

For $\text{Mo}_6\text{Br}_8\text{I}_6^{2-}$, the absorptions at 274 cm^{-1} and in the range $210\text{--}250\text{ cm}^{-1}$ can again be assigned to the $\nu_1(\text{Mo-O-X})$, $\nu_2(\text{Mo-O-X})$, and $\nu_5(\text{Mo-Mo})$ modes; that at 120 cm^{-1} , to the $\nu_3(\text{Mo-Y})$ mode, with $\delta_4(\text{Mo-Y})$ being again out of range. The small peak at 157 cm^{-1} remains unassigned.

Finally, for the $\text{W}_6\text{Cl}_{14}^{2-}$ spectrum, the following assignments seem certain: $\nu_1(\text{W-X})$ and $\nu_2(\text{W-X})$ occur at $290\text{--}320\text{ cm}^{-1}$ and $\nu_3(\text{W-Y})$, at 224 cm^{-1} . $\delta_4(\text{W-Y})$ may be occurring at $\sim 105\text{ cm}^{-1}$, but the reliability of the spectra here is questionable. Finally, in part b of

Figure 3, there is some indication of a weak absorption at 150 cm^{-1} . This is approximately where $\nu_5(\text{W-W})$ might be expected to occur assuming that only the masses and not the force constants change on going from Mo_6 to W_6 .

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Tautomeric Changes in Metal Carbonyls. I. π -Cyclopentadienyliron Dicarboxyl Dimer and π -Cyclopentadienylruthenium Dicarboxyl Dimer¹

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The problem of the structure of π -cyclopentadienyliron dicarbonyl dimer in nonpolar solvents (*e.g.*, C_6H_6 , CS_2) has been reconsidered. New data and a reanalysis of all data lead to the conclusion that the molecule exists as a doubly bridged dimer in which both C_5H_5 groups lie on one side of the mean plane of the Fe and bridging C atoms and the equivalent terminal CO groups lie on the other side. It is suggested that this structure and the centrosymmetric tautomer which exists in the solid are interconverted *via* a nonbridged structure in which rotation about the Fe-Fe bond can occur. The Ru compound has been carefully studied and the conclusion reached that in nonpolar solvents there is a tautomeric equilibrium between a bridged structure similar to that postulated for the Fe compound and a nonbridged structure of the sort which provides a pathway between the *cis*- and *trans*-bridged structures in the iron case. The precise rotational configuration of the nonbridged structure of the Ru compound could not be established definitely but appears to be *cis* (*i.e.*, eclipsed), rather than *gauche* or staggered, but definitely not *trans*. The prediction is ventured that the osmium homolog of these compounds may exist under all or most conditions entirely in a nonbridged structure.

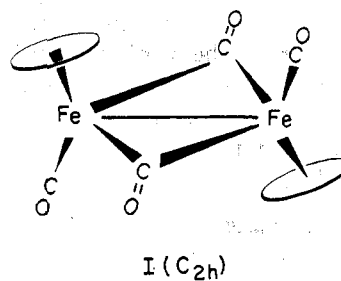
Introduction

The idea that a metal carbonyl or metal carbonyl derivative of given stoichiometry may exist in tautomeric forms is not new. However, the idea that such tautomerism may be of frequent occurrence perhaps is.

Probably the best characterized tautomeric system is $\text{Co}_2(\text{CO})_8$, which has a structure with two bridging CO groups in the crystalline state but exists as a mixture of this and a nonbridged structure in solution.^{3,4} Tautomerism also has been suggested⁵ for $\text{Co}_4(\text{CO})_{12}$. Studies in this laboratory indicate that tautomeric rearrangements and equilibria also occur in other systems, and in this paper we describe studies of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ and $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ ($\text{Cp} = \pi\text{-C}_5\text{H}_5$) which show that the existence of such equilibria provides an explanation for the heretofore puzzling infrared spectra of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$.

The preparation and infrared spectrum of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ were first reported⁶ in 1955. When X-ray study⁷

of the crystalline solid later showed it to have a centrosymmetric structure, I, with two bridging and two



terminal CO groups (molecular symmetry,⁸ C_{2h}), the interpretation of this spectrum became challenging and controversial.^{9,10} Another experimental observation which must be kept in view in these discussions is the dipole moment of about 3.1 D. possessed by $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ in benzene solution.¹¹ The work of Stammreich,

(7) O. S. Mills, *Acta Cryst.*, **11**, 620 (1958).

