led to convergence with $R_1 = 0.029$ and $R_2 = 0.037$ and the esd for an observation of unit weight equal to 0.95. All parameter shifts in the final cycle were smaller than their esd's. In the final difference electron density map the highest peak was 0.375 $\text{e } \text{Å}^{-3}$ whereas the hydrogen atoms had been located on an earlier map as peaks of density 0.6–0.7 $\text{e } \text{Å}^{-3}$. Lists of observed and final calculated structure factor amplitudes and the rms amplitudes of thermal vibration are available.¹⁸

Preparation of Compound 9. Iron dodecacarbonyl (1.15 g, 2.3 mmol) was dried under vacuum and added, along with azulene (0.4 g, 3.1 mmol), to 60 ml of heptane. The mixture was stirred for 24 h at 90 °C. The flask was allowed to reach room temperature and more iron dodecacarbonyl (1.15 g, 2.3 mmol) was added. The mixture was stirred again for 24 h at 90 °C. After removal of the solvent at low pressure the compound was isolated by chromatography on Florisil (100–200 mesh), operating as reported before for compound

Table II. Positional and Thermal Parameters^a

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.09804 (10)	0.08578 (6)	0.19166 (6)	0.0124 (2)	0.00335 (5)	0.00417 (6)	0.00096 (8)	-0.000032 (6)	-0.00077 (5)
O(1)	-0.2049 (5)	0.0581 (3)	0.1135 (3)	0.0173 (9)	0.0048 (3)	0.0051 (3)	-0.0020 (4)	-0.0034 (4)	-0.0009 (2)
O(2)	0.1210 (7)	-0.0984 (4)	0.1521 (4)	0.033 (1)	0.0042 (4)	0.0108 (5)	0.0043 (5)	-0.0075 (6)	-0.0029 (3)
C(1)	0.1422 (6)	0.2242 (4)	0.1847 (4)	0.009 (1)	0.0028 (3)	0.0032 (4)	-0.0003 (5)	0.0006 (5)	-0.0003 (3)
C(2)	0.2738 (8)	0.1766 (5)	0.2103 (6)	0.011 (1)	0.0052 (4)	0.0056 (5)	0.0016 (6)	0.0009 (6)	-0.0006 (4)
C(3)	0.3009 (9)	0.1179 (6)	0.1394 (6)	0.013 (1)	0.0066 (5)	0.0071 (6)	0.0026 (6)	0.0025 (7)	-0.0006 (5)
C(4)	0.1861 (9)	0.1265 (5)	0.0677 (6)	0.019 (2)	0.0053 (5)	0.0045 (5)	0.0010 (7)	0.0033 (7)	-0.0010 (4)
C(5)	0.0909 (8)	0.1946 (4)	0.0937 (5)	0.012 (1)	0.0041 (4)	0.0041 (5)	-0.0003 (5)	0.0017 (6)	-0.0002 (3)
C(6)	-0.0287 (8)	0.2363 (6)	0.0361 (5)	0.015 (1)	0.0056 (5)	0.0028 (4)	-0.0018 (6)	0.0000 (6)	-0.0008 (4)
C(7)	-0.0524 (8)	0.3227 (6)	0.0334 (5)	0.014 (1)	0.0056 (6)	0.0039 (5)	0.0008 (7)	0.0003 (6)	0.0013 (4)
C(8)	0.0320 (8)	0.3879 (5)	0.0883 (5)	0.015 (1)	0.0034 (4)	0.0052 (5)	-0.0007 (6)	0.0021 (6)	0.0014 (4)
C(9)	0.0987 (8)	0.3800 (4)	0.1725 (5)	0.015 (1)	0.0033 (4)	0.0045 (5)	-0.0015 (5)	0.0012 (6)	-0.0003 (3)
C(10)	0.0822 (7)	0.3007 (4)	0.2357 (5)	0.0093 (9)	0.0034 (3)	0.0032 (4)	-0.0006 (4)	0.0000 (5)	-0.0002 (3)
C(11)	-0.1129 (8)	0.0701 (4)	0.1753 (5)	0.017 (1)	0.0018 (3)	0.0044 (4)	-0.0004 (5)	-0.0004 (6)	0.0009 (3)
C(12)	0.1123 (9)	-0.0257 (5)	0.1691 (5)	0.021 (1)	0.0038 (5)	0.0057 (5)	0.0029 (6)	-0.0040 (6)	-0.0013 (4)

^a Numbers in parentheses are estimated standard deviations in the last significant digit.

8. After crystallization from a dichloroethane-hexane (1:1) mixture, the following carbonyl bands were found (CS₂): 2045 (s) 1995 (s), and 1785 (s) cm⁻¹.

The unit cell dimensions obtained from a single crystal of the compound were in agreement with those previously reported by Churchill.¹³

Spectroscopic Measurements. Infrared spectra were recorded either on a Perkin-Elmer Model 467 spectrophotometer or on a Perkin-Elmer Model 237B equipped with a scale expansion accessory and a Leeds and Northrup Model XL strip chart recorder. Frequencies were calibrated using the 2851.5- and 1601.8-cm⁻¹ absorptions of polystyrene and are accurate to ± 3 cm⁻¹. The spectrum recorded here for (η^5 -C₅H₅)₂Fe₂(CO)₃P(OPh)₃ is of higher resolution and accuracy than that reported previously by us.⁹ Proton NMR spectra were recorded in CDCl₃ containing 1% tetramethylsilane using a Varian HA100D spectrometer. Carbon-13 spectra were recorded with a JEOL 100-Nicolet 1080 Fourier transform system operating at a spectrometer frequency of 25.037 MHz. In each case the spectrometer was locked on a ²H signal of the solvent.

