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Application of a Dipole-Dipole Coupling Model to the Carbonyl Stretching Spectra of Some Dinuclear Metal Carbonyls[1a]

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A simplified treatment of the carbonyl stretching vibrations is described. The interactions between carbonyl groups, particularly intermolecular coupling and coupling between carbonyls bonded to different metal atoms, are described as being principally due to dipole-dipole forces. This force field allows a consistent interpretation of the solution and solid state spectra of a series of dinuclear metal carbonyl complexes. The molecules discussed are: $[(h^5\text{–}C_5H_5)M(CO)_2]_2$, *where* $M = Fe, Ru$; $[RhX(CO)_2]_2$, *where* $X = Cl, Br, I$; $Ru_2(O_2CCH_3)_2(CO)_4(C_5NH_5)_2$; *and* $Os_2(O_2CCH_3)_2(CO)_6$.

Introduction

Studies of the carbonyl stretching vibrations have been one of the most useful methods in investigations of the structure and bonding in metal carbonyl complexes. Because of the difficulty in conducting a comprehensive analysis which would include all the normal modes in these complexes, approximate methods have been developed to describe the carbonyl stretching modes independently of the others. Orgel[2] and independently El-Sayed and Kaesz[3] have described the carbonyl stretches in terms of local oscillating dipoles. Because the dipolar interaction potential between carbonyls is positive, band assignments can often be determined. In particular the totally symmetric stretching mode must be of highest frequency. Since the oscillating dipoles are assumed to be colinear with the C–O bond, the relative infrared intensities have also been predicted.[4,5] With respect to the coupling constants, this theory has not been made quantitative (although it has with respect to relative intensities) and of a large extent has been superceded in dealing with coupling constants by the approach of Cotton and Kraihanzel.[6]

The Cotton-Kraihanzel approximation contains a quantitative factorization yielding «stretch-stretch interaction force constants» and a description of these force constants in terms of π-bonding. The factorization is predicated on two assumption. First, that the interactions between the carbonyl stretches and the other normal modes can be neglected, either because they are very small or because they may be invariant over a series of related molecules. This assumption is generally quite good since the carbonyl stretches are between 1700 and 2200 cm^{-1} and the M–C stretches and M–C–O bends, the next highest modes, are between 300 and 700 cm^{-1}. Second, the carbonyl vibrations are taken to be simply harmonic. This approximation is often necessary since the overtone and combination bands needed for anharmonic corrections are weak. It is not, however, a particularly good approximation since anharmonicities are known to affect the fundamental frequencies by 16-43 cm^{-1}.[7]

The π-bonding force field predicts that the stretch-stretch interactions must be positive, and that for an octahedral complex the interactions between carbonyl groups *trans* to each other should be twice that for a pair of *cis* carbonyls. Because of the assumptions inherent in the factorization, these force constants have systematic errors. Jones, *et al.*,[7] have shown with a normal coordinate analysis of chromium, molybdenum and tungsten hexacarbonyls that the interactions are overestimated by the approximate method and that the *cis* interaction is greater than the *trans* one. A major source of these errors is the inadequacy of treating observed fundamental frequencies as equal to the true harmonic frequencies.

The π-bonding force field does not afford a means of predicting the magnitudes of the interaction of carbonyls bonded to different metals. Haas and Sheline[8] have treated the interactions of the carbonyls bound to different metal atoms by a dipolar exinton model in $Mn_2(CO)_{10}$. They found that, by assuming that the interactions between carbonyl groups bonded to different metal atoms are dipolar, the carbonyl stretches could be assigned in terms of the molecular geometry.

The purpose of the work described here was to explore more systematically, and in depth, the utility of a model in which dipole-dipole couplings are assigned a key role in accounting for the observed coupling between CO oscillations *when these are on different metal atoms.* It seems likely from the known results on $M(CO)_6$ and similar molecules that the na-

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(1) (*a*) This work was supported in part by the National Science Foundation under Grants GP-7034X and GP-2426. (*b*) N.S.F. Predoctoral Fellow, 1965-1970.

(2) L.E. Orgel, *Inorg. Chem.*, *1*, 25 (1962).

(3) M.A. El-Sayed and H.D. Kaesz, *J. Mol. Spectry.*, 9, 310 (1962).

(4) F.A. Cotton, A.D. Liehr, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, *1*, 175 (1955).

