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Infrared Intensities of the Carbonyl Stretching Modes in Trigonal Bipyramidal Cobalt and Iron Tetracarbonyl Compounds

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The dipole moment derivatives for the carbonyl stretching modes in monosubstituted (C_{3v}) trigonal bipyramidal metal carbonyls have been calculated assuming that each carbonyl stretching mode exhibits a characteristic MCO group moment derivative. The intensity distribution in the two A_1 modes is discussed in terms of coupling, the angle (θ) between axial and equatorial CO groups, and electron migration along the threefold axis during the vibrations. Equations for calculating the dipole moment derivatives for the A_1 (axial) and E symmetry modes are presented. The A_1 (equatorial) moment derivative is expressed as a function of the angle (θ) and the electronic migration parameter (ρ) and is represented graphically. The compounds considered in this study are $Cl_3SiCo(CO)_4$, $(C_6H_5)_3SiCo(CO)_4$ and $(C_6H_5)_3PFe(CO)_4$.

Introduction

There have been several qualitative discussions of infrared intensities of the carbonyl stretching modes in $LCo(CO)_4$ molecules (C_{3v}) in the recent literature.[1-4] However, these have been mostly concerned with the origin of the intensity distribution between the two A_1 modes and no quantitative measurements have thus far been reported.

We wish at this time to present some quantitative intensity data for $X_3SiCo(CO)_4$, X = Cl, C_6H_5 and $(C_6H_5)_3PFe(CO)_4$ along with a detailed explanation of their origin.

Coupling of the A_1 Symmetry Coordinates. The infrared spectrum of $Co(CO)_4L$ and $Fe(CO)_4L$ compounds consist of three infrared-active bands, $2A_1$ and E. The near equal intensities of the CO stretching vibrations in the A_1 modes are shown in Table I. This is explained in terms of extensive coupling between the axial and equatorial carbonyl groups. The L_{ij} matrix elements expressed in terms of symmetry coordinates are found in Table II. Calculated frequencies and force constants are listed in Table III.

Table I. Infrared Intensities of the Carbonyl Stretching Vibtions

Compound	Vibration,[a] (cm^{-1})	Intensity[b] × 10^{-4} (M^{-1} cm^{-2})
$Cl_3SiCo(CO)_4$	2120.6 (A_1)	3.05
	2064.8 (A_1)	4.37
	2039.4 (E)	21.6
$(C_6H_5)_3SiCo(CO)_4$	2100.3 (A_1)	4.22
	2033.5 (A_1)	5.87
	2005.8 (E)	25.0
$(C_6H_5)_3PFe(CO)_4$	2052.2 (A_1)	5.98
	1979.7 (A_1)	4.72
	1946.6 (E)	26.2

[a] All spectra were observed in hexane solution. [b] Defined as $\frac{2.303}{cl}\int_{band} \log \frac{I_o}{I}\, d\nu$, where c equals the concentration in moles/liter and l equals the cell pathlength in cm.

Table II. Calculated Values of the L_{ij} Matrix Elements[a]

Compound	L_{12}	L_{11}
$Cl_3SiCo(CO)_4$	0.22692	0.30703
$(C_6H_5)_3SiCo(CO)_4$	0.23901	0.29771
$(C_6H_5)_3PFe(CO)_4$	0.21892	0.31279

[a] $L_{12} = -L_{21}$ and $L_{11} = L_{22}$.

Geometrical considerations and calculation of Group Dipole Moment Derivatives. There are three ways in which the high frequency (equatorial) A_1 vibration can gain intensity: (a) coupling with the A_1 axial vibration, (b) the C_{ax}–M–C_{eq} angle departing from 90° significantly, and (c) electronic migration along the threefold axis during the stretching of the equatorial carbonyl groups.

We wish to calculate a characteristic MCO group dipole moment derivative for each of the three symmetry coordinates.

Equations (1) and (2) developed for the two A_1 modes are similar to those previously derived for the $M(CO)_5L$ (C_{4v}) molecules[5] with the added modification for effect (c).

$$I_1^{A_1(1)} = (\mu'_{MCO}{}^{(1)}L_{11} + \sqrt{3}(\cos\theta + \rho)\mu'_{MCO}{}^{(2)}L_{21})^2 \qquad (1)$$

$$I_2^{A_1(2)} = (\mu'_{MCO}{}^{(1)}L_{12} + \sqrt{3}(\cos\theta + \rho)\mu'_{MCO}{}^{(2)}L_{22})^2 \qquad (2)$$

I_1 and I_2 are the measured integrated intensities for the A_1 modes CO vibrations respectively; $\mu'_{MCO}{}^{(1)}$

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(1) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 6, 981 (1967).

(2) G. Bor, *Inorg. Chim. Acta*, *1*, 81 (1967).

(3) J. Dalton, I. Paul, J. G. Smith, and F. G A. Stone, *J. Chem. Soc.* (A), 1199 (1968).

(4) R. S. Gay and W. A. G. Graham, *Inorg. Chem.*, in press.

(5) D. J. Darensbourg and T. L. Brown, *ibid.*, 7, 959 (1968).