The spectra of compounds 6-8 were taken using samples enriched in ¹³CO. Five hundred to 2000 pulses (depending on the compound) were collected for each spectrum with a duration of 12 μ s (18.5 μ s = 90° pulse). The spectra of compound 9 were taken at natural abundance of ¹³C, with 15000-20000 pulses per spectrum and a pulse duration of 6 μ s.

The spectra of compound 6 were recorded in 1:1 CDCl₃-CH₂Cl₂ and that of compound 7 was measured in 4:1 toluene-toluene-*d*₈, while spectra for compound 8 were recorded in 85% 1,1,2,2-tetrachloroethane-15% toluene-*d*₈. For compound 9 which is relatively insoluble, ¹³CO spectra were measured in 85% DMSO-15% DMSO-*d*₆.

The variable-temperature control unit was calibrated against a thermocouple inserted into a reference sample placed in the spectrometer probe. Temperatures are accurate to ± 2 °C. All samples were prepared in serum-stoppered tubes in an inert atmosphere. From 5 to 30 mg of tris(acetylacetonato)chromium(III) was added to each sample used for ¹³C spectra.¹⁹ Carbon-13 chemical shifts were internally referenced to 1-5% added CS₂ but are listed relative to TMS employing the relationship $\delta_{TMS} = \delta_{CS_2} + 192.8$ ppm. All line shape changes are reversible with temperature.

Results

Structure of Compound 8. The final positional and thermal parameters are listed in Table II for all nonhydrogen atoms; the isotropically refined positional parameters for the hydrogen atoms are listed in Table III. The numbering scheme is defined in Figure 1 for the half of the molecule forming the asymmetric unit. The atoms in the other half of the molecule bear the corresponding primed numbers. The halves of the molecule are related by rotation about a twofold axis which bisects both the Fe-Fe' bond and the C(10)-C(10)' bond. Bond lengths are listed in Table V and bond angles in Table VI.

The structure is, expectedly, grossly similar to that¹³ of compound 9 except for the absence of the Fe(CO)₃ groups bound to butadiene portions of the seven-membered rings, but

Table III. Positional Parameters^a of the Ring Hydrogen Atoms^b

Atom	x	y	z
H(2)	0.330 (8)	0.181 (4)	0.267 (5)
H(3)	0.380 (7)	0.078 (4)	0.141 (4)
H(4)	0.176 (7)	0.094 (4)	0.010 (4)
H(6)	-0.075 (7)	0.206 (4)	-0.009 (5)
H(7)	-0.132 (7)	0.344 (4)	-0.004 (4)
H(8)	0.047 (7)	0.444 (4)	0.060 (4)
H(9)	0.142 (7)	0.427 (4)	0.203 (4)
H(10)	0.145 (7)	0.309 (4)	0.289 (5)

^a The isotropic temperature factor was held constant at 5.

^b Numbers in parentheses are estimated standard deviations in the last significant digit.

Table V. Bond Lengths (Å)

Fe-Fe'	2.500 (2)	O(1)-C(11)	1.187 (7)
Fe-C(11)	1.908 (7)	O(12)-C(12)	1.140 (8)
Fe-C(12)	1.739 (8)		
Fe-C(1)	2.154 (6)	Fe-C(4)	2.081 (7)
Fe-C(2)	2.104 (8)	Fe-C(5)	2.172 (7)
Fe-C(3)	2.069 (8)		
C(1)-C(2)	1.415 (9)	C(5)-C(6)	1.459 (9)
C(1)-C(5)	1.429 (8)	C(6)-C(7)	1.34 (1)
C(1)-C(10)	1.497 (8)	C(7)-C(8)	1.45 (1)
C(2)-C(3)	1.39 (1)	C(8)-C(9)	1.317 (9)
C(3)-C(4)	1.41 (1)	C(9)-C(10)	1.523 (9)
C(4)-C(5)	1.410 (9)	C(10)-C(10)	1.56 (1)
C(2)-H(2)	0.93 (6)	C(7)-H(7)	0.92 (6)
C(3)-H(3)	0.94 (6)	C(8)-H(8)	0.96 (6)
C(4)-H(4)	0.97 (6)	C(9)-H(9)	0.91 (6)
C(6)-H(6)	0.88 (7)	C(10)-H(10)	0.93 (6)

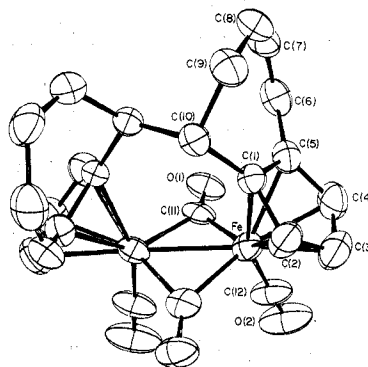


Figure 1. Molecular structure of compound 8. Ellipsoids enclose 50% of the electron density and the numbering scheme used in tables of structure parameters is defined for the unique half of the molecule. The other half of the molecule is obtained by rotation about a twofold axis. Atoms in the other half are given the corresponding primed numbers.

