A Carbon-13 Nuclear Magnetic Resonance Study of the Fluxional Character of the η^6-(Bicyclo[6.2.0]dodeca-2,4,6-triene)hexacarbonyldiiron(*Fe–Fe*) and a Triethylphosphine Derivative Thereof, and the Crystal Structure of the Latter

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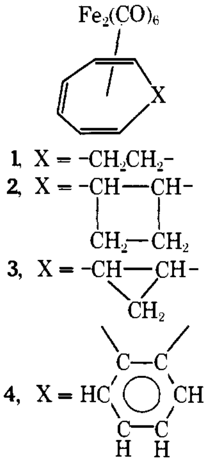
Abstract: The ^{13}C NMR spectrum of the title compound (**2**) has been recorded at various temperatures from −120 to 102°. The four resonances for the eight-membered ring which are observed at room temperature broaden at −30° and are totally collapsed at about −85°; solubility problems precluded further study of these signals. The carbonyl carbon resonances were observed using enriched samples. The six-line spectrum expected from the crystal structure is observed at −120°. Four lines collapse and disappear into the base line between −120 and −88°. From −88 to −50° these four and one other signal re-form into two signals of relative intensities 2:3. From ca. −50 to +102° the signal of intensity 2 and the previously unbroadened signal of intensity 1 collapse and re-form as a signal of intensity 3, while the signal of intensity 3 which was present at −50° sharpens. These changes can be understood in terms of a twitching process of the $Fe_2(CO)_6$ group relative to $C_{10}H_{12}$ ligand followed by local averaging in one $Fe(CO)_3$ group, followed by averaging within the other $Fe(CO)_3$ group. No gliding motion or internuclear exchange of CO groups is allowed. The interpretation here is the same as that given previously for $(C_8H_{10})Fe_2(CO)_6$ (**1**), but the interpretation is more straightforward because there is less overlap of the three processes. Moreover, by comparison of the slow exchange limit spectra of **1** and **2** a partial assignment can be made which is sufficient to allow an unequivocal determination that local scrambling occurs first about the allyl-bound iron atom. This point remained uncertain on the basis of data for **1** alone. The molecule $(C_{10}H_{12})Fe_2(CO)_5PEt_3$ was prepared and the position of the PEt_3 ascertained by X-ray crystallography. From its ^{13}C spectrum still further information is obtained which confirms all of the previous conclusions.

Although the structural and dynamical properties of molecules of the general type **1–5** have been studied for a number of years, a complete and definitive understanding of their fluxional behavior has not yet been achieved.[1] The crystal structures of four of them, namely **1**,[2] **2**,[3] **3**,[4] and **5**[5] have been determined and there is considerable NMR data available.[3,5,6-8] For **5**, the cycloheptatrienyl compound, the structure observed in the crystal has a plane of symmetry, as shown in Figure 1a. Thus, the facts that the proton NMR spectrum is invariant from room temperature to −100° and consistent with a structure having a plane of symmetry could be easily explained by assuming that this molecule is not fluxional and merely retains in solution the static structure it has in the crystal. It is known[9] that the nonequivalent CO groups, which give three separate ^{13}C resonances below −55°, are NMR equivalent at and above about 12°. It has not yet been proved whether this CO scrambling occurs locally within each $Fe(CO)_3$ group or involves passage of CO groups from one metal atom to the other, although there is indirect evidence favoring the former. It may also be noted that a 180° rotation of the entire $Fe_2(CO)_6$ group so as to give end-for-end exchange is not ruled out by any data presently available. Thus, for compound **5** several key points remain to be investigated; this compound will not be considered further at this time.



1, $X = -CH_2CH_2-$

2, $X = -CH{-}CH-$ ($CH_2{-}CH_2$)

3, $X = -CH{-}CH-$ (CH_2)

4, $X = $ HC CH, C–C, C–C, H H

5, $X = -CH_2-$

For compounds **1–3**, skew structures, Figure 1b, were found in the crystal. NMR data for the ring protons showed that motion of the ring relative to the $Fe_2(CO)_6$ group causes interconversion between the two enantiomorphous structures (Figure 1b and 1c) of this type. When this motion is rapid, as it is at room temperature for all of the compounds **1–4**, the molecules appear to have a plane of symmetry according to their NMR spectra.

Although, at first, it seemed "obvious" that a twitching motion would be the rearrangement pathway, it soon became evident[5] that a gliding motion, which would interchange the two ends of the $Fe_2(CO)_6$ unit, was also a plausible possibility. It was noted[5] that only by NMR study of the $Fe_2(CO)_6$ group itself, most likely by ^{13}C spectroscopy, could this question be resolved.

Such an investigation was first undertaken[10] on compound **1**. The low-temperature spectrum (at and below −75°) contained the expected six carbonyl carbon atom resonances and eight signals due to the ring carbon atoms. Raising of the temperature caused simultaneous collapse of the peaks due to the CO groups as well as those for the eight ring carbon atoms. At a temperature of −35° there was a signal for one CO group that had not averaged, and by +8° a 1:3:2 set was observed in the carbonyl region. A further increase in temperature caused averaging of the 1:2 portion of the set so that at +110° (above which tempera-

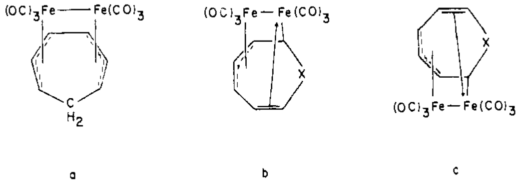


Figure 1. Schematic representation of the structures of (a) $(C_7H_8)Fe_2(CO)_6$ (**5**) and, (b and c) the enantiomorphs of molecules **1–4**.

ture decomposition occurred) two distinct, equally intense signals, attributable to averaging within each set of three CO groups, were observed.

These data allowed several rigorous conclusions to be drawn concerning **1**. The two carbonyl signals observed in the high temperature spectrum show that the two ends of the $(OC)_3FeFe(CO)_3$ moiety do not exchange environments nor do CO ligands pass from one metal to the other. Instead, site exchange of the CO groups on each metal atom is taking place as has been reported previously for other molecules.[9]

The twitching process was firmly established since a glide when coupled with the internal scrambling of the CO groups about each iron atom would equilibrate all six CO groups to yield only one peak at high temperatures. Thus, from the carbon-13 NMR of compound **1**, the nature of the relative motion of the $Fe_2(CO)_6$ moiety to the ring was demonstrated, but in doing so several new questions concerning the fluxional processes in the carbonyl portions of the molecule were brought into focus.

To allow a more detailed elucidation of the dynamic processes involved, a study has been made of *cis*-(1,2,6-η^3:3,4,5-η^3-bicyclo[6.2.0]deca-1,3,5-triene)hexacarbonyldiiron(*Fe–Fe*), $(C_{10}H_{12})Fe_2(CO)_6$ (**2**), and the triethylphosphine substituted molecule *cis*-(1,2,6-η^3:3,4,5-η^3-bicyclo[6.2.0]deca-1,3,5-triene)pentacarbonyltriethylphosphinediiron(*Fe–Fe*), $(C_{10}H_{12})Fe_2(CO)_5(PEt_3)$ (**6**). The results and interpretation of that study are reported here.

