

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843**Spectroscopic Studies of the Structural and Dynamical Properties of Bis(pentahaptocyclopentadienyl)tricarbonyl(triphenyl phosphito)diiron in Solution**

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The dynamical properties of the molecule $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{P}(\text{OPh})_3]$ in solution have been studied by ^1H and ^{13}C nmr spectroscopy. It has been shown that two processes occur: (1) cis-trans isomerization; (2) scrambling of bridge and terminal CO ligands. Line shape analysis has been conducted and the rates and activation parameters for each process have been obtained. The key result is that both processes have the same rate at each temperature and the same activation parameters within experimental error. It is then shown, from a detailed analysis of the pathways of cis-trans isomerization and of carbonyl scrambling, as these would be dictated by the previously proposed mechanism of Adams and Cotton, that that is precisely what the mechanism requires. If there were some additional mechanism for carbonyl scrambling, such as one-for-one bridge-terminal interchanges, the total rate of bridge-terminal interchange would be greater than the rate of cis-trans isomerization, contrary to the fact. Thus the Adams and Cotton mechanism is supported. The Arrhenius activation energy is 20.0 (2) kcal/mol as compared to ca. 12 kcal/mol for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$. This is also in agreement with the Adams and Cotton mechanism, since the replacement on one CO ligand by the very bulky $\text{P}(\text{OPh})_3$ ligand should appreciably raise the barrier to rotation in the nonbridged intermediate.

Introduction

Adams and Cotton have previously proposed¹⁻³ and provided considerable evidence to show¹⁻⁸ that the pathways for scrambling of carbonyl and isocyanide ligands and for isomerization of both bridged (*e.g.*, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_n(\text{CNR})_{4-n}$, $n = 1-4$) and nonbridged (*e.g.*, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_n(\text{CNR})_{6-n}$, $n = 5, 6$) dinuclear metal carbonyls have as their essential, component steps (1) concerted opening and closing of *pairs* of ligand bridges and (2) hindered internal rotations in the nonbridged tautomers.

The compound chosen for this study is one of a number of phosphine-substituted derivatives⁹ of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$, namely, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OPh})_3$. For several compounds of this stoichiometry, notably those in which the phosphorus ligand was a phosphite or PPh_3 , the infrared spectra in the carbonyl stretching region displayed two bands, of unequal intensity, in the terminal region as well as one band attributable to bridging carbonyl groups. At the same time, it was noted that the proton nmr spectrum at ambient temperature consisted of only two signals, one for each of the chemically distinct types of C_5H_5 group to be found in a $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\mu\text{-CO})_2(\text{CO})(\text{PR}_3)$ molecule. From this information, it was concluded that both cis and trans isomers were present but that they were rapidly interconverting just as in the case of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ itself.¹⁰

We report here a detailed investigation of the structural

and dynamical behavior of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{P}(\text{OPh})_3]$, employing ^1H and ^{13}C nmr spectroscopy over a range of temperatures. This study was undertaken to determine whether the behavior of this compound could be accounted for using only the same mechanistic principles that have previously been proposed¹⁻³ to explain the behavior of related molecules. The molecule studied here differs from those previously investigated in a significant way, namely, in containing one ligand which cannot occupy a bridging position and is therefore required to remain permanently attached to one of the metal atoms. For such a case, as will be explained in the Discussion, quite specific predictions can be made, using the previously developed mechanistic principles, as to the relationship between rates and activation parameters for the two independently measurable exchange processes, namely, cis-trans isomer interconversion and bridge-terminal CO exchange. Other conceivable mechanisms, such as one-for-one bridge-terminal exchanges would lead to different expectations and, in this way, the opportunity exists for testing further our earlier mechanistic proposals.

Experimental Section

All preparations were carried out in an atmosphere of pre-purified nitrogen. All solvents were dried and deoxygenated in an appropriate manner prior to use.

Preparations. $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{P}(\text{OPh})_3]$ was prepared by direct reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ and $\text{P}(\text{OPh})_3$, according to the procedure described in the literature.⁹ Purification was effected by column chromatography on silica gel (Baker 60-200 mesh). Elution of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ was accomplished with 1:2 hexane-benzene and the product was removed with benzene and then recrystallized from a 1:1 mixture of benzene and hexane.