Table VI. Bond Angles

Fe'-Fe-C(11)	49.3 (2)	Fe-C(12)-O(2)	178.4 (7)
Fe'-Fe-C(12)	100.8 (3)	Fe-C(11)-O(1)	138.6 (6)
C(11)-Fe-C'(11)	96.5 (3)	Fe-C(11)-Fe'	81.7 (3)
C(11)-Fe-C(12)	86.5 (3)		
C(1)-Fe-C(2)	38.8 (2)	C(4)-Fe-C(5)	38.6 (3)
C(2)-Fe-C(3)	38.8 (3)	C(5)-Fe-C(1)	38.6 (2)
C(3)-Fe-C(4)	39.8 (3)		
C(2)-C(1)-C(5)	106.8 (6)	C(4)-C(5)-C(6)	127.6 (7)
C(2)-C(1)-C(10)	126.5 (6)	C(5)-C(6)-C(7)	123.9 (7)
C(5)-C(1)-C(10)	126.0 (6)	C(6)-C(7)-C(8)	125.8 (7)
C(1)-C(2)-C(3)	108.9 (6)	C(7)-C(8)-C(9)	128.7 (7)
C(2)-C(3)-C(4)	108.6 (7)	C(8)-C(9)-C(10)	124.1 (7)
C(3)-C(4)-C(5)	107.6 (7)	C(1)-C(10)-C(9)	106.2 (5)
C(1)-C(5)-C(4)	108.0 (6)	C(1)-C(10)-C'(10)	120.3 (4)
C(1)-C(5)-C(6)	124.1 (6)	C(9)-C(10)-C'(10)	106.6 (5)

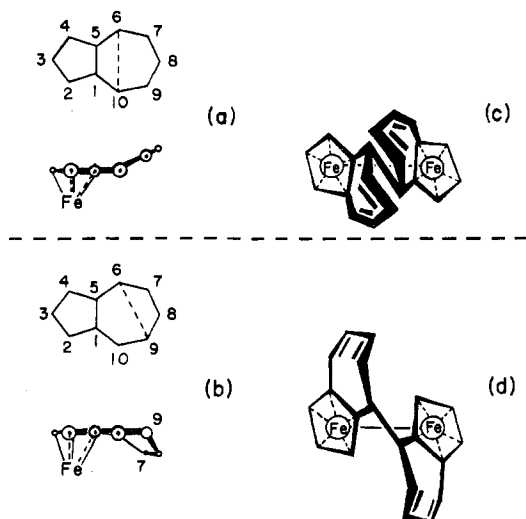


Figure 2. Some comparative aspects of the conformations of compounds 8 and 9. (a) and (c) represent, respectively, the ring folding and the internal twist for compound 8. (b) and (d) represent the same features for compound 9. These diagrams are schematic rather than precisely quantitative and are simplified slightly to afford a clearer indication of the features of interest.

there are definite conformational differences. The Fe-Fe' distances in the two compounds differ by only 1.6 times the sum of their individual esd's.

The important differences between the structures of 8 and 9 are the following. In 8 the seven-membered ring forms roughly (not exactly) two planes. One, consisting of carbon atoms 6, 5, 1, and 10, is coplanar with the cyclopentadienyl ring, while the other, consisting of carbon atoms 6, 7, 8, 9, and 10, is tilted *away from* the iron atom to which the η^5 -C₅H₅ ring is bound. This is indicated in Figure 2a. In 9 there are again two planes defined by the seven-membered ring, but the fold line is different, passing through carbon atoms 6 and 9, rather than 6 and 10, and the outer plane is tilted *toward* the iron atom, as shown schematically in Figure 2b. In addition, the pattern of C-C distances in the seven-membered rings is quite different in the two compounds. In 8 there are two short distances separated by a longer one, 1.34, 1.45, and 1.32 Å, corresponding clearly to the double bonds in the butadiene portion of the ring, whereas in 9 the three corresponding distances have the values 1.43, 1.37, and 1.44 Å as a result of the attachment of the Fe(CO)₃ group. Finally, as shown schematically in Figure 2c and d, the configurations of the ligands, from one cyclopentadienyl group through the bridging carbon atoms to the other cyclopentadienyl group, are notably different in relation to the direction of the Fe-Fe bond.

Carbon-13 NMR Spectra. The spectra of compound 6 in the ¹³CO region are shown in Figure 3. At -48 °C the resonance for the terminal carbonyl groups is at 211.7 ppm

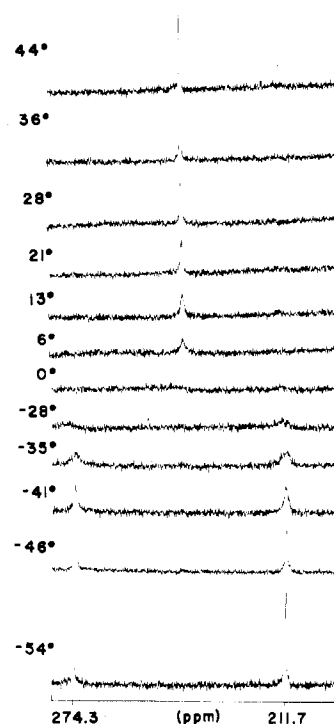


Figure 3. ¹³C NMR spectra in the CO region of (η^5 -C₅H₅C-(CH₃)₂C(CH₃)₂- η^5 -C₅H₄)Fe₂(CO)₄ (compound 6) at temperatures from -54 to +44 °C; solvent is 1:1 CDCl₃-CH₂Cl₂.

