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Structural and Dynamic Properties of the *Pentahapto*cyclopentadienylmetal Dicarbonyl Dimers[1]

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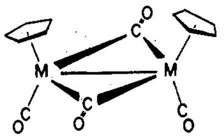
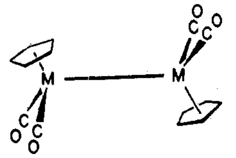
The 100-MHz pmr and infrared spectra between 1700 and 2100 cm^{-1} of $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $[(h^5\text{-}C_5H_5)Ru(CO)_2]_2$ have been investigated as functions of solvent and temperature. There are four isomers present in solutions of the ruthenium compound: cis bridged (I), trans bridged (III), trans nonbridged (IV), and a polar nonbridged structure (probably V). The thermodynamic and kinetic data measured in nonpolar solvents are consistent with the nonbridged isomers as intermediates in the interconversion of I and III. The approximate kinetic activation parameters for the I ⇄ III process in the iron compound have been evaluated from the temperature dependence of the pmr spectrum.

Introduction

The solution structures of $[CpM(CO)_2]_2$ for M = Fe, Ru, and Os and Cp = $h^5\text{-}C_5H_5$ have been the subject of some controversy. The X-ray structure of $[CpFe(CO)_2]_2$, reported in 1958, showed the molecule to have structure III.[4] However, it was soon apparent from the vibrational spectra of this compound[5,6] and from the dipole moment (3.1 D in benzene, 2.4 D in cyclohexane)[7] that some kind and degree of rearrangement was occurring for $[CpFe(CO)_2]_2$ on dissolution.



I



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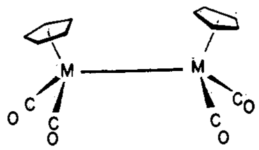
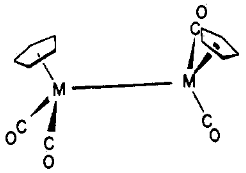
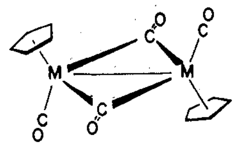


II



V



III

Two subsequent, more detailed studies attempted to resolve the problem as to the exact identities of the species present. Cotton and Yagupsky[8] studied the CO stretching fundamantals as well as overtones and combinations, using CS_2 and heptane solutions, and considered that their data (in CS_2 solution) were consistent with structure I plus a trace of some noncentrosymmetric, nonbridged isomer (probably of C_{2v}, *e.g.*, II, or C_2 symmetry). They also examined $[CpRu(CO)_2]_2$ and postulated that solutions of it in the same solvents consisted of a roughly equimolar mixture of the same two structures. Fischer, Vogler, and Noack[9] studied the CO stretching fundamentals of the iron and ruthenium molecules as a function of temperature. These authors drew essentially the same conclusions as to the presence of two isomers in solution. They also reported $[CpOs(CO)_2]_2$ to consist entirely of the nonbridged form. Noack[10] estimated that the cis-bridged isomer, I, is more stable than the nonbridged isomer by *ca.* 4 and 1.5 kcal/mol for the iron and ruthenium compounds, respectively.

Interestingly, the compound $[((CH_3)_5C_5)Fe(CO)_2]_2$, prepared by King and Bisnette,[11] exhibited an infrared spectrum most consistent with a trans-bridged structure, III; this preference for the trans structure was attributed to steric effects.

Bryan, *et al.*,[12,13] next reported the X-ray structure

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[1] Partially supported by the National Science Foundation through Grant No. 7034X.

[2] NSF Predoctoral Fellow, 1965–1969.

[3] NSF Predoctoral Fellow, 1966–1970.

[4] O. S. Mills, *Acta Crystallogr.*, **11**, 620 (1958). For a more accurate redetermination see R. F. Bryan and P. T. Greene, *J. Chem. Soc. A*, 3064 (1970).

[5] H. Stammreich, G. Wilkinson, and F. A. Cotton, *J. Inorg. Nucl. Chem.*, **9**, 3 (1959).

[6] K. Noack, *ibid.*, **25**, 1383 (1963).

[7] E. Weiss, H. Hubel, and R. Merenyi, *Chem. Ber.*, **95**, 1155 (1962).

[8] F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6**, 15 (1967).

[9] R. D. Fischer, A. Volger, and K. Noack, *J. Organometal. Chem.*, **7**, 135 (1967).

[10] K. Noack, *ibid.*, **7**, 151 (1967).

[11] R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **8**, 287 (1967).

[12] R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *Chem. Commun.*, 1477 (1969).