(8) Molecular symmetry assignments in this paper will be made treating the $(\pi\text{-C}_5\text{H}_5)\text{-M}$ groups as circular cones. A considerable body of data on π -cyclopentadienylmetal carbonyl compounds has shown that, insofar as selection rules for CO stretching modes are concerned, this is a highly satisfactory assumption.

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

(10) K. Noack, *ibid.*, **25**, 1383 (1963).

(11) E. Weiss, W. Hubel, and R. Merengi, *Chem. Ber.*, **95**, 1155 (1962).

(1) Supported by the National Science Foundation.

(2) Fellow of the Consejo Nacional de Investigaciones Cientificas y Tecnicas, Argentina.

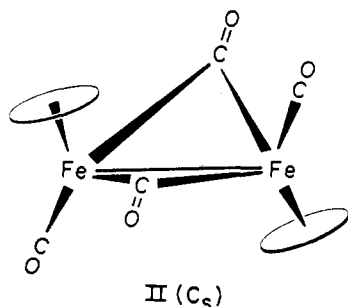
(3) K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963).

(4) G. Bor, *ibid.*, **19**, 2065 (1963).

(5) F. A. Cotton, *Inorg. Chem.*, **5**, 1083 (1966).

(6) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

Wilkinson, and Cotton led to the general conclusion that in solution the molecule could not exist exclusively as structure I but instead consisted at least in part of some structure in which a Raman-infrared coincidence is possible. Later, Noack was led to propose that the solutions contain structure II. This is obtained simply



by distortion of I by bending the $Fe(CO)_2Fe$ group along the Fe-Fe line; the two terminal CO groups are now no longer equivalent. The crucial considerations leading to the proposal of this structure appear to have been as follows.

(1) The need to explain the appearance of two terminal CO stretching modes in the infrared, while assuming that coupling between the two terminal CO groups in bridged structures such as I and II would be negligible. Structure II could have two bands because the two terminal CO groups are not equivalent to each other and thus could have inherently different force constants.

(2) The need to explain the existence of a dipole moment. We note here, however, that it is first difficult to believe that any degree of bending which is sterically reasonable in structure II could lead to a moment of as much as 3 D. and, further, that if the molecule is extensively bent, the absence of a second bridging CO band in the infrared becomes puzzling. In short, structure II seems unlikely to provide a satisfactory explanation of all the facts, even as they were known prior to the work reported below. We shall show, in fact, that a much more acceptable structure can be proposed. We shall also describe and explain the more complicated infrared spectrum of the ruthenium analog, $Cp_2Ru_2(CO)_4$.

Results and Discussion

The Iron Compound.—The spectroscopic data upon which the discussion will be based are given in Figures 1a and 2a, with the numerical values of the peak frequencies and some relative intensities given in Tables I and II. The intensities were estimated by replotting the recorded spectra on a relative molar absorbance intensity scale. All spectra were run at various dilutions and recorded on greatly expanded scales relative to the data presented in the figures. However, no significant qualitative features not evident in the figures given were ever observed. In particular, no definite asymmetry in the bridging CO fundamentals or combination overtone bands was found.

We believe that all of the experimental facts regarding the iron compound can be best explained in terms of

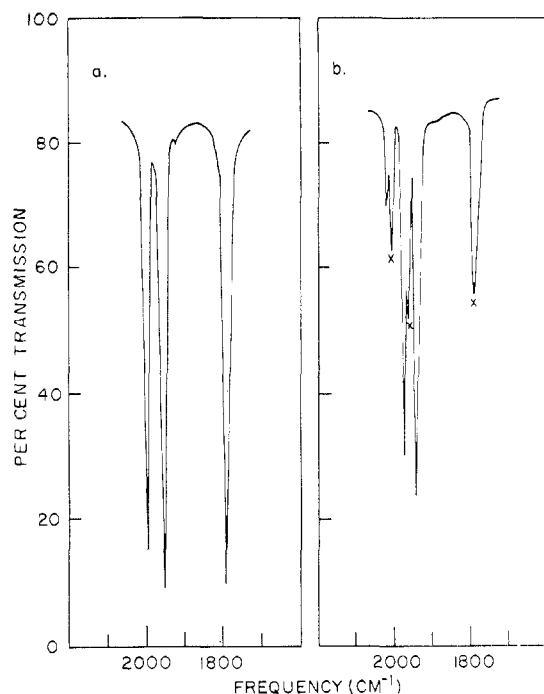
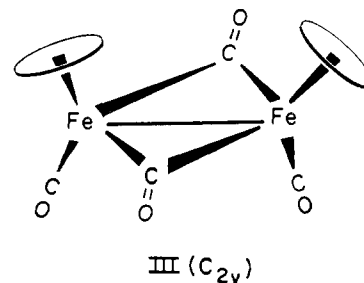


Figure 1.—The spectra of (a) $(\pi-Cp)_2Fe_2(CO)_4$ and (b) $(\pi-Cp)_2Ru_2(CO)_4$ (in CS_2 solution at 25°) in the CO stretching region.