(5) W. Beck, A. Melnikoff, and R. Stahl, *Angew. Chem.*, *77*, 719 (1965).

(6) F.A. Cotton and C.S. Kraihanzel, *J. Amer. Chem. Soc.*, *84*, 4432 (1962).

(7) L.H. Jones, R.S. McDowell, and M. Goldblatt, *Inorg. Chem.*, *8*, 2349 (1969).

(8) H. Haas and R.K. Sheline, *J. Chem. Phys.*, *47*, 2996 (1967).

ture of the CO–CO interactions is too complex to admit of explanation in terms of any single simple model. It did, however, seem to us that the dipole coupling model might be adequate to deal with couplings, both intra- and intermolecular, in which valence or electronic mechanisms as well as kinematic (*i.e.*, G-matrix) factors would probably be negligible.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer equipped with a scale expander built by J. A. Simms and Dr. Marks of This Department or a Perkin-Elmer 521 spectrometer. Raman spectra were recorded on a Cary 81 spectrometer with either a Spectra-Physics helium-neon laser source or an argon ion laser source. Solution spectra were recorded with freshly prepared solutions from solvents dried and deoxygenated in the appropriate manner. Solutions were replaced if any bands changed in intensity with time.

Theory

A dipolar approximation may be described in terms of the Cotton-Kraihanzel factorization and a dipolar force field; however, a more unified formalism is possible. Since the carbonyl stretches are completely decoupled from the remainder of the molecule by assumption, they may be described by a set of harmonic oscillating dipoles with a reduced mass μ_{CO}, harmonic force constant K and a dipole derivative $\partial\mu/\partial r$ along the C–O bond. This model may be treated rigorously. The normal modes Q_k are linear combinations of the displacements Δ_i of the charges forming the dipoles. The infrared intensity I_k of the normal mode Q_k is proportional to $(\partial\mu/\partial Q_k)^2$[9] which may be expressed in terms of $(\partial\mu/\partial r)^2$. The harmonic secular equation for this system is solvable in terms of μ_{CO}, K and the binary interactions k_{ij}. The only interactions allowed between the oscillations are dipolar

$$V(\mu_i,\mu_j)=\vec{\mu}_i\cdot\vec{\mu}_j/r^3_{ij}-3(\vec{\mu}_i\cdot\vec{r}_{ij})(\vec{\mu}_j\cdot\vec{r}_{ij})/r_{ij}^5=\mu_i\mu_jS_{ij}/r_{ij}^3$$

where $\vec{\mu}_i$ is the vector dipole of oscillator i of magnitude μ_i along carbonyl dipole i, $\vec{r}_{ij}$ is the vector joining the centers* of carbonyl groups i and j of length r_{ij}. Expanding μ_i in terms of the displacement Δ_i

$$\mu_i=\mu_{oi}+(\frac{\partial\mu}{\partial r})_j\Delta_i+(\frac{\partial^2\mu}{\partial r^2})_i\Delta_i^2+\ .\ .\ .\ .\ .$$

The component of $V(\mu_i,\mu_j)$ that is proportional to $\Delta_i\Delta_j$ is the interaction force constant k_{ij}.

$$k_{ij}=(\frac{\partial\mu}{\partial r})_i(\frac{\partial\mu}{\partial r})_jS_{ij}/r_{ij}^3$$

The frequencies** of the carbonyl modes are a function of the geometry, S_{ij}/r_{ij}^3, the harmonic force constant K and the dipole derivative.

The success of this drastic simplication depends on the validity of the various approximations. The factorization has been critically reviewed by Haines and Stiddard[10] and can be verified by two calculations. The frequencies of the carbonyl stretches for isotopically substituted carbonyl complexes, for example, due to the naturally occurring ^{13}CO, can be predicted by rediagonalizing the FG matrix formed from the measured K_K and the G matrix with the lower symmetry. Bor, *et al.*,[11] have recently estimated the effects of M–C mixing on the frequencies of isotopically substituted C–O stretches. If the molecular geometry is known, the relative intensities of the infrared modes may be calculated. Both of these calculations make implicit use of the factorization. The intensity test is particularly sensitive for weak carbonyl modes where a small amount of mixing will cause a large increase in the intensity relative to a strong mode.

