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Stereochemically Nonrigid Six-Coordinate Metal Carbonyl Complexes. II.[1] A ^{13}C Nuclear Magnetic Resonance Study of the Series $M(CO)_4(EMe_3)_2$ (M = Fe, Ru, Os; E = Si, Ge, Sn, Pb)

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Abstract: Carbon-13 NMR spectra are reported for the compounds $M(CO)_4(EMe_3)_2$ (M = Fe, E = Si, Ge, Sn; M = Ru or Os, E = Si, Ge, Sn, Pb) and for the chlorosilyl derivatives $M(CO)_4(SiMe_{3-n}Cl_n)_2$ (M = Fe, Ru, Os; n = 1–3). The study provides data on 19 cis isomers and 10 trans isomers. Spin-spin coupling in cis tin and lead derivatives leads to the assignment of the ^{13}CO resonance at higher field as the equatorial carbonyl group; *cis*-$Fe(CO)_4(SnMe_3)_2$ is anomalous in this respect. Attention is directed to the averaging of axial and equatorial carbonyl signals in the cis isomers, which at room temperature results in a single carbonyl resonance for most of the iron derivatives. The barrier for this process increases with halogen substitution and is greater for corresponding compounds of ruthenium and osmium. The preservation of ^{117,119}Sn–^{13}CO coupling in the high-temperature limiting spectrum of *cis*-$Fe(CO)_4(SnMe_3)_2$ shows that the process is nondissociative. The pattern of coalescence in cis-trans mixtures strongly suggests that axial-equatorial averaging proceeds by a cis-to-trans-to-cis isomerization process.

In 1972 we reported the results of a proton magnetic resonance study of the equilibrium mixture of *cis*- and *trans*-$Os(CO)_4(SiMe_3)_2$, which established that the isomers were rapidly interconverted on the NMR time scale at 55 °C.[2] The lack of exchange with ^{13}CO suggested that the isomers were interconverted without dissociation, a process rarely observed in six-coordinate complexes.

It was anticipated that ^{13}C NMR spectroscopy would play a key role in the continuation of these studies. Since axial and equatorial carbonyl groups of a cis tetracarbonyl derivative can be distinguished, any process which involves their interchange at an appropriate rate may be recognized. Thus, we have very recently shown that, in *cis*-$Fe(CO)_4(SiMe_3)_2$, there is rapid averaging of the signals due to axial and equatorial carbonyl groups (coalescence temperature −55 °C), and furthermore that the process does not involve ligand dissociation.[1]

The trimethylsilyl derivatives of iron and osmium mentioned above provide important new examples of six-coordinate polytopal rearrangement processes. In view of our interest in these processes and in factors governing the relative stabilities of cis and trans isomers, we have carried out an extensive ^{13}C NMR study of compounds of this type and report here the results.

Experimental Section

NMR Instrumentation and Techniques. Spectra were recorded in the pulse Fourier transform mode of operation on a Bruker HFX-90-Nicolet 1085, or a modified Varian HA-100 spectrometer interfaced to a Digilab FTS/NMR-3 Data System and pulse unit. The instruments operated at 22.6 and 25.1 MHz, respectively.

The Bruker instrument, with which the majority of the spectra were obtained, was equipped with a single coil receiver; a pulse width of 6–8 μs (90° pulse = 27 μs) was used with a dwell time of 100 μs and an acquisition time of 0.8 s. Spectra were recorded using proton broad-band decoupling conditions. The number of scans was usually 1000 (1K). However, in the cases where exchange was observed or in order to determine coupling constants as many as 8- or 12K pulses were taken. The number of data points (channels) was 8K and the sweep width was 5000 Hz. This afforded a digital resolution of 0.06 ppm or 1.25 Hz.

The temperature unit of the instrument was calibrated with a thermocouple held coaxially in the spinning sample tube partially filled with solvent. The temperature was controlled by means of a thermocouple situated just beneath the probe.

The NMR solvent and lock was either toluene-d_8 or, for the less soluble compounds, CD_2Cl_2. Tetramethylsilane was employed as an internal standard or, where this was not possible, the peaks were referenced to the quaternary carbon of toluene-d_8 and converted to the Me_4Si scale by taking the chemical shift of this latter peak as 137.46 ppm. Chemical shifts downfield from Me_4Si are taken as positive.

Approximately 2 ml of a 0.7–1.0 M solution contained in a 10 mm (o.d.) NMR tube was used to obtain the ^{13}C NMR spectrum of the compound in question. For most spectra above room temperature, a relaxation agent,[3a] tris(acetyacetonato)chromium(III) (approximately 10 mg), was employed; no relaxation reagent was used in experiments where a line-shape analysis was carried out.[3b] In one experiment, the ^{13}C NMR spectrum of $Os(CO)_4(SiMe_3)_2$ was recorded with and without $Cr(acac)_3$; no differences in the chemical shifts of the resonances were noted. The NMR tubes containing the particularly air-sensitive compounds $Fe(CO)_4(GeMe_3)_2$ and $Ru(CO)_4(SiMe_3)_2$ were sealed under vacuum before spectra were recorded. Spectra of $Fe(CO)_4(SnMe_3)_2$ in CF_2HCl-CD_2Cl_2 were also measured in a sealed tube.

The spectrum of $Ru(CO)_4(SnMe_3)_2$ above 100 °C was determined using the pure liquid. The lock consisted of dimethyl-d_6 sulfoxide contained in a 5-mm NMR tube fitted coaxially in the larger tube.

The simulation of the NMR spectra of *cis*-$Fe(CO)_4(GeMe_3)_2$ and $Os(CO)_4(SiMe_3)_2$ was carried out using a six-site exchange program written by Professor D. L. Rabenstein of this department. The computations were carried out on an IBM 360/67 computer at the University of Alberta. The following rates were found for $Fe(CO)_4(GeMe_3)_2$: −40 °C, 12.5; −30 °C, 35.71; −20 °C, 94.34; −15 °C, 169.5; −10 °C, 312.5; −5 °C, 476.2 s^{-1}. The half width used in simulation was 2.8 Hz, the value observed at −50 °C.

In most cases where collapse of the carbonyl signals was observed, line-shape analysis of the spectra was not considered worthwhile. Because of the large chemical-shift difference (2–5 ppm) between the two peaks, the signal in the region of collapse is spread over a large region and is therefore weak. Large errors are consequently involved in simulating such a spectrum with concomitant errors in the activation parameters. Several spectra having 8K scans each would have been necessary for a satisfactory analysis. The time required for 8K scans is approximately 2 h, and many of the compounds showed signs of decomposition after only one 2-h period at the temperature of collapse.