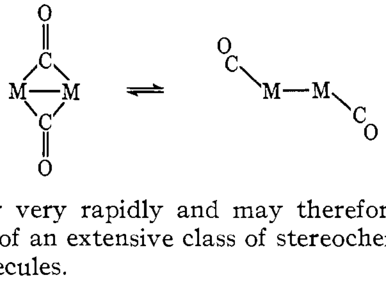
[13] R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Filed, *J. Chem. Soc. A*, 3068 (1970). This paper also reports poorly resolved low-temperature pmr spectra in $CDCl_3$.

of $[CpFe(CO)_2]_2$ in form I, which could be obtained by crystallization from polar solvents at low temperature. Thus, up to this point, what can be termed the "two-structure" hypothesis for the solution structural behavior of $[CpM(CO)_2]_2$ molecules ($I \rightleftarrows II$) seemed relatively secure.

Manning[14] soon challenged the "two-structure" hypothesis, reporting the vibrational spectrum of $[CpFe(CO)_2]_2$ as a function of solvent polarity. The solvent dependence of the spectrum had been noted earlier,[5] but it was Manning, on the basis of relatively small effects (broadenings, occasional splittings, and variations in relative intensities), who proposed a "three-structure" [14] model. This hypothesis attributed the effects in the ir spectra to a mixture in solution of structures I, II, and III, with substantial overlapping of bands being required to explain the small number of separate C–O bands which could normally be observed. Later studies on ring-substituted $[CpFe(CO)_2]_2$ molecules[15,16] and on $[CpRu(CO)_2]_2$[17] were also interpreted in terms of the "three-structure" [14] or "four-structure" [17] model.

It was our opinion that Manning, though not rigorously proving this model, had produced substantial evidence that it was plausible. We thus set out to devise some additional and, hopefully, definitive experiments which might resolve this question. This paper describes in detail the proton nuclear magnetic resonance and infrared spectroscopic studies we have conducted on solutions of $[CpFe(CO)_2]_2$ and $[CpRu(CO)_2]_2$ as a function of both temperature and solvent dielectric constant. Our results, some of which have already been communicated in a preliminary form,[18] offer unequivocal proof that for $[CpFe(CO)_2]_2$ there are two bridged species present in comparable quantities, as proposed by Manning.

In addition we have discovered that these two species are rapidly interconverting above *ca.* −40°. Analysis of the pmr and infrared spectra of the iron and ruthenium molecules as a function of temperature and solvent has yielded thermodynamic and kinetic data necessary to quantify the various aspects of a multistructure (probably four-structure) model and to map the potential energy surfaces which $[CpM(CO)_2]_2$ molecules occupy. Furthermore, and for greater generality, we offer the first direct proof that bridge–terminal interconversions of CO groups of the type



(1)

can occur very rapidly and may therefore constitute the basis of an extensive class of stereochemically nonrigid molecules.

Experimental Section

$[CpFe(CO)_2]_2$ was purchased from Alfa Inorganics, Inc., and was recrystallized from ethyl acetate or ethyl acetate–pentane mixtures. $[CpRu(CO)_2]_2$ was prepared by the reaction of $Ru(CO)_2Cl_2$ or $Ru(CO)_2I_2$ with NaC_5H_5 in 1,2-dimthoxyethane. It crystallized from benzene as the trans isomer. All solvents were dried and deoxygenated in the appropriate manner.

Infrared spectra, unless otherwise noted, were recorded on a Perkin-Elmer 337 spectrometer equipped with a scale expander built by J. A. Simms and T. J. Marks. All spectra were recorded with freshly prepared solutions and were calibrated with polystyrene film. Solutions were replaced whenever any bands were observed to have changed in intensity with time. In most cases solutions were stable for up to 9 hr after preparation if protected from visible light and kept at reduced temperatures.

The variable-temperature infrared apparatus included a Varian Associates V-6040 variable-temperature controller to regulate the temperature of a stream of dry nitrogen which was passed around a Barnes Engineering microcavity cell. This cell was held in an insulated box in a nitrogen-purged spectrometer. One such box equipped with an uncoated germanium window to filter visible radiation causing photodecomposition was used in some studies, but it had a transmission factor of only 0.05. A second box, with a transmission factor of 0.75, was used in others. Temperatures were measured with a copper–constantan thermocouple placed in a depression in the cap of the cavity cell. There was no noticeable difference between spectra taken while cooling the cell and those recorded as it returned to the ambient temperature.

Proton nuclear magnetic resonance spectra were recorded on a Varian Associates HA-100 spectrometer equipped with a variable-temperature controller. Temperature calibration was achieved by means of a calibrated copper–constantan thermocouple which was inserted in the nitrogen stream just below the sample in the probe. Measurements with this apparatus were checked against those obtained by inserting a calibrated thermocouple into a solvent sample, capped with a serum stopper, while it was in the probe. Spectra were calibrated by measuring the frequency difference in hertz from the lock signal with a Varian V-4315 electronic counter.