The preparation of a sample enriched in ^{13}C was first attempted by equilibration of the compound with ^{13}C CO. This was unsatisfactory because the ^{13}C CO displaced much of the $\text{P}(\text{OPh})_3$ thus generating a product heavily (50-80%) contaminated with ^{13}C CO-enriched $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$. A practical method consisted in enriching $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ (500 mg, 1.4 mmol) by exchange with 90% enriched ^{13}C CO (20 cm³ at 22^o (1 atm), 0.8 mmol) in 100 ml of benzene. The exchange was carried out in a three-necked flask equipped with two gas inlets and having a total accessible volume of about 120 ml. The solution was frozen and the space above it was evacuated and then refilled with the ^{13}C CO. The flask was sealed and stirred for 24 hr. The CO was then removed by several cycles of freezing and pumping followed by thawing. Triphenyl phosphite (500 mg, 1.4 mmol) was added and the standard preparative procedure followed to yield 250 mg of product which the infrared spectrum showed to be ca. 20% enriched.

Spectroscopic Measurements. Proton nmr spectra were recorded

(1) R. D. Adams and F. A. Cotton, *Inorg. Chim. Acta*, **7**, 153 (1973).

(2) F. A. Cotton, Plenary Lecture, Assemblée Annuelle, Société Chimique de France, Marseille, May 22-25, 1972; *Bull. Soc. Chim. Fr.*, (9) 2588 (1973).

(3) F. A. Cotton, Plenary Lecture, Sixth International Conference on Organometallic Chemistry, Amherst, Mass., Aug 13, 1973; see Abstracts, pp 1-8.

(4) R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, **95**, 6589 (1973).

(5) R. D. Adams, M. D. Brice, and F. A. Cotton, *J. Amer. Chem. Soc.*, **95**, 6594 (1973).

(6) R. D. Adams and F. A. Cotton, *Inorg. Chem.*, **13**, 249 (1974).

(7) F. A. Cotton and B. A. Frenz, *Inorg. Chem.*, **13**, 253 (1974).

(8) R. D. Adams, F. A. Cotton, and J. M. Troup, *Inorg. Chem.*, **13**, 257 (1974).

(9) R. J. Haines and A. L. du Preez, *Chem. Commun.*, 1513 (1968); *Inorg. Chem.*, **8**, 1459 (1969).

(10) J. G. Bullitt, F. A. Cotton, and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 2155 (1970); *Inorg. Chem.*, **11**, 671 (1972).

on a Varian HA-100D spectrometer equipped with a V-4060 variable-temperature controller. Temperatures were recorded by a copper-constantan thermocouple placed in the nitrogen stream directly below the sample and attached to a Leeds and Northrup Model 713 digital thermometer. Temperatures were calibrated vs. a methanol standard and are accurate to $\pm 2^\circ$. Chemical shifts were measured from the internal TMS lock with a Varian V-4315A frequency counter and are accurate to ± 0.5 Hz. Samples were prepared under a nitrogen atmosphere in serum-stoppered nmr tubes. Toluene- d_8 with 1% TMS was vacuum degassed and added to the sample by syringe.

A correction for the temperature dependence of the chemical shifts in toluene- d_8 was estimated from measurements of chemical shifts at several temperatures below the slow-exchange limit and extrapolation through the intermediate-exchange region. Equilibrium constants were measured at nine temperatures below the slow-exchange limit. Ten spectra at each temperature were traced and the peaks cut out and weighed. Sufficient time was allowed at all temperatures for sample equilibration.

Carbon-13 nmr spectra were recorded on a Bruker HFX-90/Nicolet 1085 Fourier transform spectrometer at 22.625 MHz. A 200-mg sample enriched to ca. 20% in ^{13}C was dissolved in 1.5 ml of dry degassed toluene- d_8 and transferred to a 10-mm diameter tube using inert-atmosphere techniques. The spectrometer was locked on the ^2H methyl signal of $\text{CD}_3\text{C}_6\text{D}_5$. The Bruker variable-temperature unit was calibrated against a thermocouple inserted into the sample tube; readings agreed to within $\pm 1^\circ$ over the entire temperature range of interest. One thousand pulses with a tilt angle of 25° were collected at each temperature. Spectra at temperatures greater than 0° were taken with 30 mg of tris-(acetoacetonato)chromium(III) added.¹¹ A slight change in line width was noted upon addition of this relaxation reagent. Chemical shifts were measured relative to the substituted aromatic carbon in $\text{CD}_3\text{C}_6\text{D}_5$ and corrected according to the relation $\delta_{\text{TMS}} = \delta(\text{C}, \text{D}_8) + 137.5$ ppm.