Experimental Section

Synthesis. Compounds **2** and **6** in the solid form are stable in air. To avoid slight decomposition that was sometimes observed in solution, the solvents were stored over Na-K alloy with benzophenone present and distilled just prior to use.

Complex **2** was prepared by literature methods[11] as well as by following the same procedure and substituting tetrahydrofuran as the solvent.[12] Diethyl ether proved to be the better solvent since it gave yields of 25% as compared to 2% when THF was employed. Quantitative data were not obtained, but it was obvious during the column chromatography step that minor products that are obtained[11] were more favored when the reaction was run in THF as compared to diethyl ether.

The phosphine substituted compound **6** was prepared by refluxing 100 mg (0.24 mmol) of **2** with 0.015 ml (0.1 mmol) of triethylphosphine in dry hexane for 3 hr under N_2. The color of the solution darkened, from an orange-red to a dark red. The solution was concentrated in vacuo, dissolved in a small portion of hexane, and charged to an alumina column (Woelm, activity grade II, 1.25 × 43 cm). The column was washed with hexane, and the compounds remained at the top. Elution with 1:2 ether:hexane gave poor resolution of trace amounts of a yellow and an orange-red compound. No attempt was made to identify these compounds. Continued elution with ether-hexane yielded a large orange band. This solution was concentrated and the residue recrystallized at −78° from hexane to give 55 mg, 45% yield, mp 134–135°. The infrared spectrum in CS_2 contained bands at 2010 s, 1969 s, 1959 s, 1940 sh, and 1917 m cm^{-1}. Crystals suitable for X-ray crystallographic studies were grown slowly from a dilute hexane solution at 0°.

A sample of **2** with carbon-13 enrichment in the carbonyl groups (>20%) was prepared by photolytically induced substitution of ^{13}CO in hexane solution. To obtain the enriched phosphine substituted molecule **6**, the preparation of **6** was carried out using an enriched sample of **2**.

Table I. Crystal Data for $(C_{10}H_{12})Fe_2(CO)_5(PET_3)$

a	13.744 (8) Å	Space group $P2_12_12_1$	
b	13.730 (5) Å	Mo Kα radiation (0.71073 Å)	
c	11.922 (7) Å	$Z = 4$	
V	2249.7 (3.5) Å^3	$\mu = 14.2$ cm^{-1}	
d_{calcd}	1.48 g cm^{-3}	$d_{obsd} = 1.48$ g cm^{-3}	

Spectroscopic Measurements. The infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The carbon-13 NMR spectra were measured on a Jeol PFT 100/Nicolet 1080 Fourier transform spectrometer at 25.036 MHz. A sweep width of 5600 Hz, a tilt angle of 49°, and a repetition rate of 1.1 sec were employed. The solvents were freeze-thaw degassed using Schlenk technique. The sample was dissolved and the solution then filtered into a 10-mm diameter NMR tube fitted with a serum stopper. The spectra below ambient temperature were obtained in CH_2Cl_2 with CD_2Cl_2 (15%) furnishing a deuterium internal lock and CS_2 (10%) serving as a reference. Below the temperature where this solution began freezing, ca. −95°, $CHClF_2$ (~50% by volume) was added to lower the freezing point of the solvent. The spectra above ambient temperatures for molecule **2** were recorded in *o*-dichlorobenzene with toluene-d_8 (15%) for internal lock and reference. A minimal quantity of $Cr(acac)_3$,[13] 0.5–1.0 mg, was added to each tube to aid in the relaxation of the carbonyl carbon atoms. The variable temperature unit was calibrated by placing a copper-constantan thermocouple in an NMR tube containing an appropriate solvent inside the probe. The temperature was read from a Leeds and Northup Model 913 digital thermometer and was constant to ±2°.

Collection of X-Ray Data. A well-formed red-orange crystal of **6**, measuring approximately 0.3 × 0.3 × 0.3 mm, was selected for data collection and mounted in a glass capillary. Preliminary examination on the diffractometer showed the crystal to be orthorhombic with the near equivalence of axes *a* and *b* being accidental. Cell constants and the orientation matrix for data collection were determined from least-squares refinement of the setting angles for 15 reflections. These dimensions and other crystal data are given in Table I. Several strong reflections showed peaks with a width at half-height of 0.2° on ω scans. Data were collected at 22° with Mo Kα radiation on a Syntex P$\bar{1}$ computer-controlled four-circle diffractometer, equipped with a graphite-crystal monochromator in the incident beam. The θ–2θ scan technique with a variable scan rate from 4.0 to 24.0°/min and a scan range from 0.9° before Mo Kα_1 to 0.9° after Mo Kα_2 was used to collect 2272 independent data up to a maximum 2θ value of 50°.

The intensities of three reflections were measured every 100 reflections as a check on crystal and electronic stability. These showed no significant variation. A correction for Lorentz and polarization factors was applied to the data. A listing of computer programs used in data reduction and in the solution and initial structure refinement has been given elsewhere.[14] No absorption corrections were made to the data. In the final refinement those 1910 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used. The parameter p^3 used in the calculation of standard deviations was set equal to 0.06. The observed systematic absences in the data, $h00$ ($h \neq 2n$), $0k0$ ($k \neq 2n$), and $00l$ ($l \neq 2n$) uniquely define the space group as $P2_12_12_1$.

Solution and Refinement of the Structure. An attempt was first made to solve the structure using conventional Patterson techniques, but unsatisfactory solutions for the two iron atoms and the phosphorus atom were obtained. Normalized structure factors (E's) were then computed using the program FAME. The 32 starting phase sets were chosen automatically using the program MULTAN which combines the cyclic application of the tangent formula with multisolution techniques employing the 265 reflections with E's greater than 1.50. From the 32 phase sets generated, the set showing the best figures of merit was used to generate an E map. The positions of the phosphorus and two iron atoms were the top peaks on the E map and their positions were refined by two cycles of full-matrix least squares to give the agreement factors[3] $R_1 = 0.359$ and $R_2 = 0.478$. Scattering factors were taken from the International Tables.[15] Anomalous dispersion effects for the Fe and