Samples were prepared by weighing the organometallic compound into a nitrogen-flushed sample tube, capping the tube with a serum stopper, and injecting degassed solvent and tetramethylsilane mixtures with a syringe. Serious solubility problems were encountered with these compounds, and it was necessary either to use dilute (usually *ca.* 0.03 *M*) solutions or to record the spectra of more concentrated samples as quickly as possible before appreciable crystallization could occur. In either case, spectra were generally of less than optimum quality.

Results and Discussion

Figure 1 shows the 100-MHz variable-temperature nmr spectra of $[CpFe(CO)_2]_2$ dissolved in 1:3 v/v $C_6D_5CD_3$–CS_2. We chose this particular solvent mixture because of its low polarity, good solvating properties, and low freezing point. As can be seen, two species of nearly, but, importantly,[19] not exactly equal populations are undergoing rapid interconversion at temperatures above *ca.* −40°. Since the infrared data supporting the "two-structure" model indicated the nonbridged form to be present in less than 0.1% at low temperatures,[9,10] it was clear that *two* bridged isomers were present. On the other hand, infrared data supporting the "three-structure" [14] model would predict structures I and III to be present in nearly equal quantities. The next step was to ascertain the effect of an increase in the dielectric constant of the medium, since this should favor the polar, cis-bridged isomer, I. Addition of 9% $CDCl_3$ (ϵ 4.8 at 20°) caused little change in the −70° spectrum, while 9% CD_2Cl_2(ϵ 9.1 at 20°) caused the low-field peak to decrease to about one-third of its original intensity, and 9% acetone (ϵ 21.0 at 20°) practically abolished the low-field peak. Such behav-

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[14] A. R. Manning, *J. Chem. Soc. A*, 1319 (1968).

[15] P. McArdle and A. R. Manning, *ibid.*, *A*, 1498 (1969).

[16] P. McArdle and A. R. Manning, *ibid.*, *A*, 2119 (1970).

[17] P. McArdle and A. R. Manning, *ibid.*, *A*, 2128 (1970).

[18] J. G. Bullitt, F. A. Cotton, and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 2155 (1970).

[19] The fact that the two signals do not have the same intensity excludes the possibility that this spectral behavior is due to the presence of one species with nonequivalent h^5-C_5H_5 rings which are rapidly interconverting at room temperature. A structure of this type was originally postulated for $[(C_5H_5)Fe(CO)_2]_2$.[6,7]