An attempt was made to assign the cyclopentadienyl proton resonances to the geometric isomers. Crystals from the same batch as were used for the single-crystal X-ray structure determination¹² were placed in a serum-stoppered nmr tube under nitrogen and the sample tube was placed in the nmr probe which had been already equilibrated at -45° . Solvent, either toluene- d_8 (with 1% TMS) or 1:1 toluene- d_8 - CS_2 (with 1% TMS) was freeze-thaw degassed, cooled to ca. -50° , and injected into the sample tube *via* syringe.¹³ The spectrometer was quickly locked and tuned and spectra were recorded. These experiments were inconclusive because of the slowness with which the solid went into solution. When pure toluene- d_8 was used, no signals had appeared after 30 min. With 1:1 toluene- CS_2 weak signals were first observed only after 20 min. These were the signals due to the isomer which predominates at equilibrium. Since the half-life of the cis-trans isomerization process is ca. 1 min at -45° , the time span of the experiment is too long to yield any indication of which signal corresponds to the isomer in the crystal (cis).

Thermodynamic parameters for the cis-trans equilibrium were calculated from the proton nmr data by a nonlinear, weighted least-squares fit of the equation $\ln K = -\Delta H/RT + \Delta S/R$ using a program (ISOMER) written by A. J. White based on Krieger's EXEN.¹⁴ K was defined as the mole ratio of the minor isomer to the major isomer. Line shape calculations were carried out using a local version of EXCHSYS by Whitesides and Krieger.¹⁵ The kinetic exchange matrix for the proton nmr must describe two simultaneous two-site exchanges suitably modified for the effects of unequal isomer population¹⁵ using values for each temperature calculated from the thermodynamic parameters described above. The kinetic exchange matrix for the ^{13}C nmr was of the form

$$\begin{bmatrix} -2 & 0 & 1/K & 1/K \\ 0 & -1 & 1/K & 0 \\ 1 & 1 & -2/K & 0 \\ 1 & 0 & 0 & -1/K \end{bmatrix}$$

(11) O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Amer. Chem. Soc.*, **94**, 2550 (1972).

(12) F. A. Cotton, B. A. Frenz, and A. J. White, *Inorg. Chem.*, **13**, 1407 (1974).

(13) Independent experiments showed that the equilibrium ratio of isomers is essentially independent of solvent composition from pure toluene to 1:1 toluene- CS_2 .

(14) J. K. Krieger, Ph.D. Thesis, Massachusetts Institute of Technology, 1971.

(15) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

where K is the equilibrium constant at the appropriate temperature as defined above. Suitable correction was made for the line broadening due to addition of the chromium relaxation reagent at temperatures greater than 0° .

Results

Some of the ^1H and ^{13}C nmr spectra of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{P}(\text{O}^-\text{Ph})_3]$ recorded at various temperatures are displayed in Figures 1 and 2. As Figure 1 shows, at 42° the proton spectrum represents the fast-exchange limit. Only two resonances, of equal intensity, are present. The upfield resonance is a doublet ($J_{\text{P-H}} = 1.1$ Hz) and may be assigned to the C_5H_5 ring on the iron atom bearing the phosphite ligand, while the downfield resonance is due to the other ring. As the temperature is lowered, each of these signals broadens and, at ca. -31° , re-forms into a pair of resonances which are unequal in intensity. At no temperature within the range of our investigations was there evidence that the two distinct ring environments were averaged *via* either intra- or intermolecular exchange of the phosphite ligand between the iron atoms. It thus appears that the behavior of the ^1H nmr spectra shown in Figure 1 can be accounted for entirely by the process of interconversion of cis and trans isomers, unaccompanied by phosphite exchange. These spectra provide no information as to the occurrence, or nonoccurrence, of bridge-terminal carbonyl ligand exchange.

Representative ^{13}C spectra in the region of the carbonyl carbon atoms are shown in Figure 2. At -40° two terminal carbonyl resonances appear, in the same intensity ratio as that between the two pairs of cyclopentadienyl proton resonances at the same temperature. In the bridging carbonyl region only one doublet is observed. The doublet structure is attributable to ^{31}P - ^{13}C coupling ($J_{\text{P-C}} = 20$ Hz). The absence of an observable weak doublet can only be attributed to its being practically identical in chemical shift with the larger doublet.

As the temperature is raised, the weaker of the two signals in the terminal carbonyl region first begins to collapse. Eventually, all signals broaden and collapse. At about 30° all signals have disappeared into the base line. At 87° a single, broad resonance can be observed at a position approximately one-third of the way between the bridge and terminal chemical shifts.

The proton nmr spectra obtained at temperatures below the slow-exchange limit yielded the following thermodynamic parameters for the isomer equilibrium in 1:1 toluene- CS_2 : $\Delta H = 1.9$ (2) kcal mol $^{-1}$, $\Delta S = 4.0$ (8) cal mol $^{-1}$ deg $^{-1}$, $\Delta G_{298} = 0.8$ (3) kcal mol $^{-1}$.