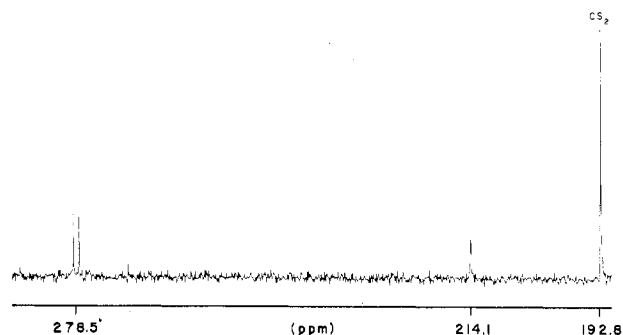


Figure 4. ¹³C NMR spectrum in the CO region of (η^5 -C₅H₄C-(CH₃)₂C(CH₃)₂- η^5 -C₅H₄)Fe₂(CO)₃P(OC₆H₅)₃ (compound 7) at 100 °C. CS₂ added as internal reference; solvent is toluene containing 20% toluene-*d*₆.

and that for the bridging carbonyl groups is at 274.3 ppm. A sharp single peak representing the averaged resonances of the four carbonyl groups appears at 242.8 ppm at temperatures above 36 °C. The free energy of activation for the exchange process may be estimated using the two-site exchange approximation.^{1,20} For the observed frequency separation of 1612 Hz and a coalescence temperature of ca. -10 °C, $\Delta G^{\ddagger}_{263} = 11 \pm 1.5$ kcal/mol which is equivalent to that found for (η^5 -C₅H₅)₂Fe₂(CO)₄.¹⁰

For compound 7, the ¹³C NMR spectrum in the CO region is invariant with temperature from 22 to 100 °C, except, perhaps, for slight changes in chemical shifts. Figure 4 shows the spectrum at 100 °C. The spectrum is consistent with the rigid *cis* structure in which there is one terminal CO group giving a resonance of relative intensity 1 at 214.1 ppm and two equivalent bridging CO groups giving rise to a resonance of relative intensity 2 at 278.5 ppm. The latter is split into a doublet by coupling to the phosphorus atom ($J_{P-C} = 24$ Hz).

For compound 8 the ¹³CO spectrum is shown in Figure 5. The bridge and terminal signals begin to broaden at about 20 °C and disappear into the noise at about 80 °C. It was not

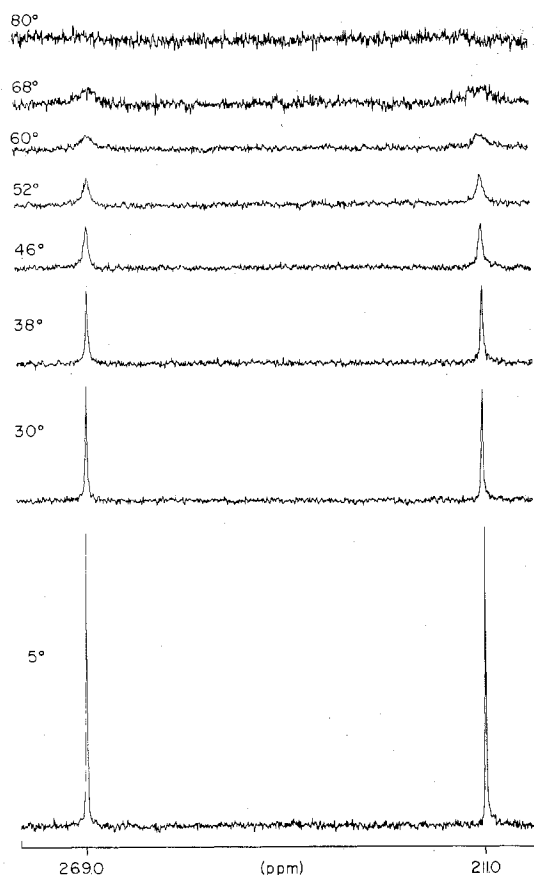


Figure 5. ^{13}C NMR spectra in the CO region of (diazulenyl) $\text{Fe}_2(\text{CO})_4$, compound 8, at temperatures from 5 to 80 °C. A sample (0.15 g) approximately 15% enriched in ^{13}C was dissolved in 2 ml of $\text{C}_2\text{H}_2\text{Cl}_4$ and 0.2 ml of toluene- d_6 .

possible to record spectra at higher temperatures due to the onset of thermal decomposition.

For compound 9, the ^{13}C CO spectra from room temperature to 65 °C are shown in Figure 6. The sharp signal at 210.4 ppm is due to the $\text{Fe}(\text{CO})_3$ groups and it is evident that the internal averaging within these groups is already very rapid at 22.0 °C. This is in keeping with previous results on (1,3-diene) $\text{Fe}(\text{CO})_3$ systems where coalescence temperatures of about -60 °C were found.^{21,22} The signals for the bridge and terminal CO groups of the $\text{Fe}_2(\text{CO})_4$ portion of the molecule broaden and collapse above room temperature. As nearly as can be judged, their behavior parallels that of the corresponding signals in compound 8, indicating that the rates in the two compounds 8 and 9 are essentially the same.

Infrared Spectrum of 7. The infrared spectra in the carbonyl stretching region of 7 and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ are shown in Figure 7a and b, respectively. Absorptions for the two compounds attributable to the antisymmetric stretch of bridging carbonyl groups occur at 1755 and 1751 cm^{-1} , respectively, while weaker peaks assignable to the symmetric stretching mode occur at 1789 and 1786 cm^{-1} , respectively. In the terminal carbonyl region 7 exhibits one strong stretch at 1968 cm^{-1} . Since the $-\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2-$ linkage constrains 7 to exist as the cis isomer, the strong bands at 1963 and 1943 cm^{-1} in Figure 7b may be assigned to *cis*- and *trans*- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\mu\text{-CO})_2(\text{CO})\text{P}(\text{OC}_6\text{H}_5)_3$, respectively. The weak peaks observable in Figure 7a at 1996 cm^{-1} and in Figure 7b at 1983 and 2030 cm^{-1} may be assigned to small amounts of nonbridged isomers present in solution, as has been proposed for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ itself.^{23,24} The two bridging absorptions for the *trans* isomer are not expected to differ much in frequency from those of the *cis* isomer and they should

be weaker. They are not, therefore, separately observed.

