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Structural and Dynamic Properties of Dicyclopentadienylhexacarbonyldimolybdenum in Various Solvents*

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The structural and dynamical properties of $[(h^5\text{-}C_5H_5)\text{-}Mo(CO)_3]_2$ *have been studied by infrared and nmr spectroscopy in various solvents. The infrared results indicate that as solvent dielectric constant increases an increasing proportion of the molecules rearrange from the trans* (C_{2h}) *rotamer to a gauche* (C_2) *rotamer. The free energy (25), enthalpy and entropy changes for the gauche to trans rearrangement in acetone are:* -0.57 ± 0.33 *Kcal/mole,* 0.44 ± 0.15 *Kcal/mole, and* 3.38 ± 0.61 *cal/mole-degree. The rate of trans-gauche interconversions as a function of temperature was determined by fitting of computer-simulated to measured nmr spectra. The Arrhenius parameters of activation are* $E_a = 15.3\pm1$ *Kcal/mole, Log* $A = 13.0\pm1$. *The substantial energy for interconversion of rotamers found here implies that barriers to rotation may play critical roles in* cis-trans *interconversion in other systems, such as* $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$. *A modification of the previously suggested diagram of energy* vs *molecular configuration of* $[h^5\text{-}C_5H_5)Fe(CO)_2]_2$ *is proposed.*

Introduction

Recent investigations of the rearrangement processes which occur in binuclear metal carbonyl compounds have established that there is a general category of bridge-terminal equilibria and related *cis-trans* isomerizations.[1-4] Implicit in the *cis-trans* rearrangement mechanisms are internal rotations about the metal-metal bond in the nonbridged tautomers. Until now little attention has been focused on the details of this step.[1] We report here the first direct study of such a process which reveals that the rearrangement is not facile and might, at least in some cases, be the rate determining step in such *cis-trans* isomerizations.

Cyclopentadienyltricarbonylmolybdenum dimer exists in solution solely in a non-bridged form. The infrared spectrum should show three bands for a *trans* (C_{2h}) structure, five for a *cis* (C_{2v}) rotamer and six for a gauche (C_2) rotamer. On the basis of the number of observed peaks, all previous studies[5-7] have been interpreted in terms of the trans structure as found in the solid.[8] However, the assignment of three peaks to the presumed C_{2h} rotamer has been inconsistent from study to study. Lewis and coworkers[5] reported the peaks at 2018 m, 1960 vs, and 1915 vs cm^{-1}. Braterman and Thompson[6] reported the same two low energy peaks but showed that the lower was actually a composite of two. In a thorough study Fischer and Noack[7] reported all four but for reasons not made clear, discussed only the three low energy absorptions.

Results

We have reinvestigated the infrared spectrum in a variety of solvents of varying dielectric strength. The results are reported in Table I. Generally three peaks were observed (Figure 1): a relatively sharp high-energy peak at ~2020 cm^{-1}, which varied in

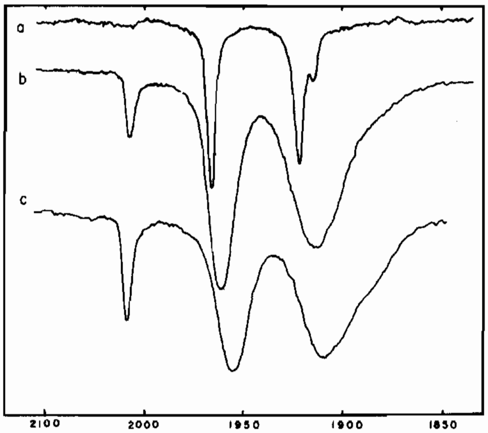

Figure 1. The carbonyl infrared spectra of $[(h^5\text{-}C_5H_5)Mo(CO)_3]_2$ in various solvents. (a) cyclohexane. (b) nitrobenzene. (c) dimethyl sulfoxide.

