A Carbon-13 and Proton Magnetic Resonance Examination of Solute Structures, Equilibria, and Structural Interconversions in Some Dinuclear η^5-Dienylruthenium, -iron, and -nickel Carbonyls

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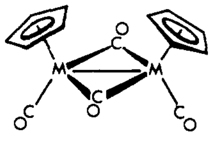
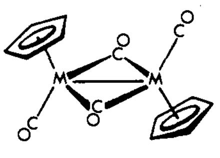
Abstract: As a part of an NMR investigation of carbonyl molecular interconversion mechanisms, temperature dependent proton and ^{13}C NMR spectra have been obtained for eight dinuclear η^5-dienyliron and -ruthenium carbonyls of general structure (η^5-dienyl)$M_2(CO)_4$ (M = Fe, Ru; dienyl = C_5H_5, $CH_3C_5H_4$, indenyl, and tetrahydroindenyl). Resonances characteristic of both cis and trans bridged carbonyl isomers of the four iron complexes could be detected and both thermodynamic and kinetic parameters measured for molecular interconversions of their species in solution. Spectral data for the ruthenium complexes are, however, substantially at variance with those measured in the iron systems in that resonances are seen to be characteristic both of the bridged and a nonbridged isomer. An explanation for this variance and for other poorly understood previous studies of the ruthenium complexes is provided by reference to a detailed mechanism first put forth by Cotton and co-workers and later by Roberts and co-workers. Briefly, the barrier to rotation of the nonbridged iron dimers is seen to be markedly greater than that for the analogous ruthenium systems. These data, together with similar already published studies[51] of the isoelectronic $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ and $[(\eta^5\text{-}C_5H_5)_2Mn(CO)(NO)]_2$, show that the steric considerations of the Cotton mechanism do not fully explain the observed data. We are led to suspect that metal-metal bonding in these complexes may be directional and, hence, that at least a part of the rotational barrier of nonbridged isomers may be due to hindered internal rotation about the metal-metal bond. Spectral data for the related $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ and $[(\eta^5\text{-}C_5H_5)_2FeNi(CO)_3]$ are also reported.

Since the initial synthesis[3] by Piper, Cotton, and Wilkinson, numerous articles in the chemical literature have dealt with applications of spectral[4-17] and x-ray crystallographic[11,18-23] methods to structural studies of the η^5-cyclopentadienyliron dicarbonyl dimer and related compounds. A renewed interest in such studies[23-27] has been generated by development and application in our laboratory[28,29] and elsewhere[30] of techniques useful for obtaining carbon-13 NMR spectra of metal carbonyls. Our present study reports the results of a proton and ^{13}C NMR investigation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (I) and of nine related compounds chosen to elucidate and test mechanisms for structural interconversions observed for these molecules in solution. X-ray crystallographic studies[11,18,19] have determined that, in the solid state, I is found to exist in both the cis **1** and trans **2** isomeric forms, whereas only the trans structure is known[21] for the similar $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$.

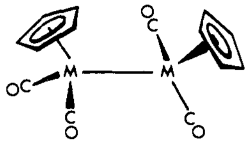
The solution structures of molecules of this type have been the subject of some controversy. Investigations of vibrational spectra of I showed that the molecule must undergo substantial structure rearrangement in solution. Subsequent early Raman and infrared spectral studies[5-7] together with dipole moment measurements[31] led to the view that, in nonpolar solvents, the molecule existed mostly as structure **1**, plus a small amount of a nonbridged form such as **3**. These results were strongly challenged by Manning[14] who measured solvent polarity dependencies of ir spectra of the iron dimer I and concluded that the suggested predominance of isomer **1** was not acceptable and that the presence of cis, trans, and nonbridged isomers was required to explain fully his observations. The amount of nonbridged isomer present was thought to be quite small. Bullitt, Cotton, and Marks[10] confirmed the presence of major quantities of only two different, rapidly interconverting isomeric forms of I in solution by measuring its solvent and temperature dependent ^{1}H NMR spectra. The marked variation with solvent polarity seen for ^{1}H NMR resonances assigned to the two forms strongly indicated the presence of isomers **1** and **2**.



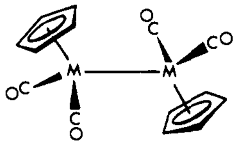
1,**5**



2,**6**



3,**7**



4,**8**

1 - 4, M = Fe
5 - 8, M = Ru

A lack of complete understanding has also typified the results of spectral studies of the analogous dinuclear ruthenium carbonyl, $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$. Early ir studies[7,9] suggested the presence in solution of both bridged and open isomers of the type **5** and/or **6** and **7**. Thermodynamic parameters were estimated by ir for the bridged ⇄ nonbridged equilibria,[7] but previous proton and ^{13}C NMR studies failed[10,27] to provide either kinetic or thermodynamic data concerning structural equilibria in solution.

The recent development of techniques for observing ^{13}C NMR spectra of metal carbonyls allowed us to conduct the first ^{13}C NMR study of fluxional metal carbonyls.[29] Our study of I in solution provided the first truly definitive evidence that structures **1** and **2** were the two predominant forms present in solution and that both forms could undergo rapid intramolecular bridged-terminal carbonyl interconversions of the type **9** ⇄ **10** in I as well as cis-trans structural interchange.[32] To

9

10

test these conclusions, we began the present ^{13}C NMR study of several $[(\eta^5\text{-dienyl})Fe(CO)_2]_2$ complexes in which the η^5-dienyl ligands were either indenyl or substituted cyclopentadienyl moieties (II-IV). During the course of this study, Adams and Cotton[24] and later Harris, Rosenberg, and Roberts[27] proposed a mechanism to explain the occurrence of this type of carbonyl interchange.

The postulated mechanism for carbonyl interconversion within the trans isomer of I requires pairwise opening of the carbonyl bridges followed simply by random bridge reclosing ($\mathbf{1} \rightleftarrows \mathbf{3}$) of any two trans disposed carbonyls. To accomplish carbonyl interconversion for the cis isomer **2**, in addition to bridge opening ($\mathbf{2} \rightleftarrows \mathbf{4}$), rotations about the iron–iron bond in the nonbridged isomer **4** must also occur. The conformer rotation $3 \rightleftarrows 4$ would accomplish simultaneous cis–trans isomerization and carbonyl interconversion.

The mechanism suggested to us certain experiments by which we might test its underlying assumptions and conclusions and from which we might be able to deduce additional information about the relative importance of steric and electronic effects on the rates and activation energies of the structural interconversion processes. Our studies for I provide further definition of the molecular interconversion processes and, therewith, are confirmatory of several major aspects of the proposed mechanism. However, the present investigations of analogous ruthenium systems V-VIII reveal that the nature of the central metal atom importantly and understandably influences the activation energy profile for these reactions. Our examination of several η^5-dienylruthenium dicarbonyl dimers has proven conclusively that in contrast to the analogous iron systems, $\mathbf{5}, \mathbf{6} \rightleftarrows \mathbf{8}$ equilibria may be detected between open and bridged forms present in solution and that rates of interconversion between such forms are too rapid to be measured by ^{13}C NMR techniques. We were, however, able to obtain rate constants and activation parameters for the cis-trans interconversion process $\mathbf{5} \rightleftarrows \mathbf{6}$.

These data, together with that from previously reported studies of rotational barriers for nonbridged isomers of I and for the isoelectronic compounds $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ and $[(\eta^5\text{-}C_5H_5)Mn(CO)(NO)]_2$ indicate that the steric considerations of the proposed mechanism do not fully explain the observed activation energy data. Rather, other considerations, perhaps directional metal-metal bonding must be considered. It is possible that at least a part of the rotational barrier may be due to hindered internal rotation about the metal-metal bonds.

Experimental Section

All preparative procedures were carried out under an atmosphere of prepurified nitrogen. Solvents were deoxygenated prior to use.