The *trans* to *cis* ratio of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\mu\text{-CO})_2(\text{CO})\text{P}(\text{OC}_6\text{H}_5)_3$ is therefore about 0.5, which is smaller than that found in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\mu\text{-CO})_2(\text{CO})_2$.¹ This is probably due to increased steric strain when a carbonyl ligand is replaced by the bulkier $\text{P}(\text{OC}_6\text{H}_5)_3$. This increase is greater for the *trans* isomer, where the repulsive intramolecular nonbonded contacts are between the $\text{P}(\text{OC}_6\text{H}_5)_3$ and the cyclopentadienyl ring on the opposite iron, than for the *cis* isomer, where the contacts are between the $\text{P}(\text{OC}_6\text{H}_5)_3$ and the remaining terminal carbonyl.

The result obtained by comparing the ir spectrum of 7 with that of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{P}(\text{O}^i\text{Pr})_3$, namely, that in the latter the *cis* isomer predominates, had been anticipated⁹ from preliminary data obtained on a similar compound in which the two $\eta^5\text{-C}_5\text{H}_5$ rings are also tied together by a two-carbon bridge.

Discussion

The mechanistic hypothesis proposed by Adams and Cotton³⁻⁷ to account for the fluxional behavior of 1, 2, and various derivatives thereof involves, first, the opening of bridges, second, internal rotation within nonbridged species, and third, re-formation of the bridges. Points of particular importance within this general scheme are the following.

(1) The process of bridge opening occurs in such a way as to lead directly to a staggered rotational conformation of the nonbridged form. For the *cis*-bridged isomer either of two enantiomorphous *gauche* rotamers would be initially formed, while for the *trans*-bridged isomer only the *anti* rotamer is directly accessible.

(2) For bridge-terminal exchange to occur in the *cis* isomer the initially formed *gauche* rotamer must execute an internal rotation which converts it into its *gauche* enantiomer. This may be achieved directly via a rotation by about $2\pi/3$ in which the two $\eta^5\text{-C}_5\text{H}_5$ groups must pass each other or, less directly, by a rotation of about $4\pi/3$, which has as its midpoint the *anti* rotamer. However, once the *anti* rotamer is reached, the *trans*-bridged isomer is directly accessible. Thus, if the barrier to the rotation of one *gauche* rotamer directly to the other (i.e., the $\sim 2\pi/3$ rotation) is as high or higher than that for rotation from a *gauche* to an *anti* conformation, then both CO scrambling within the *cis* isomer and *cis*-*trans* interconversion are predicted to have very similar if not identical activation energies. This is in accord with observation.^{2,10}

If there were another independent mechanism for bridge-terminal CO exchange in the *cis* isomer, with an activation energy as low as or lower than that for the one just discussed, one would expect to observe bridge-terminal exchange in the *cis* isomer occurring significantly more rapidly than *cis*-*trans* interconversion. This is not observed.

The rationale of the work reported here was to see if the behavior of compounds in which the two cyclopentadienyl rings are tied together, so as to make a *trans*-bridged structure as well as an *anti* rotamer of the nonbridged structure inaccessible, is in accord with that expected from the Adams and Cotton scheme. The literature recorded three compounds with the rings tied together, namely, 6, 9, and a compound similar to 6 but having $-\text{CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)-$ instead of $-\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2-$ as the chain connecting the two cyclopentadienyl rings.^{25,26} Since the latter was more complex than 6 but otherwise of no greater utility, we elected to prepare and study 6. As described below, a derivative of 6 in which one terminal carbonyl group is replaced by a ligand incapable of occupying a bridging position affords a clear mechanistic test and so compound 7 was prepared. As for compound 9, it was so cumbersome that we felt it advisable to try to prepare compound 8 in which the $\text{Fe}(\text{CO})_3$ addenda were not present. This has been done and 8 has been fully characterized