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[8] F.C. Wilson and D.P. Shoemaker, *J. Chem. Phys.*, *27*, 809 (1957).

Table I. Infrared Peak Positions and Relative Intensities for $[(h^5\text{-}C_5H_5)Mo(CO)_3]_2$.

Solvent	Frequencies, cm^{-1} (Relative Intensities) Peak 1	Peak 2	Peak 3	Solvent Dielectric Constant
Dimethyl Sulfoxide	2003 (1.98)	1949 (5.63)	1906 (10.0)	47.6
Acetonitrile	2015 (1.64)	1959 (6.73)	1912 (10.0)	36.2
Acetone	2015 (1.50)	1960 (6.81)	1916 (10.0)	20.7
Nitrobenzene	2014 (1.10)	1958 (6.72)	1908 (10.0)	34.6
Tetrahydrofuran	2014 (1.00)	1959 (6.66)	1916 (10.0)	7.36
Methylene Chloride	2017 (0.50)	1963 (6.99)	1915 (10.0)	8.9
Chloroform	2017 (0.44)	1964 (6.75)	1919 (10.0)	4.7
d_6-Benzene	2018 (0.30)	1961 (7.22)	1916 (10.0)	2.27
Carbon Disulfide	2017 (0.20)	1963 (9.16)	1918 (10.0)	2.64
Cyclohexane *	—	1966 (10.0)	1922 (10.0)	2.02

* Contains an additional low energy peak resolved from peak 3 at 1914 cm^{-1} with an estimated relative intensity of 1.0.

intensity in a manner roughly proportional to the dielectric constant of the solvent, and two relatively broad low-energy absorptions at ~1960, and ~1920 cm^{-1}. The lowest-energy absorption band was quite asymmetric on the low-energy side, and in non polar solvents could be resolved into two peaks. In solvents of very low dielectric constant the peak at ~2020 was either extremely weak (benzene, CS_2) or unobserved (cyclohexane).

We propose the following interpretation of these spectra. The predominant form of the molecule, and the only one detectable in the least-polar solvent, cyclohexane, is the *trans* (C_{2h}) rotamer. The three infrared-active fundamental CO-stretching modes which are expected for this species are observed at 1966, 1922, and 1914 cm^{-1}, in cyclohexane. In polar solvents a second rotamer becomes significantly populated. Figure 2 shows a schematic representation of rotational configurations formed by partial rotations around the metal: metal bond. A, B and B′ are staggered rotamers; C, C′ and D are eclipsed rotamers.

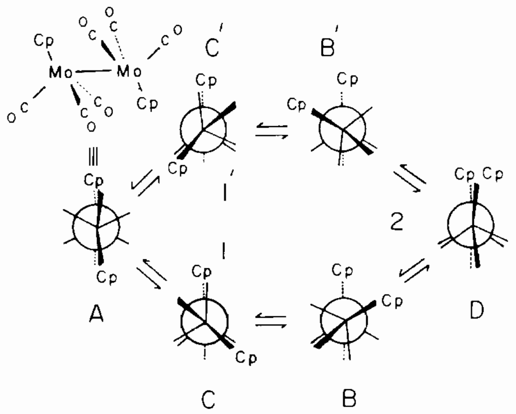


Figure 2. Schematic representation of the interconversion pathways for the rotamers.

All of the eclipsed rotamers entail very severe nonbonded repulsions. The rotational potential energy function is of the 3-maximum, 3-minimum type, since one CO group on each metal atom points away from the other end of the molecule. In effect, then, only three rotamers can be expected to be stable enough to have significant population: A, B and B′, and of these B and B′ are enantiomorphs. Form A, the trans rotamer, may also be described as the 180° rotamer. Similarly, the *cis* C_{2v} rotamer, D may be called the 0° rotamer. Two types of gauche rotamers B, B′ and C, C′ of C_2 symmetry are formed by partial rotations of 60° and 120°, respectively. Rotamers A and B, B′ show comparable steric interaction between the two halves. The form of the second rotamer is undoubtedly the gauche rotamer B, B′.