Preparation of ^{13}CO Enriched $[(\eta^5\text{-dienyl})Fe(CO)_2]_2$ Compounds. Iron pentacarbonyl enriched to 33 mol % ^{13}CO (by mass spectroscopy) was prepared for use in synthesis by twice stirring a heptane solution of $Fe(^{12}CO)_5$ (Ventron Corp.) in an atmosphere of 90% carbon-13 monoxide (Mound Laboratories, Monsanto Corp.) over 10% Pd on charcoal catalyst.[33]

By using 1.5 ml of enriched $Fe(CO)_5$ in 1.5 ml of heptane solution, ^{13}CO enriched $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (I) may be prepared according to the procedure outlined by King and Stone.[34] Modified versions of this method were similarly used to prepare enriched $[(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2]$ (II) and $[(\eta^5\text{-indenyl})Fe(CO)_2]_2$ (IV). Complex II was prepared by refluxing 1.5 ml of enriched $Fe(CO)_5$, 1.5 ml of heptane, and 1.5 ml of purified[35] methylcyclopentadiene dimer (Aldrich Chemical Co.) until gas evolution ceased (ca. 4 h). The red-brown reaction mixture cooled to −15 °C overnight yielded the desired product in 80% yield which was further purified by chromatography on alumina (Woelm activity grade 1) with dichloromethane elution, followed by solvent evaporation and recrystallization from dichloromethane–pentane. Anal. Calcd for $[(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2]_2$: C, 50.3; H, 3.8. Found: C, 50.1; H, 3.8. (All analyses were performed on ^{12}CO products.)

Complex IV was similarly prepared by refluxing 1.5 ml of enriched $Fe(CO)_5$, 1.5 ml of heptane, and 15 ml of purified (by distillation) indene (Aldrich Chemical Co.) until cessation of gas evolution (ca. 6 h). The red-brown solution obtained was slowly cooled to ambient temperature and poured into 60 ml of cold (0 °C) pentane, giving the product in 63% yield. Further purification was performed by using chromatography and recrystallization as described for II above. Anal. Calcd for $[(\eta^5\text{-}C_9H_7)Fe(CO)_2]_2$: C, 58.2; H, 3.1. Found: C, 57.5; H, 3.5.

Enriched $[(\eta^5\text{-tetrahydroindenyl})Fe(CO)_2]_2$ (III) was obtained by catalytic hydrogenation[36] of ^{13}CO enriched IV in ethanol over PtO_2 (Strem Chemicals). Recrystallization from ethanol yielded the pure product.

Preparation of ^{13}CO Enriched $[(\eta^5\text{-dienyl})Ru(CO)_2]_2$ Compounds. $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ (V) was prepared and purified as described by Fischer and Vogler.[37] Enrichment was accomplished as described for IX below. After chromatography on alumina, sublimation yielded the enriched complex.

To prepare $[(\eta^5\text{-}CH_3C_5H_4)Ru(CO)_2]_2$ (VI), a solution of the nonstoichiometric $Ru(CO)_nCl_m$ was first formed by passing CO through a refluxing 2-ethoxyethanol solution of hydrated $RuCl_3$ (Ventron Corp.), as described by Dawes and Holmes.[38] To this solution was added sodium methylcyclopentadienide (200% excess based on $RuCl_3$). After heating at 80 °C for 8 h, solvent was removed under vacuum and the residue extracted with CH_2Cl_2 until colorless extracts were observed. The orange CH_2Cl_2 solution was then chromatographed on alumina with CH_2Cl_2 elution. The orange band on the column was collected and solvent removed on a rotary evaporator. Recrystallization from CH_2Cl_2–pentane yielded the pure product. Anal. Calcd for $[(\eta^5\text{-}CH_3C_5H_4)_2Ru(CO)_2]_2$: C, 40.68; H, 2.97. Found: C, 40.82; H, 2.89. Enrichment with ^{13}CO was effected by stirring a CH_2Cl_2 solution of VI in an atmosphere of 90% ^{13}CO for 3 days.

$[(\eta^5\text{-indenyl})Ru(CO)_2]_2$ (VIII) was prepared by using a new method described by Knox and Humphries[39] for preparation of V. Distilled indene (10 ml) and $Ru_3(CO)_{12}$ (1 g) were refluxed in heptane (50 ml) for 24 h without exclusion of air. The rust-colored precipitate formed was filtered and air dried. The crude product was purified by overnight sublimation at 115 °C (0.3 mm) to remove unreacted $Ru_3(CO)_{12}$. Further purification by chromatography on alumina with dichloromethane elution and final recrystallization from CH_2Cl_2–pentane was needed. This complex was enriched in ^{13}CO as described for VI above. Anal. Calcd for $[(\eta^5\text{-}C_9H_7)Ru(CO)_2]_2$: C, 48.53; H, 2.57. Found: C, 48.3; H, 2.51.

Catalytic hydrogenation of VIII in tetrahydrofuran over PtO_2 (10 h) yielded $[(\eta^5\text{-tetrahydroindenyl})Ru(CO)_2]_2$ (VII), which was purified by chromatography and recrystallization from CH_2Cl_2–pentane. ^{13}CO enrichment was achieved in the same manner as described for VI. Anal. Calcd for $[(\eta^5\text{-}C_9H_{11})Ru(CO)_2]_2$: C, 47.83; H, 3.99. Found: C, 47.60; H, 3.92. $[(\eta^5\text{-}C_9H_{11})Ru(CO)_2]_2$: mp 123–124 °C; ir (CO region, tetrahydrofuran) 1986 (17.9), 1972 (17.5), 1954 (15.4), 1835 (2.1), 1809 (10); NMR ($CDCl_3$) δ 4.90 (1), 4.88 (2), 2.56 (4), 1.87 (4).

Preparation of ^{13}CO Enriched $[(\eta^5\text{-}C_5H_5)_2FeNi(CO)_3]$ and $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$. $[(\eta^5\text{-}C_5H_5)FeNi(CO)_3]$ (IX) was prepared by using isotopically natural $Fe(CO)_5$ in the synthesis described by Tilney-Bassett.[40] Enrichment with ^{13}CO was effected by stirring a dichloromethane solution of IX in an atmosphere of 90% carbon-13 enriched CO for 2 weeks under fluorescent light. After enrichment, purification by chromatography and recrystallization as described for II above was required to remove traces of I, $Ni(CO)_4$, and nickelocene.

Enriched $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$(X) was obtained[41] by stirring overnight, in an atmosphere of 90% ^{13}CO, a dichloromethane solution of the commercially purchased compound (Strem Chemicals).

Spectral Measurements. Infrared spectra were recorded by using a Perkin-Elmer 457 spectrophotometer and were calibrated by using polystyrene film. Solutions were prepared under nitrogen and were transferred via syringe to matched NaCl ir cells. Solid state spectra were recorded as Nujol mulls.

Proton NMR data were obtained either on a Varian A-56/60 or an HA-100 spectrometers. Carbon-13 NMR spectra at 22.628 MHz were measured by using a Bruker HFX-10 spectrometer modified for wide-band spectral measurements as described[42] by Traficante et al. and equipped with a Nicolet 1083 computer, a Diablo disk memory unit, and a Nicolet 293 I/O controller.

Three solvent systems were employed to extend the range of temperature-dependent ^{13}C NMR studies from +100 to −160 °C. For work above +9 °C, samples were prepared under nitrogen in either chloroform, dibromomethane, or toluene solution with 20% 1,2-difluorotetrachloroethane added to serve as an ^{19}F heteronuclear NMR lock. In the temperature range +9 to −130 °C, Genetron 21 (dichlorofluoromethane, Matheson Gas Products) was used both as solvent and NMR lock. Spectra measured below −130 °C employed samples dissolved in a 2:1 mixture of Freon 22 (chlorodifluoromethane, Matheson Gas Products) and Genetron 21, with the former serving as ^{19}F lock. All samples contained 0.03 M tris(acetylacetonato)chromium (III), recrystallized from benzene-pentane, added to reduce carbonyl relaxation times.[28] Most samples contained ca. 5% carbon disulfide present as an internal ^{13}C chemical shift reference. Chemical shifts are reported in positive ppm downfield from TMS; the conversion from CS_2 to TMS being $\delta_{TMS} = \delta_{CS_2} + 192.4$ ppm.

Temperature calibration was achieved by reading values either from a thermocouple or a small thermometer inserted directly into a solvent-filled sample tube in the NMR probe. Optimum signal to noise in ^{13}C spectra was obtained by using in excess of 2000 pulse transients per spectrum. Most spectra were recorded over a spectral width of 5000 Hz. When higher resolution data were required, smaller spectral windows were employed.

The thermodynamic parameters for equilibria between the various isomers of the compounds studied were determined from the temperature dependence of equilibrium constants measured from changes in chemical shifts or integrated signal intensities as a function of temperature. Data were processed by using the least-squares program KINFIT.[43]

Analysis of NMR Data. Treatment of the dynamic NMR data was accomplished by using either the program DNMR-3 or a version of the program EXCHSYS.[44] The chemical shift differences between bridge and terminal carbonyls were sufficiently large so that thermally (but not kinetically) induced changes in chemical shift could be neglected.