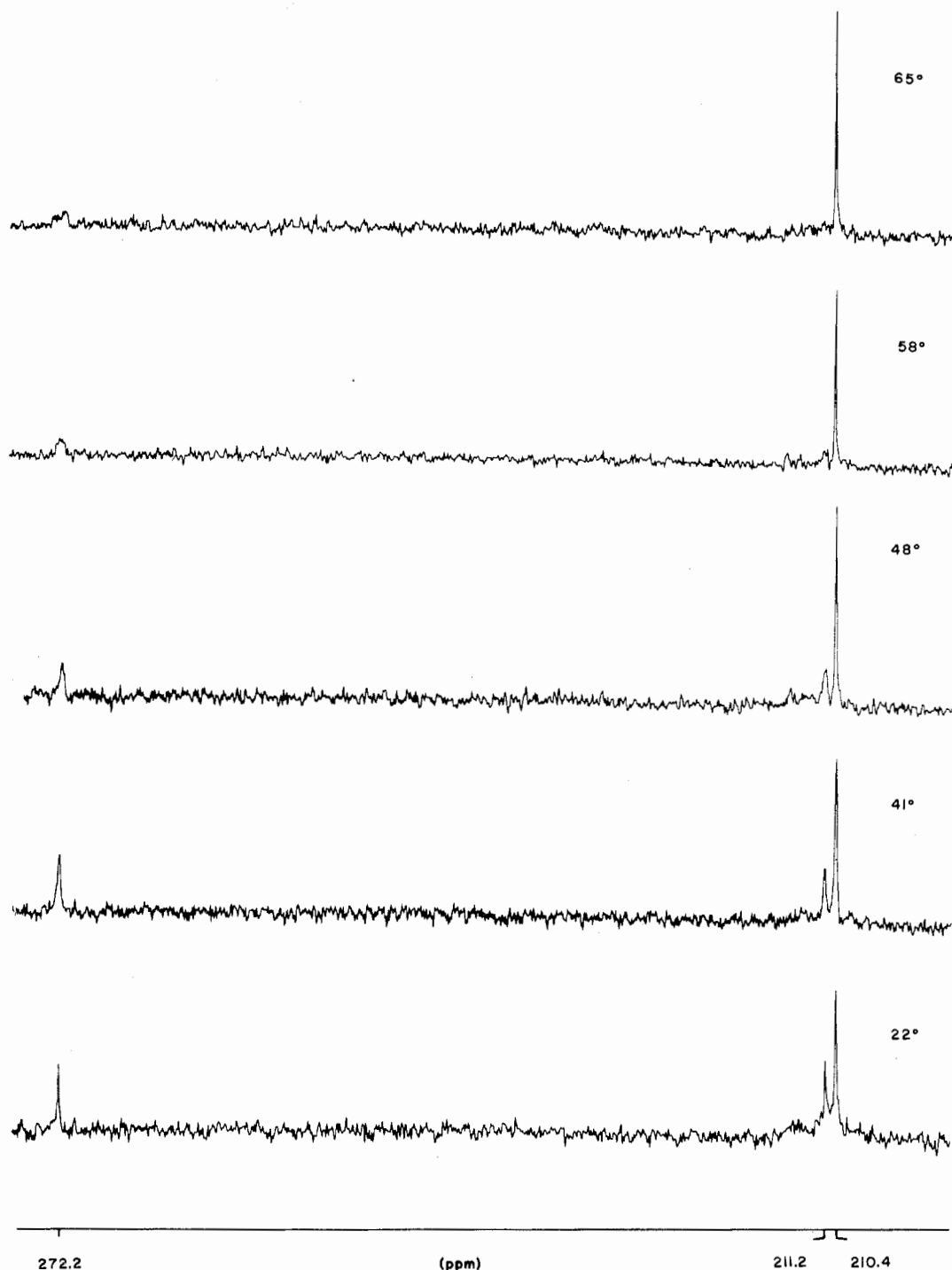


Figure 6. ^{13}C NMR spectra of compound 9 at temperatures from 22 to 65 °C.

structurally by means of x-ray crystallography.

The tying together of the rings, as in **6**, does not prevent bridge-terminal exchange in the cis isomer, but, as shown in Figure 8, it does restrict the available route, within the Adams-Cotton scheme, to that involving direct $2\pi/3$ type rotation. Thus, by examining a compound such as **6** we can determine whether this pathway is an effective one as compared to the alternative one in which there is a $4\pi/3$ rotation traversing the anti rotamer at its midpoint. As mentioned already, compound **6** does, in fact, engage in bridge-terminal exchange with an activation energy scarcely different from that previously found for **1**.

The fact that the bridge-terminal exchange process in **6** is not appreciably slower than that in **1** might seem surprising

from the point of view that in **6** rotation about the Fe-Fe bond must be accompanied by rotation about the bridging C-C bond, and some barrier to the latter rotation might be expected. However, this is not necessarily so since it is possible that in the most stable configuration of **6** there is partial eclipsing of the methyl groups of the bridge system so that any increase in rotational barrier per se would be offset by a decrease in the stability of the bridged ground state of the molecule relative to the nonbridged gauche form.

It is interesting that in **8**, where one of the two gauche forms of the nonbridged intermediate must be considerably more strained than the other, the process of bridge-terminal exchange is slowed considerably, but still proceeds rapidly enough to cause the lines to coalesce at a temperature (ca. 80 °C)

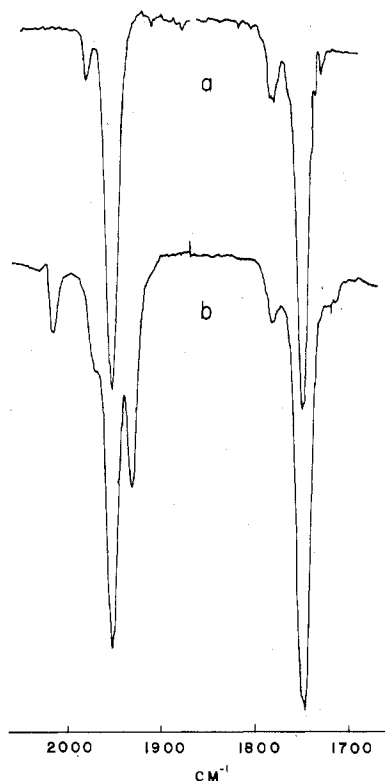


Figure 7. (a) Infrared spectrum of the CO stretching region of $(\eta^5\text{-C}_5\text{H}_4\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{-}\eta^5\text{-C}_5\text{H}_4)_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ (compound 7). (b) Infrared spectrum of the CO stretching region of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$.