The rate and activation parameters for the isomer interconversion were obtained by line shape analysis of the proton nmr data. Simulated spectra are shown matched to observed spectra in Figure 1. From the mean residence times at the various temperatures the activation parameters listed in Table I were obtained. Similarly, computer simulation of the ^{13}C line shapes was carried out and activation

Table I. Activation Parameters Obtained from Line Shape Analysis^a

Parameter	Process	
	Isomerizn	CO scrambling
E_a , kcal mol $^{-1}$	20.0 (2)	19.8 (2)
$\log A$	17.4 (6)	17.3 (7)
ΔH^\ddagger , kcal mol $^{-1}$	19.5 (2)	19.3 (2)
ΔS , cal mol $^{-1}$ deg $^{-1}$	19.3 (6)	18.6 (7)
ΔG_{298} , kcal mol $^{-1}$	13.7 (3)	13.7 (3)

^a Numbers in parentheses are the estimated standard deviation in the least significant digit.

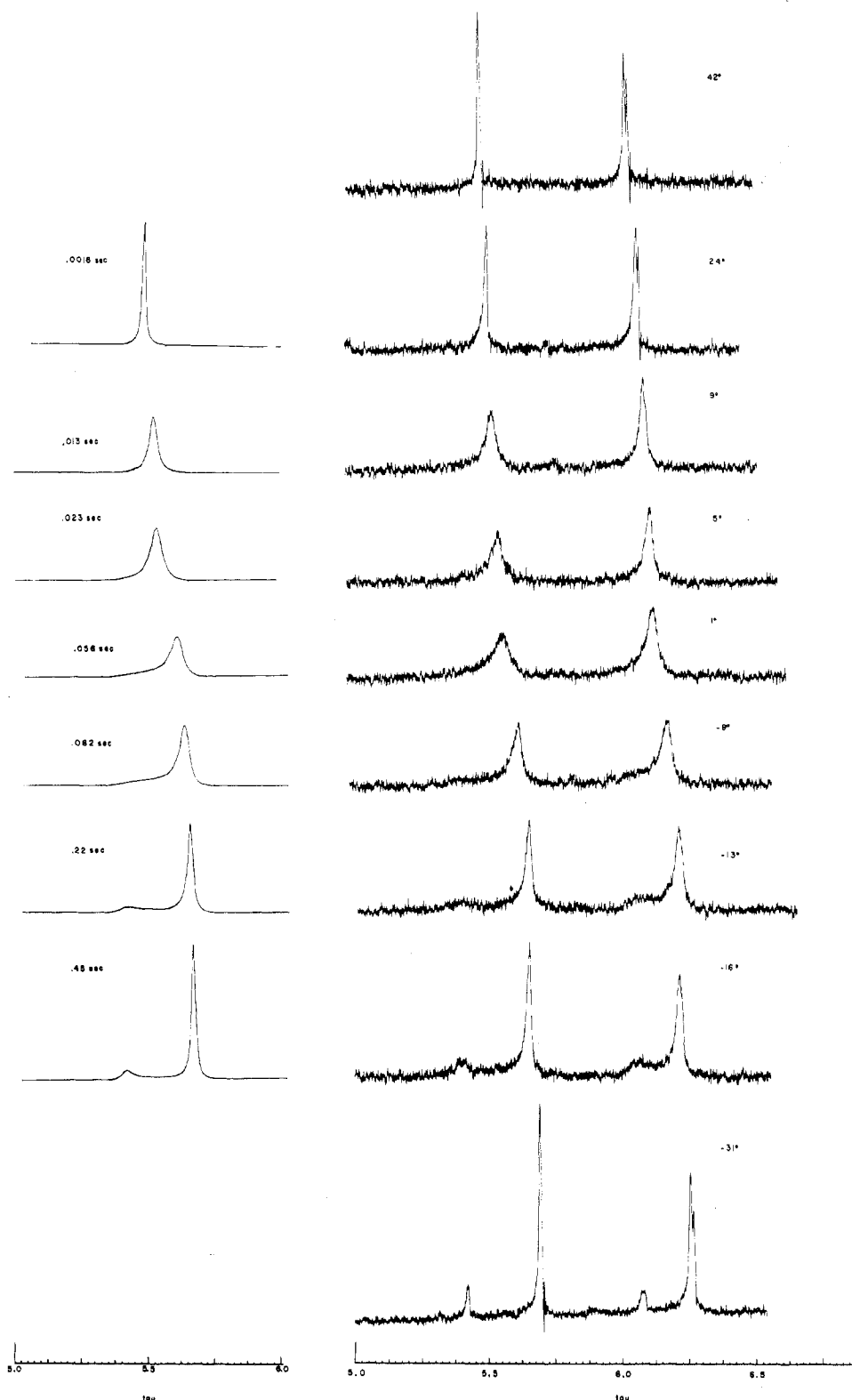


Figure 1. The ^1H nmr spectra of the title compound at various temperatures. Experimental spectra are shown in the right column and simulated spectra of the uncoupled cyclopentadienyl ring for various mean residence times are shown on the left.

parameters for the bridge-terminal exchange process were calculated. These are also listed in Table I.