Use of the program DNMR-3,[45] as described in detail by Roberts et al.,[27] allowed calculation of multiline ^{13}C spectra as a function of exchange rates. Both cis and trans isomer exchange rate constants at particular temperatures were determined by fitting calculated to observed spectra.

Exchange rates for the iron system trans isomers were also independently calculated by using a two site exchange matrix for the EXCHSYS program to generate a series of spectra and to fit the broadening at low temperatures of the bridge-terminal averaged carbonyl signal. Additional rate data were obtainable for the indenyl complex IV by fitting the collapse of the separated bridge and terminal carbonyl resonances of the trans isomer. This program could also be used to model the three site exchange process describing the higher temperature cis ⇄ trans isomerization. The exchange matrix, **K**, is given in (2) below.

$$\mathbf{K} = \begin{bmatrix} -1.0 & \dfrac{0.5C}{T + 0.5C} & \dfrac{T}{T + 0.5C} \\ 0.5T & -T & 0.5T \\ \dfrac{T}{T + 0.5C} & \dfrac{0.5C}{T + 0.5C} & -1.0 \end{bmatrix} \qquad (2)$$

Therein T and C represent relative populations of the trans and cis isomers ($T = 1 - C$) determined at each temperature from integrated carbonyl signal intensities. In these calculations, some additional line broadening of the averaged trans ^{13}CO resonance could be anticipated due to trans isomer carbonyl interchange. This was accounted for by using as the value of T_2 in the input parameters the trans carbonyl exchange determined lifetime. A simple two site exchange matrix sufficed to obtain rates for carbonyl exchange in the ruthenium and iron-nickel carbonyls. Rate constants provided by the two computational procedures fortunately agreed to within the error of the NMR measurements. Arrhenius and Eyring plots were constructed to obtain activation parameters from rate data.

Results

Proton and carbon-13 NMR spectra of ca. 0.2 M solutions of the ten dimetallic η^5-dienyl metal carbonyls listed in Table I have been obtained at numerous sample temperatures between −160 and 100 °C. The wide separations of chemical shifts and the facile, line broadening chemical exchange processes observed for these metal bonded carbonyls required, for resonance detection, the preparation of ^{13}CO enriched compounds and the use of several different solvents. Spectra representative of those obtained for the iron I–IV and ruthenium V–VIII carbonyls examined are displayed in Figures 1 and 2. A tabulation of carbonyl chemical shifts measured and solvents employed at various temperatures is provided in Table I.

Table I. Carbonyl ^{13}C Chemical Shifts

Compd	T, °C	$\delta_{ter}{}^a$	$\delta_{av}{}^a$	$\delta_{br}{}^a$
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (I)	$+55^b$		239.4	
	−40	210.2^c	241.9^d	273.2^c
	−70	210.2^c	242.4^d	274.1^c
	−126	210.4		275.9
$[(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2]_2$ (II)	$+74^b$		240.4	
	−24	210.5^c	242.6^d	274.7^c
	−69	210.8^c	243.4^d	276.0^c
	−125	211.1		277.4
$[(\eta^5\text{-}C_9H_{11})Fe(CO)_2]_2$ (III)	−7	211.2^c	242.8^d	275.5^c
	−52	211.4^c	244.0^d	277.0^c
	−61	211.5		277.3
	-141^e	211.6		278.7
$[(\eta^5\text{-}C_9H_7)Fe(CO)_2]_2$ (IV)	19^b	210.5^c	240.0^d	267.1^c
	−20	210.2^c	240.8^d	269.3^c
	−60	210.2		270.6
	−70	$210.3,^c$ 211.5^d		$271.0,^c$ 272.5^d
	−101	$210.3,^c$ 211.6^d		$271.9,^c$ 273.2^d
$[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ (V)	$+96^f$		208.7	
	−20		221.5	
	−82		225.4	
	−118	199.3		251.7
	-136^e	198.9		252.8
$[(\eta^5\text{-}CH_3C_5H_4)Ru(CO)_2]$ (VI)	50		222.5	
	25		223.0	
	−46		225.3	
	−121	199		255.6
$[(\eta^5\text{-}C_9H_{11})Ru(CO)_2]_2$ (VII)	100^f		220.7	
	55^f		221.5	
	−116	200.2		252.9
$[(\eta^5\text{-}C_9H_7)Ru(CO)_2]_2$ (VIII)	64		220.5	
	−111	198.5		250.0
$[(\eta^5\text{-}C_5H_5)_2FeNi(CO)_3]$ (IX)	−14		238.5	
	−112	209.4		254.5
$[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ (X)	25^b			225.5
	−98			226.8

[a] Chemical shifts in ppm vs. CS_2. Spectra taken in 95% $CHFCl_2$, 5% CS_2 solvent, unless noted. Subscripts refer to terminal (ter), averaged (av), or bridged (br) carbonyls. Resonances assigned to appropriate carbonyls of all isomers detected, unless noted otherwise. [b] Solvent: 75% CH_2Br_2, 20% $(CFCl_2)_2$, 5% CS_2. [c] Resonance assigned exclusively to cis isomer. [d] Resonance assigned exclusively to trans isomer. [e] Solvent: 63% CHF_2Cl, 32% $CHFCl_2$, 5% CS_2. [f] Solvent: 75% toluene, 20% $(CFCl_2)_2$, 5% CS_2.

In every case, the more downfield of the two or more ^{13}CO signals detected at low temperatures were assigned as bridged carbonyl resonances.[46] Higher sample temperatures resulted ultimately in broadening of all carbonyl resonances, followed by coalescence, except for the easily decomposed indenyl derivatives III and IV into a single averaged line which for the iron systems and for VIII remained chemical shift invariant with temperature. In contrast, the averaged resonances of the ruthenium complexes V–VII were seen to move upfield as

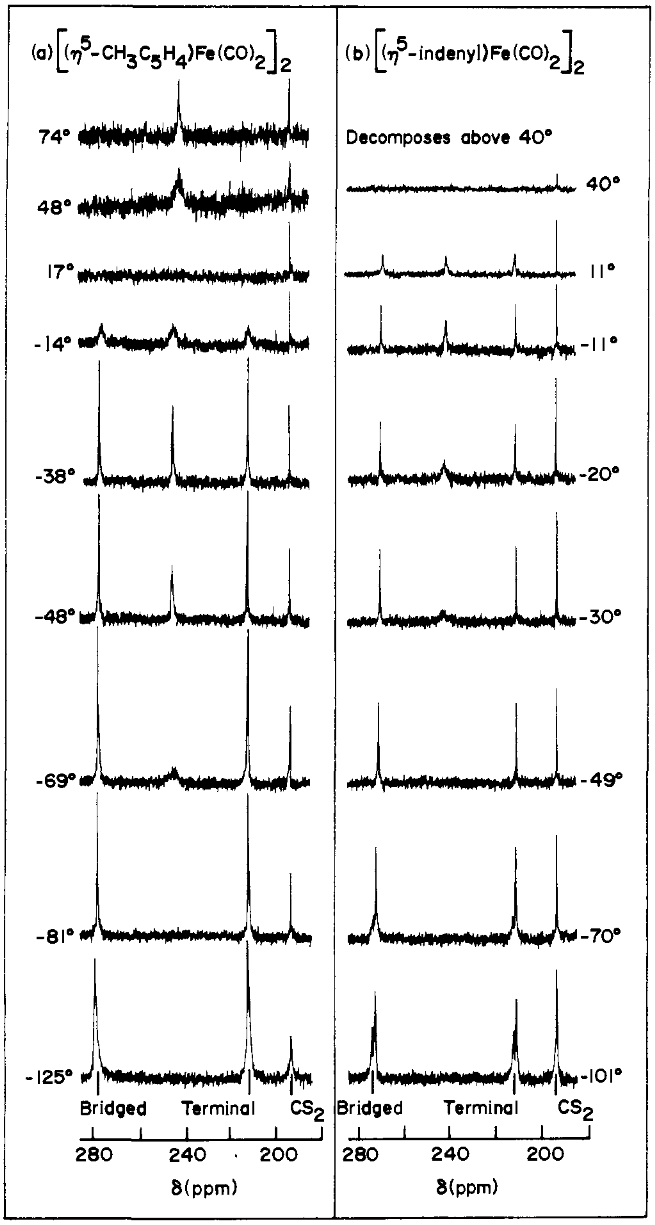


Figure 1. Temperature dependent ^{13}C NMR spectra (carbonyl region only) of (a) $[(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2]_2$ and (b) $[(\eta^5\text{-}C_9H_7)Fe(CO)_2]_2$.