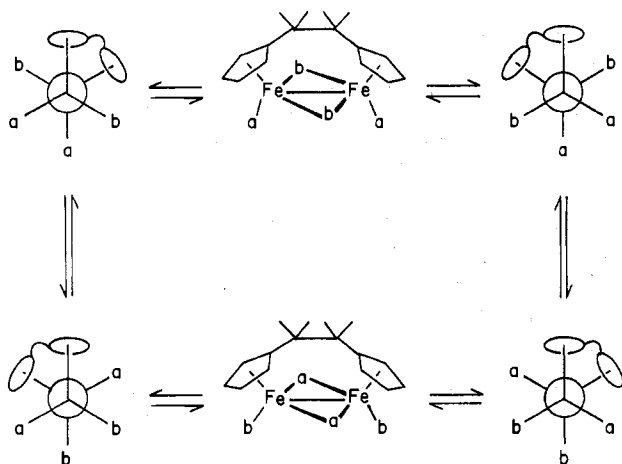


Figure 8. Rearrangements available to the carbonyl ligands of 6 according to the Adams-Cotton scheme.

below the temperature of decomposition. We estimate that the activation energy is raised by about 5 kcal/mol, relative to 1 and 6, based on the increase of about 80–100 °C in coalescence temperature and assuming that the frequency factors are the same in all cases.

Even though the affixing of two $\text{Fe}(\text{CO})_3$ groups to 8 so as to produce 9 causes noticeable changes in the conformation of the diazulenyl system and presumably rigidifies the seven-membered rings considerably, the rate of bridge-terminal exchange in 9 is essentially the same as that in 8. We had anticipated a higher activation energy in 9 compared to 8, but because of the complexity of these molecules no such prediction can be considered reliable and the actual result is in no way inconsistent with our views as to the mechanism.

The behavior of compound 7 affords very clear evidence for the view that in these iron-containing species only the Ad-

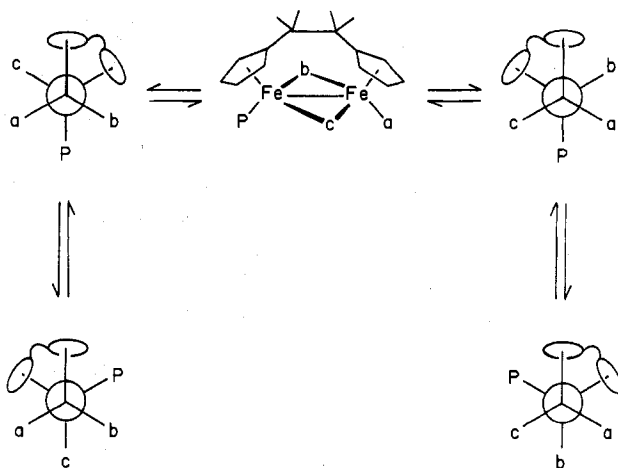


Figure 9. The Adams-Cotton scheme applied to compound 7. No path for carbonyl ligand scrambling is present.

ams-Cotton pathways for fluxionality are important. In a recent study⁹ of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{P}(\text{O}^i\text{Pr})_3$ further support was obtained for the mechanistic scheme of Adams and Cotton. The scheme predicts⁹ that for such a molecule, in which one of the ligands, $\text{P}(\text{O}^i\text{Pr})_3$, is incapable of occupying a bridging position, bridge-terminal exchange must occur via the anti rotamer of the nonbridged form, which, in turn, requires that bridge-terminal exchange and cis-trans isomerization must proceed with the same activation parameters. This was observed. A conclusion of particular importance was that any pathway allowing direct bridge-terminal exchange (such as simple 1 for 1 switches) must be appreciably slower. Compound 7 provides an opportunity to see if there is any alternative process for bridge-terminal exchange that is fast enough to be observed at all on the NMR time scale, even if it is not fast enough to be seen simultaneously with the Adams-Cotton pathway. As shown in Figure 9, it is completely impossible for this molecule to engage in bridge-terminal exchange within the scope of the Adams and Cotton mechanism. Both bridge opening processes leading to gauche rotamers are abortive, allowing only the restoration of the original bridges. The experimental result is that, up to 100 °C, not the slightest line broadening is observed for the ^{13}C O resonances of 7, whereas for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{P}(\text{O}^i\text{Pr})_3$ line broadening becomes evident at about -10 °C and just above 30 °C the bridge and terminal resonances have disappeared into the baseline. Clearly, in this set of diiron compounds²⁷ neither the 1 for 1 bridge-terminal switch process, nor any other process which is outside of the Adams-Cotton scheme, is effective enough to cause any observable line shape effects up to 100 °C.

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Registry No. 6, 57774-48-8; 7, 57774-49-9; 8, 57774-50-2; 9, 57774-51-3; $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$, 51056-17-8; $\text{Fe}(\text{CO})_5$, 13463-40-6; ω,ω -dimethylfulvene, 2175-91-9; triphenyl phosphate, 101-02-0; iron dodecacarbonyl, 17685-52-8; azulene, 275-51-4.

Supplementary Material Available: listing of structure factor amplitudes and Table IV showing root-mean-square amplitudes of vibration (7 pages). Ordering information is given on any current masthead page.