The gauche isomer should have six infrared-active, fundamental CO stretching modes, one of which should correspond approximately to the inactive A_{1g} mode of the *trans* rotamer. This involves the in-phase stretching of all CO groups and should have the highest frequency of all the six modes. It is responsible for the band at ~2020 cm^{-1}. Each of the five other modes of the gauche form presumably has a frequency similar to one of those infrared-active modes of the *trans* isomer, or is relatively weak. Therefore, these bands are not resolved in the polar solvents, where all CO stretching bands are very broad.

Since $[(h^5\text{-}C_5H_5)Mo(CO)_3]_2$ is commonly prepared[9] from $Mo(CO)_6$, care was taken to prove that the high energy band at ~2020 did not result from $Mo(CO)_6$ as an impurity or decomposition product. Spectra of mixtures of the two compounds in both acetone and acetonitrile showed the same bands as are recorded in Table I plus an additional band at ~1995 cm^{-1}, attributable to $Mo(CO)_6$.

(9) R.B. King, *Organometal. Syn.*, *1*, 109 (1965).

Further evidence for the proposed solvent-dependent equilibrium mixture of trans and gauche rotamers has been obtained from the proton nmr spectra in acetone at various temperatures. These are shown in Figure 3. A single sharp peak at $+62^\circ$ collapses and reforms as two peaks of unequal intensity which are sharp at -15°. The addition of toluene-d_8 to decrease the dielectric strength of the nmr solvent has the appropriate effect of shifting the equilibrium from gauche to trans.

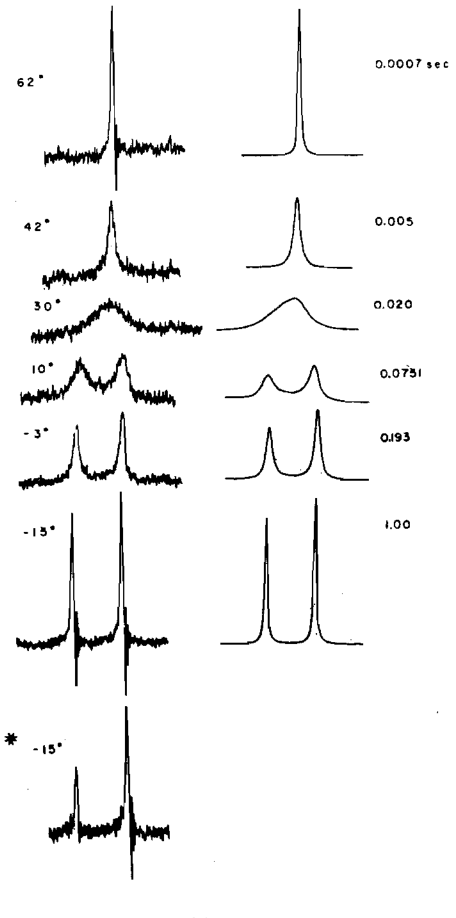


Figure 3. Observed and computed 100 MHz pmr spectra for $[(h^5\text{-}C_5H_5)Mo(CO)_3]_2$ in acetone. The numbers on the computed spectra are the mean residence times in seconds. The -15° spectrum marked * was taken with 20% toluene in acetone solvent.

The pathway for interconversion of the rotamers can be envisioned most simply as an internal rotation around the Mo-Mo bond, as shown in pathway 1 in Figure 2. An interconversion of the two enantiomorphic gauche forms by pathways 2 is in principle possible, but is not detectable by pmr. Interconversion of the trans and gauche tautomers via one or more intermediates in which one or both halves of the molecule assume a *quasi* trigonal bipyramidal (*tbp*) configuration[10] cannot be ruled out with the data at hand. The rotational pathway and those involving *tbp* intermediates are in principle distinguishable by their different consequences in permuting the CO groups. A ^{13}C nmr study might resolve this problem.