III as the structure of the molecule when dissolved in nonpolar solvents.¹² Considering first that the dipole moment of $(\pi-Cp)Mn(CO)_3$ is 3.1 D.,¹³ it seems quite reasonable that structure III might have a moment of



about the same magnitude.

In order to account for the spectral data of Table I in terms of this structure we must, of course, renounce the assumption, made by Noack,¹⁰ that coupling between the two equivalent terminal CO groups would be too small to afford a splitting of *ca.* 30 cm^{-1} between the symmetric and antisymmetric combinations of terminal CO stretching motions. In view of the fact (which was not known at the time of Noack's suggestion¹⁰ of structure II) that there is a 55- cm^{-1} separation between the terminal modes in the similar cisoid¹⁴ molecule $[(\pi-Cp)Fe(CO)]_2(\mu-CO)(\mu-CNC_6H_5)$, which has virtually the same structure as III except that one of the bridges is formed by CNC_6H_5 instead of by CO, the assumption we now make of a significant coupling appears entirely justified.

(12) In certain polar solvents, notably alcohols, the spectra are more complicated, especially in the region of bridging CO stretching frequencies. This indicates that other tautomeric and/or distorted structures may arise, but a detailed explanation is not yet at hand.

(13) W. Strohmeier and D. von Hobe, *Z. Elektrochem.*, **64**, 945 (1960).

(14) K. K. Joshi, O. S. Mills, P. L. Pauson, B. W. Shaw, and W. H. Stubbs, *Chem. Commun.*, 181 (1965).

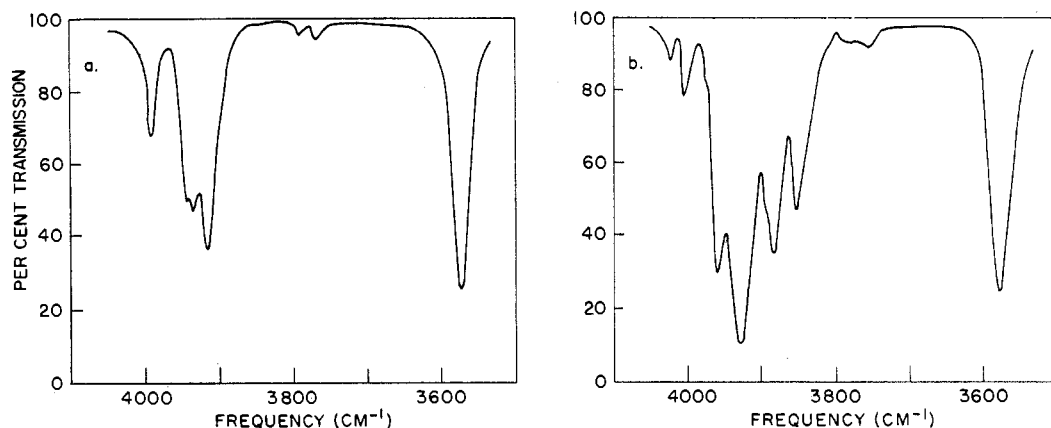


Figure 2.—The spectra of (a) $(\pi\text{-Cp})_2\text{Fe}_2(\text{CO})_4$ and (b) $(\pi\text{-Cp})_2\text{Ru}_2(\text{CO})_4$ (in CS_2 solution at 25°) in the region of combinations and overtones of CO stretching fundamentals.

TABLE I
FUNDAMENTAL CO STRETCHING MODES OF
 $(\pi\text{-Cp})_2\text{Fe}_2(\text{CO})_4$ AND $(\pi\text{-Cp})_2\text{Ru}_2(\text{CO})_4$ IN
NONPOLAR SOLVENTS (CM^{-1})

In octane ^a		In carbon disulfide	
$(\pi\text{-Cp})_2\text{Fe}_2(\text{CO})_4$	$(\pi\text{-Cp})_2\text{Ru}_2(\text{CO})_4$	$(\pi\text{-Cp})_2\text{Fe}_2(\text{CO})_4$	$(\pi\text{-Cp})_2\text{Ru}_2(\text{CO})_4$
2005 (4.5)	2021 (3.8)	1999	2016
	2011 (4.4)		2005
	1972 (33)		1967
1961 (10)	1964 (10)	1956	1959
	1943 (46)		1936
1794 (9.4)	1794 (7.4)	1785	1783

^a Relative intensities estimated from peak heights plotted on an arbitrary molar extinction scale.