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations

Atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Fe(1)	0.50181 (7)	0.15578 (6)	0.18764 (8)	0.00375 (4)	0.00346 (5)	0.00438 (6)	0.00055 (9)	0.0005 (1)	0.0007 (1)
Fe(2)	0.56717 (7)	0.18658 (7)	0.96769 (8)	0.00377 (4)	0.00373 (5)	0.00477 (6)	0.00014 (10)	0.0006 (1)	0.0010 (1)
P	0.4476 (1)	0.1156 (1)	0.3568 (2)	0.0058 (1)	0.0040 (1)	0.0049 (1)	0.0027 (2)	0.0024 (2)	0.0020 (2)
O(1)	0.3435 (4)	0.2948 (4)	0.1782 (6)	0.0076 (3)	0.0090 (4)	0.0118 (6)	0.0125 (5)	0.0016 (8)	0.0068 (9)
O(2)	0.6438 (4)	0.2924 (5)	0.2770 (6)	0.0069 (3)	0.0077 (4)	0.0141 (7)	−0.0056 (7)	−0.0028 (8)	−0.0066 (9)
O(3)	0.4013 (4)	0.3169 (4)	−0.0553 (6)	0.0069 (3)	0.0084 (4)	0.0111 (5)	0.0082 (6)	0.0007 (8)	0.0091 (8)
O(4)	0.7090 (4)	0.3379 (4)	0.0113 (6)	0.0078 (4)	0.0054 (3)	0.0158 (8)	−0.0044 (6)	0.0031 (9)	−0.0027 (9)
O(5)	0.6059 (5)	0.2090 (5)	0.7284 (5)	0.0141 (5)	0.0082 (5)	0.0065 (5)	−0.0024 (9)	0.0027 (9)	0.0012 (8)
C(11)	0.4020 (6)	0.2381 (6)	0.1760 (7)	0.0067 (5)	0.0054 (4)	0.0054 (5)	−0.0011 (8)	−0.0009 (9)	0.0036 (9)
C(12)	0.5884 (6)	0.2364 (6)	0.2415 (7)	0.0065 (5)	0.0057 (5)	0.0066 (6)	0.0002 (9)	0.0018 (10)	0.0009 (10)
C(21)	0.4652 (5)	0.2691 (6)	−0.0372 (7)	0.0049 (4)	0.0074 (5)	0.0056 (5)	0.0020 (8)	0.0023 (8)	0.0042 (18)
C(22)	0.6572 (5)	0.2810 (5)	0.9982 (6)	0.0048 (4)	0.0043 (4)	0.0069 (6)	−0.0021 (7)	0.0033 (8)	−0.0013 (9)
C(23)	0.5885 (6)	0.1952 (6)	0.8227 (7)	0.0063 (5)	0.0055 (5)	0.0055 (5)	−0.0007 (9)	0.0001 (9)	0.0008 (10)
C(1)	0.5070 (5)	0.9812 (6)	0.8993 (6)	0.0041 (4)	0.0054 (4)	0.0068 (5)	−0.0007 (8)	−0.0006 (9)	−0.0012 (9)
C(2)	0.4644 (4)	0.0763 (5)	−0.0408 (7)	0.0031 (3)	0.0042 (4)	0.0063 (5)	−0.0009 (6)	−0.0004 (7)	−0.0002 (9)
C(3)	0.4406 (5)	0.0496 (5)	0.0761 (5)	0.0039 (3)	0.0033 (3)	0.0065 (5)	−0.0025 (7)	0.0004 (8)	−0.0007 (7)
C(4)	0.5083 (5)	0.0103 (5)	0.1536 (5)	0.0050 (4)	0.0036 (4)	0.0056 (5)	0.0005 (7)	0.0015 (8)	−0.0003 (7)
C(5)	0.6048 (5)	0.0427 (5)	0.1611 (6)	0.0049 (4)	0.0037 (4)	0.0052 (5)	0.0012 (7)	0.0004 (7)	−0.0021 (9)
C(6)	0.6613 (4)	0.0879 (5)	0.0739 (6)	0.0033 (3)	0.0046 (4)	0.0061 (5)	0.0007 (7)	−0.0017 (7)	−0.0004 (9)
C(7)	0.6672 (5)	0.0647 (5)	0.9594 (7)	0.0043 (4)	0.0050 (4)	0.0062 (5)	0.0001 (7)	−0.0011 (9)	−0.0002 (10)
C(8)	0.6213 (5)	0.9749 (6)	0.9130 (5)	0.0038 (3)	0.0051 (4)	0.0045 (5)	−0.0002 (7)	0.0019 (7)	−0.0021 (8)
C(9)	0.6308 (5)	0.9664 (7)	0.7798 (7)	0.0046 (4)	0.0081 (6)	0.0065 (6)	0.0019 (9)	0.0015 (9)	−0.0035 (11)
C(10)	0.5179 (6)	0.9844 (7)	0.7703 (6)	0.0052 (5)	0.0077 (5)	0.0057 (5)	−0.0011 (9)	0.0004 (9)	−0.0049 (9)
C(1P)	0.3361 (7)	0.0411 (6)	0.3562 (8)	0.0090 (6)	0.0060 (5)	0.0090 (7)	−0.0005 (11)	0.0033 (12)	0.0041 (11)
C(2P)	0.4153 (7)	0.2195 (6)	0.4477 (7)	0.0136 (7)	0.0056 (5)	0.0047 (5)	0.0056 (11)	0.0072 (11)	−0.0013 (9)
C(3P)	0.5320 (6)	0.0462 (7)	0.4432 (7)	0.0094 (6)	0.0083 (6)	0.0070 (6)	0.0083 (10)	0.0023 (11)	0.0043 (11)
C(4P)	0.2460 (7)	0.0767 (10)	0.3065 (10)	0.0060 (6)	0.0216 (14)	0.0140 (10)	−0.0019 (18)	0.0039 (15)	0.0122 (25)
C(5P)	0.3723 (7)	0.1957 (8)	0.5610 (8)	0.0126 (7)	0.0075 (7)	0.0083 (13)	0.0801 (13)	0.0093 (12)	0.0001 (13)
C(6P)	0.6240 (6)	0.0937 (9)	0.4757 (8)	0.0078 (6)	0.0170 (11)	0.0876 (8)	0.0054 (15)	−0.0042 (12)	−0.0006 (13)

P atoms were included in the calculated structure factors using $\Delta f'$ and $\Delta f''$ values given by Cromer and Liberman.[16]

A series of two successive difference Fourier maps allowed location of all non-hydrogen atoms except the methyl carbon atoms in triethylphosphine. Two cycles of refinement with the P and two Fe atoms allowed to vary anisotropically yielded discrepancy indices $R_1 = 0.099$ and $R_2 = 0.147$ after which a difference map revealed positions for the remaining non-hydrogen atoms. Two more cycles of least-squares refinement employing isotropic thermal parameter for all except the P and Fe atoms as above gave R values of $R_1 = 0.062$ and $R_2 = 0.090$.

An anisotropic refinement of all non-hydrogen atoms was completed using the PDP 11/45 computer and software at the Molecular Structure Corporation.[17] Following four cycles of full-matrix least-squares refinement the refinement was completely converged with no parameter shift exceeding 0.15 times the standard deviation in the parameter. The final agreement indices were $R_1 = 0.049$ and $R_2 = 0.067$ with the esd in an observation of unit weight equal to 1.73.