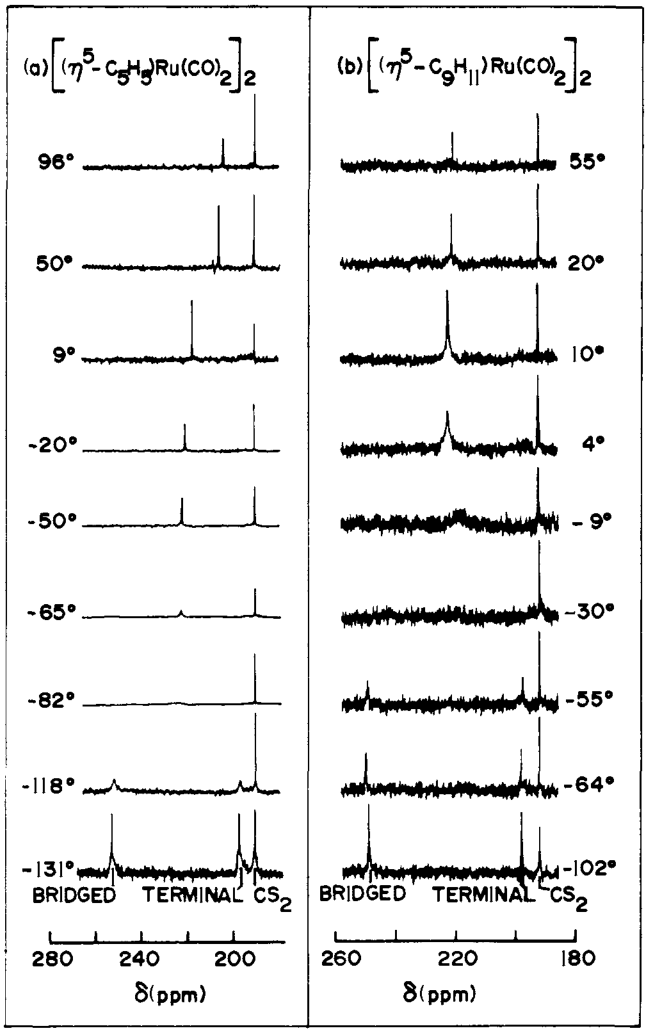


Figure 2. Temperature dependent ^{13}C NMR spectra (carbonyl region only) of (a) $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ and (b) $[(\eta^5\text{-}C_9H_{11})Ru(CO)_2]_2$.

sample temperatures were raised. This chemical shift dependence was utilized for V to determine thermodynamic parameters for the equilibrium between bridged and nonbridged tautomers present in solution. Similarly, the integrated intensities of carbonyl resonance lines measured as a function of temperature for I–IV were employed to obtain the thermodynamic parameters for the cis–trans equilibrium between structural isomers of the form **1** ⇄ **2**. Analyses of NMR line shapes were performed to obtain rate constants and activation parameters for the structural interconversions detected.

Spectral Data. Carbon-13 NMR spectra measured in this study for the iron carbonyls I–IV are reminiscent of those previously communicated[29] by us for I and, as such, provide evidence for two separate carbonyl exchange processes, the most facile of which can be viewed by NMR in Figure 1 for the methylcyclopentadienyl iron compound II as occurring between −125 and −35 °C and for the similar indenyl iron carbonyl IV between −102 and −9 °C. This low temperature process is clearly seen for IV to average two equally intense bridged (273.2 ppm) and terminal (211.6 ppm) carbonyl resonances. Studies at even very low temperatures, ca. −160 °C, failed to resolve similar, separate bridged, terminal resonances for I–III, although careful examination of the signals observed for I and II at −125 °C reveals that they are asymmetric. Activation energy data reported below leave little doubt that, at the solvent temperatures studied, separate signals should, in principle, be seen. It is likely that viscosity broadening, which below −120 °C limits resolution to ca. 1.0 ppm, as measured from the CS_2 reference lines, prevents their detection.

The source of the lower temperature exchange process is easily understood. Cotton et al. have reported[10] that it is possible to alter the ratio of the two separated cyclopentadienyl resonances seen for I at low temperatures by increasing solvent polarity and have argued that the more dipolar cis form **2** would reasonably be expected to be more stable in the higher dielectric medium. Similarly, if less polar solvents than $CHFCl_2$ are used to obtain ^{13}C NMR spectra of I–IV the intensity of the low temperature averaged carbonyl resonance increases in favor of the other as yet stationary ^{13}CO signals. The lower temperature carbonyl averaging process is therefore assigned to trans isomer bridge-terminal carbonyl interchange.[29]

The higher temperature exchange process, which occurs for II and IV above −14 and +11 °C, respectively, results in broadening and coalescing of all carbonyl resonances. Above 40 °C, the indenyl compounds decompose; however, spectra of the two remaining di-iron carbonyls taken at and above this temperature display the growth of an averaged, chemical shift invariant resonance found for II at 240.2 ppm. Concurrent with this process, both the proton and ^{13}C signals of the cyclopentadienyl ligands of I are observed to broaden and coalesce into a sharp line. Similar, though not so straightforward, data are obtained for the more complex ligand spectra of compounds II–IV. This set of spectral observations can be neatly accounted for by postulating that, at the higher sample temperatures, simultaneous cis–trans isomerization and cis isomer carbonyl interconversion become energetically allowed.[24,29]

Spectra recorded for the diruthenium compounds V–VIII may be compared with those obtained for the homologous diiron series. Low temperature spectra again evidence the presence of both bridged and terminal carbonyls, which, as illustrated for V and VII in Figure 2, are seen to broaden and coalesce at higher temperatures into a single sharp line, thereby providing evidence for only one bridge-terminal carbonyl exchange process. Yet another feature of the high temperature carbonyl spectra of the cyclopentadienyl ruthenium dicarbonyl solutions is of particular interest. As sample temperatures are raised, the bridge-terminal averaged carbonyl signals monotonically shift upfield toward the terminal carbonyl chemical shift region, without appreciable line broadening, from the averaged position which for V is a shift from 223.2 ppm at −50 °C to 208.7 ppm at 96 °C. Only relatively small shifts of the averaged resonance are observed for VI and VII and none for VIII. The marked chemical shifts seen for V indicate that we are detecting a population redistribution between open and bridged isomers of the form **5**, **6** ⇄ **7**, **8**, as has been postulated from ir spectral studies.[7]

Concurrent, temperature dependent proton NMR studies have been performed for the several diruthenium complexes V, VI, and VIII. As previously reported,[10] even at −110 °C only one sharp ^1H NMR signal may be observed for the cyclopentadienyl carbonyl V and, under similar conditions, we detect only one methyl proton and carbon resonance for VI. However, ^1H NMR spectra of the indenyl complex VIII are more informative. The spectrum in Figure 3a is typical of those obtained above −30 °C in a variety of polar solvents, i.e., $CHFCl_2$, CD_2Cl_2, and $(CD_3)_2CO$. Spectral features detected are easily assigned by reference to those reported[47] for the analogous $(\eta^5\text{-indenyl})_2Ru$. The cyclopentadienyl ring protons form an A_2B pattern, $J_{AB} = 0.5$ Hz, $(\nu_A - \nu_B) = 11$ Hz, while one relatively broad, slightly structured resonance is observed for the protons of the aromatic six-membered ring. In more nonpolar solvents such as 50% CS_2-$CDCl_3$, the $J_{AB}/\Delta\nu_{AB}$ ratio became ca. 1.0, giving rise to a complex multiplet.[48] At −54 °C in polar media (Figure 3b), both the benzenoid and cyclopentadienyl resonances are coalesced into two indistinct multiplets. Below −70 °C, benzenoid resonances are narrowed somewhat into one relatively sharp line at ~732 Hz and a broader line centered at ~670 Hz. Simultaneously, the A_2B multiplet is converted into a well defined, unsymmetrical five-line pattern, as illustrated in Figures 3c and 3d. The character of the low temperature ^1H NMR spectra is strongly influenced by solvent polarity. In CD_2Cl_2 solution, the integrated intensity ratio of the two benzenoid resonances is 1.58:1, whereas in the less polar 25% CS_2, 75% CD_2Cl_2 medium, that ratio becomes 1.22:1. The intensity of the most upfield cyclopentadienyl line may also be observed to markedly increase upon addition of CS_2. This signal becomes the dominant spectral feature of the C_5 ring proton region at −70 °C when the least polar solvent (50% CS_2, $CDCl_3$) available to us is used.