TABLE II
CALCULATED AND OBSERVED OVERTONE AND COMBINATION
BANDS DERIVED FROM CO STRETCHING MODES OF
BRIDGED STRUCTURES^a (CM^{-1})

A. For $(\pi\text{-Cp})_2\text{Fe}_2(\text{CO})_4$		B. For $(\pi\text{-Cp})_2\text{Ru}_2(\text{CO})_4$	
Calcd	Obsd	Calcd	Obsd
$2 \times 1785 = 3570$	3775, vs, b	$2 \times 1783 = 3566$	3580 vs, b
$1785 + 1956 = 3741$	3760, vw	$1783 + 1959 = 3742$	3767 vw
$1785 + 1999 = 3784$	3785 vw	$1783 + 2005 = 3788$	3788 vw
$2 \times 1956 = 3912$... ^b	$2 \times 1959 = 3918$... ^b
$1956 + 1999 = 3955$... ^b	$1959 + 2005 = 3964$... ^b
$2 \times 1999 = 3998$	3990, m	$2 \times 2005 = 4010$	4000, m

^a Using data from CS_2 solutions throughout. ^b Region overlapped by bands of other origin as noted in text.

Model III would also lead one to expect, in principle, the appearance of two bridging CO stretching modes in the infrared. The actual observation of only one could be due to one or both of two things: (a) the frequency difference between the two is very slight; (b) the symmetric mode has negligible intensity. Both are reasonable possibilities. (a) could be due to a lack of coupling between the two bridging CO groups, which, in contrast to the terminal ones, presumably have no significant π interaction with the metal atoms and hence no suitable electronic mechanism to effect a coupling *via* the F matrix. (b) could well be true if the two bridging CO groups are essentially collinear and only loosely coupled to modes of vibration other than CO stretching.

The overtone and combination bands for $(\pi\text{-Cp})_2\text{Fe}_2(\text{CO})_4$ in solution are in accord with the foregoing

interpretation. Figure 2a shows the relevant spectral region. It is important to note that because of certain second overtones and/or ternary combination bands arising from the $\pi\text{-Cp}$ rings (as observed, for example, in ferrocene and $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{I}$) (Figure 3), the range $3900\text{--}3950\text{ cm}^{-1}$ must be omitted when interpreting the CO overtone spectrum. Table IIA lists the calculated overtones and combinations using the observed fundamentals and correlates these with the observed bands whose assignment to CO motions is not obscured by known occurrence of bands with different origins.

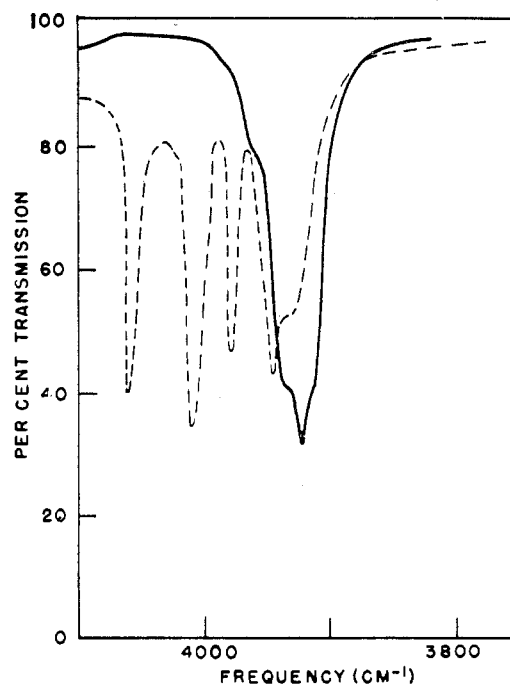


Figure 3.—The spectra of ferrocene, $(\text{C}_5\text{H}_5)_2\text{Fe}$ (—), and $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{I}$ (-----) showing the overtones of ring modes which interfere in the spectra of Figure 2.