No systematic trends were observed in the data as a function of $\lambda^{-1} \sin \theta$, $|F_o|$, Miller indices, or reflection number. The primary purpose in obtaining the X-ray crystal structure was to determine which carbonyl group the phosphine ligand had replaced. With this goal satisfied and considering the excellent agreement for the calculated and observed density no attempt was made to locate the hydrogen atoms. The atomic coordinates and the anisotropic thermal parameters are given in Table II. Structure factors for $(C_{10}H_{12})Fe_2(CO)_5(PEt_3)$ are available elsewhere.[18]

Results

$(C_{10}H_{12})Fe_2(CO)_6$. The spectrum in the region of the ring carbon atoms was not studied in detail, because of the combination of low solubility and the impracticability of preparing a suitably enriched sample. However, spectra recorded between 25 and −84° indicate that pairwise averaging of the ring carbon atoms, rather than a static plane of symmetry, is, as previously proposed,[3] the reason why only five, equally intense signals are observed at room temperature.[19] The four signals which may be assigned to carbon atoms of the eight-membered ring[19] are observed to broaden below −30°. At −84° they have disappeared into the baseline. The upfield signal, which is due to the two carbon atoms that complete the four-membered ring, only begins to show appreciable broadening at −84°. This is presumably because there is only a small chemical shift difference between the two signals which would occur in the slow exchange limit that would average to the upfield signal above −84°.

The carbon-13 NMR spectra in the carbonyl region of the unsubstituted molecule **2** are shown in Figure 2. The chemical shifts measured downfield from CS_2 are indicated on the figure. The spectrum at −120° is consistent with the ground state structure established by X-ray crystallography[3] which requires the presence of six signals of equal intensity.

The use of selective line shape changes to provide mechanistic information is well established.[1] The changes within the CO group resonances as the temperature is raised indicated that several processes are occurring. As the solution is warmed, at first only four of the six lines collapse. They do so uniformly, and at −88° only the signals at 26.5 and 17.7 ppm remain. This shows that from −120 to −88° a process which causes only four CO groups to undergo site exchange is accelerating.

As the temperature is raised from −88 to −30° the peak at 17.7 ppm also collapses and by −50° two discrete new peaks have appeared, one of relative intensity 3 at 19.0 ppm and the other of intensity 2 at 18.3 ppm. The resonance at 19.0 ppm is fully sharpened by −14°, whereas the peak at 18.3 never becomes fully sharpened. The two signals at 26.2 and 18.3 ppm are completely collapsed at around room temperature. At 30° only a single peak is observed, at 19.0 ppm, as reported by Deganello.[19]

The spectra above room temperature were obtained with a sample that contained naturally abundant ^{13}CO groups to avoid decomposition of the enriched sample. Thus, the signal to noise ratio is poorer. Nevertheless, as seen in the 90 and 102° spectra (above which temperature decomposition precluded further study), a second signal appears at 20.5 ppm, with an integrated intensity about equal to that of the signal at 19.0 ppm.

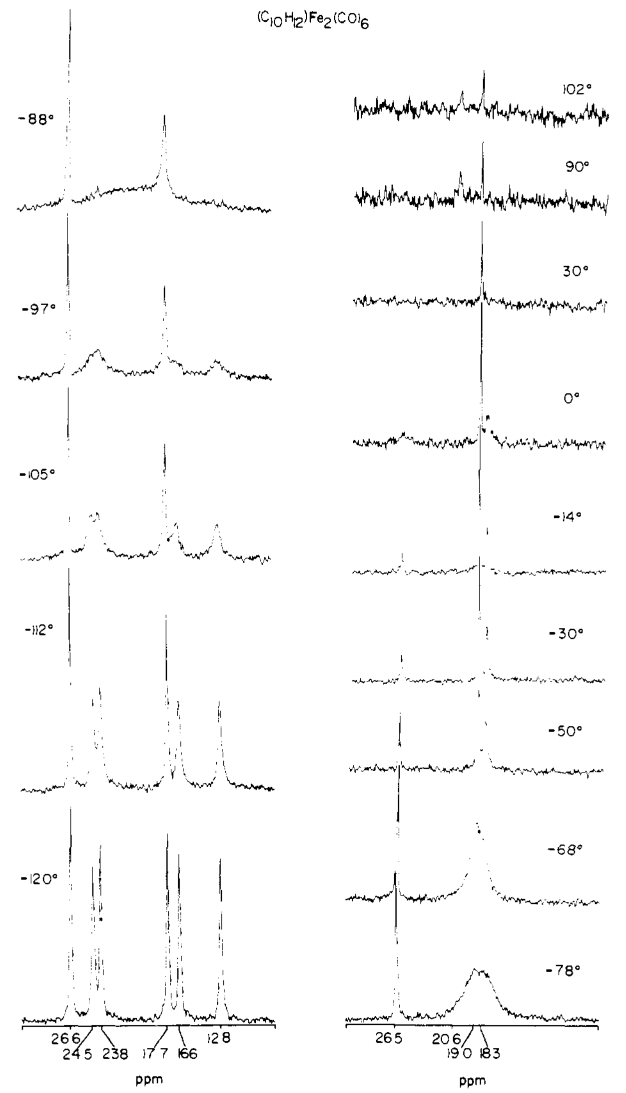


Figure 2. The ^{13}C spectra in the carbonyl region for $(C_{10}H_{12})Fe_2(CO)_6$ at various temperatures from −120 to +102°.

Table III. Bond Lengths (Å) for $(C_{10}H_{12})Fe_2(CO)_5(PEt_3)$

Fe(1)–Fe(2)	2.804 (1)	C(1)–O(1)	1.119 (8)
Fe(1)–P	2.220 (2)	C(12)–O(2)	1.161 (9)
Fe(1)–C(11)	1.783 (8)	C(21)–O(3)	1.117 (8)
Fe(1)–C(12)	1.784 (8)	C(22)–O(4)	1.068 (8)
Fe(1)–C(3)	2.145 (6)	C(23)–O(5)	1.164 (9)
Fe(1)–C(4)	2.040 (6)	P–C(1P)	1.842 (9)
Fe(1)–C(5)	2.125 (6)	P–C(2P)	1.845 (7)
Fe(2)–C(21)	1.804 (7)	P–C(3P)	1.821 (8)
Fe(2)–C(22)	1.829 (7)	C(1P)–C(4P)	1.46 (1)
Fe(2)–C(23)	1.757 (7)	C(2P)–C(5P)	1.51 (1)
Fe(2)–C(2)	2.073 (6)	C(3P)–C(6P)	1.48 (1)
Fe(2)–C(6)	2.261 (6)	C(5)–C(6)	1.438 (9)
Fe(2)–C(7)	2.167 (6)	C(6)–C(7)	1.404 (9)
C(1)–C(2)	1.600 (9)	C(7)–C(8)	1.492 (9)
C(1)–C(8)	1.581 (9)	C(8)–C(9)	1.597 (9)
C(1)–C(10)	1.55 (1)	C(9)–C(10)	1.575 (9)
C(2)–C(3)	1.478 (9)		
C(3)–C(4)	1.417 (9)		
C(4)–C(5)	1.403 (9)		

$(C_{10}H_{12})Fe_2(CO)_5PEt_3$. The structure of this molecule, as determined X-ray crystallographically, is shown in Figure 3. Bond lengths and angles are listed in Tables III and IV, respectively, and some least-squares planes are presented in Table V. The structure is qualitatively the same as that of $(C_{10}H_{12})Fe_2(CO)_6$[3] except for the presence of PEt_3 in place of one CO ligand. The site of substitution is seen to be that labeled a in Schemes I and II. The bond distances pertaining to the eight-membered ring and its attachment to the iron atoms are very similar to those found in compounds **1** and **2** (see Figure 4) and, insofar as possible, to those in $(C_8H_8)Ru_2(CO)_6$.[20]