Two interpretations of the temperature dependent ^1H NMR data seem possible: (a) as temperature is lowered, the rate of cis–trans isomerization is decreased and separate resonances characteristic for ligands on each isomer are seen, or (b) rotation of the indenyl ligand about the ligand–metal bond slows and this in some complex way alters the ^1H NMR spectra.

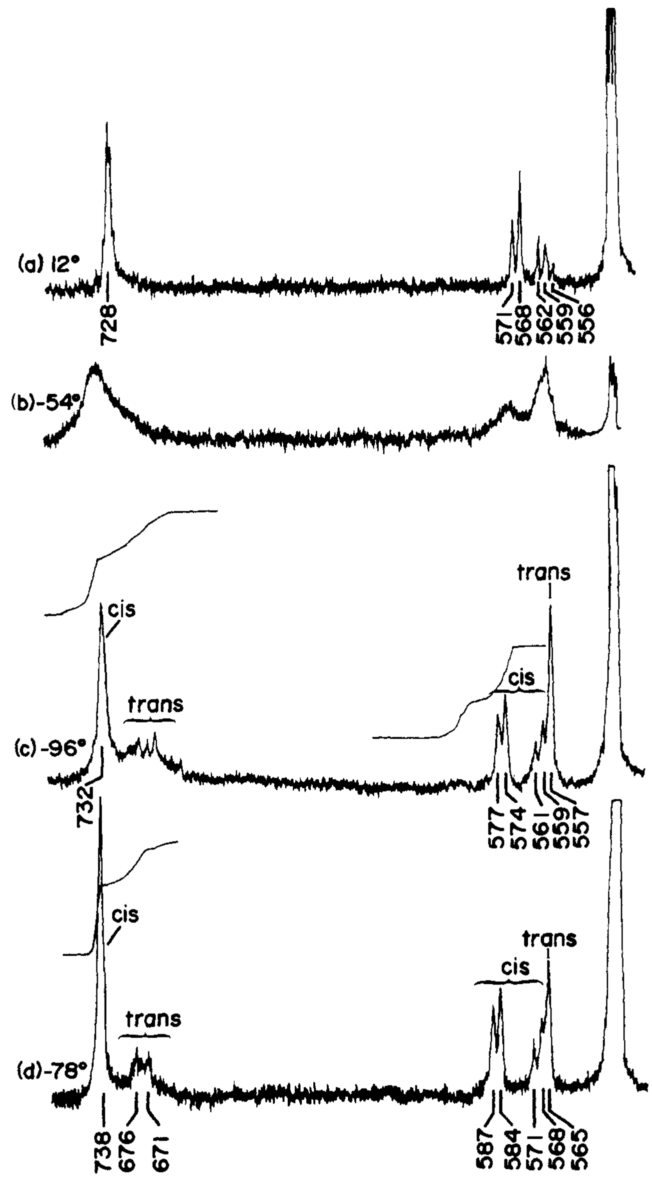


Figure 3. Temperature dependent 100 MHz ^1H NMR spectra of $[(\eta^5\text{-}C_9H_7)Ru(CO)_2]_2$. Spectra (a–c), 50% CD_2Cl_2 CS_2 solution, (d), CD_2Cl_2 solution. Chemical shifts in hertz.

The possibility (b) may be safely discarded on several grounds. First, activation energies for rotations of symmetrically bonded η^5-C_5 ring moieties are typically quite small,[49] <1 kcal for $(\eta^5\text{-}C_5H_5)_2Fe$.[50] The temperature required for coalescence of C_5 ring ^1H NMR signals 11 Hz apart for VIII was −54 °C, which, by assuming any reasonable frequency factor, leads to an estimated $E_a > 10$ kcal, far in excess of that required for this type of ring rotation. Furthermore, ligand ^1H NMR data obtained under conditions of slow ligand rotation are expected to be complex A_2B_2, A_2X_2, etc., and ABC, ABX, etc., spectra which should show solvent independent, whole number intensity ratios of separated resonances. Our observations are entirely at variance with these expectations.

We now must account for the observed ^1H NMR spectra in terms of possibility (a). It is well established that solvent polarity affects the equilibrium ratio of cis–trans isomers.[10,16] We are therefore led to assign the sharp C_6 ring signal to the cis isomer, and correspondingly, the broad multiplet which increases in intensity in nonpolar media is attributed to those protons of the trans structure. The intense, most upfield C_5 ring resonance is the only signal to similarly increase its intensity in CS_2 solutions. It must therefore be assigned as an A_3 signal arising from all three protons on the trans isomer C_5 ring; the

A_2B multiplet, the A_2 portion of which is clearly observed at 574 and 577 Hz in Figure 3c, remains for those protons of the cis isomer. These assignments can be tested for internal consistency by examining the relative integrated intensities of the several sets of well separated spectral lines in Figure 3c. The cis–trans isomer ratio of 1.22:1 obtained from integration of the C_6 ring proton data may be used to predict an intensity ratio 1.69 for the two separated C_5 ring multiplets if indeed the cis B resonance is overlapped by the intense trans A_3 line. The measured ratio of upfield:downfield multiplets is 1.62, in good agreement with our signal assignments.

A ^{13}C NMR study of the iron-nickel system IX evidences only one bridged-terminal carbonyl exchange process. No carbonyl interchange was detected for the related dinickel dimer X in either temperature dependent ^{13}C or proton NMR spectra, since, apparently, only bridging carbonyls are present.

Thermodynamic and Activation Parameters. Integrated signal intensities of widely separated resonances ascribed to isomeric forms of the type **1, 2** for the iron systems I–IV were compared to determine cis $\rightleftarrows$ trans equilibrium constants.

Accurate integral values were assured by both electronically integrating and by cutting and weighing of recorded spectral lines. Thermodynamic parameters collected in Table II were obtained from a plot of ln K vs. $1/T$. The accuracy of the reported data is somewhat limited due to the small temperature range over which suitable spectral information could be obtained. Overlap between NMR lock and ligand ^{13}C resonances precluded their use in similar studies. Data reported are consistent with those previously determined for I from ^1H NMR studies.[10] Some difference in thermodynamic parameters is to be expected since our experiments were performed in very polar Freon solvents.

The rather large temperature dependence of chemical shift observed for the bridge-terminal averaged resonance of the cyclopentadienylruthenium carbonyl V allowed us to estimate equilibrium constants for the open $\rightleftarrows$ closed structure equilibrium, **5, 6** $\rightleftarrows$ **7, 8**. At −82 °C the lowest temperature where the bridge-terminal averaged carbonyl resonance can be seen, we measured its chemical shift to be quite precisely midway between the separate bridge and terminal resonances detected at lower temperatures. We therefore can assume that, at this temperature, the concentration of the nonbridged species is negligibly small. The averaged resonance may be observed to shift *linearly* upfield with increase in sample temperature. By assuming that the chemical shifts of the carbonyls of the nonbridged isomers **7, 8** were identical and were approximately that of the terminal carbonyls seen at low temperatures for the bridged species **5, 6**, we calculated equilibrium constants, $K = P_{nb}/P_b$, for **5, 6** $\rightleftarrows$ **7, 8** by using the equation $\delta_{(av)} = \delta_{nb}P_{nb} + \delta_bP_b$ where δ_{nb}, δ_b, P_{nb}, P_b are the chemical shifts (δ) and mole fractions (P) of the nonbridged (nb) and bridged (b) isomers. The approximate thermodynamic parameters ΔH = 2.6 kcal/mol, ΔS = 6.9 eu, ΔG_{298} = 0.5 kcal/mol were determined from a graph of ln K vs. $1/T$. To justify our assumption of the terminal carbonyl chemical shift value, we note that resonance positions measured (Table I) for several other terminal η^5-dienylruthenium carbonyls are very near to those assumed for the nonbridged structures. Additionally, terminal ^{13}CO chemical shifts reported for numerous other organoruthenium carbonyls in general do not differ markedly from our assumed chemical shift.[46] Attempts to analyze the bridged $\rightleftarrows$ nonbridged equilibria of the several ruthenium derivatives VI–VIII were unfortunately thwarted by the small temperature dependence of their bridge-terminal averaged resonances.

Rate constants for carbonyl interchange were obtained by line shape analysis of ^{13}C NMR spectra. Details of the computational methods utilized have been provided in the Experimental Section. Both plots of ln k vs. $1/T$ and ln (k/T) vs. $1/T$ were linear; least-squares data fits yielded the Arrhenius and Eyring activation parameters set out in Table III.