An approximate method of calculating $\Delta G^\dagger$ from the chemical-shift separation (at slow exchange), and the collapse temperature was therefore carried out using the relationships $\tau = 1/\pi(2)^{1/2}\Delta\nu$ and $1/\tau = \kappa(kT/h)\exp(-\Delta G^\dagger/RT)$, where τ = lifetime at temperature T, κ = transmission coefficient = 1, T = temperature of collapse, and $\Delta\nu$ = chemical shift difference in the low temperature limiting spectrum.

In cases where $\Delta G^\dagger$ was calculated by both this method and from the results of the line-shape analysis, it was found that the two values agreed within experimental error.

Variable Temperature ^{13}C NMR Spectra and Line-Shape Analysis for $Os(CO)_4(SiMe_3)_2$. The sample (1.0 g) was enriched with ^{13}CO to approximately 25%. The solvent was freshly distilled decalin (1.5 ml), and dimethyl-d_6 sulfoxide in a sealed capillary was used as the lock. No relaxation reagent was used. The NMR sample tube was sealed under vacuum. At 140 °C slight refluxing of solvent in the tube occurred, resulting in some loss of resolution. For this reason, spectra at higher temperatures were not attempted.

The line-shape analysis was complicated by two factors: the chemical-shift difference between the methyl peaks of the trans and cis isomers varied with temperature, and the ratio of isomers changed with temperature.

Study of the change in the methyl-carbon chemical-shift difference with temperature at temperatures below the region of collapse suggested the following relationship between the chemical-shift difference ($\Delta\delta$) with temperature (T, K) as established by a least-squares fit:

$$\Delta\delta = -0.0844T + 54.08$$

From this relationship, $\Delta\delta$ in the region of coalescence could be estimated.

Similarly from the ratio of isomers, as obtained by integration at temperatures below 50 °C, the following equation was established by least-squares:

$$\log K = -185.9/T + 0.870$$

where K is the ratio trans:cis. Thus the ratio of isomers at temperatures greater than 50 °C could be estimated. The equation implies that $\Delta H° = 0.85$ kcal mol^{-1} and $\Delta S° = 4$ eu for the equilibrium:

$$cis\text{-}Os(CO)_4(SiMe_3)_2 \rightleftharpoons trans\text{-}Os(CO)_4(SiMe_3)_2$$

These results are in good agreement with values obtained using ^1H NMR data (CH_2Br_2 solvent).[2]

Low-temperature limiting half-widths (−20°) used in spectral simulation were 2.0 Hz for trans Me, and 2.2. Hz for cis Me, leading to the following rates. The first value given after the temperature (°C) is k_{ct}, the rate of isomerization of cis to trans in s^{-1}, and the second figure is the corresponding rate (k_{tc}) for the trans to cis process: 35 °C, 5.00, 2.70; 40 °C, 6.67, 3.52; 45 °C, 11.1, 5.75; 50 °C, 15.4, 7.81; 55 °C, 25.2, 12.5; 60 °C, 35.3, 17.2; 65 °C, 42.2, 20.2; 70 °C, 76.3, 35.7; 75 °C, 100, 45.5; 80 °C, 147, 66.7; 90 °C, 297, 130; 100 °C, 575, 244; 110 °C, 1220, 500.

From these results, activation parameters of $\Delta H^\dagger_{ct} = 16.4 \pm 0.3$ kcal mol^{-1}, $\Delta S^\dagger_{ct} = -2.3 \pm 0.8$ eu, $\Delta H^\dagger_{tc} = 15.6 \pm 0.3$ kcal mol^{-1}, and $\Delta S^\dagger_{tc} = -6.3 \pm 0.8$ eu were calculated from a least-squares fit to the Eyring equation.

In the calculation of the activation parameters, only rate constants between 35 and 110 °C were used since values outside this range were subject to larger experimental error; this was especially the case with the spectrum at 140 °C.

From the Eyring equation, rate constants at particular temperatures were calculated and used to simulate the spectra in the carbonyl region. The model used in calculating the simulated spectra assumed that the trans signal gave rise to axial or equatorial resonances in the cis molecule with equal (0.5) probability; that the axial and equatorial resonances each produced the trans resonance with unit probability; and that the probability for direct axial-equatorial interchange was zero. Half-widths of ^{13}CO resonances in the low-temperature limiting spectrum (−20 °C) were 2.4 Hz for the trans isomer and 2.8 Hz for both axial and equatorial signals of the cis isomer.

The small peak observed between the cis carbonyl resonances is due to an impurity, possibly $[Os(CO)_4SiMe_3]_2$.

Sources of Compounds. Of the compounds studied here, the following have appeared in the literature before: $Fe(CO)_4(SiMe_3)_2$,[4] $Fe(CO)_4(SiMeCl_2)_2$,[5] $Fe(CO)_4(SiCl_3)_2$,[6] $Fe(CO)_4(SnMe_3)_2$,[7] $Ru(CO)_4(SiMe_3)_2$,[8] $Ru(CO)_4(GeMe_3)_2$,[9] $Ru(CO)_4(SnMe_3)_2$,[10] $Ru(CO)_4(PbMe_3)_2$,[11] $Os(CO)_4(SiMe_3)_2$,[12] $Os(CO)_4(GeMe_3)_2$,[9] $Os(CO)_4(SnMe_3)_2$,[12] $Os(CO)_4(PbMe_3)_2$.[11] The preparation of the other compounds along with improved syntheses of some of the above complexes will be described in a separate paper.[13] Attempts to prepare $Fe(CO)_4(PbMe_3)_2$ and $Os(CO)_4(CMe_3)_2$ were unsuccessful. Compounds were characterized by elemental analysis, and infrared, ^1H NMR, and mass spectroscopy, as well as the ^{13}C NMR spectra reported here.

The $M(CO)_4(EMe_3)_2$ compounds are, with the exception of $Fe(CO)_4(SiMe_3)_2$, air-sensitive liquids at room temperature and are very soluble in the solvents used. In all cases, the ^{13}C NMR carbonyl resonances could be easily obtained.