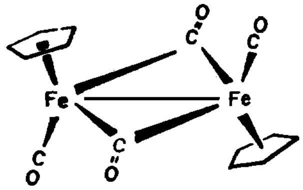
For the gauche/trans equilibrium in acetone solution, the thermodynamic parameters have been determined by least squares analysis of the nmr data in the slow exchange temperature region to be: $\Delta H^\circ = 0.44 \pm 0.15$ Kcal/mole and $\Delta S^\circ = 3.38 \pm 0.61$ Kcal/mole-degree. By extrapolation $\Delta G^\circ_{298} = [\text{gauche}]/[\text{trans}] \approx 0.8$. This is consistent with the appearance of the infrared spectrum at room temperature.

The Arrhenius activation energy, E_a, for the trans/gauche interconversion has been estimated to be 15.3 Kcal/mole, with $\log A = 13.0$ by fitting of computed to observed spectra. Representative fittings are shown in Figure 3.

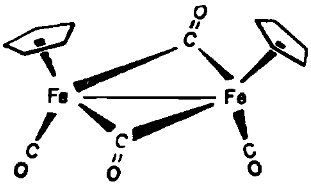
Discussion

The results of this study have two important implications. First, and most obvious, is that the previous uncertainty about the structure of $[(h^5\text{-}C_5H_5\text{-}Mo(CO)_3]_2$ in solution has been cleared up. In all solvents used, which span a range of dielectric constants from 2.0 to 47.6, the trans form, which is found in the crystal, is the most stable tautomer, but the gauche form becomes increasingly populated as solvent dielectric constant increases. It should be noted that since there are two enantiomorphous gauche rotamers, the actual stabiliy of a gauche structure relative to that of the trans structure is overestimated in the equilibrium constant by a statistical factor of 2.

The observation of a high rotational barrier in this case, coupled with the recently published ^{13}C observations of Gansow, Burke and Vernon[4] on $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$ leads us to suggest a modification of the previously proposed diagram of energy *vs* configuration for the diiron species. In the first study of this molecule,[1] only the resonances of the $h^5\text{-}C_5H_5$ protons were studied, whereby only the overall rate of the interconversion of its cis (**1**a) and terans (**1**b) isomers was observable. It was necessary to postulate that this isomerization proceeds through at least two non-bridged tautomers. By combining the activaion energy for the **1**a$\rightleftarrows$**1**b interconversion (12 ± 1 Kcal/mole) with estimates of enthalpy differences be-



1a



1b

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(10) J.W. Faller and A.S. Anderson, *J. Amer. Chem. Soc.*, *92*, 5852 (1970).

tween other pairs of tautomers, a potential energy diagram of the type shown in Figure 4 was developed. We now believe that Figure 4a requires modification and that Figure 4b gives a more nearly correct picture of energy as a function of molecular configuration.

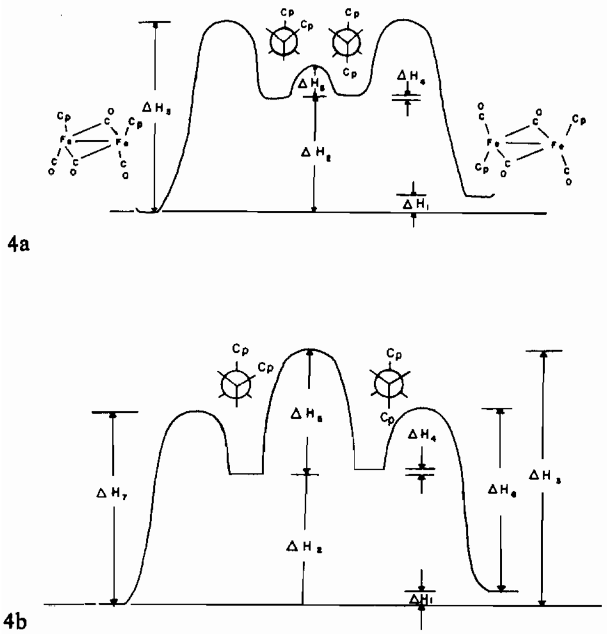

Figure 4. Two possible diagrams of potential energy *vs* molecular configuration for $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$. (a) The diagram suggested earlier in ref. 1. (b) A modified diagram which is considered more realistic.