Table II. Thermodynamic Parameters for Cis–Trans Equilibria

Compd	ΔH^a	ΔS^b	$\Delta G_{298}{}^a$
I	1.3 ± 0.5	1.0 ± 0.5	1.0 ± 0.3
II	2.4 ± 0.2	2.2 ± 0.2	1.8 ± 0.2
III	2.5 ± 0.5	1.7 ± 0.6	1.7 ± 0.3
IV	3.5 ± 0.1	3.3 ± 0.1	2.5 ± 0.1

[a] kcal/mol. [b] eu.

Computer analysis of ^1H NMR spectra of VIII proved largely unrewarding because of both the complexity of the spectra and the small chemical shift differences measured between spectral lines. It is possible, however, to extract some information from the coalescence temperature (−54 °C) of the sets of cyclopentadienyl resonances in order to test whether cis–trans isomerization and bridge-terminal carbonyl exchange occur at similar rates. By assuming the Arrhenius frequency factor measured for carbonyl interchange, an activation energy may be predicted for the cis–trans interconversion. Since k = 11 Hz = $10^{15.9\pm0.5}\exp(E_a/RT)$ at coalescence (−54 °C), we can calculate E_a (cis $\rightleftarrows$ trans) = 14.9 ± 0.4 kcal, in excellent agreement with E_a = 14.5 ± 0.5 measured for bridge-terminal carbonyl exchange.

Discussion

The results of this investigation clearly demonstrate that structural interconversions in solution of dinuclear η^5-dienyliron and -ruthenium carbonyls are very general and facile processes. Both cis–trans isomerization and intramolecular bridge-terminal carbonyl interchange could be examined by ^{13}C and/or proton NMR techniques. The trans structure of the iron systems I–IV is seen to interconvert carbonyls at different rates and with very different activation energies than the corresponding cis isomers. Carbonyl exchange for the cis isomer is always slower than for trans and, moreover, is always accompanied by simultaneous cis–trans structural interconversion. In contrast, concurrent proton and ^{13}C NMR studies of the ruthenium homologues V–VIII show that in these systems both cis and trans isomers simultaneously undergo the isomerization **5** $\rightleftarrows$ **6** and interchange bridged and terminal carbonyls. The sizable temperature dependent upfield chemical shifts detected for bridge-terminal averaged carbonyl of V–VII suggest that nonbridged structures like **7, 8** are appreciably more stable in solution than for the corresponding iron system tautomers.

These spectral results offer strong confirmatory evidence for the NMR interpretations we have previously presented[29] for I and as well support much of the mechanistic explanation of these data recently put forth by Cotton et al.[10] and, later, by Harris et al.[27] Our initial observations were explained as follows: "(a) both cis–trans interconversion and intramolecular (carbonyl) exchanges (for I) are occurring above ca. 35 °C, (b) cis and trans forms interconvert bridging and terminal carbonyls, but with differing activation energies". The mechanism offered to rationalize these interpretations (Figure 4) requires concerted, pairwise opening of the carbonyl bridges of both **1** and **2** to form the most easily accessible, noneclipsed rotamers **11, 12,** and **13.** Since the rotamer **11** has C_{2h} symmetry, bridge opening renders the four carbonyls homotopic and random pairwise closing of two anti carbonyls completes carbonyl interchange. However, carbonyl interconversion within the cis isomer **2** requires, in addition, 120° rotations about the metal–metal bond. These are diagrammed in Figure 4 as (a) **1** $\rightleftarrows$ **12** $\rightleftarrows$ **13** $\rightleftarrows$ **1** or (b) **1** $\rightleftarrows$ **12** $\rightleftarrows$ **11** $\rightleftarrows$ **13** $\rightleftarrows$ **1.** Pathway (b) has two advantages; it avoids a transition state

Table III. Activation Parameters for Bridge-Terminal Carbonyl Interchange Processes

Compd	Log A	E_a[a]	$\Delta H^{\ddagger}$[a]	$\Delta S^{\ddagger}$[b]	$\Delta G^{\ddagger}_{298}$[a]
I(trans)	12.6 ± 0.9	7.1 ± 0.8	6.5 ± 0.8	−3.4 ± 4.0	7.5 ± 0.7
I(cis)	11.8 ± 0.5	11.2 ± 0.3	10.7 ± 0.3	−5.9 ± 1.1	12.4 ± 0.5
II(trans)	13.0 ± 0.7	8.0 ± 0.6	7.1 ± 0.6	−2.5 ± 2.5	7.8 ± 0.2
II(cis)	11.6 ± 0.5	11.3 ± 0.6	11.4 ± 1.3	−7.2 ± 2.0	13.5 ± 0.8
III(trans)	12.8 ± 0.9	8.8 ± 0.6	8.0 ± 0.8	−0.4 ± 3.5	8.1 ± 0.2
III(cis)	16.9 ± 1.8	18.3 ± 2.2	17.8 ± 0.9	17.0 ± 8.3	12.8 ± 2.4
IV(trans)	13.8 ± 0.5	10.4 ± 0.6	10.5 ± 0.9	5.5 ± 3.5	8.9 ± 0.2
IV(cis)	23.7 ± 1.5	28.8 ± 2.0	30.2 ± 0.4	26.0 ± 0.2	22.5 ± 0.4
V	13.2 ± 0.4	7.8 ± 0.4	7.6 ± 0.3	2.1 ± 1.8	7.0 ± 0.15
VI	14.8 ± 0.4	10.0 ± 0.3	10.1 ± 0.7	2.3 ± 1.0	9.4 ± 0.4
VII	16.8 ± 0.4	14.9 ± 0.5	13.9 ± 0.6	14.7 ± 2.7	9.5 ± 0.15
VIII	15.9 ± 0.5	14.0 ± 0.5	13.4 ± 0.4	12.2 ± 1.6	9.8 ± 0.1
IX	13.8 ± 0.4	9.5 ± 0.4	9.2 ± 0.3	4.1 ± 1.5	8.0 ± 0.13

[a] kcal/mol. [b] eu.

in which the bulkier organic ligands are eclipsed, and it provides a mechanism by which cis-trans isomerization and carbonyl interconversion are accomplished in concert.

There is no experiment apparent to us which differentiates between the two rotameric pathways. Rather, we have been able to test the applicability of the mechanism by performing experiments which attempt to answer the following questions: (i) Can the (presumably steric) barrier to rotation be tractably altered by changing the η^5-dienyl ligand? (ii) Does changing the inductive character of the ligand have a measurable and understandable effect on structural interchange rates? (iii) Will the mechanistic considerations apply to structural interconversions of homologous ruthenium V–VIII, or the analogous manganese XI and chromium XII systems?

To answer these questions, the dinuclear molecules I–VIII were chosen for study since they offered systematic variation of two properties: (1) extent of alkyl substitution and (2) ligand size. The portion of space which must be subtended by the rapidly rotating metal bonded η^5-dienyl moiety increases from I to IV and alkyl substitution similarly increases the electron donating properties of the C_5 ring for I → III.

Activation parameters recorded in Table III demonstrate that decreasing the bulkiness of the ligand has a remarkable lowering effect on the free energies ($\Delta G^{\ddagger}_{298}$) and enthalpies ($\Delta H^{\ddagger}$) of activation measured for cis isomer carbonyl interconversions in the iron system. Parallel observations of temperature dependent ^{1}H NMR spectra for I–IV leave little doubt that this process is accompanied by and integral to cis-trans isomerization. Activation energies for the two processes in I agree to within a few tenths of a kilocalorie.[2,10,27,51] This evidence is strongly supportive of the proposed mechanism in that, at least for III and IV and probably for I and II the rate-determining step for cis-trans interconversion must be attributed in rotation over the steric barrier in the pathways above.[25] It is also interesting to note that the large excursions in $\Delta H^{\ddagger}$ with ligand size are accompanied by parallel changes in activation entropy ($\Delta S^{\ddagger}$). Inspection of molecular models for *cis*-IV reveals that the two ligands may not freely rotate against each other. The C_6 ring protons in the most eclipsed conformer would overlap by ca. 1.3 Å, and indeed would still interact strongly in **12** and **13** where the ligands are gauche. Passage to the intermediate **11** would allow free ligand rotation and could account for the increased entropy. The ^{1}H NMR spectrum of the trans bridged isomer **2** does in fact contain a collapsed A_3 signal for all three protons on the C_5 ring of IV and VIII indicating that they experience similar, averaged environments.[2]

The large excursion in activation parameters is not, however, seen for iron system trans isomer carbonyl interconversions. Instead, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ increase in series I–III, V–VII as alkyl substituents are added to the C_5 ring. This can be understood in terms of a picture developed by Braterman for bonding in these complexes.[52] Bridged metal carbonyl bonds are thought of as having, in addition to a metal-metal σ bond, two three-center components. One, **14**, is formed by overlap of the filled ligand σ orbital with two empty metal σ orbitals and the second, **15**, is constructed from back donation from two filled metal nonbonding d orbitals to empty ligand π^* orbitals. Electron-donating alkyl substituents on the η^5-C_5 ring would tend to increase its electron density which might then be transported to the metal carbonyl dative π bond, since carbonyl π^* orbitals tend to act as electron sinks. This would make bridge breaking more difficult and could be the source of the small increase in $\Delta H^{\ddagger}$ seen for CO interconversion of *trans*-I → III.