Because of anharmonicity, an overtone will generally have a frequency equal to or less than that calculated from the frequency of the fundamental. For the band observed at 3900 cm^{-1} and calculated as 3998 cm^{-1} , this is true. However, the band at 3575 cm^{-1}

lies 5 cm^{-1} higher than twice the frequency of the observed bridging fundamental at 1785 cm^{-1} , and the observed band is relatively very intense and nearly twice as broad as the other overtone bands. Presumably this band results from a superposition of both bridging overtones and the combination of bridging modes, and it would appear that the unobserved fundamental may lie about $5\text{--}10\text{ cm}^{-1}$ higher than the one observed. This is not inconsistent with the fact that the bridge-terminal combination bands, only two of which are observed, at 3760 and 3785 cm^{-1} , are at higher frequencies than those calculated using the 1785 cm^{-1} fundamental. These bridge-terminal combination bands are all very weak, in accord with the idea that the bridging CO oscillators are only weakly coupled to the others in the molecule.

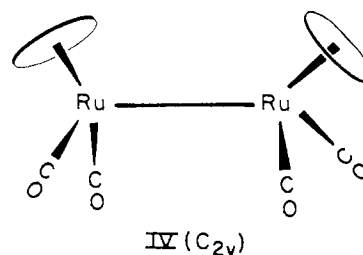
If structure III is accepted as the structure (or at least the overwhelmingly predominant structure) of $(\pi\text{-Cp})_2\text{Fe}_2(\text{CO})_4$ in the octane and CS_2 solutions, the question immediately arises as to how it is obtained from I, the structure of the molecule in the solid. We believe that the rearrangement takes place *via* an intermediate in which the bridge bonds open up, one initially bridging CO swinging over entirely to each iron atom. Rotation can then occur about the unbridged Fe-Fe bond, and, when the proper relative rotational orientation of the two $(\pi\text{-Cp})\text{Fe}(\text{CO})_2$ entities is reached, the bridges can be reestablished to give structure II. The process of crystallization requires a reversal of this sequence.

The intermediate, internally rotating $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2$ species evidently has practically no permanent existence under the conditions of our observations. However, the presence of a trace of it is suggested by the observed weak peak¹⁰ at $\sim 1938\text{ cm}^{-1}$ corresponding to the strongest peak in the spectrum of a $(\pi\text{-Cp})_2\text{Ru}_2(\text{CO})_4$ molecule, which, as we shall show below, is a nonbridged one.

It may also be noted here that structure II makes the C_5H_5 rings nonequivalent, as well as the terminal CO groups. However, the proton nuclear resonance spectrum of the compound in CS_2 shows but one sharp resonance. This in itself does not necessarily constitute evidence against structure II, because it could be explained in terms of either an unresolvably small chemical shift difference or a relatively rapid intramolecular rearrangement process. Indeed, the latter sort of phenomenon definitely appears to occur in the ruthenium case, *vide infra*.

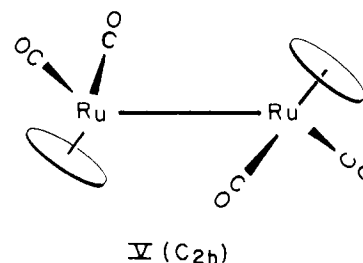
The Ruthenium Compound.—As Figure 1 and Table I show, the ruthenium compound has a far richer spectrum than the iron compound, indicating moreover that more than one tautomeric form must be present, since no one structure, however unsymmetrical, could account for the six observed bands in the CO stretching region. We propose the following assignment in terms of two structures, one of which is the Ru analog of III, the other being structure IV.

As indicated in Table I, when the relative positions and, especially, the relative intensities of the bands in



the spectrum of the Ru compound are closely compared with the corresponding data for the iron compound, it is rather clearly indicated which three bands are attributable to the molecule with structure III. Moreover, as indicated in Table II, the overtone and combination region matches closely that for the iron compound in respect to bands for this tautomer.

There remain then three strong bands, at $2021\text{--}2016$, $1972\text{--}1967$, and $1943\text{--}1936\text{ cm}^{-1}$, where the two figures are for the hydrocarbon and CS_2 solutions, respectively. Since there is no bridging frequency among them, we must seek a model with only an Ru-Ru bond and two terminal CO groups on each metal atom. The least symmetrical structures of this kind would have C_2 symmetry and hence, in principle, four infrared-active CO stretching modes. A structure of intermediate symmetry, C_{2v} , is IV, which should have three infrared-active CO stretching modes. The most symmetrical structure is V, which has C_{2h} symmetry and,



in principle, a maximum of two infrared-active CO stretching modes. The observation of three bands rules out V and tends to favor IV, but does not eliminate one of the rotomers of C_2 symmetry. However, in order to explain the data using a C_2 structure, it would be necessary to postulate either an accidental degeneracy of two fundamentals, an accidental ~ 0 intensity for one of the fundamentals, or an accidental overlap of one of the bands with a band due to the bridged tautomer. The last seems unlikely because the relative intensities of the three bands assigned to the bridged tautomer are in good accord with the data for the iron compound (*cf.* Table I). Either of the first two assumptions is, in principle, possible but not very likely. Moreover, as will now be shown, when the overtone and combination data are considered, structure IV can give a satisfactory account without recourse to such assumptions.