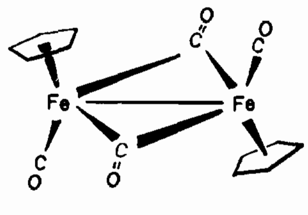
For intramolecular coupling both the π-bonding and dipole-dipole contributions to the force constant are positive. If through-bond coupling is important, assigning all the coupling to dipolar forces will lead to an overestimation of the dipole derivative.

Since the carbonyl stretches are generally the most intense bands in the infrared spectrum of these complex, the carbonyl dipole derivatives are usually the largest in the molecule. Moreover, the dipole derivative is large enough to cause significant interactions with the solvent, which are manifested both as solvent shifts[12] which show the sign of the dipole gradient to be positive and in dipolar broadening of the carbonyl bands in polar and polarizable solvents.

Results and Discussion

1. *$[h^5\text{-}C_5H_5M(CO)_2]_2$ Molecules.*

Using the bridged isomers of $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$ and related compounds, the dipole derivatives of the bridging and terminal carbonyls have been calculated for three cases. Intermolecular coupling, intramolecular coupling and infrared intensities. The intermolecular coupling, must depend on some "through space" interaction. Intramolecular coupling may contain both "through space" dipolar contributions and valence contributions. Since these compounds have both terminal and bridging carbonyls, the ratio of the dipole derivatives is easily obtainable from the infrared intensities. The *trans* isomers, I, have C_{2h}



I(C_{2h})

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(9) D. Steele, *Quart. Rev.*, *18*, 21 (1964).

* It is an additional assumption of the model that the dipoles are centered on the C—O bonds instead of at the center of mass of carbon monoxide. This has the effect of correcting, at least partially, for the bonding of the carbon atom to the metal atom.

** The frequency ν_K in cm^{-1} is related to the force constant K_K in millidynes per Ångstrom (mdyn / A) by the equation $4\pi^2c^2\nu^2=\mu_{CO}K_K$ or for $^{12}C^{16}O$ by $\nu_K^2=247583\ K_K$.

(10) L.M. Haines and M.H.B. Stiddard, *Adv. in Inorg. Chem. and Radiochemistry*, *12*, 53 (1969).

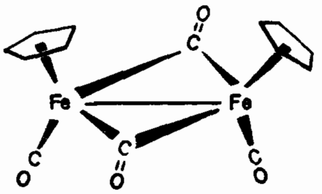
(11) (a) G. Bor, B.F.G. Johnson, J. Lewis ,and P.W. Robinson, *J. Chem. Soc. (A)*, 696 (1971). (b) J.R. Miller, *ibid.*, 1885 (1971).

Table I. Dipole Gradients Calculated for $[(h^5{-}C_5H_5)Fe(CO)_2]_2$ and Related Compounds.

Geometrical Data[a] S_T	S_B	T_1	T_2	T_3	T_4	Ref.	Spectral Method	Spectral Data[b] 1	2	3	4	Ref.	$\frac{\partial\mu}{\partial r_t}$	$\frac{\partial\mu}{\partial r_b}$	$\frac{\partial\mu}{\partial r_t}/\frac{\partial\mu}{\partial r_b}$
							trans$[(h^5{-}C_5H_5)Fe(CO)_2]_2$, I								
Table III		0	0.775	0	1.0	*d*	intermolecular coupling	1958	1936	1775	1757	*c*	1.4	0.9	1.56
							cis$[(h^5{-}C_5H_5)Fe(CO)_2]_2$, II								
0.262	0.300	0.97	0.03	0.019	0.986	*e*	intramolecular coupling								
							solid state	1974	1933	1800	1768	*e*	1.1	0.88	1.25
							solution	1998	1954	1810	1777	*f*	1.2	0.87	1.30
							cis$[Fe_2\{(h^5{-}C_5H_4)\cdot CH(NMe_2)\cdot(h^5{-}C_5H_4)\}(CO)_4]$								
0.267	0.296	0.957	0.043	0.116	0.884	*g*	intramolecular coupling								
							solid state	1980	1939	1805	1775	*k*	1.11	0.89	1.24
							solution	2002	1964	1817	1793	*h*	1.16	0.75	1.55
							relative intensities	21.5	3.5	<1	10	*h*			1.4
							$[(h^5{-}C_5H_5)_2Fe_2(CO)_3]_2\cdot(C_6H_5)_2PCCP(C_6H_5)_2$								
—	~0.3	—	—	0.116	0.884	*i*	intramolecular coupling								
							solid state			1765	1724	*i*		~1.0	
							solution	—	—	1780	1732	*i*		~1.0	
							trans$[(\pi\text{-}2,3\text{-}(CH_3)_2C_2H_2)Co(CO)_2]_2$								
		0	0.820	0	1.0	*j*	relative intensities	—	19.3	—	10	*k*			1.5
							cis$[(\pi\text{-norbornadiene})Co(CO)_2]_2$								
		1.0		1.0		*l*	relative intensities	16.8	4.7	sh	10	*k*			1.3