Enrichment with ^{13}CO. General. The following compounds were enriched with ^{13}CO: $Fe(CO)_4(SiCl_3)_2$, $Fe(CO)_4(SnMe_3)_2$, *cis*-$Ru(CO)_4(SiCl_3)_2$, $Os(CO)_4(SiMe_3)_2$, and $Os(CO)_4(SnMe_3)_2$. The exchange of ^{13}CO with *cis*-$Ru(CO)_4(SiCl_3)_2$ has been described before;[14] the enrichment of the other three complexes was similar and is only reported in detail for $Os(CO)_4(SnMe_3)_2$. Enrichment of $Fe(CO)_4(SiCl_3)_2$ was carried out since it was not sufficiently soluble in CD_2Cl_2 to give a satisfactory spectrum otherwise. The tin derivatives were enriched to obtain the tin to carbonyl carbon coupling constants.

The ^{13}CO used was of 92% isotopic purity (Monsanto Research Corporation, Miamisburg, Ohio). Enriched carbon monoxide was manipulated in a glass vacuum system of conventional design by means of a Toepler pump. The reaction vessel consisted of a round-bottomed flask (50 ml) sealed to a condenser resulting in a total volume of approximately 100 ml. The vessel could be attached to the vacuum line by means of a ball joint. The unit was also fitted with a Teflon valve so that once filled with CO it could be transferred to other areas of the laboratory. Samples for infrared analysis could be withdrawn with the aid of a 1-ml syringe through a serum cap covering a side arm on the bulb.

Irradiation with ultraviolet light was usually required to bring about exchange with ^{13}CO. The bulb was positioned 3 or 4 cm from a 140-W lamp (Engelhard-Hanovia Inc., Newark, N.J.), and cold water was passed through the condenser during irradiation.

Enrichment of $Os(CO)_4(SnMe_3)_2$. A sample of $Os(CO)_4(SnMe_3)_2$ (0.60 g, 0.95 mmol) in toluene-d_8, previously used in a ^{13}C NMR experiment and containing $Cr(acac)_3$, was diluted to 15 ml with toluene. The solution was placed in the appropriate vessel, cooled to −78 °C and evacuated. Vigorous stirring during the evacuation served to degas the solution. A pressure of 1 atm of ^{13}CO was admitted to the flask. The flask was then heated at 55 °C for 1 h. The infrared spectrum (in heptane) showed that no enrichment had occurred. It may be noted that this is the temperature at which collapse of the cis and trans signals occurs in the ^1H NMR spectrum.[2] Subsequent irradiation with ultraviolet light for 30 min with vigorous stirring afforded the enriched product. Excess ^{13}CO and toluene were removed on the vacuum line, and the resulting product was sublimed [50-60 °C (0.1 mmHg)] onto a probe cooled with liquid nitrogen. On warming the probe, the enriched sample of $Os(CO)_4(SnMe_3)_2$ (0.35 g) was obtained as a pale yellow liquid. From mass spectrometry, it was estimated that 40-60% of the molecules contained at least one ^{13}CO group, or in other words that each carbonyl group was 10-15% enriched with ^{13}CO.

The enrichment of $Fe(CO)_4(SnMe_3)_2$ was carried out in n-hexane. No enrichment was observed after stirring for 1 h at room temperature. Irradiation with ultraviolet light for 1 h achieved the desired enrichment.

Table I. ^{13}C Chemical Shifts in *cis*-$M(CO)_4(ER_3)_2$ Derivatives[a]

Compd	CO_{ax}		CO_{eq}	Me	Temp, K
$Fe(CO)_4(SiMe_3)_2$	208.50		207.64	7.50	183[b]
		208.07		7.61	298[b]
		207.96		7.71	301
$Fe(CO)_4(SiMe_2Cl)_2$	205.70		203.27	12.09	253
		204.53		12.30	303
$Fe(CO)_4(SiMeCl_2)_2$	202.46		200.14	17.16	253
	202.46		200.04	16.89	303
$Fe(CO)_4(SiCl_3)_2$	199.44		197.34		303
	199.71		197.88		308[b]
$Fe(CO)_4(GeMe_3)_2$	208.94		207.15	6.96	223[b]
		208.07		7.34	293[b]
$Fe(CO)_4(SnMe_3)_2$[c]	207.86		208.07	−3.67	163[d]
		207.75		−3.29	273
		207.75		−3.24	293[d]
		208.07		−2.75	300[b]
$Ru(CO)_4(SiMe_3)_2$	198.53		191.62	7.72	253
$Ru(CO)_4(SiMe_2Cl)_2$	194.54		188.12	12.36	303
$Ru(CO)_4(SiMeCl_2)_2$	190.60		185.42	17.37	305
$Ru(CO)_4(SiCl_3)_2$	187.46		183.63		293[b]
$Ru(CO)_4(GeMe_3)_2$	198.04		191.30	7.02	303
$Ru(CO)_4(SnMe_3)_2$	197.39		192.27	−4.74	300
$Ru(CO)_4(PbMe_3)_2$	196.96		192.21	−0.86	303
$Os(CO)_4(SiMe_3)_2$	181.48		172.58	6.74	303
$Os(CO)_4(SiMe_2Cl)_2$	177.54		169.61	11.44	303
$Os(CO)_4(SiMeCl_2)_2$	173.71		167.23	16.51	303
$Os(CO)_4(GeMe_3)_2$	180.40		171.88	5.24	293
$Os(CO)_4(SnMe_3)_2$	179.05		172.26	−6.63	303
	179.21		172.58	−6.69	293[b]
$Os(CO)_4(PbMe_3)_2$	179.32		172.31	−3.18	303

[a] Chemical shifts in parts per million downfield from Me_4Si. Solvent is toluene-d_8 except as noted. [b] CD_2Cl_2 as solvent. [c] See text. [d] CD_2Cl_2–methylcyclohexane-d_{14} (1:1) as solvent.

Results and Discussion

Compounds of the type $M(CO)_4(EMe_3)_2$ or $M(CO)_4(SiMe_{3-n}Cl_n)_2$ may exist in solution as pure cis, pure trans, or as a mixture of observable amounts of cis and trans isomers (which may or may not be in rapid equilibrium at a given temperature). All these possibilities have been observed among the compounds investigated here.