Gansow's study[4] of the ^{13}C nmr spectrum of **1**a and **1**b as a function of temperature provided the follwing important information: (1) From the reported coalescence temperature (–10°C) we calculate E_a for the process **1**a$\rightleftarrows$**1**b to be 11.0 Kcal/mole, which is in excellent agreement with the best value (11.7 Kcal/mole) which we can estimate from our previously reported proton nmr data. (2) Gansow's results show that bridge-terminal interchange (*bti*) occurs rapidly only for the trans isomer, as low as about –80°C. If this is taken as the approximate coalescence temperature and the frequency factor is assumed to be 10^{13}, E_a for this process can be estimated as about 8.0 Kcal/mole. (3) *Bti* in the cis isomer has a much higher activation energy and becomes rapid at or about the same temperature at which cis-trans isomerization (*cti*) becomes rapid.

We believe that the information derivable from the results of Gansow, *et al.* combined with our demonstration that the barrier to internal rotation in a nonbridged $[(h^5\text{-}C_5H_5)M(CO)_n]_2$ molecule may be quite high indicates that diagram 4b is preferable to 4a. The main qualitative difference is that the barrier to rotation, ΔH_5 is substantially larger in the revised diagram.

The estimates of ΔH_1 and ΔH_2 remain unchanged. ΔH_3 is obtained from the observed activation energy for *cis*-bridged/*trans*-bridged interconversion. *Bti* for the *cis*-bridged isomer has approximately the same activation energy because internal rotation, presumably via the transoid rotamer, is required in order to transform the gauche rotamer first formed upon bridge opening into the other one, whence the alternate set of bridges may be obtained. The new diagram correctly incorporates this common barrier to both *bti* in the *cis*-bridged isomer and *cti*, while acounting for the appreciably lower activation energy, ΔH_6, for *bti* in the *trans*-bridged isomer.

Table II. Enthalpy parameters for $[h^5\text{-}C_5H_5Fe(CO)_2]_2$ in Kcal/mole, as in Figure 4b.

ΔH_1 [a]	0.9±0.1
ΔH_2 [a]	4.9±1.0
ΔH_3 [a]	~12
ΔH_4 [a]	~0
ΔH_5 [b]	~7
ΔH_6 [c]	<8
ΔH_7 [d]	<8

[a] From ref. 1. [b] ΔH_3 - ΔH_2. [c] Calculated assuming the entropy of activation equals zero. [d] See text.

Table II lists our numerical estimates of the various ΔH_i in Figure 4b. We have assumed that $\Delta H_7 \approx \Delta_6$ and that ΔH_4 is small. An estimate of ~7 Kcal/mole for ΔH_5 results from the relationship $\Delta H_5 = \Delta H_3 – \Delta H_2 = (\sim 12) – (\sim 5) = \sim 7$

It should be noted that because $\Delta H_3 = \Delta H_2 + \Delta H_5$, the question of whether the *bti* processes in the *cis*-bridged and *trans*-bridged isomers will have appreciably different activation energies depends on more than just the presence of a high rotational barrier. If ΔH_2 becomes smaller or if ΔH_6 ($\approx \Delta H_7$) become larger, ΔH_2 may become relatively unimportant. This seems to be the case for $[(h^5\text{-}C_5H_5)Mn(CO)\text{-}(NO)]_2$ where Marks and Kristoff find that the activation energies for the two *bti* processes differ by less than 1 Kcal/mole.

It is clear that great diversity of behavior is possible in systems of the kind discussed here. We are, however, beginning to appreciate the roles of the different factors and further studies should prove fruitful and interpretable within the general scheme discussed here.