Discussion

Using the detailed mechanism proposed by Adams and Cotton for the fluxional processes which occur generally in dinuclear metal carbonyl type molecules,¹⁻³ certain quite specific predictions can be made concerning the

dynamical behavior of a $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{L}$ type molecule (where L is a ligand which cannot serve as a bridge) in solution. Qualitatively, of course, one expects both cis-trans isomerization and bridge-terminal CO exchange to be facile processes, as is observed. Closer examination of the mechanism leads to a very explicit prediction of the relative rates of these two processes. This can best be seen by first examining the rearrangements shown in Figure 3.

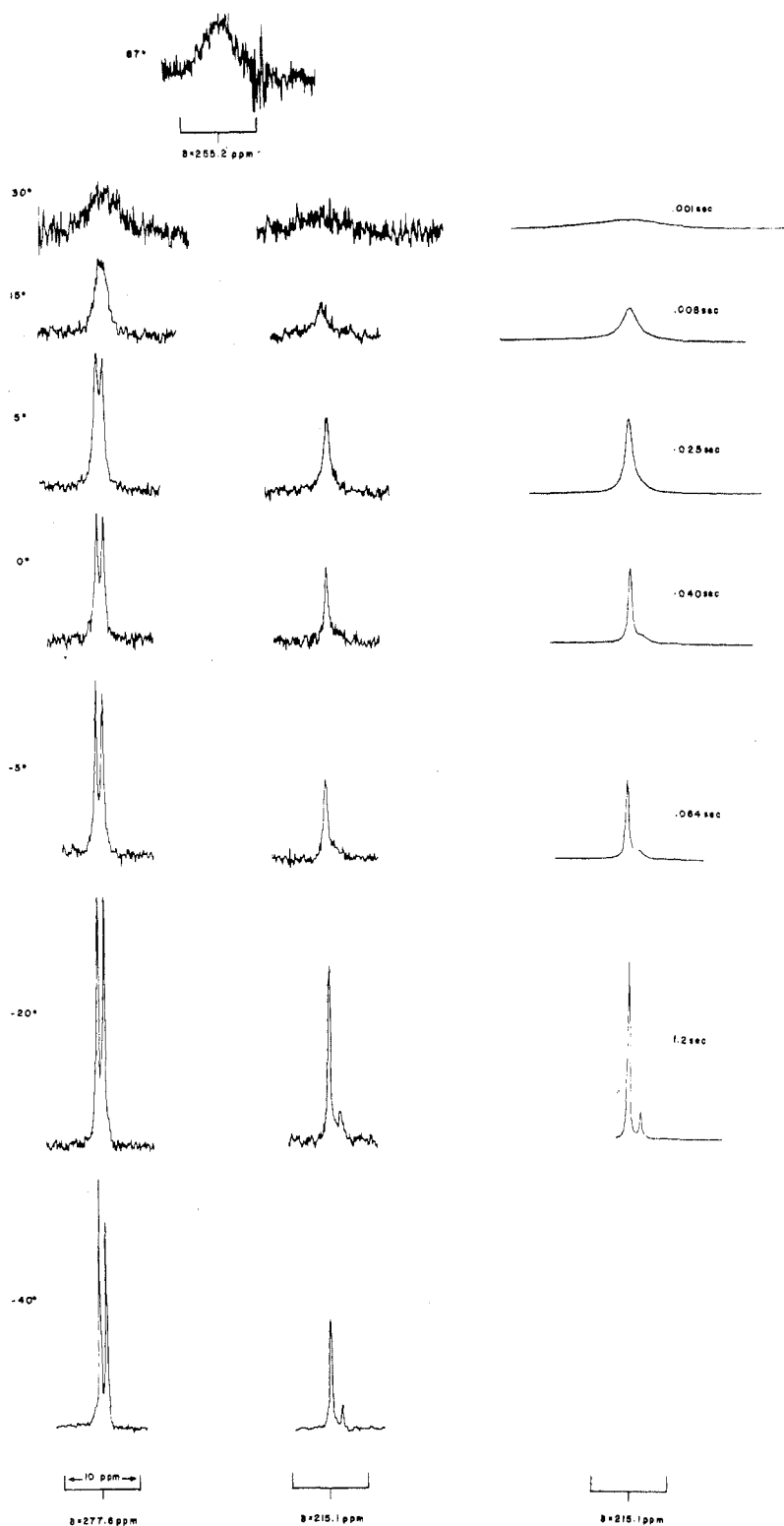


Figure 2. The ^{13}C nmr spectra in the CO region for the title compound at various temperatures. From left to right are the bridging carbonyl region, the terminal carbonyl region, and computer simulation of the exchange process for the terminal carbonyl region.