[a] The dipolar coupling constants are defined $k_t = S_t(\frac{\partial\mu}{\partial r})^2$ and $k_b = S_b(\frac{\partial\mu}{\partial r})^2$ for the terminal and bridging carbonyls respectively. The intensity of a given band is proportional to $T_k(\frac{\partial\mu}{\partial r})^2$ where for the *cis* C_{2v} compounds k = 1,...,4 are A_1,B_1,A_1,B_2 and for the *trans* C_{2h} compounds k = 1,...,4 are A_g,B_u,A_g,A_u modes. [b] For coupling experiments the data are frequencies in cm^{-1}. For intensity experiments the data are relative intensities. [c] This work, Fig. 1. [d] R.F. Bryan and P.T. Greene, *J. Chem. Soc.* (*A*), 3064 (1970). [e] R.F. Bryan, P.T. Greene, M.J. Newlands and D.S. Field, *ibid.*, 3068 (1970). [f] J.G. Bullit, F.A. Cotton, and T.T. Marks, *Jnorg. Chem.*,in press [g] F.S. Stevens, *J. Chem. Soc.* (*A*), 1722 (1970), [h] P. McArdle and A.R. Manning, *ibid.*, 2119 (1970). [i] A.J. Carty, T.W. Ng, W. Carter, G.J. Palenik, and T. Birchall, *Chem. Comm.*, 1101 (1969). [j] P.A. McArdle, A.R. Manning, and F.S. Stevens, *ibid.*, 318 (1970). [k] P.A. Mc Ardle and A.R. Manning, *J. Chem. Soc.* (*A*), 2123 (1970). [l] By definition the sum of $T_1+T_2=1.0$ and $T_3+T_4=1.0$ for *cis* complexes.

symmetry with terminal carbonyl modes belonging to the A_g and B_u representations and bridging modes to A_g and A_u. The *cis* isomers, II, are of C_{2v} symmetry with terminal modes of A_1 and B_1 symmetry and bridging modes of A_1 and B_2 symmetry stretches, the infrared intensity of the weak A_1 bridging mode of the *cis* isomers would be enhanced. No enhancement is observed; in fact, the band is so weak that it is often difficult to measure, see Table I. At least to first order, the mixing between the terminal and briging carbonyls is very small. Because the observed relative intensities for the *cis* isomers, I, generally agree well with those calculated from the crystallographic structure parameters, the mixing in of non-carbonyl modes also appears to be very small.



II (C_{2v})

The *trans*-bridged isomer of $[(C_5H_5)Fe(CO)_2]_2$ has two terminal and two bridging carbonyl stretches in the solid state infrared spectrum, Fig. 1. This splitting has been ascribed to two non-equivalent molecular sites.[10,13]

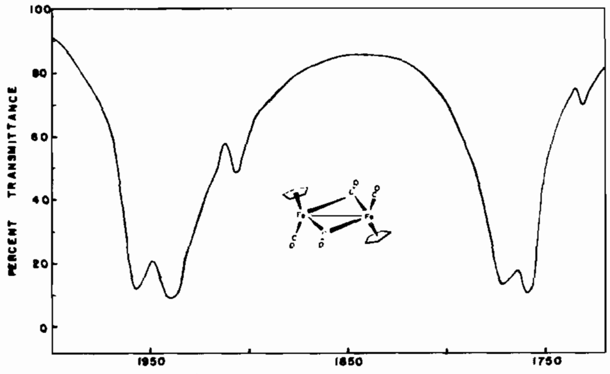


Figure 1. The solid state infrared spectrum of the carbonyl stretches of *trans*-$[(h^5{-}C_5H_5)Fe(CO)_2]_2$.

As in many other carbonyl complexes,[14] the interactions of the two molecules in the unit cell in equivalent sites but in different orientations cause the split-

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(12) W.D. Horrocks, Jr. and R.H. Mann, *Spectrochim. Acta*, *19*, 1375 (1963); *ibid.*, *21*, 394 (1965).