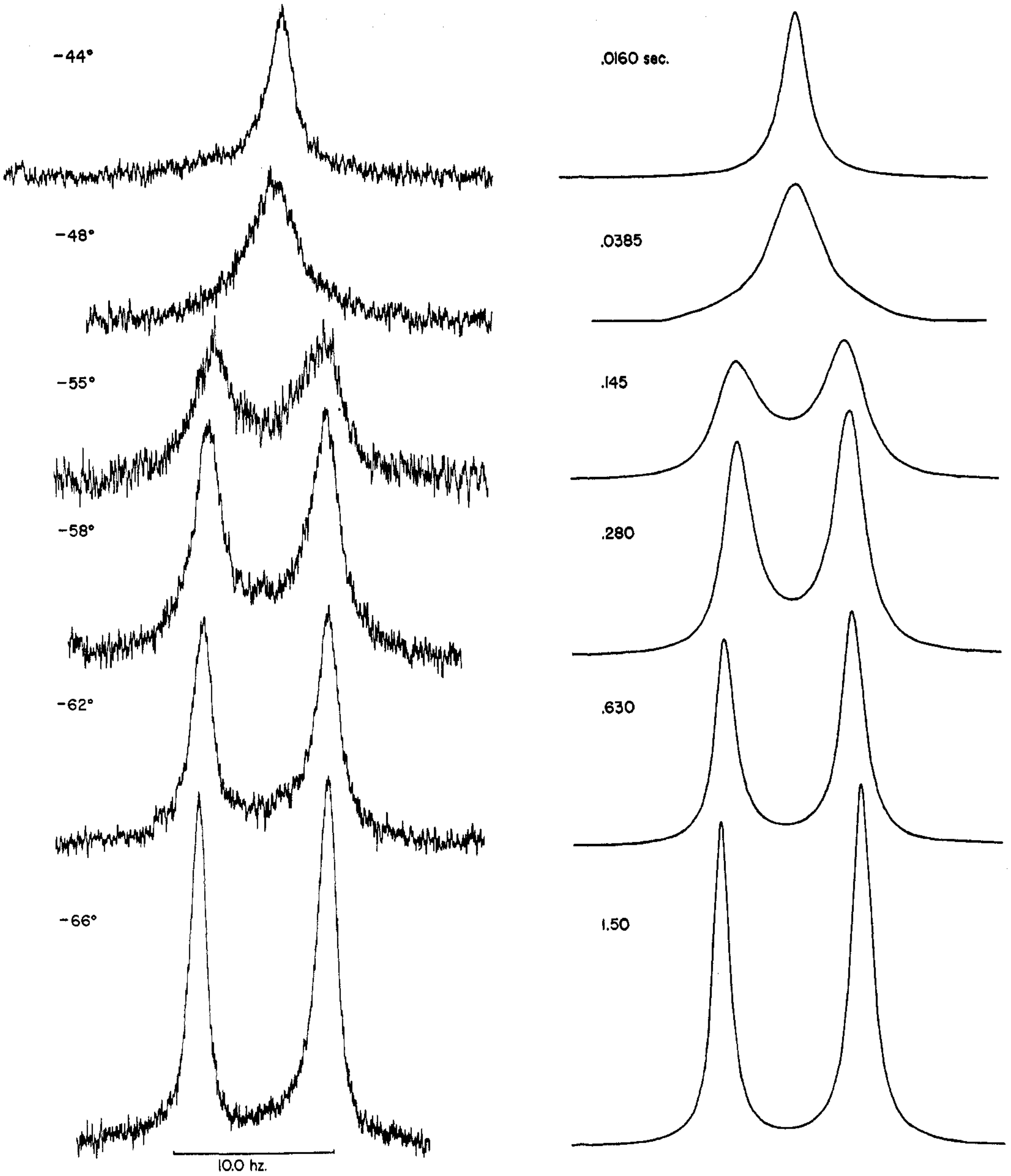

Figure 1.—Observed and computed 100-MHz pmr spectra for $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$. The numbers on the computed spectra are mean residence times in seconds.

ior and its consistency with infrared correlations (*vide infra*) are to be expected from the I $\rightleftarrows$ III equilibrium.

Kinetic analysis of the $[CpFe(CO)_2]_2$ pmr data was performed using the Kubo–Sack method[20,21] to generate spectra by computer simulation.[22] Besides problems encountered in spectral resolution, it was necessary to correct for both temperature-dependent changes in the chemical shifts of the two exchanging singlets and the temperature dependence of the equilibrium constant. These corrections were made by extrapolating the peak separation *vs.* T data and also the log K *vs.* $1/T$ data, to be reported below, taken at temperatures below the slow-exchange limit to temperatures where the exchange process was fast.

Since the peaks influenced by exchange are separated by less than 10 Hz at 100 MHz, what are in many cases negligible changes in the chemical shifts with temperature assume, in this case, major importance. These difficulties, combined with the fact that reliable data (data taken in the region where broadening was appreciable) were only available for a temperature range of about 35°, greatly limit the accuracy of the kinetic studies. Figure 1 shows the observed and computed nmr spectra. A least-squares fit of the Arrhenius plot yielded the parameters $E_a = 16.7 \pm 1.6$ kcal/mol and log $A = 17.5 \pm 1.6$. In view of the difficulties encountered in this system, the high activation energy and frequency factor probably carry even greater errors than the stated uncertainty intervals, which are based purely on the fit, would imply.[23,24] A more accurate quantity, $\Delta G^{\ddagger}$,[25] is calculated to be 10.4 kcal/mol at

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[20] G. M. Whitesides and J. S. Fleming, *J. Amer. Chem. Soc.*, **89**, 2855 (1967).

[21] F. A. Cotton, J. W. Faller, and A. Musco, *ibid.*, **90**, 1438 (1968).

[22] EXCNMR written by Professor G. M. Whitesides of this department.

[23] H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970).

[24] T. Deakenberg, K.-I. Dahlquist, and S. Forsen, *Acta Chem. Scand.*, **24**, 694 (1970).

[25] $\Delta G^{\ddagger} = \Delta H_{\ddagger} - T\Delta S_{\ddagger}$ in Figure 3. Calculated from the relationship $1/\tau = (kT/h)e^{-\Delta G^{\ddagger}/RT}$.

220°K. Alternatively, if it is assumed that the activation entropy (ΔS_3 in terms of the numbering of Figure 3) is equal to 0 (*i.e.*, $\log A = 13$) and a rate value near the center of the Arrenhius plot is chosen, an activation enthalpy (ΔH_3 of Figure 3) of about 12 kcal/mol is obtained.

The equilibrium between I and III was studied both by means of the pmr spectrum between −70 and −90° and by observing the infrared spectrum of the carbonyl stretches between +30 and −90°. It was found that the line shapes of the pmr spectrum near coalescence were invariant over a concentration range of 4 and the relative intensities of the carbonyl stretching bands of $[CpFe(CO)_2]_2$ are constant over a concentration range from 0.25 to 5.0 m*M*. The interconversion of I and III is thus indubitably unimolecular and a nonbridged form (or perhaps several) is presumably an intermediate through which the interconversion is effected. The thermodynamic parameters for the equilibration of I and III were obtained from the nmr data by measuring the relative intensities of the two singlets at temperatures below the slow-exchange limit. Ample time was allowed for equilibration at each temperature. The equilibrium constant was calculated by integrating each spectrum six times (three scans in each direction) and taking the average or by cutting out the peaks from the spectra and weighing them. Both sets of data were fitted to a $\log K$ *vs.* $1/T$ plot by computer using the method of least squares; the results are recorded in Table I. The limited temperature range available for these measurements no doubt limits the accuracy of these parameters.