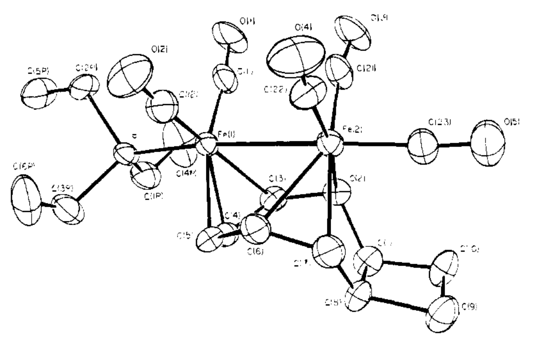


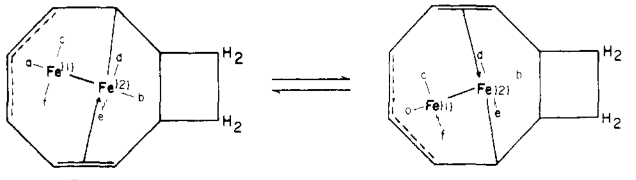
Figure 3. An ORTEP drawing of the molecular structure of compound **6**, $(C_{10}H_{12})Fe_2(CO)_5PEt_3$. Ellipsoids enclose 40% of the electron density and the numbering scheme used in the tables of crystallographic results is defined.

Table IV. Selected Bond Angles (deg) for $(C_{10}H_{12})Fe_2(CO)_5(PEt_3)$

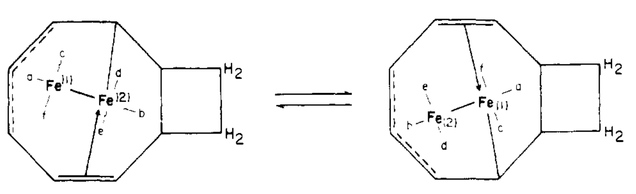
Fe(2)–Fe(1)–P	174.14 (6)	C(6)–Fe(2)–C(7)	36.9 (2)
Fe(2)–Fe(1)–C(11)	94.5 (2)	Fe(1)–P–C(1P)	114.4 (3)
Fe(2)–Fe(1)–C(12)	91.7 (2)	Fe(1)–P–C(2P)	115.0(3)
Fe(2)–Fe(1)–C(3)	69.4 (2)	Fe)1)–P–C(3P)	115.5 (3)
Fe(2)–Fe(1)–C(4)	87.0 (2)	C(1P)–P–C(2P)	103.4 (4)
Fe(2)–Fe(1)–C(5)	76.0 (2)	C(1P)–P–C(3P)	104.0 (4)
P–Fe(1)–C(11)	88.3 (2)	C(2P)–P–C(3P)	103.0 (4)
P–Fe(1)–C(12)	93.0 (3)	P–C(1P)–C(4P)	121.5 (7)
P–Fe(1)–C(3)	105.2 (2)	P–C(2P)–C(5P)	116.8 (6)
P–Fe(1)–C(4)	87.3 (2)	P–C(3P)–C(6P)	117.6 (7)
P–Fe(1)–C(5)	100.3 (2)	Fe(1)–C(11)–O(1)	172.7 (7)
C(11)–Fe(1)–C(12)	98.7 (4)	Fe(1)–C(12)–O(2)	177.8 (7)
C(3)–Fe(1)–C(4)	39.5 (3)	Fe(2)–C(21)–O(3)	170.5 (7)
C(3)–Fe(1)–C(5)	70.9 (2)	Fe(2)–C(22)–O(4)	176.7 (7)
C(4)–Fe(1)–C(5)	39.3 (3)	Fe(2)–C(23)–O(5)	174.0 (7)
Fe(1)–Fe(2)–C(21)	82.9 (2)	C(2)–C(1)–C(8)	111.3 (5)
Fe(1)–Fe(2)–C(22)	97.9 (2)	C(2)–C(1)–C(10)	117.1 (6)
Fe(1)–Fe(2)–C(23)	169.6 (2)	C(8)–C(1)–C(10)	90.4 (5)
Fe(1)–Fe(2)–C(2)	73.6 (2)	C(1)–C(2)–C(3)	107.4 (5)
Fe(1)–Fe(2)–C(6)	64.5 (2)	C(2)–C(3)–C(4)	124.3 (5)
Fe(1)–Fe(2)–C(7)	97.4 (2)	C(3)–C(4)–C(5)	122.8 (6)
C(21)–Fe(2)–C(22)	95.0 (3)	C(4)–C(5)–C(6)	127.0 (7)
C(21)–Fe(2)–C(23)	93.2 (3)	C(5)–C(6)–C(7)	129.5 (6)
C(22)–Fe(2)–C(23)	92.0 (3)	C(6)–C(7)–C(8)	121.6 (6)
C(2)–Fe(2)–C(6)	88.8 (3)	C(1)–C(8)–C(7)	114.4 (6)
C(2)–Fe(2)–C(7)	82.3 (2)	C(1)–C(8)–C(9)	89.0 (5)
		C(7)–C(8)–C(9)	113.3 (6)
		C(8)–C(9)–C(10)	88.8 (5)
		C(1)–C(10)–C(9)	91.1 (5)

Because of solubility limitations even more severe than for **2**, the ring carbon resonances were not studied for **6**.

Scheme I



A. The Twitching Process



B. The Gliding Process

Table V. Least-Squares Planes in $(C_{10}H_{12})Fe_2(CO)_5(PEt_3)$

		Equations of planes[a]			
		A	*B*	*C*	*D*
Plane I[b]		0.1990	−0.9014	−0.3845	0.4130
Plane II		0.0558	0.9730	−0.2239	1.4846
Plane III		0.0451	0.4537	−0.8900	1.2182
Plane IV		0.0850	0.9958	−0.0347	0.4269
Plane I	C(2) 0.100 (7)	C(3) −0.171 (7)	C(4) 0.145 (7)	C(5) −0.026 (7)	C(6) −0.031 (7)
Plane III		C(1) 0.047 (7)	C(2) −0.023 (8)	C(7) 0.079 (8)	C(8) −0.044 (7)
Plane IV		C(1) −0.050 (8)	C(8) 0.041 (8)	C(9) −0.058 (9)	C(910) 0.060 (9)

[a] Equations have the form $Ax + By + Cz - D = 0$ where x, y, and z are orthogonalized coordinates. [b] Plane 1, II, III, and IV are identified in Figure 5.