As shown in Figure 3, a particular permutamer of the cis isomer, C(1), where **a**, **b**, and **c** are labeled CO ligands, can open its bridges in two ways. Each of these non-bridged structures can then execute rotations by $\pm 120^\circ$ to give two other rotamers. In each case, one of the rotations (that leading to the rotamer shown above) is abortive, in the sense that it does not have an anti pair of CO ligands and cannot therefore reclose a pair of bridges to generate

a bridged structure. In each case, there is also one rotation (that leading to the rotamer shown below) which gives a rotamer with cyclopentadienyl groups anti to each other and with an anti pair of CO ligands. From each of these, a pair of bridges can be formed and a trans bridged isomer, T(1) or T(3), is obtained. In each case, the quondam terminal CO group, **a**, is now in a bridging position.

Similar processes can now be repeated with each of the

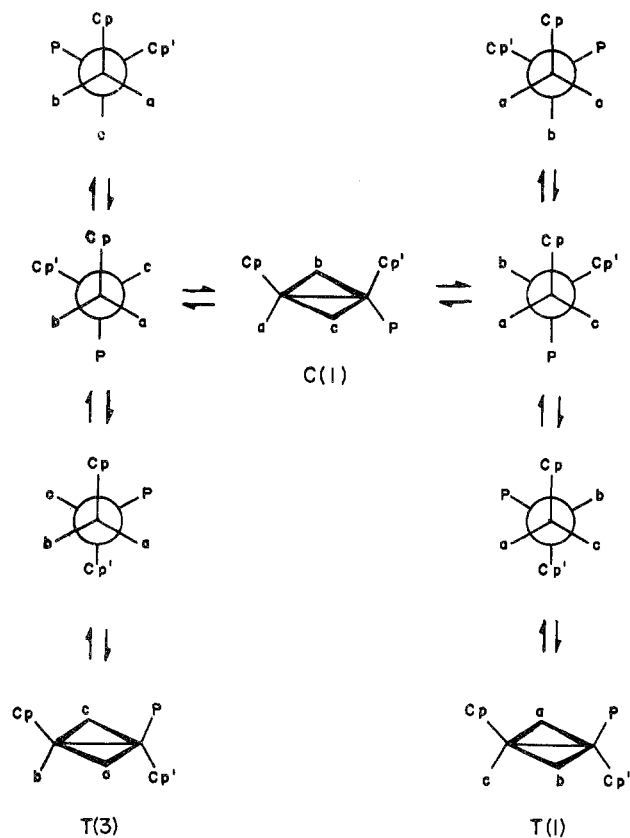


Figure 3. The rearrangements directly available to a cis isomer of the title compound, according to the mechanism of Adams and Cotton. The letters *a*, *b*, and *c* are used to label the three CO ligands, Cp and Cp' represent cyclopentadienyl groups, and P stands for the entire P(OPh)₃ ligand. C(1), T(1), and T(3) identify particular permutamers of the cis and trans isomers, as indicated in more detail in Figure 4.

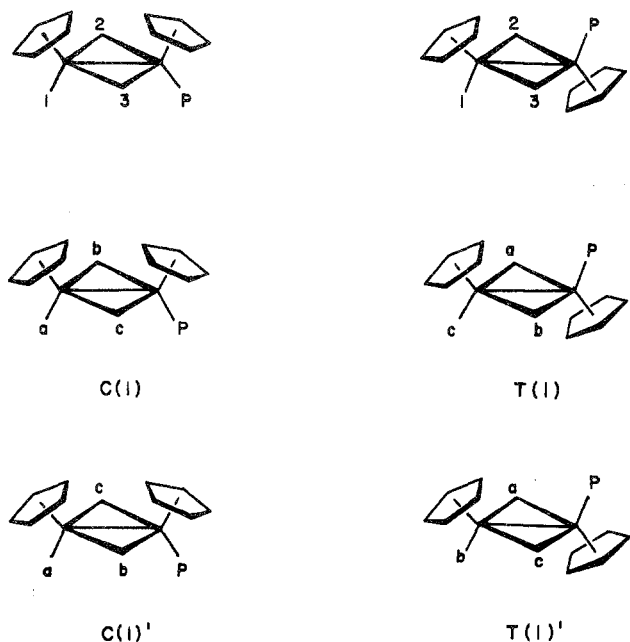


Figure 4. Diagrams showing how the notation for the 12 possible permutamers is defined. The upper two drawings show how the sites for CO ligands are numbered. The middle two show how two members, one cis and one trans, in one interrelated set of permutamers are defined. Note that a right-handed (clockwise) permutation takes C(1), with abc into T(1), with cab. In exactly the same way two of the permutamers in the second, primed set are defined.