TABLE I

THERMODYNAMIC PARAMETERS FOR THE CIS-BRIDGED ⇄ TRANS-BRIDGED ISOMERIZATION FOR $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$

Method	ΔH_1[a]	ΔS_1[b]
Pmr, electronic integration[c]	0.87 ± 0.07[g]	3.5 ± 0.4
Pmr, weighing[c]	0.94 ± 0.13	3.5 ± 0.7
Ir, calcd intensities[c]	0.37 ± 0.03	1.4 ± 0.14
Ir, calcd intensities[d]	0.54 ± 0.02	3.6 ± 0.1
Ir, calcd intensities[e]	0.23 ± 0.03	1.9 ± 0.1
Ir, nonlinear fit[c,f]	0.79 ± 0.8	2.5 ± 1.5

[a] $K = [III]/[I] = \exp[-\Delta H_1/RT + \Delta S_1/R]$; ΔH_1 in kcal/mol. [b] In eu; results from ir data assume calculated relative intensities. [c] A 3:1 v/v CS_2–$C_6D_5CD_3$ mixture. [d] Methylcyclohexane. [e] CS_2. [f] $A_0 = 0.0 \pm 0.5$. [g] Estimated standard deviations from the least-squares analysis.

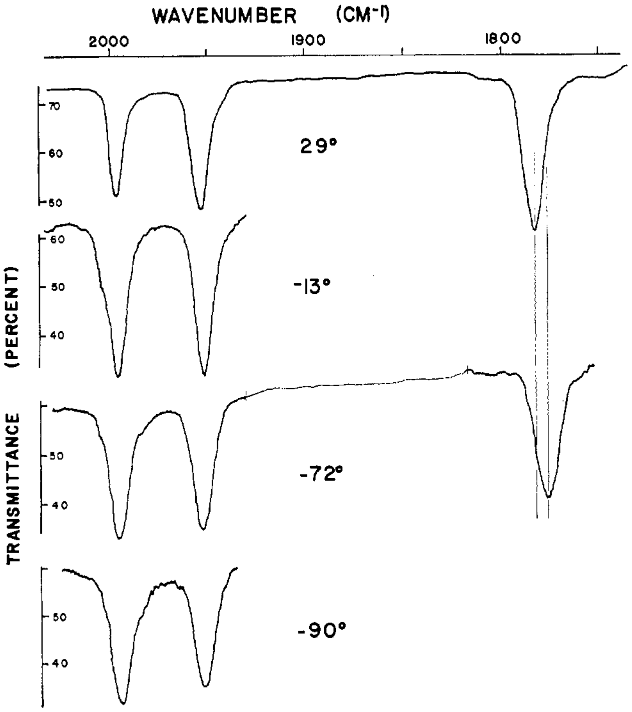

Figure 2.—The variable-temperature infrared spectrum of $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$ in a 3:1 v/v mixture of CS_2 and $C_6D_5CD_3$ recorded on a Perkin-Elmer 521 spectrometer.

The infrared spectrum of $[(C_5H_5)Fe(CO)_2]_2$ in the carbonyl stretching region has previously been assigned from its solvent dependence.[14] This assignment is consistent with the temperature-dependent ir spectrum, shown in Figure 2, which contains three well-defined bands: a broad band due to antisymmetric stretching of the bridging carbonyl groups, whose maximum shifts from 1781 cm^{-1} at 30° to 1777 cm^{-1} at −72° in CS_2–toluene mixtures. From the asymmetry and temperature dependence of the band at ~1780 cm^{-1}, we infer that it consists of the strong antisymmetric A_u stretch of III lying between the weak A_1 and strong B_2 stretches of I. The band at 1954 cm^{-1} must then contain the antisymmetric stretches of the terminal carbonyls: the strong B_u mode of III and the weak B_1 mode of I. In the analysis of the equilibrium between I and III for $[CpFe(CO)_2]_2$ the nonbridged form may be ignored. Noack[10] has estimated its concentration to be about 1% of that of the bridged species at 30° and about 0.1% at −30°.