Infrared spectroscopy has commonly been used to distinguish among the possibilities, on the basis that a single carbonyl stretching band is expected for a trans isomer, and four for the cis. We wish to stress, however, that infrared spectroscopy will not reliably detect a cis–trans mixture because the single carbonyl band of the trans isomer is often coincident with one of the four cis bands.[15] A further problem arises in molecules such as $M(CO)_4(SiMe_{3-n}Cl_n)_2$ (n = 1, 2) where extra bands result from various conformations of the unsymmetrical ligands.[6]

Proton NMR spectroscopy may in certain cases reveal the presence of two isomers, but even so it is generally not possible to assign the signals to the individual isomers without other evidence. On the other hand, ^{13}C NMR is broadly applicable to $M(CO)_4(EMe_3)_2$ and related complexes. Two ^{13}C resonances of equal intensity are expected in the metal carbonyl region for a cis isomer, whereas a single resonance is expected for the trans isomer. Assignment of peaks in mixtures can normally be made on an intensity basis; ambiguities which might result if the intensities of the three ^{13}CO resonances were very similar (i.e., a cis:trans ratio near 2 in the mixture) could be resolved by examining the spectrum over a range of temperatures at different equilibrium ratios.

Assignment of Axial and Equatorial Resonances. From the proton-coupled ^{13}C NMR spectrum of $Os(CO)_4H_2$, it was possible to assign unambiguously the resonance at lower field (A_2X pattern) to the axial carbonyl group, and the resonance at higher field (AA′X) to the equatorial carbonyl.[18,19] Evidence is now presented that the same assignment also holds for several of the *cis*-$M(CO)_4(ER_3)_2$ derivatives of Table I. It may hold for most of the compounds, although there is at least one exception.

When the element E has a significant proportion of an isotope of spin ½, coupling is observed between this element and the carbonyl carbons. The equatorial carbon is expected to show two different couplings, one due to the E atom trans to it, the other to the mutually cis E atom. The axial carbonyl carbon is expected to show a single coupling, with satellites of twice the intensity of those centered around the equatorial resonance.

This possibility exists for tin (^{117}Sn, 7.6%; ^{119}Sn, 8.6%) and lead (^{207}Pb, 22.6%) derivatives and it has been observed in this work. It is illustrated in Figure 1 for $Os(CO)_4(SnMe_3)_2$, in which the equatorial carbonyl resonance, flanked by two satellite pairs, lies at higher field. The coupling constants will be discussed more fully below.

A quite different method leads to a similar assignment in the case of *cis*-$Ru(CO)_4(SiCl_3)_2$. It has been shown by a detailed infrared analysis that the equatorial carbonyl groups of this molecule undergo exchange with ^{13}CO in a completely stereospecific way.[14] Figure 2 compares the ^{13}C NMR spectra of the molecule at natural abundance with that of the equatorially ^{13}CO enriched species. The natural abundance spectrum shows two ^{13}CO resonances of equal intensity, as expected; the equatorially enriched compound shows a single peak at the higher field resonance of the upper spectrum, thereby confirming the assignment. It should also be pointed out that the ^{13}C NMR experiment provides a striking confirmation of the stereospecificity of the exchange.[14]

In summarizing our findings to date on the ^{13}C chemical shifts of axial and equatorial carbonyls in *cis*-

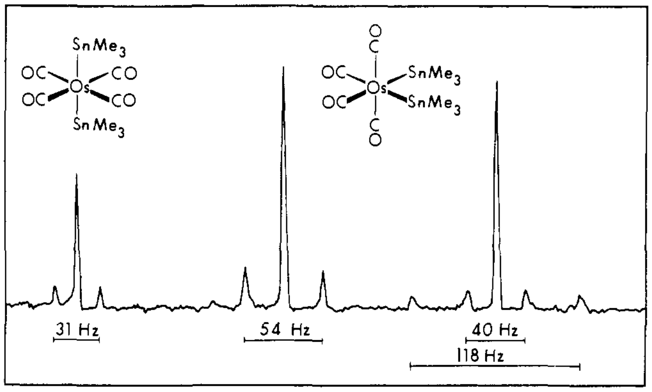

Figure 1. Carbonyl portion of Fourier transform ^{13}C NMR spectrum of an equilibrium mixture of cis and trans isomers of Os$(CO)_4(SnMe_3)_2$ in CD_2Cl_2 at 253 K. The sample is enriched in ^{13}CO. Satellites of main peaks are due to coupling to ^{117}Sn and ^{119}Sn (not resolved, total abundance 16.2%). Unambiguous assignments are possible from a consideration of peak intensities and satellite patterns; the peak at highest field with two satellite pairs is due to equatorial carbonyl groups of cis isomer.

Table II. ^{13}C Chemical Shifts in *trans*-$M(CO)_4(ER_3)_2$ Derivatives[a]

Compd	CO	Me	% trans	Temp, K
$Fe(CO)_4(SiMeCl_2)_2$	203.59	18.78	8[d]	253
$Fe(CO)_4(SiCl_3)_2$	199.49		21[d]	308[b]
	199.12		19[d]	303
$Ru(CO)_4(SiMeCl_2)_2$	191.14	18.94	12[c]	305
$Ru(CO)_4(SiCl_3)_2$	187.03		*e*	293[b]
$Os(CO)_4(SiMe_3)_2$	186.17	8.04	63[c]	303
$Os(CO)_4(SiMe_2Cl)_2$	179.53	13.38	60[c]	303
$Os(CO)_4(SiMeCl_2)_2$	174.36	19.26	*e*	303[b]
$Os(CO)_4(SiCl_3)_2$	170.31		*f*	303[b]
$Os(CO)_4(GeMe_3)_2$	184.99	6.21	20[c]	293
$Os(CO)_4(SnMe_3)_2$	185.47	−6.75	23[d]	303
	185.50	−6.78	20[d]	293[b]

[a] Shifts in parts per million downfield from Me_4Si. Solvent is toluene-d_8 except as noted. Percent trans refers to mole percent of that isomer present in solution at time of measurement. [b] CD_2Cl_2 solvent. [c] Estimated from integrated areas of methyl resonances in ^{13}C spectrum. [d] Estimated from integrated areas of carbonyl resonances in ^{13}C spectrum. [e] Measurements on pure trans isomer after separation from cis; rate of isomerization negligible at temperature of measurement. [f] Pure trans isomer; cis isomer unknown.

$M(CO)_4(ER_3)_2$ or *cis*-$M(CO)_4X_2$ (X represents a formal one-electron donor to the zerovalent metal), we may state that, with the exception of $Fe(CO)_4(SnMe_3)_2$ (see below), *the ^{13}C resonance of the carbonyl trans to the one-electron donor ligand is at higher field.* This assignment applies also to a number of pentacarbonylmanganese and pentacarbonylrhenium compounds which have been investigated[20,21] and differs from that in complexes of the type *cis*-$M(CO)_4L_2$, where L is an electron-pair donor ligand.[22]

^{13}C Chemical Shifts. Values of chemical shifts measured for cis derivatives are presented in Table I, and those for the trans derivatives in Table II. In several cases, values for the two isomers were obtainable only from low-temperature spectra, and this aspect will be fully discussed below. We remark here upon some trends in chemical shifts which are apparent from Tables I and II.