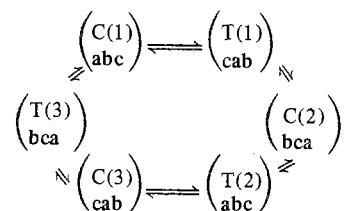
trans-bridged isomers, T(1) and T(3), leading either back to C(1) or on to two other cis permutamers, C(2) and C(3). Rather than draw all of the transformations out in detail, we adopt a compact notation which enables us to specify each permutamer and set out the entire sequence of rearrangements in a simple way. In Figure 4 we show how the three sites of CO ligands are numbered in the cis and trans structures. We then designate the cis permutamer with *a* at site 1, *b* at site 2, and *c* at site 3 as C(1). Figure 4 also shows the (arbitrary) definition of trans permutamer T(1). We can express the ordering of *a*, *b*, and *c* on the sites 1, 2, and 3 in C(1) by the expression *abc*; in the same way the ordering in T(1) may be written *cab*. Complete symbols for these two permutamers are

$$\begin{pmatrix} C(1) \\ abc \end{pmatrix} \text{ and } \begin{pmatrix} T(1) \\ cab \end{pmatrix}$$

A little reflection will show that the type of process depicted in detail in Figure 3 leads entirely to *cyclic* permutations of *a*, *b*, and *c*. Thus we have

$$\text{etc.} \rightleftharpoons \begin{pmatrix} T(3) \\ bca \end{pmatrix} \rightleftharpoons \begin{pmatrix} C(1) \\ abc \end{pmatrix} \rightleftharpoons \begin{pmatrix} T(1) \\ cab \end{pmatrix} \rightleftharpoons \text{etc.}$$

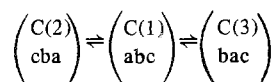
When the entire sequence is worked out, it is found to be the closed cycle



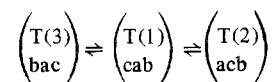
There is another set of six permutamers, the primed set, of which C(1)' and T(1)' shown in Figure 4 are representative. The two sets are not, of course, physically distinguishable unless *a*, *b*, and *c* are distinguishable; in the present case they are not.

It is immediately obvious from the above cyclic set of interconverting species, C(1), T(1), C(2), T(2), C(3), and T(3), that the Adams and Cotton mechanism makes the following explicit prediction: *Cis-trans isomerization and bridge-terminal exchange are tied together mechanically in such a way that they must have the same rate.* This, within experimental error, is precisely what is observed.

If there were another effective mechanism for bridge-terminal CO scrambling, then that process would proceed measurably faster than cis-trans isomerization. The fact that this is not observed indicates that there is no other CO scrambling process except that which is intrinsic to the Adams and Cotton mechanism. One class of such additional CO exchange pathways that can therefore be ruled out are direct, one-for-one bridge-terminal interchanges, such as those represented by



or



It is noteworthy that the entire analysis is conducted in such a way that it is unnecessary to know which isomer

(cis or trans) gives rise to which nmr signals. This is very convenient as there is no sure way, with the data at hand, to make such an assignment.^{16,17} Since the energy difference between the two is so small, arguments depending on estimates of steric strain are inconclusive, even though we

(16) It is possible to design an experiment which can resolve this ambiguity, and such work is now in progress. If it is successful, the results will be reported later.

(17) Note Added in Proof. Although, as noted explicitly, the uncertainty as to which isomer is the predominant one in solution does not interfere at all with the kinetic analysis, we nevertheless desired to make an identification. This was done by preparing the compound [C₅H₄CH(NMe₂)CH(NMe₂)C₅H₄]Fe₂(CO)₃P(OPh)₃, measuring its ir spectrum, and comparing with that of (C₅H₅)₂Fe₂(CO)₃P(OPh)₃. The former, which can exist only in a cis form, was prepared by reaction of P(OPh)₃ with [C₅H₄CH(NMe₂)CH(NMe₂)C₅H₄]Fe₂(CO)₄ [P. McArdle and A. R. Manning, *J. Chem. Soc. A*, 2119 (1970)]. In CS₂ the new compound, which is constrained to be cis, has bands at 1958 and 1745 cm⁻¹, of essentially equal intensities. (C₅H₅)₂Fe₂(CO)₃P(OPh)₃ has bands at 1961 (s), 1940 (w), 1751 (sh), and 1748 (s) cm⁻¹. These results clearly indicate that the cis isomer predominates and has bands at 1961 and 1748 cm⁻¹ while the trans isomer has bands at 1940 and 1751 cm⁻¹.

know the structure of the cis isomer in detail.¹² We also think it doubtful that any reliable answer could be obtained from study of how solvent polarity affects the infrared spectrum since both isomers are inherently polar (unlike the case of (η^5 -C₅H₅)₂Fe₂(CO)₄ where the trans isomer is rigorously nonpolar).