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

(14) H.J. Battery, G. Keeling, S.F.A. Kettle, J. Paul, and P.J. Stamper, *Disch. Faraday Soc.*, *47*, 48 (1969).

ting, Table II. Since the wavelength of infrared electromagnetic radiations is much longer than the molecular contacts, only the orientation of the oscillators determines the symmetry of the solid state bands. Intermolecular and intramolecular dipolar contributions to the force constants have been calculated using the formalism of Vedder and Hornig[15] with dipolar contributions, S_{ij}/r_{ij}^3, Table III, summed out to distances of 40 unit cells.[16]

Table II. Symmetry Correlation Diagram for *Trans*-$[C_5H_5Fe(CO)_2]_2$.

Isolated Molecule (C_{2h})	Site Group(C_i)	Factor Group(C^5_{2h}) $P2_1/c$
A_g(Raman)	A_g	A_g B_g
B_u(IR)	A_u	A_u B_u
A_g(Raman)	A_g	A_g B_g
A_u(IR)	A_u	A_u B_u

Table III. Dipolar Contributions[a] to Carbonyl Coupling in $[C_5H_5Fe(CO)_2]_2$.

Orientation Operation	$\bar{1}$	2	m
terminal	0.0614	—0.1062	—0.0222
bridging	0.2024	—0.0832	0.0406

[a] In millidyne Angstroms per Debye squared (mdyn A/D²).

For both the terminal and bridging carbonyl the force constants for the four normal modes are:

$$K_{Ag} = K + k_{\bar{1}} + k_2 + k_m$$

$$K_{Bg} = k + k_{\bar{1}} - k_2 - k_m$$

$$K_{Au} = k - k_{\bar{1}} + k_2 - k_m$$

$$K_{Bu} = K - k_{\bar{1}} - k_2 + k_m$$

where k_1, the interaction force constant between carbonyl related by the molecular and crystallographic center of symmetry, contains intramolecular and intermolecular coupling whereas k_2, the interaction between carbonyls related by the 2_1 screw axis, and k_m, which pertains to interaction between carbonyls related by the c glide, are intermolecular only. Because the deep color prevented obtaining a Raman spectrum, the dipole derivatives were estimated from $|K_2—K_m|$ obtainable from the solid state infrared spectrum. The intermolecular dipole derivatives are 1.4 D/Å for the terminal carbonyls and 0.9 D/Å for the bridging carbonyls. The Raman and infrared spectra of the carbonyl stretches of the isomorphous *trans* $[(C_5H_5)Ru(CO)_2]_2$,[17] Fig. 2, show factor group splitting as predicted by the sign and magnitude of the dipolar interactions in $[C_5H_5Fe(CO)_2]_2$.

For the *cis* isomer of $[CpFe(CO)_2]_2$ all four carbonyl vibrations are infrared active and the solid state structure and spectra have been reported.[18]

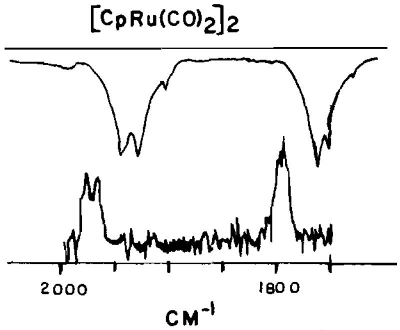

Figure 2. The solid state infrared and Raman spectra of the carbonyl stretches of *trans*-$[(h^5—C_5H_5)Ru(CO)_2]_2$.

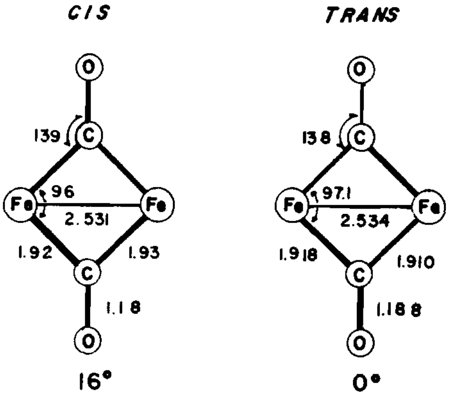

Figure 3. The geometry of the bridging carbonyls in *cis* and *trans*-$[(h^5—C_5H_5)Fe(CO)_2]_2$. The angle below is the dihedral angle between the Fe—(CO)—Fe planes.