Because the antisymmetric stretches of I and III overlap, the ratio of the intensities of any two bands is not directly proportional to the equilibrium constant. The ratio *R* of the intensity of the antisymmetric to symmetric terminal carbonyl bands, however, should be a linear function of the equilibrium constant *K*, *i.e.*

$$R_0 = (\epsilon_{B_1}[I] + \epsilon_{B_u}[III])/\epsilon_{A_1}[I]$$
$$= \epsilon_{B_1}/\epsilon_{A_1} + (\epsilon_{B_u}/\epsilon_{A_1})K$$

where $K = [III]/[I] = \exp[\Delta S_1/R_0 - \Delta H_1/RT]$. Manning[14] has used a similar relation to determine the equilibrium constant as a function of solvent; however, he has assumed that $\epsilon_{B_u} = \epsilon_{A_1} + \epsilon_{B_1}$ whereas we have calculated[26] that $\epsilon_{B_u} = 0.775(\epsilon_{A_1} + \epsilon_{B_1})$. The various ΔH_i's are defined by Figure 3; a ΔS_i with the same subscript refers to the same process as ΔH_i. The ratio of the extinction coefficients was calculated assuming that the carbonyl modes are decoupled from the remainder of the molecule, that the symmetric carbonyl stretches do not mix, and that the dipole derivatives of the terminal carbonyls of I and III are the same.[27] The appropriate equations are then

$$R_0 = 0.031 + 0.80 \exp[\Delta S_1/R - \Delta H_1/RT]$$

$$\ln[R_0 - 0.031] = 0.223 + \Delta S_1/R - \Delta H_1/RT$$

where $K = \exp[\Delta S_1/R - \Delta H_1/RT]$. The results are given in Table II. The ΔS_1 and ΔH_1 resulting from a

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(26) J. G. Bullitt and F. A. Cotton, *Inorg. Chim. Acta*, in press.

(27) Using these assumptions the intensity of the bridging carbonyl band should be independent of the temperature. This was observed to be true except at the lowest temperatures, below −70° where crystallization occurred.

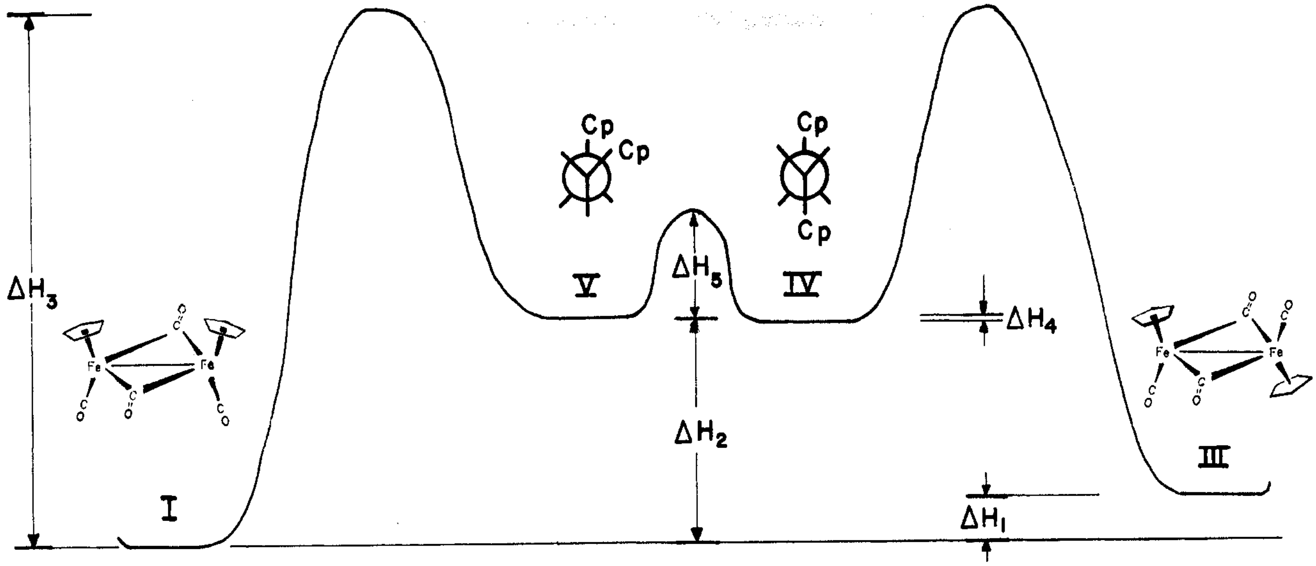

Figure 3.—Schematic diagram of the reaction coordinate for interconversion of cis-bridged (I), trans-bridged (III), and nonbridged structures (IV, V) of $[(h^5\text{-}C_5H_5)M(CO)_2]_2$. This diagram is based on the energies estimated for $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$.