The range of ^{13}CO shifts is 209–197 ppm for iron, 199–183 for ruthenium, and 181–167 ppm for osmium derivatives. This upfield shift on descending the group is typical of metal carbonyl derivatives[21] and was also observed for the closely related chelate complexes $M(CO)_4(Me_2SiCH_2CH_2SiMe_2)$.[19]

The ^{13}CO resonance of the trans isomer is usually at lower field than the axial ^{13}CO resonance of the cis isomer (as shown in Figure 1). The compounds $Fe(CO)_4(SiCl_3)_2$ and $Ru(CO)_4(SiCl_3)_2$ are exceptions, in which the ^{13}CO resonance of the trans isomer is at slightly higher field than the axial cis resonance.

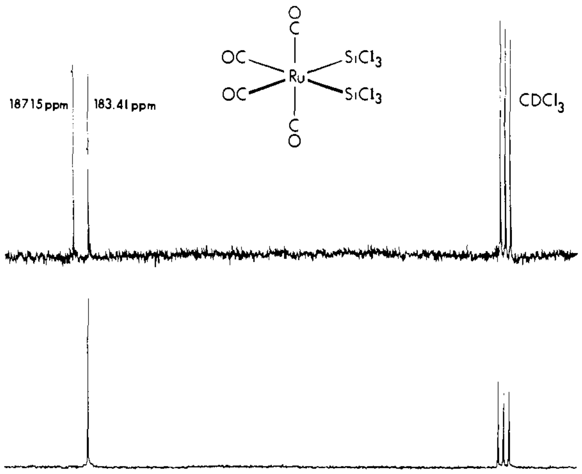

Figure 2. Fourier transform ^{13}C NMR spectrum of *cis*-$Ru(CO)_4(SiCl_3)_2$ in $CDCl_3$ at 25 °C. Upper trace: natural abundance ^{13}CO. Lower trace: after ^{13}CO enrichment stereospecifically in the equatorial positions.

In the *cis*-$M(CO)_4(EMe_3)_2$ derivatives, keeping the EMe_3 ligand constant, the difference between axial and equatorial ^{13}CO shifts increases as the central atom changes from Fe to Ru to Os. On the other hand, holding M constant, the axial-equatorial separation decreases as E is varied from Si to Pb. In the series *cis*-$M(CO)_4(SiMe_{3-n}Cl_n)_2$, for a given M, axial-equatorial separation decreases with an increase in n.

It is of interest to observe that, among the cis derivatives of Table I, a change in the noncarbonyl ligand often causes a greater change in the shift of the axial carbonyl than in that of the equatorial carbonyl.

Table II lists the percent of trans isomer present as NMR measurements were made. These values are approximate only, having been obtained by integration of the ^{13}C NMR spectra. They do not necessarily represent equilibrium values at the temperature in question. Those compounds of Table I for which no reference is made to a trans isomer in Table II can be assumed to be completely cis, within the limits of detection of ^{13}C NMR, under the conditions stated.

^{13}C Coupling Constants. Coupling constants are listed in Table III. One-bond coupling of the methyl carbon to tin and lead is observed, and the values may be compared with those reported for the related compounds $Me_3SnRe(CO)_5$ and $Me_3PbRe(CO)_5$.[20] The two-bond coupling of the group 4 atom to ^{13}CO is believed to be the first reported, with the exception of ^{29}Si-Fe-^{13}C coupling found in our laboratory for $Fe(CO)_4(SiMe_3)_2$.[1]

Two E-$^{13}CH_3$ coupling constants are possible for *cis*-$M(CO)_4(EMe_3)_2$ molecules, namely the one- and three-bond types. These were observed in the lead derivatives, where $^3J(^{207}Pb\text{-}^{13}CH_3)$ was approximately one-tenth the magnitude of $^1J(^{207}Pb\text{-}^{13}CH_3)$. No three-bond couplings were observed for the tin analogues despite a careful search. Coupling to ^{117}Sn and ^{119}Sn could only be resolved in the case of methyl groups directly bonded to tin.

Although $^2J(E\text{-}CO_{ax})$ was unambiguously defined by satellite intensities, $^2J(E_{trans}\text{-}CO_{eq})$ and $^2J(E_{cis}\text{-}CO_{eq})$ could not be experimentally distinguished, and it was assumed that the larger was due to trans coupling, i.e., $^2J(E_{trans}\text{-}CO_{eq})$. In every case save *cis*-$Fe(CO)_4(SnMe_3)_2$,

Table III. Carbon-13 Coupling Constants[a]

Compd	${}^2J(\mathrm{E{-}CO_{ax}})$	${}^2J(\mathrm{E_{trans}{-}CO_{eq}})$	${}^2J(\mathrm{E_{cis}{-}CO_{eq}})$	${}^1J(\mathrm{E{-}CH_3})$	${}^3J(\mathrm{E{-}CH_3})$
cis-$\mathrm{Fe(CO)_4(SnMe_3)_2}$[b]	101[b]	65[b]	33[b]	262, 274	
cis-$\mathrm{Ru(CO)_4(SnMe_3)_2}$[c]	61	143	36	255, 267	
cis-$\mathrm{Os(CO)_4(SnMe_3)_2}$[d]	54	118	40	266, 278	
cis-$\mathrm{Ru(CO)_4(PbMe_3)_2}$	94	252	66	108	12
cis-$\mathrm{Os(CO)_4(PbMe_3)_2}$	78	221	53	138	13

[a] Values in hertz. E = ^{117,119}Sn or ^{207}Pb. Temperature 253 K except as noted. Solvent toluene-d_8 except as noted. [b] $\mathrm{CD_2Cl_2}$–methylcyclohexane-d_{14} (1:1) at 163 K; at 293 K in same solvent, average ${}^2J$(Sn–CO) = 60 Hz (see text). [c] Neat liquid, 303 K. [d] In $\mathrm{CD_2Cl_2}$.