Calculations on the solid state and solution intramolecular coupling yield 1.1 and 0.89 D/Å for the dipole derivatives of the terminal and bridging carbonyls, respectively. These calculations and similar ones are summarized in Table I. Because of the similarty in bonding and geometry, Fig. 3, the interactions of the bridging carbonyls in *cis* and *trans*-$[CpFe(CO)_2]_2$ should be almost equal. In the *cis* isomer it is 0.230 mdyn/Å and in the *trans* isomer it is calculated to be 0.154 mdyn/Å from the intermolecular dipolar coupling.

The dipole gradients calculated appear to form a consistent set for the *cis* and *trans* isomers for intermolecular and intramolecular coupling. Moreover, the ratio of the terminal to bridging carbonyl dipole gradients is consistent with the infrared intensities and Noack's[19] observation that terminal carbonyls are roughly twice as intense as bridging carbonyls. Moreover these dipole gradients are of the same magnitude as that of the antisymmetric stretch of carbon dioxide, 6 D/Å for two 'CO' oscillators, measured from gas phase intensities.[9]

2. *Rhodium Dicarbonyl Halide Dimers.*

Rhodium dicarbonyl chloride and similar C_{2v} di-

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(15) W. Vedder and D.F. Hornig, *Advances in Spectroscopy*, Vol. II, H.W. Thompson, Ed., Interscience, N.Y., 1961, p. 189.
(16) R.F. Bryan and P.T. Greene, *J. Chem. Soc.* (*A*), 3064 (1970).
(17) O.S. Mills and J.P. Nice, *J. Organometal. Chem.*, 9, 339 (1967).
(18) R.F. Bryan, P.T. Greene, D.S. Fields, and M.J. Newlands, *J. Chem. Soc.* (*A*), 3068 (1970).
(19) K. Noack, *Helv. Chim. Acta*, 65, 1847 (1962).

meric compounds, Fig. 4, are especially favorable systems to test the quantitative features of the dipolar model. The four carbonyl groups span the irreducible representations of C_{2v}. The force constants for the four carbonyl stretching modes are

$$K_{A_1}=K+k_g+k_c+k_t$$
$$K_{B_1}=K+k_g-k_c-k_t$$
$$K_{B_2}=K-k_g+k_c-k_t$$
$$K_{A_2}=K-k_g-k_c+k_t$$

where k_g is the geminal interaction force constant between carbonyls A and B, k_c is the cisoid interaction between A, and D, and k_t is the transoid interaction between A and C. From the qualitative features of the dipolar model, we may assume

$$K \gg k_g > k_c > k_t > 0;$$

thus

$$\nu_{A_1} > \nu_{B_1} > \nu_{B_2} > \nu_{A_2}$$

Using a coordinate system similar to that of Beck *et al.*,[5]* the relative intensities of the three infrared active modes give angular values close to those of the crystal structure.[20]

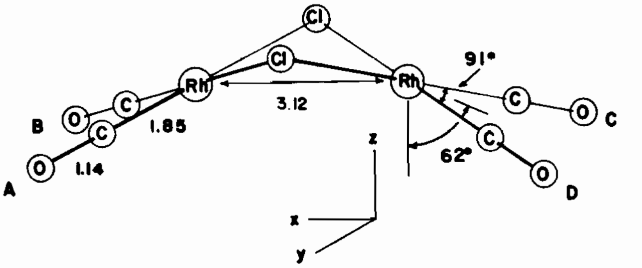
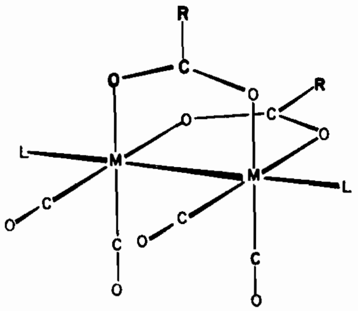


Figure 4. The solid state geometry of $[Rh(CO)_2]_2$.