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Oxidation of Tris(*N,N*-disubstituted-dithiocarbamato) Complexes of Ruthenium(III). X-Ray Structure Determination of Bis(*N,N*-diethyldithiocarbamato)- μ -tris(*N,N*-diethyldithiocarbamato)-diruthenium(III) Tetrafluoroborate, $[\text{Ru}_2(\text{Et}_2\text{dtc})_5]\text{BF}_4$

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The products of the oxidation reaction of tris(*N,N*-disubstituted-dithiocarbamato)ruthenium(III), $\text{Ru}(\text{R}_2\text{dtc})_3$, with BF_3 gas open to the air have been characterized by standard analytical and spectroscopic means. The novel metal-containing product has the formula $[\text{Ru}_2(\text{R}_2\text{dtc})_5]\text{BF}_4$ and the crystal structure has been determined for R = ethyl by three-dimensional single-crystal x-ray analysis. The space group is *Pna*2₁ with lattice constants $a = 18.303$ (6) Å, $b = 20.713$ (9) Å, and $c = 12.416$ (5) Å. The structure was solved by conventional heavy-atom techniques and refined by least-squares methods to weighted and unweighted *R* factors of 0.089 and 0.095, respectively, for 2100 independent reflections. The density of 1.54 g/cm³ computed from the unit cell volume of 4707 Å³ on the basis of four $[\text{Ru}_2(\text{Et}_2\text{dtc})_5]\text{BF}_4 \cdot \text{C}_3\text{H}_6\text{O}$ molecules per unit cell agrees well with the 1.55 g/cm³ determined by flotation methods. The structure of the cation consists of a triply bridged diruthenium compound (see Figures 1–3) with a Ru–Ru distance of 2.743 (3) Å. This distance and the diamagnetism of the compound are consistent with a bond order equal to ~ 1 . The structure is novel because it is the first example where dithiocarbamate ligands connect two metals in both bridging fashions simultaneously. The mechanism of the oxidation reaction is discussed and compared to the analogous reaction of $\text{Fe}(\text{R}_2\text{dtc})_3$ which gives a monomeric tris-chelate complex of iron(IV). A thorough electrochemical study has also been carried out on $\text{Ru}(\text{R}_2\text{dtc})_3$ and $[\text{Ru}_2(\text{R}_2\text{dtc})_5]\text{BF}_4$ complexes.

Introduction

Recently it has been shown that the *N,N*-disubstituted-dithiocarbamato ligand, R_2dtc^- , can stabilize metals in unusually high oxidation states including Cu(III),¹ Ni(IV),^{1–4} Fe(IV),^{5–10} Mn(IV),^{11–13} Co(IV),^{5,13} Pd(IV),^{4,14} and Pt(IV).^{4,14} For example, the reaction of $\text{Fe}(\text{R}_2\text{dtc})_3$ complexes, where R = alkyl or aryl, with oxidizing agents such as $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ or BF_3 gas open to the air gives stable paramagnetic tris-chelate complexes of Fe(IV),^{5–10} $[\text{Fe}(\text{R}_2\text{dtc})_3]\text{X}$, where $\text{X}^- = \text{ClO}_4^-$ or BF_4^- , respectively. One of these Fe(IV) complexes, $\text{R}_2 = (\text{CH}_2)_4$, has been shown by x-ray crystallography⁸ to be monomeric with no evidence for intra- or interligand oxidation to a disulfide linkage. Similar results have been obtained for $\{\text{Mn}[(\text{CH}_2)_5\text{dtc}]_3\}\text{ClO}_4$ ^{11,12} and $\{\text{Ni}[(n\text{-C}_4\text{H}_9)_2\text{dtc}]_3\}\text{Br}_2$ by x-ray analysis.

The oxidation reaction using BF_3 gas under aerobic conditions has very recently been carried out on $\text{M}(\text{R}_2\text{dtc})_3$ complexes of Co(III), Rh(III), and Ru(III) to give diamagnetic products.¹⁵ Monomeric tris-chelate complexes of Co(IV) and Rh(IV) (d^5), and Ru(IV) (d^4) are expected to be paramagnetic. Indeed, a recent report¹³ claims evidence for $[\text{Co}(\text{R}_2\text{dtc})_3]\text{BF}_4$ where R = cyclohexyl which has a

magnetic moment of 3.48 BM.¹⁶ It is now firmly established that the diamagnetic cobalt oxidation product has the stoichiometry $[\text{Co}_2(\text{R}_2\text{dtc})_5]\text{BF}_4$ and that the diamagnetism results from the low-spin d^6 Co(III) ion.¹⁷ The rhodium and ruthenium complexes presumably have the same stoichiometry. It is interesting that with these metals the ligand and not the metal is oxidized. A recent polarographic study¹⁸ showed that the one-electron oxidation half-wave potentials for $\text{M}(\text{Et}_2\text{dtc})_3$ ¹⁹ in DMF where M = Fe(III) and Ru(III) are +0.423 and +0.382 V vs. sce, respectively. In view of the similarity of these potentials and the apparent difference in the structures of oxidation product, $[\text{Fe}(\text{Et}_2\text{dtc})_3]\text{BF}_4$ vs. $[\text{Ru}_2(\text{Et}_2\text{dtc})_5]\text{BF}_4$, a complete characterization and x-ray investigation of the ruthenium oxidation product have been carried out. A preliminary account of this work has been published.²⁰

Experimental Section

Synthesis of $[\text{Ru}_2(\text{R}_2\text{dtc})_5]\text{BF}_4$ Complexes. The complexes with R = methyl, ethyl, or benzyl and $\text{R}_2 = \text{pyrrolidyl}$ were synthesized by oxidation of the respective tris chelates, $\text{Ru}(\text{R}_2\text{dtc})_3$, according to the method of Pasek and Straub.⁵ For example, boron trifluoride gas was slowly bubbled through a benzene solution of $\text{Ru}(\text{Et}_2\text{dtc})_3$ ²¹