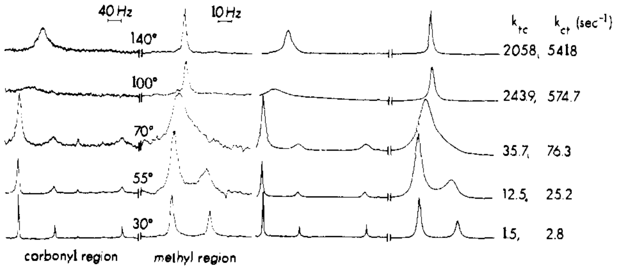

Figure 3. Variable-temperature Fourier transform ^{13}C NMR spectra of the equilibrium mixture of *cis*- and *trans*-$\mathrm{Os(CO)_4(SiMe_3)_2}$ in decalin. The sample is enriched with ^{13}CO. Carbonyl and methyl portions of spectra are shown on different scales. Rate constants for cis → trans and trans → cis processes were chosen for best fit of the methyl region, then used to simulate the carbonyl region.

the value of the trans coupling constant was much larger than the other two.

Stereochemical Nonrigidity and Isomerization. Our previous study of *cis*-$\mathrm{Fe(CO)_4(SiMe_3)_2}$ established that averaging of axial and equatorial ^{13}CO resonances was rapid on the NMR time scale at room temperature, and that ligand dissociation did not occur during the averaging process.[1] A favored averaging mechanism involved isomerization to the trans form (in which all ^{13}CO groups are equivalent) and back to the cis form; this mechanism would not require that an observable amount of the trans intermediate be present, and indeed it was not observed in the ^{13}C NMR spectrum of *cis*-$\mathrm{Fe(CO)_4(SiMe_3)_2}$. The stereochemically rigid character of the chelate *cis*-$\mathrm{Fe(CO)_4(Me_2SiCH_2CH_2SiMe_2)}$,[19] in which the trans isomer is inaccessible, was consistent with such a mechanism.[1]

Alternative axial-equatorial averaging processes which do not involve the trans form can readily be imagined. If the activation energy for any of these alternative processes is lower than that for isomerization, then averaging will occur in the cis molecule independently of the trans. A test of this possibility is afforded by several of the compounds reported here, for which both cis and trans isomers are clearly observable in the ^{13}C NMR spectrum below coalescence. In such cases, *all three ^{13}CO peaks of the spectrum appeared to coalesce to a single peak at the same rate as the temperature was raised.* Qualitatively, there was no indication of earlier coalescence of the two peaks of the cis compound as would have been expected had an averaging mechanism of lower barrier been available in the cis isomer.

In order to show more quantitatively that the trans isomer is involved as an intermediate in the averaging process, a detailed study was made of the cis–trans isomer mixture of $\mathrm{Os(CO)_4(SiMe_3)_2}$. This compound was chosen in view of the quality of the spectra obtainable and the fact that reasonable amounts of both isomers were present. Its thermal stability was such that spectra could be obtained up to 140 °C, where coalescence was well advanced. Moreover, the dynamics of the cis–trans isomerization of the compound had been investigated earlier by ^{1}H NMR.[2]

Carbon-13 spectra of the carbonyl and methyl regions of $\mathrm{Os(CO)_4(SiMe_3)_2}$ between 30 and 140 °C are shown in Figure 3. The rate constants indicated are those which best simulate the methyl region; they lead to $\Delta H^\dagger$ = 16.4 kcal mol^{-1}, $\Delta S^\dagger$ = −2.3 eu for the cis-to-trans reaction, in satisfactory agreement with the values $\Delta H^\dagger$ = 17.9 kcal mol^{-1}, $\Delta S^\dagger$ = 1.6 eu obtained by ^{1}H NMR in dibromomethane.[2]

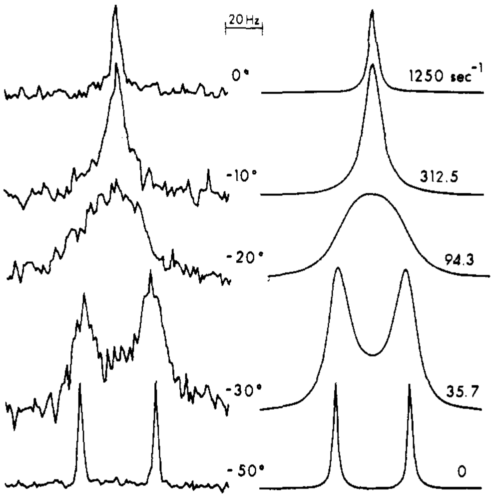

Figure 4. Variable-temperature Fourier transform ^{13}C NMR spectra of *cis*-$\mathrm{Fe(CO)_4(GeMe_3)_2}$ in $\mathrm{CD_2Cl_2}$. Chemical-shift values for low-temperature limiting spectrum (−50 °C) are 208.94 and 207.15 ppm downfield from tetramethylsilane, and half-width of both peaks is 2.8 Hz. Derived activation parameters from simulated spectra at right are $\Delta H^\dagger = 12.5 \pm 0.4$ kcal mol^{-1} and $\Delta S^\dagger = 0.6 \pm 1.5$ eu.

The rate data obtained from the methyl region were then used to calculate the spectra for the carbonyl region, under the assumption that axial-equatorial averaging occurs only via the trans isomer. The excellent agreement between observed and simulated spectra in the carbonyl region justifies the assumption and must be regarded as strong evidence that this is the major, if not the only, process occurring for axial-equatorial averaging in the cis isomer. Line-shape analysis reveals that any other process which interchanges the axial and equatorial carbonyls must have a rate less than about one-tenth that for cis–trans isomerization; otherwise, detectable broadening of the cis carbonyl signals would result.[23] This conclusion is entirely in accord with the results of a study of the isomerization of stereospecifically labeled *cis*-$\mathrm{Ru(CO)_4(SiCl_3)_2}$ which will be reported shortly.[24]

Trends in Activation Energies. We discuss here the variation over the family of compounds studied of the barrier to axial-equatorial averaging. In view of the foregoing, this is assumed to be equivalent to the barrier for cis-to-trans isomerization in all cases.