Table II

Frequencies and Calculated Relative Intensities of the Carbonyl Stretches of *cis*- and *trans*-$(h^5\text{-}C_5H_5)_2Fe_2(CO)_4$

	Terminal CO		Bridging CO	
	Sym	Antisym	Sym	Antisym
		Cis		
Symmetry	A_1	B_1	A_1	B_1
Freq[a]	1998	~1954	~1810	1777
Intens[b]	3.80	0.12	0.30	1.60
		Trans		
Symmetry	A_g	B_u	A_g	A_u
Freq[a]	...	1954	...	1781
Intens[b]	0.0	3.04	0.0	1.63

[a] In cm^{-1}, in a 3:1 v/v CS_2–$C_6D_5CD_3$ mixture measured on a Perkin-Elmer 521 spectrometer with 1.5-cm^{-1} slits. [b] Relative to one carbonyl oscillator with a dipole derivative of 1 D/Å using dipole derivatives of 1.4 D/Å for the terminal CO's and 0.9 D/Å for the bridging CO's.

least-squares fit of 20 or more spectra, Table I, are similar to but significantly different from the nmr results.

Assuming that the calculated infrared intensities are in error, R was fitted directly by a nonlinear least-squares procedure[28] to determine $A_0 = \epsilon_{B_1}/\epsilon_{A_1}$, $B = \epsilon_{B_u} \exp\{\Delta S_1/R\}/\epsilon_{A_1}$, and ΔH_1. Intensities estimated both as the product of the maximum absorbance and bandwidth and by weighing a tracing of the absorbance curve gave similar convergent results; however, ΔH_1 is so small that the parameters are strongly correlated causing large estimated standard deviations. The consistency between the nmr and ir results is important because it shows that the reaction responsible for the temperature-dependent variation in the C_5H_5 pmr spectrum is the same one responsible for the variation in the infrared spectrum with temperature.

The equilibrium between I and III was not studied quantitatively in $[CpRu(CO)_2]_2$. In the pmr spectrum the slow-exchange limit was not reached at −100°. In the ir the terminal carbonyl stretches of the nonbridged form, which is present in appreciable fraction,[8,9] overlap those of I and III. It should be noted here that the fact that the relative energy of II is lower with respect to I and III for the ruthenium system than for the iron system and that the activation energy for I $\rightleftarrows$ III for the ruthenium system is also lower strongly suggests that the two bridged forms interconvert *via* a nonbridged form in which there is relatively free rotation about the metal–metal bond.

The solvent and temperature dependence of the carbonyl stretches indicate that ΔH_1 and ΔS_1 have values about equal to those in $[CpFe(CO)_2]_2$.

Since a nonbridged form of $[CpM(CO)_2]_2$ is presumably intermediate in the interconversion of I and III, $[CpRu(CO)_2]_2$, in which the nonbridged form is present in sizable quantities, was studied to elucidate its structure. Because three infrared bands have been assigned to this form,[8,9] it has been assumed to have C_{2v} symmetry[9] or C_2 symmetry with low intensity in the fourth band.[5,8] McArdle and Manning[17] observed the infrared carbonyl stretches as a function of solvent, temperature, and cyclopentadienyl substituent and concluded that the nonbridged form is a mixture of the cis (C_{2v}) rotamer II and the trans (C_{2h}) ethane-like rotamer IV. The data available on $[CpOs(CO)_2]_2$[9] agree with this interpretation. The solid-state infrared spectrum is consistent with structure IV and the dipole moment of 2.58 D in benzene is consistent with a mixture of polar and nonpolar forms in comparable amounts.

The infrared spectra of the carbonyl stretches recorded in methylcyclohexane, carbon disulfide, and carbon tetrachloride show slight solvent dependence in the relative intensities of the bands assigned to nonbridged isomers. In methylcyclohexane these bands show no temperature dependence from +30 to +90° where nonbridged forms predominate. A polar structure that may be responsible for the highest frequency band is the staggered rotamer of C_2 symmetry, V. If so, the weak band near 1900 cm^{-1} may be the lowest frequency fundamental of V. This band is present in the spectrum which Fischer, *et al.*,[9] reported in hexane and those reported here in methylcyclohexane and carbon disulfide. More polar or even polarizable solvents broaden the band so that it becomes obscure. Since this band does not increase in intensity with time, it is not a decompo-

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(28) BMD-06R, an asymptotic regression analysis developed by the UCLA Health Sciences Computing Facility and implemented at the MIT Information Processing Center.

sition product. Since it is present in spectra recorded in various solvents and from samples synthesized by various methods, this peak does not appear to be caused by impurity. It is close to the 1910-cm^{-1} position predicted[8] for the silent A_2 mode of II from the overtone and combination bands. This peak cannot be assigned as the ^{13}C satellite of the B_u band of III which has been observed at 1924 cm^{-1} in nonane solutions of $[CpFe(CO)_2]_2$.[10] This band could be the ^{13}C satellite of the A_u or B_u modes of IV, but they probably occur at higher frequencies. Whereas the relative intensities of the three higher frequency bands cannot be rationalized with a reasonable C_{2v} geometry,[29] the relative intensities of the highest and lowest frequency bands (ratio between $^4/_1$ and $^{10}/_1$) of the nonbridged forms are consistent with reasonable staggered structures. Assuming that IV and V are present in comparable quantities, probably in a $^2/_1$ or $^3/_1$ ratio, the lack of temperature dependence in the carbonyl bands indicates that the ΔH_4 must be less than 0.2 kcal/mol.