Finally, we note that the activation energy here, ca. 20 kcal mol⁻¹, is some 8 kcal mol⁻¹ higher than that for the comparable processes in (η^5 -C₅H₅)₂Fe₂(CO)₄. This would be expected from the Adams and Cotton mechanism, since the replacement of one CO ligand by the very bulky P(OPh)₃ ligand should increase the barrier to the rotation which is required in each step of the cycle.

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Registry No. (η^5 -C₅H₅)₂Fe₂(CO)₃[P(OPh)₃], 51056-17-8; ¹³C, 14762-74-4.

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Crystal and Molecular Structures of cis-Bis(pentahaptocyclopentadienyl)tricarbonyl(triphenyl phosphito)diiron

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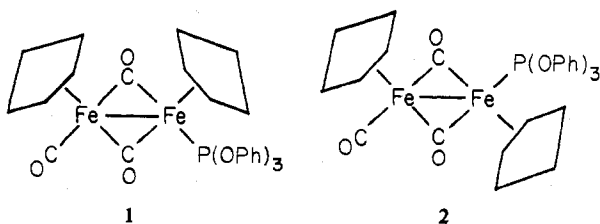
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Bis(pentahaptocyclopentadienyl)tricarbonyl(triphenyl phosphito)diiron crystallizes in space group $P\bar{1}$ with unit cell dimensions $a = 14.331$ (5) Å, $b = 17.335$ (9) Å, $c = 12.482$ (7) Å, $\alpha = 102.12$ (4)°, $\beta = 92.02$ (4)°, $\gamma = 66.44$ (4)° and $Z = 4$. The asymmetric unit is formed by two cis molecules. The structure has been solved and refined using 3605 independent reflections with intensities greater than 3σ , where σ is the estimated standard deviation for the intensity. The cyclopentadienyl rings and the phenyl groups were refined as rigid bodies and anisotropic thermal parameters were assigned to the iron and phosphorus atoms only. Refinement converged at reliability indices of $R_1 = 0.075$ and $R_2 = 0.090$. Each molecule has the expected structure, with an Fe-Fe bond (Fe-Fe = 2.543 (3) and 2.548 (3) Å) and two bridging carbonyl groups. Aside from the replacement of one terminal CO group by (C₆H₅O)₃P each molecule closely resembles the cis isomer of (η^5 -C₅H₅)₂Fe₂(CO)₄. This supports our earlier assumption that the structural and dynamical behavior of the two systems should be qualitatively very similar and that information obtained on one should have relevance to the understanding of the other.

Introduction

In the preceding paper¹ the structural and dynamic behavior of cis and trans isomers of bis(cyclopentadienyl)tricarbonyl(triphenyl phosphito)diiron in solution have been reported and interpreted on the assumption that the structures are, schematically, **1** and **2**. The results help to support



and lend emphasis to the picture previously developed in this laboratory of the way in which binuclear metal carbonyl species undergo isomerization and carbonyl scrambling reactions.²⁻⁷

(1) F. A. Cotton, L. Kruczynski, and A. J. White, *Inorg. Chem.*, **13**, 1402 (1974).

(2) R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, **94**, 6193 (1972).

In connection with the solution studies we have undertaken an X-ray crystallographic study of the molecular structure. A secure knowledge of the molecular structure in the crystal lends support to the interpretation of solution spectra and demonstrates in detail the close relationship of the structure of this molecule to the structure of what we had presumed to be related species such as the (η^5 -C₅H₅)₂Fe₂(CO)₄ isomers^{8,9} and the several methyl isocyanide substitution products thereof.¹⁰⁻¹²

(3) R. D. Adams and F. A. Cotton, *Inorg. Chim. Acta*, **7**, 153 (1973).

(4) F. A. Cotton, Plenary Lecture, Assemblée Annuelle, Société Chimique de France, Marseille, May 23-25, 1973; *Bull. Soc. Chim. Fr.*, (9) 2588 (1973).

(5) F. A. Cotton, Plenary Lecture, Sixth International Conference on Organometallic Chemistry, Amherst, Mass., Aug 13, 1973; see Abstracts, pp 1-8.

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