The most striking fact is that barriers are lowest for the iron compounds. All of the *cis*-$\mathrm{Fe(CO)_4(EMe_3)_2}$ derivatives exhibit a single ^{13}CO resonance at room temperature, as shown in Figure 4 for *cis*-$\mathrm{Fe(CO)_4(GeMe_3)_2}$. Activation parameters for *cis*-$\mathrm{Fe(CO)_4(GeMe_3)_2}$ derived from spectral simulation are $\Delta H^\dagger = 12.5 \pm 0.4$ kcal mol^{-1} and $\Delta S^\dagger$ = 0.6

Table IV. Coalescence Temperatures and Free Energies of Activation for Axial–Equatorial Averaging in *cis*-$M(CO)_4(ER_3)_2$ Derivatives[a]

Compd	$\Delta\delta$, Hz	Coalescence temp, °C	$\Delta G^\dagger$, kcal mol^{-1}, at coalescence
$Fe(CO)_4(SiMe_3)_2$[b,c]	19.5	−55	10.7 (10.9)[j]
$Fe(CO)_4(GeMe_3)_2$[b]	40.5	−20	12.1 (12.3)[j]
$Fe(CO)_4(SnMe_3)_2$[d]	4.7	−75	10.2
$Fe(CO)_4(SiMe_2Cl)_2$[e]	55.0	5	13.2
$Fe(CO)_4(SiMeCl_2)_2$[e,f]	52.5	70	16.5
$Fe(CO)_4(SiCl_3)_2$[e,f]	47.5	90	17.5
$Ru(CO)_4(SnMe_3)_2$[g]	112.3	100	17.4
$Ru(CO)_4(SiCl_3)_2$[h]			25.7
$Os(CO)_4(SiMe_3)_2$[f,i]	199.0	100	17.0 (16.8)[j]

[a] From ^{13}C NMR spectra with the single exception noted. $\Delta\delta$ is the chemical-shift difference between axial and equatorial carbonyl groups in the low-temperature limiting spectrum. [b] CD_2Cl_2 solvent. [c] From ref 1. [d] CD_2Cl_2–methylcyclohexane-d_{14} (1:1) solvent (see text). [e] Toluene-d_8 solvent. [f] Trans isomer also present (see text and Table II), the peaks of which are involved in coalescence. [g] As neat liquid. [h] Free energy of activation for cis to trans isomerization in *n*-octane by conventional kinetic methods as calculated from data in ref. 2. [i] Decalin solvent. [j] Values in parentheses are $\Delta G^\dagger$ calculated for coalescence temperature from $\Delta H^\dagger$ and $\Delta S^\dagger$ obtained from complete line-shape analysis treatment.

± 1.5 eu. Corresponding values for the silicon analog *cis*-$Fe(CO)_4(SiMe_3)_2$ are $\Delta H^\dagger = 10.4 \pm 0.6$ kcal mol^{-1} and $\Delta S^\dagger = 2.3 \pm 2.6$ eu.[1] The tin derivative presents some special problems and is discussed below, but its barrier is very similar to those of the silicon and germanium analogues.

Although it was an objective of the present investigation to characterize the nonrigid behavior of these compounds quantitatively, the quality of ^{13}C NMR spectra in the region of collapse for most derivatives was rather poor despite all reasonable efforts (see Experimental Section). Attempts at simulation were not justified in these cases. However, to permit at least a qualitative assessment of barriers, we present in Table IV values of $\Delta G^\dagger$ calculated at the coalescence temperature from the axial-equatorial ^{13}CO separation at the low-temperature limit. As Table IV shows, the crude $\Delta G^\dagger$ values so calculated are in excellent agreement with those from a complete line-shape analysis where available. This is true even in the case of $Os(CO)_4(SiMe_3)_2$, where the involvement of the trans form in coalescence is ignored in the crude calculation. Thus, we consider that the $\Delta G^\dagger$ values of Table IV are useful as an indication of trends.

Free energies of activation for the averaging process are 6–8 kcal higher for the ruthenium and osmium derivatives than for the corresponding iron compounds (of Table IV). A similar trend was noted among the hydrides $MH_2[P(OR)_3]_4$ (M = Fe, Ru) insofar as the barrier to rearrangement was concerned;[25] thus $\Delta G^\dagger$ for $FeH_2[P\text{-}C_6H_5(OEt)_2]_4$ was 12.2 kcal, while for $RuH_2[P\text{-}C_6H_5(OEt)_2]_4$ it was 17.2 kcal. An explanation suggested for this trend in the hydride series was that the complex of the smaller iron atom was more distorted from octahedral, favoring the proposed tetrahedral jump mechanism.[25]

There is at present insufficient evidence to know whether a similar rationale is appropriate for the trend in $M(CO)_4(EMe_3)_2$ complexes. It is by no means certain that the tetrahedral jump, heretofore suggested only for hydride derivatives, could reasonably be invoked for bulky EMe_3 ligands. In contrast to the $FeH_2[P(OR)_3]_4$ complexes,[25] the simple NMR spectra of the present compounds permit no mechanistic inferences. A considerable range of distortion in the ground state is possible, from the pseudo-bicapped tetrahedral *cis*-$Fe(CO)_4(SiMe_3)_2$[1] to the almost perfectly octahedral *cis*-$Ru(CO)_4(GeCl_3)_2$.[26]

A final important trend arises in the series $Fe(CO)_4(SiMe_{3-n}Cl_n)_2$, where the barrier increases steadily with increasing chlorine substitution. Thus (Table IV), $\Delta G^\dagger$ = 10.7 kcal for $n = 0$, 13.2 kcal for $n = 1$, 16.5 kcal for $n = 2$, and 17.5 kcal for $n = 3$. The same trend was previously noted in the osmium series $Os(CO)_4(SiMe_3)_2$, $Os(CO)_4(SiMe_2Cl)_2$, and $Os(CO)_4(SiMeCl_2)_2$,[2] but no information is available for $Os(CO)_4(SiCl_3)_2$, for which only the trans isomer is known. An independent determination of activation parameters for cis–trans isomerization by ^1H NMR in $Os(CO)_4(EMe_3)_2$ derivatives is in progress.

The Case of *cis*-$Fe(CO)_4(SnMe_3)_2$. This compound is one of the most interesting members of the series. It exhibits a single ^{13}CO resonance down to −80 (CD_2Cl_2) and −90 °C (toluene-d_8). Attempts to reach lower temperatures using methylcyclohexane-d_{14} failed because of high viscosity of the solution below −60 °C. Using a ^{13}CO-enriched sample in the solvent CF_2HCl-CD_2Cl_2 (4:1), a single resonance was again observed at −110 °C. However, all three Sn-^{13}CO couplings were observed, which established that the compound is stereochemically rigid at −110 °C, and that the single carbonyl resonance is due to accidental degeneracy of the axial and equatorial peaks.