If we number the four CO groups in structure IV as 1 and 2 on one Ru atom and 3 (opposite 1) and 4 (opposite 2) on the other, we may write the following expressions for the normal coordinates of CO stretching modes

$$S(A_1) = \frac{1}{2}(\Delta_1 + \Delta_2 + \Delta_3 + \Delta_4)$$

$$S(B_1) = 1/2(\Delta_1 - \Delta_2 + \Delta_3 - \Delta_4)$$

$$S(B_2) = 1/2(\Delta_1 + \Delta_2 + \Delta_3 - \Delta_4)$$

$$S(A_2) = 1/2(\Delta_1 - \Delta_2 - \Delta_3 - \Delta_4)$$

The A_2 mode is inactive in the infrared.

If we now let K represent the stretching constant, k_g represent the stretch-stretch interaction constant for geminal CO groups (on the same metal atom), k_c represent the cisoid (*i.e.*, $\Delta_1\Delta_3$ and $\Delta_2\Delta_4$) interactions, and k_t represent the transoid (*i.e.*, $\Delta_1\Delta_4$ and $\Delta_2\Delta_3$) interactions, the following secular equations¹⁵ are obtained

$$\lambda(A_1) = \mu_{CO}(K + k_g + k_c + k_t)$$

$$\lambda(B_2) = \mu_{CO}(K + k_g - k_c - k_t)$$

$$\lambda(B_1) = \mu_{CO}(k - k_g + k_c - k_t)$$

$$\lambda(A_2) = \mu_{CO}(K - k_g - k_c + k_t)$$

If we assume that the magnitudes of the force constants fall in the order: $K \gg k_g > k_c > k_t \simeq 0$, then the frequencies of the modes should be in the order: $\nu(A_1) > \nu(B_2) > \nu(B_1) > \nu(A_2)$. Thus the fundamental which is absent from the spectrum must have a frequency less than 1936 cm^{-1} (in CS_2).

Turning now to the overtone spectrum, we see, in Table III, that, using only the observed fundamentals, not all of the observed bands in the combination-overtone region can be explained. However, if we follow the indication of the preceding discussion of the selection rules and secular equations, we can assign the A_2 mode a frequency of $\sim 1910 \text{ cm}^{-1}$, whence the absorption at $\sim 3820 \text{ cm}^{-1}$ can be assigned as $2\nu(A_2)$ and the band at 3850 cm^{-1} can be assigned as $\nu(B_1) + \nu(A_2)$ (calcd, 3846 cm^{-1}). The $\nu(A_2) + \nu(B_2)$ combination would then be expected at about 3877 cm^{-1} and is presumably part of the strong absorption peaking at 3872 cm^{-1} . The $\nu(A_1) + \nu(A_2)$ combination is not allowed in the infrared; its calculated frequency, 3926 cm^{-1} , is in the region completely obscured by non-CO absorption.

It is, of course, possible, that a structure with C_2 symmetry having a mode, roughly corresponding to the A_2 mode discussed above, which by accident has ~ 0 intensity, could also be invoked. However, we prefer the C_{2v} model (IV) for which no arbitrary assumptions need be made.

If we accept the preceding analysis on the basis of the C_{2v} model (IV), the fundamentals are: $\nu(A_1)$, 2016 cm^{-1} ; $\nu(B_2)$, 1967 cm^{-1} ; $\nu(B_1)$, 1963 cm^{-1} ; $\nu(A_2)$, $\sim 1910 \text{ cm}^{-1}$. Inserting these frequencies into the secular equations, the force constants (in mdyne/A) are: $K = 15.48$, $k_g = 0.54$, $k_c = 0.30$, $k_t = 0.1$.