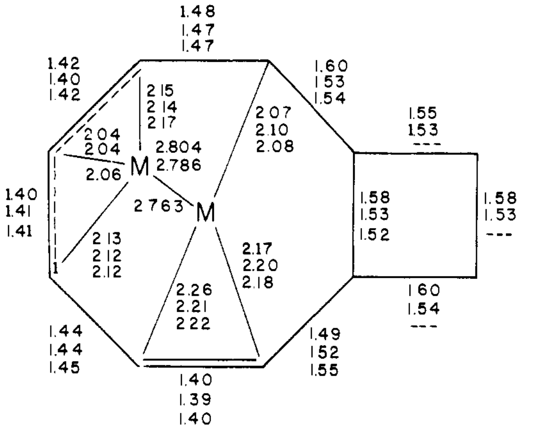
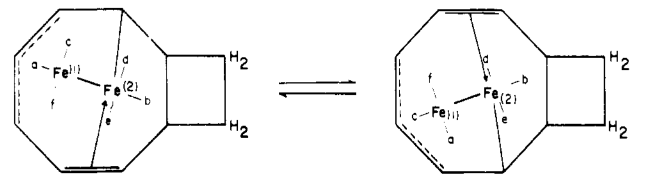
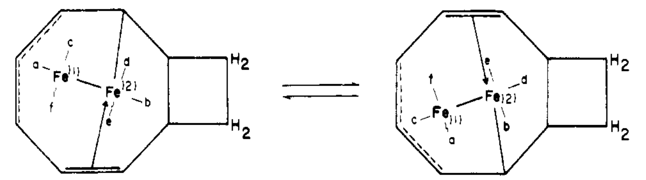


Figure 4. A comparison of bond distances in compounds **6**, **2**, and **1**. The distances are listed in that order next to each bond.

Scheme II



A. Twitch + Rotation on Fe(1)



B. Twitch + Rotation on Fe(1) & Fe(2)

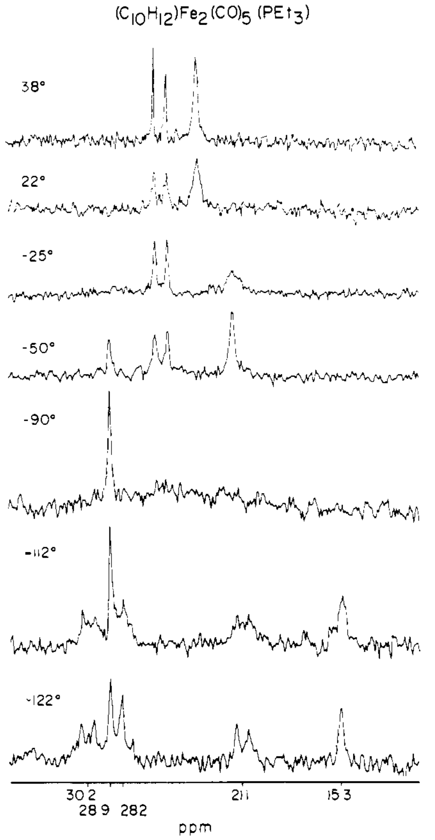


Figure 5. The ^{13}C NMR spectra in the carbonyl region for compound **6**, $(C_{10}H_{12})Fe_2(CO)_5PEt_3$, at various temperatures from −122 to 38°. The signals at 30.2 and 21.1 ppm at −122° and the one at 23.1 ppm at −50, −25, 22, and 38° are doublets because of coupling to the ^{31}P nucleus.

Spectra in the carbonyl region are shown in Figure 5. The spectrum at −122° is consistent with the structure shown in Figure 3. The number of lines has been reduced to five, two of which, at ca. 30.2 and 21.1 ppm, show a coupling to the phosphorus atom with $J_{P\text{-}C} \approx 19$ Hz. The coupling validates assignment of these signals to carbon atoms c and *f* since the PEt_3 group occupies the site of carbon a. As the temperature is raised to −90°, four of the five signals collapse uniformly with the resonance at 28.9 ppm showing no exchange. Since it has been previously determined that one CO group in **1** and two in **2** do not undergo site exchange during the beginning stages of the twitching process, the signal at 28.9 ppm can be assigned to carbon atom b. By −50° the two signals which show coupling to the phosphorus atom have averaged to 25.2 ppm. Also the two signals at 28.2 and 15.3 ppm have reappeared as an average at 21.2 ppm. The spectrum observed here at −50° is analogous to the 1:3:2 spectra previously observed in molecules **1** and **2**. Further increase in temperature caused collapse of the signals at 28.9 and 21.2 ppm until at +40° a completely averaged spectrum was observed, with two signals, a singlet at 23.1 ppm of relative intensity 3 and a doublet ($J_{P\text{-}C} \approx 19$ Hz) at 25.2 ppm of relative intensity 2.

An approximate line shape analysis was made for each compound. For practical reasons, stemming from the inexactness of intensity relations in the ^{13}C spectra and the relatively poor signal to noise ratios, we have only attempted to estimate the rates at the approximate coalescence temperatures. Then, assuming a frequency factor of $10^{13.3}$ (equivalent to $\Delta S^\ddagger = 0$), the values of E_a were calculated.

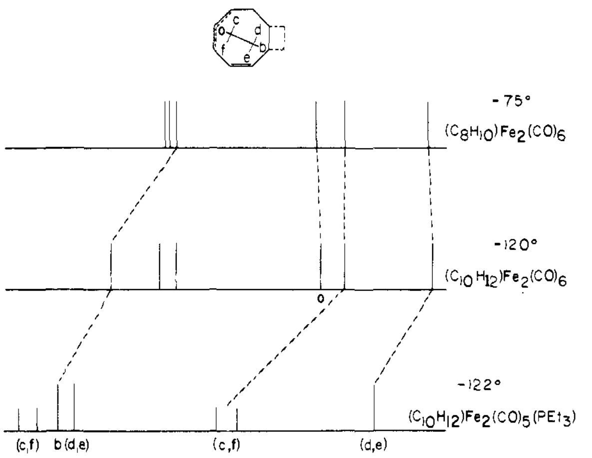


Figure 6. A chart showing the proposed correlation of the spectra of compounds **1**, **2**, and **6** and the partial assignment implicit therein.

Discussion

The purpose of the work reported here was to obtain answers to questions left unresolved, as well as to confirm the conclusions that were obtained, in the previous investigation[10] of **1**, $(C_8H_{10})Fe_2(CO)_6$, by ^{13}C NMR spectroscopy. The previous study ruled out the gliding process, ruled out internuclear exchange of CO groups, and showed that scrambling of CO groups occurred locally within each $Fe(CO)_3$ unit. By implication, the twitching mechanism was thus supported. However, because line shape effects caused by both scrambling within one $Fe(CO)_3$ group and the twitching process occurred in the same temperature range, some of the details which could unambiguously establish the occurrence of the twitch motion were not observed. Moreover, the possibility that the twitch and a concerted, partial, local exchange of CO groups on the iron atom bound to the allyl moiety of the ring might be interdependent could not be ruled out because of the similar temperature ranges for twitching and one of $Fe(CO)_3$ local scrambling processes. Finally, there is no way to determine directly which $Fe(CO)_3$ group is the more labile.