In the mixed solvent methylcyclohexane-d_{14}-CD_2Cl_2 (1:1), two ^{13}CO peaks separated by 4.7 Hz were observed at −110 °C. At the end of data collection, it was noted that the solution had separated into two layers. However, we believe that there was a genuine separation of the axial and equatorial resonances since two sets of ^{13}CO-Sn couplings were observed to be centered about the peak to low field and one stronger set centered about the high-field peak. The couplings were identical in magnitude with those found in the CF_2HCl-CD_2Cl_2 experiment.

The ^{13}C NMR spectrum of *cis*-$Fe(CO)_4(SnMe_3)_2$ at −110 °C is anomalous in two ways. From Sn-^{13}CO couplings, the axial carbonyl resonance can be assigned as that at higher field, which is in contrast with all other members of the series where assignment has been possible. It is also found (Table III) that $^2J(\text{Sn-}^{13}CO_{ax})$ is greater than either $^2J(\text{Sn}_{trans}\text{-}^{13}CO_{eq})$ or $^2J(\text{Sn}_{cis}\text{-}^{13}CO_{eq})$, again in contrast to the ruthenium and osmium analogues. Because of this anomaly, assignments of the cis and trans couplings of the equatorial carbonyls must be regarded as uncertain. These peculiarities may be the consequence of a severe distortion of *cis*-$Fe(CO)_4(SnMe_3)_2$ from octahedral geometry, as has been found in the solid state structure of *cis*-$Fe(CO)_4(SiMe_3)_2$.[1]

On warming, the two carbonyl peaks coalesced at −75 °C. Similarly the ^{13}CO-Sn couplings collapsed but, because of their large separation, did not reappear—as a single doublet about the main peak—until 20 °C. The retention of coupling in the high-temperature limiting spectrum establishes the crucial point that the averaging process occurs *without ligand dissociation.* This has been shown to be the case in a similar way for *cis*-$Fe(CO)_4(SiMe_3)_2$,[1] and it is assumed that all the compounds of this type behave similarly.

The weighted average (75 Hz) of the coupling constants in $Fe(CO)_4(SnMe_3)_2$ from the slow exchange spectrum was not quite equal to the value (60 Hz) found in the high temperature limiting spectrum. This may be due to the presence of a small amount of *trans*-$Fe(CO)_4(SnMe_3)_2$ at high temperatures. In *trans*-$Os(CO)_4(SnMe_3)_2$, $^2J(\text{Sn-}^{13}CO)$ is 31 Hz, smaller than any coupling constant in the cis isomer (Table III).

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(15) An interesting example is $Fe(CO)_4(SiCl_3)_2$, which on the basis of its infrared spectrum, was taken to be the cis isomer.[6] It was claimed that the trans isomer was recognized by its infrared spectrum as a more volatile component from the reaction of $Fe_3(CO)_{12}$ and $HSiCl_3$.[16] However, in view of the low barrier for interconversion of *cis*- and *trans*-$Fe(CO)_4(SiCl_3)_2$ shown in the present work, all normal infrared solution measurements would involve the equilibrium cis-trans mixture. The suggestion[17] that bands attributed to *trans*-$Fe(CO)_4(SiCl_3)_2$ are due in reality to *cis*-$Fe(CO)_4(H)SiCl_3$ is almost certainly correct. In fact, the trans isomer of $Fe(CO)_4(SiCl_3)_2$ does exist (about 20% at equilibrium), but there is no valid evidence for it from infrared studies.

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Carbon-13 Nuclear Magnetic Resonance Study of the Fluxional Behavior of Cyclooctatetraenetricarbonyliron and -ruthenium

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Abstract: The fluxional behavior of the title compounds has been investigated by ^{13}C NMR. The 1,2 shift mechanism for the ruthenium compound, previously deduced from ^1H NMR spectra, has been confirmed and a new assessment of the activation parameters, which is in satisfactory agreement with the previous one, has been made. The main new result, however, is that for the iron compound, where proton NMR had failed to reveal the mechanism because of the low temperature required to attain the slow exchange limit, the mechanism has now been proved, directly and unambiguously, to be 1,2 shifts. The Arrhenius parameters obtained by a complete line shape analysis are: $E_a = 8.1$ (2) kcal and log $A = 13.5$ (2) for the iron compound; $E_a = 8.6$ (1) kcal and log $A = 13.3$ (1) for the ruthenium compound. The averaging of the CO signals is also observed in the same general temperature range, but the mechanistic relationship between the two processes is not unambiguously revealed by the available data, contrary to an earlier assertion by others.

One of the earliest fluxional organometallic molecules to be subjected to study by nuclear magnetic resonance spectroscopy was $C_8H_8Fe(CO)_3$, but proton NMR spectra proved unable to resolve the mechanistic problem umambiguously,[1-3] in part because the slow exchange limit was not reached at the lowest practicable temperature of measurement (ca. −150 °C).[3-8] Fortunately, the ruthenium analogue reached the limiting spectrum at about −140 °C, and this spectrum was sufficiently simple to allow mechanistic analysis.[9,10] It was possible to show that rearrangement of $C_8H_8Ru(CO)_3$ takes place by 1,2 shifts and also to make an estimation of the activation parameters, viz., $E_a = 9.4 \pm 0.5$ kcal/mol and log $A = 14.0 \pm 0.7$. Because of the uncertainties in line widths introduced by the proton-proton coupling, which could only be treated approximately, the true uncertainties in these parameters (the limits quoted reflect only the statistical errors in the least-squares plots) should be two-three times higher than those quoted. Since the 1,2 shift mechanism was found to operate for $C_8H_8Ru(CO)_3$ it was suggested[9,10] that it probably operates also for $C_8H_8Fe(CO)_3$, but this has been only a plausible supposition and not a proven fact.

With the availability of Fourier transform carbon-13 NMR, we were prompted to reexamine $C_8H_8Fe(CO)_3$ and also, for comparison, $C_8H_8Ru(CO)_3$. The advantages of ^{13}C spectroscopy,[11] particularly the greater range (in hertz) of chemical shifts and the absence of spin-spin coupling (if the abundance of ^{13}C is kept low and protons are decoupled) seemed likely to make possible the mechanistic analysis that had not been attainable previously. We have noted a brief report[4] on the ^{13}C spectrum of $C_8H_8Fe(CO)_3$ which showed only that the structure in solution is of the (1-4)-tetrahapto type since a four-signal spectrum for the ring carbon atoms can be observed below −120°. Apparently no mechanistic conclusions were drawn; in any event, none was stated. It was stated that no spectra in the temperature range between −120 and −20° were recorded. We have carried out carbon-13 NMR studies of the rearrangement mechanisms of both the iron and ruthenium compounds and the results are reported in detail here.