Using the crystal structure parameters and a dipole derivative of 1.14 D/Å, the dipolar force constant k_g, k_c, and k_t are 0.525, 0.078, and 0.061 mdyn/Å. Johnson *et al.*[21] have measured the force field from isotopic substitution as k_g = 0.541, k_c = 0.078, and k_t = 0.057 mdyn/Å. One factor contributing to the very good fit in this case is the small polarizability of the carbonyls. Neither Johnson *et al.*[21] nor C. M. Lukehart and M. Debeau of This Laboratory were able to measure the carbonyl Raman spectrum of $[RhCl(CO)_2]_2$. From the spectrum reported by Wilt for $[RhBr(CO)_2]_2$ there appears to be no significant changes in η or Ψ. Assuming that the geometry is not significantly different for either $[RhBr(CO)_2]_2$ or $[RhI(CO)_2]_2$, the dipolar model fits quite well except that there may be more valence coupling between the geminal carbonyls.

3. *Cisoid Di-μ-acetatodimetal Tetracarbonyls.*

Di-μ-acetato-tetracarbonyl-dipyridine diruthenium, $Ru_2(CH_3CO_2)_2(CO)_4(C_5H_5N)_2$. This molecule resembles the rhodium dicarbonyl halide dimers in having a C_{2v} sawhorse arrangement (III) of carbonyl groups.[22]



III, L=py
IV, L=CO

The relative infrared intensities and interaction constants have been estimated from Kilbourn's structure,[23] η = 44.3°, Ψ = 6.9°, r_m = 2.68 Å, r_μ = 2.42 Å, yielding 1.0, 0.15 and 0.96 for the relative intensities I_{A_1}, I_{B_1} and I_{B_2} and $k_g = 0.397\ (\partial\mu/\partial r)^2$, $k_c = 0.445\ (\partial\mu/\partial r)^2$ and $k_t = 0.123\ (\partial\mu/\partial r)^2$. The relative infrared intensities in $CHCl_3$ solution, Figure 5, are 1.0, 0.28 and 0.89 for the 2035, 1980 and 1945 cm^{-1} bands. The most likely cause of the enhanced intensity of the B_1 mode is mixing between the carbonyl stretches and the acetate C–O stretches. Since the B_1 acetate C–O stretch should have 80% of the total acetate intensity, such mixing could contribute significantly only to the intensity of the B_1 carbonyl mode.

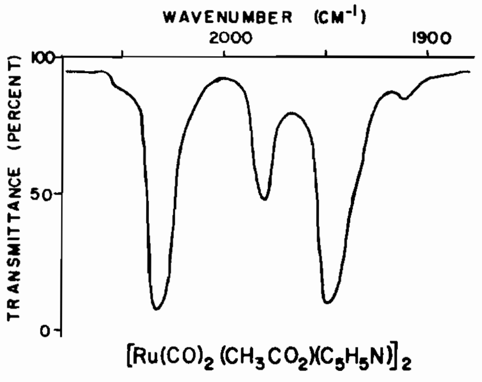


Figure 5. Infrared spectrum of $[Ru(CH_3CO_2)(CO)_2(C_5H_5N)]_2$, IV between 1900 and 2100 cm^{-1} in chloroform.

Assuming only dipolar coupling, the band assignment based on the relative intensities does not agree with that based on the coupling constants. From the intensities one assigns the 2035 cm^{-1} band as an A_1 mode, the 1980 cm^{-1} band as a B_1 mode and the 1945 cm^{-1} band as the B_2 mode, where as the dipolar coup-

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* If η is one-half the (OC)—Rh—(CO) angle, if Ψ is one-half the dihedral angle between the $Rh(CO)_2$ planes, if r_m is the distance in A between the rhodium atoms and if r_{mu} is the distance in Angstroms between the metal atom and the dipole,

$$k_g = 10 \cdot [1+\sin^2\eta] \cdot [2r_{mu}\sin\eta]^{-3}(\frac{\partial\mu}{\partial r})^2$$

for k_g in mdyn/Å and $\partial\mu/\partial r$ in D/A. The coordinate system in Fig. 4 then is $x=r_{mu}\cos\eta\sin\Psi$, $y=r_{mu}\sin\eta$, $z=r_{mu}\cos\eta\cos\Psi$.

(20) L.F. Dahl, C. Martell, and D.L. Wampler, *J. Amer. Chem. Soc.*, 83, 1761 (1961).

(21) B.F.G. Johnson, J. Lewis, P.W. Robinson, and J.R. Miller, *J. Chem. Soc.* (*A*), 2693 (1969).