These force constants are in the previously assumed order, indicating internal consistency in the argument. Moreover, they are individually reasonable when compared with results for similar or related molecules. Thus for $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{I}$, using the observed funda-

TABLE III
CALCULATED AND OBSERVED COMBINATION AND OVERTONE
BANDS FOR THE NONBRIDGED TAUTOMER
OF $(\pi\text{-Cp})_2\text{Ru}_2(\text{CO})_4^a$ (cm^{-1})

Calcd	Obsd ^c	Assignment
	~ 3820 (?)	$2\nu(A_2)$
	3850	$\nu(A_2) + \nu(B_1)$
	3872	$\nu(A_2) + \nu(B_2)$
$2 \times 1936 = 3872$		$2\nu(B_1)$
$2 \times 1967 = 3934$...	$2\nu(B_2)$
$1936 + 2016 = 3952$...	$\nu(B_1) + \nu(A_1)$
$1967 + 2016 = 3983$	3960 (?)	$\nu(B_2) + \nu(A_1)$
$2 \times 2016 = 4032$	4030	$2\nu(A_1)$

^a Using data from CS_2 solutions. ^b Region overlapped by bands of different origin as noted in text. ^c The question marks are meant to alert the reader to the facts that (1) the ~ 3820 absorption is unresolved but appears quite definite from the asymmetry of the 3850 band and (2) the 3960 band is partly overlapped by the non-CO absorption but does appear to represent, at least in part, genuine CO absorption.

mentals (2040 and 1998 cm^{-1} in CS_2), we calculate the constants $K = 16.46$ and $k_g = 0.35$ mdyne/A. Similarly, for $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{CH}_3$ and $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{H}$, using data obtained in CS_2 solution by Davison, McCleverty, and Wilkinson,¹⁶ we obtain the sets of force constants $K = 15.92$, $k_g = 0.49$, and $K = 15.94$, $k_g = 0.43$ mdyne/A, respectively. Also, from the frequencies of the symmetric and antisymmetric terminal stretching modes in the *cis*-bridged iron and ruthenium molecules, we obtain $K \simeq 15.9$ mdyne/A and an interaction constant comparable to k_c of 0.35 mdyne/A.

Finally, we note that the proton nmr spectrum of the ruthenium compound, like that of the iron compound, contains but one sharp peak.¹⁷ However, in this case we are postulating the existence of two nonequivalent sets of protons—in the two tautomers—so that this observation requires comment. It could be due to the lack of any measurable chemical shift difference between the two tautomers. However, while the difference might be small, it is unlikely to be undetectable. It seems more likely that the rate of interconversion of the two tautomers is sufficiently rapid in relation to the presumably small inherent chemical shift difference that the two environments are time averaged to give but one line.

General Conclusions.—The main conclusions of this study, which we believe to be valid regardless of certain ambiguities in respect to structural details, are given below.

(1) The centrosymmetric structure of $(\pi\text{-Cp})_2\text{Fe}_2(\text{CO})_4$ in the crystal (I) does not persist in solution. Instead, it tautomerizes to III, presumably by means of a nonbridged structure similar to IV or V which is not, however, present in more than minute concentration in the iron case.

(2) The ruthenium analog exists as a mixture of two tautomers, III and either IV or possibly a rotomer of IV (but not V).

(16) A. Davison, J. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, 1133 (1963).

(17) This observation was first made by E. O. Fischer and A. Vogler, *Z. Naturforsch.*, **17b**, 421 (1962), and has been confirmed by us.

(15) Cf. F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962), for definitions of symbols.

(3) The increasing tendency of these molecules to be stable without CO bridges as the group is descended appears to be a significant structural principle. It is reflected also in the fact that while $\text{Co}_4(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$ have bridging CO groups,¹⁸ $\text{Ir}_4(\text{CO})_{12}$ which has an otherwise similar structure, with a tetrahedron of metal atoms, has no bridging CO's¹⁸ in the crystalline phase.

(4) On the basis of the principle enunciated in (3), we might expect that $(\pi\text{-Cp})_2\text{Os}_2(\text{CO})_4$, which incidently appears not to be isomorphous with its Fe and Ru analogs,¹⁹ may have a nonbridged structure under all or nearly all conditions.²⁰

Experimental Section

$(\pi\text{-Cp})_2\text{Fe}_2(\text{CO})_4$ was kindly given to us by Professor A. Davison. It was further recrystallized from mixtures of ethyl

(18) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966).

(19) E. O. Fischer and A. Vogler, *Z. Naturforsch.* **17b**, 421 (1962).

(20) NOTE ADDED IN PROOF.—We have been informed by R. D. Fischer, K. Noack, and A. Vogler of the Technische Hochschule, Munich and Cyanamid European Research Institute that they have also carried out similar studies on these molecules and reached the same major conclusions. Their studies included experimental work on the osmium compound which directly demonstrates the correctness of our tentative conclusion (4).

acetate and heptane immediately before use, affording beautiful, well-formed crystals.