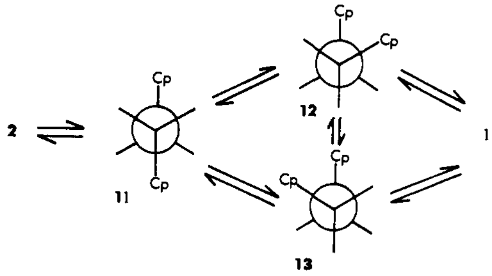
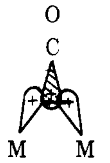


Figure 4. A mechanism for cis-trans isomerization and carbonyl interchange in dimetallic η^5-dienyl carbonyls.[24,27]



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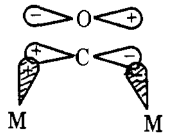

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Alkyl substitution also has a measurable and understandable effect on both the iron and ruthenium system ^{13}CO chemical shifts reported in Table I. Downfield shifts are seen for nonbridged (terminal) carbonyls in sequence I → III, V → VII. Correspondingly, electron-donating ligands X have been observed to cause downfield shifts of $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ and $R_3XM(CO)_5$ complexes.[53] Electron-donating groups substituted into the aromatic rings of (arene)$M(CO)_3$, M = Cr, Mo, W, also induce a similar effect.[46c,54] Either increases in the average excitation energy (ΔE) or decreases in the π mobile bond order terms of the Pople equation[55] for paramagnetic screening have been invoked to account for these ^{13}C chemical shifts. We wish to point out that, in terms of molecular orbital theory, the two explanations are synergic and seemingly inseparable. In any event, the observed shifts are consistent with

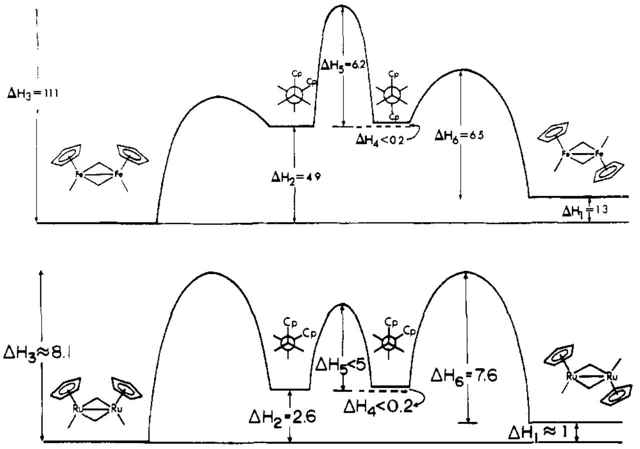

Figure 5. Schematic diagram of potential energy vs. reaction coordinate for structural interconversion in (a) $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and (b) $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$.

our interpretation of the effects of alkyl substitution on rates of carbonyl interconversion.

By using the thermodynamic data in Tables II and III, a schematic representation of enthalpy vs. reaction coordinate may be constructed (Figure 5) for structural interconversions in the iron systems. Our work provides clarification of the several already published, differing portrayals[10,12,51] of these processes in that ΔH_3, the barrier to rotation of nonbridged conformers, is shown to be sizable and to determine the rates of cis-trans isomerization for III and IV and probably I and II.

The enthalpy difference ΔH_2 between nonbridged and bridged isomers was obtained for I and V by Noack[7] from ir studies. Manning and co-workers reported that ir bands assigned to nonbridged species of I and V may also be observed for II and VI but that intensities were sharply reduced.[14-17] No such bands could be seen for IV and VIII. Our ir results also follow this pattern as only barely detectable nonbridged isomer absorptions were seen for III and VII. It is apparent that alkyl substitution on or aromatic fusion with the η^5-C_5 ring decreases the stability of nonbridged conformers. This indicates that ΔH_2 values increase somewhat in the sequences I → IV, V → VIII. Alkyl substitution in the iron systems certainly increases both the enthalpy for the cis-trans equilibrium (ΔH_1) and the barrier to trans isomer carbonyl interconversion (ΔH_6). At least a portion of the increase in ΔH_6 can probably be attributed to the greater ΔH_2 since ΔH_4 values are estimated to be <0.2 kcal/mol.[10,13] Barriers to bridge opening in 1,2 are assumed to be identical in Figure 5. That ΔH_4 is also quite small for the complexes I-IV (13-15) is evidenced by the lack of temperature dependence of ir bands seen for the open isomer. An alternative drawing for Figure 5 which might also be considered is that in which the barrier to bridge breaking of the cis isomer was larger than ΔH_5, thus the system could traverse **2** ⇄ **11** ⇄ **12** (or **13**) without reaching **1**. This seems less likely to us because of the large steric effects to the barrier to rotation observed for I-IV.

Results of our NMR investigations of the η^5-dienylruthenium carbonyls reveal a striking difference in their solution behavior as compared to the iron systems in that only one bridge-terminal carbonyl interconversion may be observed in the ^{13}C spectra. Concurrent, temperature dependent ^1H NMR studies of VII and VIII demonstrate that bridge-terminal carbonyl interconversion and cis-trans isomerization occur simultaneously. The presence in solution of sizable quantities of nonbridged isomers for V → VII again suggests these species as intermediates in the structural interconversion processes and renders probable the mechanistic pathways described in Figure 4 above.[56]

Table IV. Structural and Activation Energy Data for Some Valence Orbital Isoelectronic η^5-Dienyl Metal Carbonyls

Compd	r_{M-M}	∠M–B–M,[a] deg	E_a[b]	Ref
$[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ (XII)	2.615	86.7	≥21.5	51[c,d]
$[(\eta^5\text{-}C_5H_5)Mn(CO)(NO)]_2$ (XI)	2.571	84.8	≥13.8 ± 0.6	51[c,d]
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (I)	2.531	82.9	10.7 ± 0.8[e]	19[c]
$[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ (V)	2.73	87.0	≤7.8 ± 0.4[e]	21[c]

[a] M = metal, B = bridging ligand. [b] Activation energy (kcal) for rotation about the metal-metal bond in bridge opened conformers. See text. [c] References to x-ray structures. [d] Reference to E_a data. [e] This work.

Comparison of activation parameters for cis-trans isomerization (cis data for iron systems and the ruthenium parameters in Table III) shows that for ruthenium, the bulkier ligands change $\Delta H^{\neq}$ and $\Delta S^{\neq}$ appreciably, but not nearly so dramatically as for iron. Increased $\Delta S^{\neq}$ values still indicate some release of steric compression in the transition state, but the barrier to rotation of nonbridged tautomers is markedly reduced. The increase of $\Delta H^{\neq}$ in sequence V → VIII in fact parallels similar values for trans isomer carbonyl interconversions of the homologous iron compounds. Alkyl substitution effects on rate for I-III parallel V-VII. This evidence together with the observed simultaneous isomerization and carbonyl interconversion suggest strongly that bridge opening to nonbridged rotamers is the rate-determining step for the ruthenium system structural interconversions.

A reaction coordinate diagram may be constructed to portray the energetics of structural interconversions for V-VIII. The actual thermodynamic values represented in Figure 5 are those for V taken from Table III and include our measured value for ΔH_2. While precise values for ΔH_1 could not be obtained, ^1H NMR spectra for VII and VIII leave little doubt that both cis and trans isomers are present in about the same quantities and have the same solvent polarity dependencies as measured for the analogous iron systems. The exact barrier to rotation ΔH_5 cannot at present be determined but for simultaneous isomerization and carbonyl interconversion to occur, it must certainly be smaller than the enthalpies required for bridge opening in both isomers. For purposes of the diagram, equal activation enthalpies for opening cis and trans isomers were assumed.