All of these questions are now resolved, as will be shown below. This was made possible by two factors, each of which was deliberately introduced in the design of the experiment. First, it was already known[3] that for **2**, the motion which averages the ring atoms in pairs proceeds rapidly at much lower temperatures than it does in **1**. It was thus anticipated that, if the twitch and the faster of the $Fe(CO)_3$ scrambling processes were not interdependent but occurred together only by coincidence in **1**, they would be observable separately in **2**. Second, the additional data available from **2** and its phosphine-substituted derivative, **6**, were expected to provide enough guidance to make assignments that could distinguish between CO groups on the two ends of the $Fe_2(CO)_6$ unit. To show how these expectations were realized, we first discuss the NMR data for $(C_{10}H_{12})Fe_2(CO)_6$ and then the data for the PEt_3 derivative thereof.

Compound 2. The six carbonyl carbon atom signals shown in the −120° spectrum of Figure 2 are consistent with the crystal structure.[3] The symmetrical collapse of four of the six peaks can be explained by the twitching process, shown in Scheme IA. The two signals that do not collapse must be assigned to carbon atoms a and b, while the pairs of resonances which coalesce must be due to (c, f) and (d, e). This spectral change observed from −120 to −88°, cannot be described by the glide mechanism shown in Scheme IB as it would lead to averaging of (a, b), (c, d), and (e, f) giving three peaks of equal integrated intensity. Thus, the data from −120 to −88° allow unobscured observation of the twitching process and thus demonstrate unequivocally its occurrence. However, in addition to the simple twitching process shown in Scheme IA, an alternative one, suggested for reasons explained elsewhere,[10] in which the invariant resonances would be those due to c and b, while the exchanging ones would be the pairs (a, f) and (d, e), is also consistent with the data for **2**. It will be shown later that the data for **6** rule out this second possibility.

In addition to showing in a clear way that the twitch and not the glide is occurring, the results for compound **2** show which $Fe(CO)_3$ group in **1** and **2** undergoes internal scrambling first. This choice can be made unequivocally if the correct assignment of the two resonances which remain sharp from −120 to −88° can be made. We know that one is due to a and the other to b; the problem is simply, which is which. Figure 6 shows how the slow exchange limit spectra change from **1** to **2** to **6**. The first significant fact is that the only change from **1** to **2** is that the invariant resonance at lower field for both compounds is shifted 2.8 ppm while no other resonance moves more than 0.3 ppm.

An inspection of the structures of these molecules[2,3] shows clearly that the addition of the $-CH_2CH_2-$ group to convert **1** to **2** occurs close to b, and could influence its chemical shift substantially, whereas it could not possibly affect the chemical shift of a significantly, or indeed, the chemical shifts of the other four CO groups. The structure of **6** shown in Figure 3 serves to make this clear, since there is no significant difference (as already noted) among the structures of **1**, **2**, and **6** in respect to the relationship of the $Fe_2(CO)_6$ or $Fe_2(CO)_5PEt_3$ group to the eight-membered ring. We thus establish conclusively that the resonances at 23.8 ppm in **1** and 26.6 ppm in **2** are assigned to carbonyl group b. This in turn shows conclusively that internal scrambling occurs first about Fe(1), that is, in the allyl-bound $Fe(CO)_3$ group, as shown in Scheme IIA.

Compound 6. The ^{13}C NMR spectra of this molecule at various temperatures (Figure 5) show changes which allow us to confirm and extend all of the interpretation previously made for compounds **1** and **2**. We turn first to the assignment of the slow exchange spectrum which is juxtaposed with those of **1** and **2** in Figure 6.

The replacement of carbonyl group a by PEt_3 would be expected to affect the spectrum in three ways. (1) One ^{13}C resonance, that of a must disappear. The spectrum of **6** therefore shows only five signals. (2) The signals for the two carbonyl groups on Fe(1) should become doublets, with substantial splitting, while the other three, from CO groups on Fe(2), should show little or no splitting. This is observed. Thus, the two signals with pronounced doublet structure must be due to c and f. The other three signals are not observably split. (3) All resonances should be shifted downfield since there is both theoretical[21] and empirical[22] evidence that increased back-bonding to CO groups (as would be expected when one CO is replaced by a ligand with inferior π-acidity) causes a decrease in shielding. This is observed. We would assume further, that the shift would be greater for the CO groups on Fe(1). On this assumption, we propose the correlation shown in Figure 6. The correlation for b is made independently because of the behavior of this signal as the twitching process sets in. The shift for b gives an estimate of the magnitude that can also be expected for d and e, the other CO's on Fe(2). Thus, since the shift for b is 2.3 ppm the indicated shift of 2.5 ppm for d or e is very reasonable. For the other resonance that must be assigned to d or e, the shift is 3.7 or 4.4 ppm depending on which of the two signals (at 23.8 or 24.5 ppm) is chosen in the spectrum of **2**. We think that the correlation which gives a shift of only 3.7 ppm is preferable, though admittedly not cer-

Table VI. Energies of Activation[a]

		Twitch			Scrambling on Fe(1)		Scrambling on Fe(2)	
			E_a					
No.	Compound	T, °K	(c,f)	(d,e)	T, °K	E_a	T, °K	E_a
1	$(C_8H_{10})Fe_2(CO)_6$	238	11.6	11.4	238	11.4	333	15.6
2	$(C_{10}H_{12})Fe_2(CO)_6$	185	9.0	8.9	195	9.3	303	14.2
6	$(C_{10}H_{12})Fe_2(CO)_5(PEt_3)$	185	8.8	8.8	...	...	258	12.0
3	$(C_9H_{10})Fe_2(CO)_6$[b]	163	7.9	7.8	178	8.5	273	12.9

[a] The method of estimation is explained in the final paragraph of the results section. In view of the approximations involved the absolute accuracy of any given value is probably no better than ±2 kcal mol^{-1}. However, due to cancellation of systematic errors, the differences are probably quite meaningful. [b] We thank Professor J. Takats for allowing us to use his spectra to estimate the parameters for **3**.

Table VII. Dihedral Angles between Least-Squares Planes (deg)

	I–II	I–III	II–III	Ref
$(C_8H_{10})Fe_2(CO)_6$	44.7	86.6	45.2	5
$(C_{10}H_{12})Fe_2(CO)_6$	41.2	84.3	43.6	5
$(C_{10}H_{12})Fe_2(CO)_5(PEt_3)$	38.7	86.7	50.0	This work
$(C_9H_{10})Fe_2(CO)_6$	38.2	84.6	49.5	4

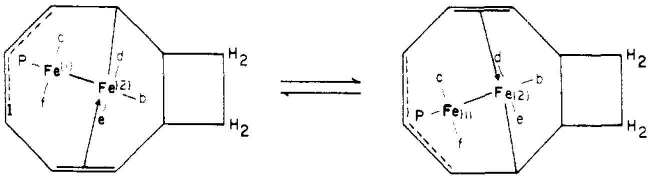
tain. From this, it follows automatically that the doublet at 30.2 ppm must correlate to the signal of **2** at 23.8 ppm, making the shift of 6.4 ppm. The doublet at 21.1 ppm then correlates to the signal at 16.6 ppm (since that at 17.7 ppm is due to a as will be shown below) for a shift of 4.5 ppm.

The uncertainty in how to assign the bands at 23.8 and 24.5 ppm cannot be resolved by testing for which assignment best accounts for the positions of the averaged resonances at higher temperatures, since the fit is about equally good with either.