(22) G.R. Crooks, B.F.G. Johnson, J. Lewis, I.G. Williams, and G. Gamlen, *J. Chem. Soc.* (*A*), 2761 (1969).

(23) B.T. Kilbourn, unpublished results, privately communicated.

Table IV. Structural Data for $[Rh(CO)_2Cl]_2$.

	Crystal Structure[a]	Beck et al.[b]	This Work	Wilt[c]	Wilt[c] for $[Rh(CO_2Br]_2$
Ψ	45.5°	46°	43.8°	46.5°	45°
η	62°	68°	61.2°	55°	55°
r_m	3.12Å				
r_{mu}	2.42Å				

[a] Ref. 19. [b] Ref. 4. [c] J.R. Wilt, B.S. Thesis, M.I.T., 1960, and C.W. Garland and J.R. Wilt, *J. Chem. Phy.*, *36*, 1094 (1962).

Table V. Carbonyl Stretching Frequencies of $Os_2(CH_3CO_2)_2(CO)_6$.

$IR(CHCl_3)$[a]	2093	2063		2010	2000(s)		1979(s)	1966(sh)
	(2.1)[b]	(6.1)	2024(sh)	(3.5)	1995(m)		1983(vs)	1970(s)
IR(Nujol)[a]	2111(s)	2076(s)		2012(s)		1993		
Raman(powder)[c]	2100(vs)	2065(s)		2010(vs)		(10)		

[a] Perkin Elmer 337. [b] Relative intensities. [c] Cary 81 with a Coherent Radiation ion laser source. Other strong Raman bands are: 90(vs), 135(?), 166(vs), 442, 524(vs), 603, 855, 961, 1360, 1450.

ling constants of $k_c > k_g$ predict that $\nu_{A1} > \nu_{B2} > \nu_{B1} > \nu_{A2}$. Either there is significant valence coupling or anharmonity in the geminal coupling or the perturbations from the acetate modes shift the B_2 mode more than the B_1 mode. Because the O–C–Ru–C–O system is planar, both through-bond and dipolar coupling are expected to be much larger than couplings between the nearly orthogonal bridging and terminal carbonyl groups, discussed in Sec. 1.

Di-μ-acetatohexacarbonyldiosmium, $Os_2(CH_3CO_2)_2(CO)_6$. This related osmium compound, IV, in addition to the A_1, B_1, B_2, and A_2 carbonyl stretches of the equatorial carbonyls, has A_1 and B_1 streches from the axial carbonyls. In the solution infrared spectrum four bands are resolved, Table V. The lowest frequency band is broad and undoubtedly contains the two lowest frequency ir active modes. Since the Os—C bond of the axial carbonyls is longer than that of the equatorial carbonyls,[24] (1.96(2) Å and 1.79(1) Å) the carbonyl stretching force constant of the two axial carbonyls should be higher than that of the four equatorial carbonyls. Using the same assignment for the equatorial carbonyls as in the ruthenium compound above, a reasonable band assignment is $\nu_{A1} > \nu_{B1} > \nu_{A1} >_{B1} \approx \nu_{B2} > \nu_{A2}$, where the two highest frequency modes would be largely from the axial carbonyls.

The splittings resolvable in the solid state carbonyl spectrum, Table V, are consistent with the higher pseudospace group C2/c rather than the full $P2_1/c$ space group.[24] In $P2_1/c$ with eight molecules per unit cell, each molecular mode would be expected to be split into eight crystal modes: four Raman-active and four ir-active modes. In C2/c with four molecules per unit cell, the two orientations of the dimer are related by a center of inversion. Each molecular mode forms a Raman-ative symmetric mode and an ir-active antisymmetric mode. The band assignment based on solution data is consistent with the crystal spectra split by the C2/c factor group. The two highest frequency bands, due principally to the axial carbonyls, have large negative intermolecular coupling constants. Since the closest intermolecular contact is between axial carbonyls related by the inversion center, the intermolecular coupling should be large. It is also expected to be negative since stretching an axial carbonyl on one molecule favors contracting that carbonyl group on the molecule related by inversion in order to minimize dipolar and van der Waals forces. The splittings observed here are another example of the *caveat* of Buttery *et al.*[14] Because of «effective symmetry operations», the factor group determined by the carbonyl stretches may be higher than that determined by X-ray crystallography.

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(24) J.G. Bullitt and F.A. Cotton, *Inorg. Chim. Acta*, submitted for publication.