Now that solution structural interconversion studies have been performed for at least ten isoelectronic $(\eta^5\text{-dienyl})_2M_2(L)_2(L')_2$ complexes (M = Cr; L = L′ = NO) (M = Mn; L = NO; L′ = CO) (M = Ru, Fe; L = L′ = Co) as well as for numerous iron systems in which one carbonyl was replaced by an isocyanide or a phosphite, it seems profitable to consider more carefully the exact nature of the barrier to rotation of the nonbridged conformers by examining the structural and activation energy data in Table IV. The tabulated E_a values for $[(\eta^5\text{-}C_5H_5)Mn(CO)(NO)]_2$ (XI) and $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ (XII) were obtained by a more detailed consideration of previously reported NMR data[51] in terms of the mechanism in Figure 4 above. Within the framework of that mechanism, direct cis-trans interconversion of XI through the nonbridged conformed obtained by concerted, pairwise bridge opening of the cis isomer cannot occur. Rather, rotation about the Mn-Mn bond is also required, as has been discussed above for carbonyl interconversions. Similar considerations apply to the ^1H NMR data for XII.

Several factors which determine the magnitude of the barrier to rotation of nonbridged conformers can easily be extracted from Table III and Figure 5. Both the enthalpy difference between bridged and nonbridged structures (ΔH_2) and the size of the steric barrier (included in ΔH_5) are important. The ΔH_2 value for I is nearly twice that of V, at least partially accounting for the decreased rotational barrier observed for the ruthenium systems.

The barrier to rotation $E_a \simeq \Delta H_3$ is measured to increase from 10.7 to 28.8 kcal upon substitution of indenyl for the η^5-C_5H_5 ligand in the iron system. Probably only a small portion of this difference can be attributed to ΔH_2 so there is at least ~15 kcal increase in the steric barrier. Yet, in the ruthenium complexes, upon similar substitution, less than 7 kcal total increase in E_a is observed, and a portion of this, at least 1-2 kcal, must be due to the larger ΔH_2. This marked difference between the iron and ruthenium systems seems at first glance surprising because the change in M—M bond distances from I to V is only 0.2 Å. It may be that the Ru—Ru bond is substantially longer in VIII, but, that seems unlikely although, at present, its crystal structure has not been determined. Alternatively, the steric barrier may simply be unusually sensitive to even small changes in bond distance. The M—M bond distances for the more crowded $[(\eta^5\text{-}C_5H_5)_2M_2(CO)_6]$, M = Cr, Mo, W, complexes decrease as Cr(3.281 Å) > Mo(3.235 Å) > W(3.222 Å), yet changes in $\Delta G^{\ddagger}$ (kcal) are sizable, Cr(12.1) < Mo(15.0) < W(16.2).[57] Since bond distances measured for both *cis*- and *trans*-I are the same to within experimental error, it is unlikely that nonbonded repulsion used to explain the above group VI carbonyl data can be important for I-VIII.

Steric considerations alone certainly cannot account for the increased rotational barrier measured for XII > XI > I. Bond distances are measured to increase regularly with decreasing metal atomic number leading us to expect corresponding, regular decrease in the steric barrier. Increases in strength of metal-nitrosyl vs. metal-carbonyl bonds could, as suggested, account for larger E_a values for trans isomer interconversions, but could not account for the increased rotational barrier, assuming no change in mechanism. Rather, we must suspect that ΔH_2 increases substantially in order I < XI < XII. Unfortunately, no ΔH_2 data are available for XI and XII. The very large changes in ΔH_2 which would be required to explain the E_a data in Table IV lead us to speculate that yet another factor may be of importance. The ability of the first row transition metals to form metal-metal d_π-d_π bonds is expected to increase with decreased nuclear charge for isoelectronic systems. The order of d_π-d_π bond strength predicted is Cr > Mn > Fe in the order of decrease in rotational E_a values. The more diffuse 4d orbitals of V might also be less able to form such bonds further lowering the barrier to rotation in ruthenium dimers. An inspection of d orbitals in the nonbridged conformers reveals that d_π-d_π overlap is indeed possible for I, V, XI, and XIId. No evaluation of the possible importance of directional M-M bonds is now possible. If so, the above data would be evidence of hindered internal rotation about a metal-metal bond. No independent studies relevant to this speculation are evident to us. Further work is in progress.

Finally, the iron-nickel dimer IX is seen to undergo carbonyl interconversion. In this case, ^{1}H NMR spectra are, however, unchanged with temperature, in agreement with ir studies[58] which indicate the presence of only the trans isomer in solution. In this case, a mechanism involving concerted bridge making and breaking rather than Figure 4 could also effect carbonyl interconversion.[59] However, the pathway depicted above seems more likely if the trans structure is appreciably more stable than cis in solution.

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A Crystal Field Model for Calculating Mössbauer Quadrupole Splittings of Iron Complexes. Application to Pseudo-D_3 and Pseudo-D_{2h} Low-Spin Ferrous Complexes

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Abstract: In this paper we present a crystal field method for calculating an approximate Mössbauer quadrupole splitting specially designed for iron complexes with low symmetry. The main features of the method are (1) evaluation of the entire efg tensor from the point charges and the 3d crystal field orbital populations, and (2) diagonalization of the efg tensor to obtain the principal tensor elements. Application of the method to two classes of low-spin ferrous compounds having either pseudo-D_3 or pseudo-D_{2h} symmetry indicates that the crystal field approach correctly predicts the sign of the quadrupole splitting for these complexes. Calculations performed on model coordination polyhedra for the two classes of complexes show which geometrical and/or charge parameters are important in determining the sign of the quadrupole splitting.

I. Introduction

The availability of Mössbauer spectra for a rather wide variety of iron complexes has stimulated the development of models which are intended to account for and effectively predict the relationship between (1) the magnitude and sign of the quadrupole splitting (qs) obtained from the spectra and (2) the nature of the structure and bonding exhibited by the complexes. The qs arises from the interaction of the quadrupole moment of the ^{57}Fe nucleus in its excited state ($I = \frac{3}{2}$) with the asymmetric electronic charge distribution surrounding the iron nucleus. Having the ability to interpret the qs data, therefore, can lead directly to some understanding of the changes in the electron distribution at the iron atom which are caused by substituting one kind of ligating atom for another (i.e., oxygen for nitrogen) and/or changing the geometrical arrangement of the ligating atoms.

Various approaches have been employed to predict the sign and magnitude of the qs for iron complexes.[1–6] The central element in each of these approaches is the manner in which the electric field gradient (efg) at the iron nucleus is estimated. The methods for approximating the efg at the iron nucleus span the range from semiempirical models using partial field gradients[1] to highly theoretical models[2] including the consideration of Coulomb repulsion of 3d electrons in the point symmetry of the complex and spin-orbit interactions. Between these extremes various models have been put forth utilizing the features that (1) the major contribution to the efg at the iron nucleus stems from the partially filled 3d shell[3–5] and other valence electrons are either neglected[1] or included[6] when suitable MO calculations are available, (2) the efg arising from the polarization of core electrons by the asymmetric, partially filled valence shell is either neglected[6] or approximated by use of the Sternheimer coefficients,[1,7] and (3) the chosen coordinate system is the principal one,[1] i.e., diagonalization of the efg tensor is "automatically" done by selection of the coordinate system in order to calculate the quadrupole coupling parameters. The latter assumption greatly simplifies the calculation in that only the diagonal elements of the efg tensor need be evaluated. Unfortunately for low symmetry complexes the a priori assignment of the orientation of the principal axes is difficult if not impossible.

Our goal in this paper is to generalize the well-known methods for calculating the efg from valence orbital and point charge contributions and to test the application to low symmetry complexes. The principal feature of the model being presented here is that the major source of the efg is assumed to be the asymmetric d electron distribution arising from the incomplete population of the d shell combined with the mixing of the d orbitals by the interaction of the crystal field. Strong support for this feature comes from the recent calculation of Goddard and Olafson[8] for the hemoglobin case in which it was shown that the populated d orbitals alone can account for the observed large quadrupole splitting. This concept is in direct contrast to the partial field gradient method which assumes that the source of the field gradient is covalency effects in which ligands donate electrons into the unoccupied hybridized orbitals.[9] The experimentally observed quadrupole splittings are undoubtedly caused by a combination of both effects; however, it has not been generally appreciated that the occupied d orbitals alone may be responsible for the greatest share in determining the qs for complexes such as those of low-spin iron(II) with ligands capable of substantial covalent interaction.[1a] The model being presented here is also distinguished from other similar treatments in that the *entire* efg tensor is first evaluated from the occupied 3d crystal field orbitals and point charges and is then diagonalized to obtain the principal elements.

The method is applied to two classes of low-spin iron(II) complexes, one characterized by pseudo-D_3 symmetry and the other by pseudo-D_{2h} symmetry. A series of calculations on model coordination polyhedra is presented to illustrate which