The important conclusion that can be drawn from the limited assignments that can be made is that the twitch mechanism is directly supported. It is clear in **6** that the c and f signals, the doublets, average with each other, and *only* with each other. This confirms that there is never any scrambling or averaging of CO groups on Fe(1) with those on Fe(2). Further, the assignment inferred for **2**, despite the uncertainties, clearly requires that one member of each of the c, f and d, e pairs is upfield and the other downfield. The first averaging process is observed to involve pairs which each consist of one upfield and one downfield signal. Since the twitch is predicted (Scheme I) to average c with f and d with e, we find yet another aspect of the data which conforms to the requirements of the twitch but not to those of any other process.

As mentioned earlier, one of the important contributions of compound **6** is in showing that the twitching process that occurs in **1** and **2** is the simple one, i.e., the one in which a and b cause the invariant signals, rather than the alternative[10] in which the nonexchanging carbonyl groups are b and c or b and f. As shown in detail earlier,[10] in the alternative twitch process, if c is invariant, a and f must exchange. In **6**, however, a is no longer equivalent chemically to f, since the crystal structure shows that a is now PEt_3. Thus, the alternative process in compound **6** cannot cause the two CO groups on Fe(1) to interchange, whereas, in fact, they do. There is no doubt of that since the splitting of two resonances by the nuclear moment of ^{31}P unequivocally identified them as the signals from the carbonyl groups on Fe(1). Thus, the twitch process in **6** must be that shown in Scheme III. We think it safe to assume that since this process occurs with virtually the same coalescence temperature and activation energy (see Table VI) in **6** as does the twitching process in **2**, that the process is qualitatively the same one in both compounds.

Scheme III



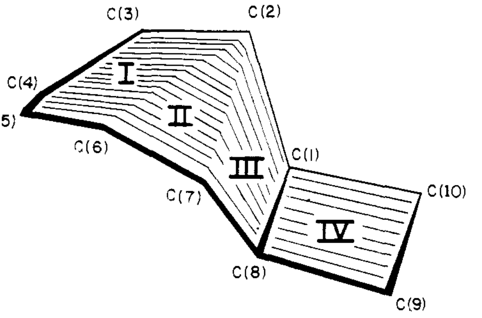


Figure 7. A set of four planes defined by the carbon atoms of $C_{10}H_{12}$ in compounds **2** and **6**. The planes I, II, and III are common to all four of the molecules, **1**, **2**, **3**, and **6**, and can be used to assess the extent of buckling of the eight-membered rings.

The ease of the twitching process increases (i.e., the activation energies and coalescence temperatures decrease) in the order **1** ≫ **2** ≈ **6** > **3**. While this may be an oversimplification, we note that this trend for the unsubstituted compounds **1–3** seems to be correlated with the degree of buckling of the cyclooctatrienyl portion of the ligand in each of the molecules. This buckling is represented approximately by the planes shown in Figure 7. Planes I and III are only mean planes and could be further subdivided, but the deviations from them are small and the division of the eight-membered ring into only three main planes seems to us to be a satisfactory approximation. The planes of particular interest are planes I and II since these planes include the atoms that are bound to the $Fe_2(CO)_6$ moiety. Table VII shows the dihedral angles for the four molecules. The angles quoted are those between intersecting lines perpendicular to the planes. Thus, the greater these angles, the more buckled the ring. For molecules **1–3** there is a linear relationship between the dihedral angles and the temperature of the slow exchange spectrum for the twitching process indicating that the ease of the twitch varies inversely with the extent of the buckling. The angle of I–II for the substituted compound **6** suggests the low limit for the twitch should be about −140°.

One final point regarding compound **6** requires comment. The internal averaging of the CO groups on Fe(2) is considerably more facile in **6** than in **1** or **2**, as reflected by the coalescence temperatures and approximate activation energies in Table VI. We had not anticipated that the substitution of PEt_3 for one CO on Fe(1) would affect the rate of scrambling on Fe(2) as much as it does, since there is scarcely any observable effect on the structure parameters of the $Fe-Fe(CO)_3$ group in question. The possibility that we have assigned the order of the two $Fe(CO)_3$ scrambling processes incorrectly in **1** and **2** was, of course considered, but in view of the strong arguments for assigning the b resonance as we have done, this does not appear to be possible. The effect that phosphine substitution has on the activation energy is presently under investigation.

General Conclusion

All of the evidence now available allows us to specify completely and unambiguously the fluxional processes which occur in $(C_8H_{10})Fe_2(CO)_6$, $(C_{10}H_{12})Fe_2(CO)_6$, and $(C_{10}H_{12})Fe_2(CO)_5PEt_3$. These processes are summarized in Schemes IA and II. The three principal stages are the following. (1) A simple twitching motion of the Fe_2L_6 moiety with respect to the cyclooctatriene unit. In all cases (see Table VI) this is the process of lowest activation energy. (2) Internal scrambling in the allyl-bound $Fe(CO)_3$ group. This is the process of next highest activation energy, although, for **1**, it accelerates almost simultaneously with the twitching process and thus the line shape changes observed at lower temperatures in this molecule are not, in themselves, subject to easy interpretation.[10] (3) Internal scrambling of the CO groups on Fe(2). An interesting, and, we think, somewhat surprising feature, is that this process is markedly easier (T_c is lower by ca. 45 to 75°; E_a is lower by ca. 2-3 kcal mol^{-1}) in **6** than in **1** and **2**.

Remarks on Related Compounds. It is worthwhile to note that the occurrence of only the twitch and not the glide process in compounds **1**, **2**, and **6** is in harmony with the behavior of $C_8H_{10}Rh_2(\eta^5\text{-}C_5H_5)_2$. Nuclear magnetic resonance study of this molecule by Evans, Johnson, Lewis, and Watt[23] has established (a) that the structure is of the same type as in the iron compounds, with $\text{-}Rh(\eta^5\text{-}C_5H_5)$ groups replacing $\text{-}Fe(CO)_3$ groups, and (b) that this molecule undergoes a twitching rearrangement between −50 and +65°. In this case the observation that the proton signals for the two $(\eta^5\text{-}C_5H_5)$ groups never coalesce allows the glide process to be ruled out easily and conclusively. Of course, uncritical reliance cannot be placed on analogies between molecules related by $Rh(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)_3$ substitutions, since the $C_8H_{10}M_2L_n$ (M_2L_n = $Fe_2(CO)_6$; $Rh_2(\eta^5\text{-}C_5H_5)_2$ molecules are not isostructural.[23]

The results obtained here are very similar to those obtained for compound **3** by Professor Takats,[4] including the marked shift of one signal in the spectrum of **1** which allows it to be assigned to carbonyl group b.

The position of the PEt_3 substituent in **6** is that which had been proposed from NMR results in the related molecule **4**, where one CO has been replaced by PPh_3.[8]

Acknowledgments. We are grateful to the National Science Foundation for support under Grant No. 33142X. We thank Professor J. Takats of the University of Alberta, Edmonton, for communicating his crystallographic and NMR results on compound **3** to us in advance of publication. We also thank Dr. B. R. Stults for assistance with the crystallography.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-5739

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