$(\pi\text{-Cp})_2\text{Ru}_2(\text{CO})_4$ was prepared according to Fischer and Vogler.¹⁹ It also was given final purification by recrystallization from ethyl acetate–heptane mixtures, whence excellent crystals were again obtained.

Infrared Spectra.—These were recorded using a Perkin-Elmer 521 spectrograph, under conditions of 1-cm^{-1} resolution and using gaseous CO as calibrant. The solutions were studied with and without compensation in 1-mm standard liquid cells.

The overtone and combination spectra were recorded, using both Perkin-Elmer 521 and Cary Model 14 spectrographs, in 10-cm quartz cells. In the region below 3800 cm^{-1} the spectra were recorded without compensation and the base line was subtracted by running a spectrum, under the same conditions, with the same cell plus the solvent. Owing to the strong absorption of the quartz windows around 3600 cm^{-1} , the quality of the spectra in that range was reduced.

All of the spectra were recorded with freshly prepared solutions of recently recrystallized samples—all in the absence of light. It was noted, as pointed out by Noack,³ that the solutions were sensitive to the beam of the spectrograph and were slowly decomposed by it. To avoid contamination of the solutions with decomposition product, the samples were allowed to stay in the beam path for only very short periods of time; hence different samples were used to record the different bands. Also some very weak bands, which increased their intensity when the samples were exposed to light, were not taken to be genuine.

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π Coordination of Unsaturated Bonds Containing Heteroatoms. II. Iron Carbonyl Complexes of Azomethine Analogs of 1,3-Dienes. Preparation and Nature of the Coordination Bondings

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The following mononuclear iron carbonyl complexes were prepared: (cinnamaldehydeanil)iron tricarbonyl (1), (crotonaldehyde-*n*-butylimine)iron tricarbonyl (2), (cinnamaldehydeanil)(triphenylphosphine)iron dicarbonyl (3), (diacetylanil)iron tricarbonyl (4), and (diacetyl-*n*-butylimine)iron tricarbonyl (5). On the basis of the nmr spectra, it was inferred that the coordination of the enimine ligands in 1, 2, and 3 may be of π -1,3-diene type, analogous to butadiene iron tricarbonyl, while the α -diimine in 4 and 5 coordinates through its nitrogen lone pairs forming a chelate ring similar to the well-known α -diimine Fe(II) chelate complexes. Attempted preparations of (π -benzalazine)- or (π -acetalazine)iron carbonyl complexes were unsuccessful.

Introduction

Although numerous π -olefin complexes are known, the possibility for this type of π coordination, *i.e.*, "side-on coordination," is very limited for a double bond containing oxygen, nitrogen, or a like atom. For simple molecules or anions such as carbon monoxide, cyanide, etc., their coordination bondings to metal are well recognized to involve π bonding generally in synergic interaction with the σ -type bonding, but they are not "side-on"; instead, they are of, say, "linear type." So far only a few examples have been reported where the "side-on" π coordination is claimed, *viz.*, coordination of the C=O group in $(\text{CH}_2=\text{CH}-\text{CH}=\text{O})_2\text{Mo}(\text{CO})_2$ ^{1a} or $[\text{CH}_2=\text{CH}-\text{C}(\text{CH}_3)=\text{O}]_3\text{W}$,^{1b} the

$-\text{N}=\text{N}-$ group in cyclopentadienyl-*o*-(phenylazo)phenylnickel,^{2a} and the $-\text{C}\equiv\text{N}$ group in $(\text{R}_2\text{N}-\text{C}\equiv\text{N})_2\text{Ni}_2(\text{CO})_2$.^{2b} We have recently reported³ a successful preparation of keteniminediiron hexacarbonyl complexes whose spectral data corroborated participation of both C=C and C=N double bonds in the coordination of the cumulated double bonds.

Our present interest is to see if π coordination of this type is possible for conjugated diene systems containing

(1) (a) D. P. Tate, A. A. Buss, J. M. Augl, B. L. Ross, J. G. Grasselli, W. M. Ritchey, and F. J. Knoll, *Inorg. Chem.*, **4**, 1323 (1965); (b) R. B. King and A. Fronzaglia, *Chem. Commun.*, 274 (1966).

(2) (a) J. P. Kleiman and M. Dubeck, *J. Am. Chem. Soc.*, **85**, 1544 (1963); (b) H. Bock and H. T. Dieck, *Chem. Ber.*, **99**, 213 (1966).

(3) S. Otsuka, A. Nakamura, and T. Yoshida, *J. Organometal. Chem.* (Amsterdam), in press.