The equilibrium in $[CpM(CO)_2]_2$ compounds thus involves four isomers for ruthenium and presumably also for iron: I $\rightleftarrows$ V $\rightleftarrows$ IV $\rightleftarrows$ III. These equilibria have been investigated in nonpolar solvents and the results referenced to isomer I as given in Table III. ΔH_2 and ΔS_2 have been calculated from the values reported by Noack[10] assuming ΔH_1, ΔS_1, and the relative extinction coefficients in Table II. Since ΔH_2 for $[CpRu(CO)_2]_2$ is 3 kcal/mol less than ΔH_2 for $[CpFe(CO)_2]_2$, ΔH_3 of $[CpRu(CO)_2]_2$ has been estimated as 9 kcal/mol; interconversion of all four isomers is expected to be rapid on the nmr time scale even at −100°. The barrier ΔH_5 between IV and the polar nonbridged form, probably V, can be no greater than 8 kcal/mol and is probably much less. The rapid interconversion of IV and V may be fast even on the ir time scale. $[CpOs(CO)_2]_2$ would provide a better vehicle for structural studies of IV and V, for it should show this fast equilibrium uncomplicated by the presence of I or III.

TABLE III

THERMODYNAMIC PARAMETERS FOR $[CpM(CO)_2]_2$

	Fe	Ru
$\Delta H_1{}^a$	0.9 ± 0.1	~1
$\Delta S_1{}^b$	3.5 ± 0.5	~3
$\Delta H_2{}^{a,c}$	4.9 ± 1	1.7 ± 0.5
$\Delta S_2{}^{b,c}$	6.5 ± 2	6.9 ± 1
$\Delta H_3{}^a$	~12	~9
$\Delta S_3{}^b$	~0	~0
$\Delta H_4{}^a$	. . .	<0.2
$\Delta H_5{}^a$	. . .	<8

[a] In kcal/mol. [b] In eu. [c] Recalculated from ref 10 assuming ΔH_1 and ΔS_1.

Conclusions

The immediate conclusion reached by this work is that a four-structure model as shown in Figure 3 best describes the potential energy surfaces available to $[CpFe(CO)_2]_2$ and $[CpRu(CO)_2]_2$. Internally consistent, complementary results obtained by infrared and nmr spectroscopy allow us to identify the different isomers present in solution and yield quantitative kinetic and thermodynamic data necessary to map out accurately areas of the potential energy surface. This quantitative information also strongly supports a mechanism whereby cis- and trans-CO-bridged isomers can interconvert *via* nonbridged isomers: I $\rightleftarrows$ V $\rightleftarrows$ IV $\rightleftarrows$ III. Thus, we furnish the first strong proof that bridged–nonbridged structure interconversions, of the type shown in eq 1, occur with low activation energy. Examination of the chemical literature as well as other results obtained in this laboratory indicate that this type of rearrangement may occur with great generality in metal carbonyl chemistry and may thus provide a basis for an extensive class of stereochemically nonrigid and fluxional molecules.

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(29) The angle between the carbonyls bound to the same metal is calculated to be about 90°, but the dihedral angle between the $Ru(CO)_2$ planes is calculated to be about 140° which would crowd the cyclopentadienyl rings excessively.

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The Spectra of Bis(tertiary arsine) Complexes. III.[1a] Tetragonal Iron(III)

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The magnetic susceptibilities, electron spin resonance, and Mössbauer spectra of the complexes *trans*-$[FeX(NO)(das)_2]^+$ and *trans*-$[FeX_2(das)_2]^+$ have been obtained. These complexes have one unpaired electron per iron, with magnetic moments ranging from 1.81 to 2.31 BM at room temperature. The Mössbauer spectra consist of quadrupole-split doublets with the quadrupole splitting ranging from 2.2 to 2.5 mm/sec for *trans*-$[FeX_2(das)_2]^+$ and being 1.0 mm/sec for *trans*-$[FeX(NO)(das)_2]^+$. Both the magnetic susceptibilities and esr spectra show that the *trans*-$[FeX(NO)(das)_2]^+$ complexes have rhombic fields, while the *trans*-$[FeX_2(das)_2]^+$ compounds are tetragonal. These data can be accommodated by the ligand field model for Fe(III) in rhombic or tetragonal fields.

Introduction

The electronic structure of nitrosyl complexes has been investigated by several authors.[2-4] The previous investigators have dealt with transition metal nitrosyl complexes in which the M–N–O grouping was linear or

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