Table III. CO Force Constants, Calculated and Observed Frequencies for $LCo(CO)_4$ and $LFe(CO)_4$ Molceules

Molecule (Symmetry)	Vibrations	Calcd. (cm^{-1})	Obsd. (cm^{-1})	Force constants [a] k_1	k_2	k_c'	k_c
$Cl_3SiCo(CO)_4$	A_1	2120.6	2120.6				
(C_{3v})	A_1	2064.8	2064.8	17.56	17.14	0.347	0.260
	E	2038.8	2039.4				
		2038.8					
Mono-^{13}CO	A'	2113.9	2113.0				
radially substiuted	A'	2062.2					
(C_s)	A'	2002.4	2001.1				
	A''	2038.8	2039.4				
$(C_6H_5)_3SiCo(CO)_4$	A_1	2100.3	2100.3				
(C_{3v})	A_1	2033.5	2033.5	17.14	16.63	0.379	0.315
	E	2005.4	2005.8				
		2005.4					
Mono-^{13}CO	A'	2093.7	2089.6				
radially subst.	A'	2030.6					
(C_s)	A'	1969.9	1969.1				
	A''	2005.4	2005.8				
$(C_6H_5)_3PFe(CO)_4$	A_1	2052.2	2052.2				
(C_{3v})	A_1	1979.7	1979.7	16.22	15.74	0.441	0.320
	E	1946.2	1946.6				
		1946.2					
Mono-^{13}CO	A'	2044.7	2046.2				
radially subst.	A'	1977.0					
(C_s)	A'	1912.5	1911.6				
	A''	1946.2	1946.6				

[a] k_1 and k_2 are the stretching force constants of the axial and equatorial CO groups respectively, and k_c' and k_c refer to the interaction constants for CO_{eq}—CO_{eq} and CO_{eq}—CO_{ax} respectively. These are in units of mdynes/Å.

and $\mu'_{MCO}{}^{(2)}$ are the dipole moment derivatives for the axial and equatorial symmetry coordinates; θ is the angle between axial and equatorial carbonyl groups; and ρ is a parameter which allows for a contribution from electronic migration along the threefold molecular axis during the equatorial carbonyls' symmetrical stretching motion. The analogous quantity for the axial CO group is built into the value of the dipole moment derivative for this particular A_1 vibration.

We can solve equations (1) and (2) for $\mu'_{MCO}{}^{(1)}$ with only a knowledge of the L_{ij} matrix elements and the measured intensities of the two A_1 CO vibrations. This results in equation (3).[6]

$$\mu'_{MCO}{}^{(1)} = \frac{L_{22}\sqrt{I_1} - L_{21}\sqrt{I_2}}{L_{11}L_{22} - L_{12}L_{21}} \qquad (3)$$

However, it is also necessary to known what the signs are for $I_1^{1/2}$ and $I_2^{1/2}$. As is shown in Figure 1 these are both taken as positive quantities. It is possible for the equatorial component in the $A_1^{(2)}$ vibration to be dominating resulting in a negative value for $I_2^{1/2}$. However, since the axial component contributes so significantly to this vibration it would take an unusually large deviation from planarity for this to result.

The dipole moment derivative for the E mode vibration is calculated from equation (4). $\mu'_{MCO}{}^{(3)}$ is not very dependent on the

$$I_3 = G_{tt}\mu'_{MCO}{}^{(3)2}\, 3\sin^2\theta \qquad (4)$$

value chosen for θ. For example, for a value of θ equals 90°±6° in $Cl_3SiCo(CO)_4$, $\mu'_{MCO}{}^{(3)}$ changes by less than 0.6%. Calculated values for $\mu'_{MCO}{}^{(1)}$ and $\mu'_{MCO}{}^{(3)}$ are shown in Table IV.

The dipole moment derivative for the equatorial A_1 vibration can be calculated as a function of both

Table IV. Values of μ'_{MCO}, the MCO Group Dipole Moment Derivatives [a]

Compound	$\mu'_{MCO}{}^{(1)}$	$\mu'_{MCO}{}^{(3)}$ [b]
$Cl_3SiCo(CO)_4$	7.12	7.03
$(C_6H_5)_3SiCo(CO)_4$	8.32	7.56
$(C_6H_5)_3PFe(CO)_4$	8.33	7.74

[a] The μ'_{MCO}'s are effective group dipole moment derivatives which involve both MC and CO stretching motions.[7] The units employed here are arbitrary; the intensities are expressed in units of $10^4 M^{-1}$ cm^{-2}, and L and G terms are based on atomic mass units. [b] These are all calculated fro a θ value of 90°.

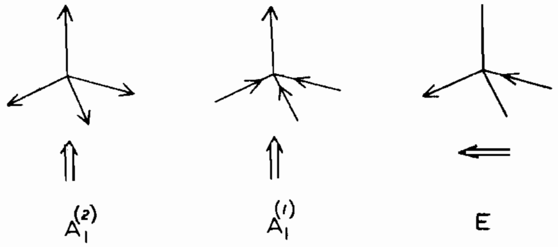

Figure 1. Directions of dipole moment changes in the symmetry vibrations of $M(CO)_4L$ molecules. Only one component of the E modes is shown. Large arrows indicate the direction of dipole moment change. The direction chosen here is consistent with the signs of the L_{ij} matrix elements, $L_{11} = L_{22}$, $L_{12} = -L_{21}$.

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(6) The denominator, $L_{11}L_{22}-L_{12}L_{21}$, is simply equal to G_{tt}, the inverse mass of a CO group.

(7) T. L. Brown and D. J. Darensbourg, *Inorg. Chem.*, 6, 971 (1967).

θ and ρ (Figure 2).[8] For molecules in which θ is known from structural data, $\mu'_{MCO}{}^{(2)}$ can be calculated as a function of ρ (vertical line in Figure 2a). θ has been found to have an average value of 98.3° in the gas phase for $H_3SiCo(CO)_4$;[9] 94.4° and 94.8° for $F_3SiCo(CO)_4$[10] and $Cl_3SiCo(CO)_4$[11] in the solid state respectively. There are no crystal packing forces in the latter two structures to indicate that θ should vary drastically between the solid state and solution. This bending away from the axial carbonyl has been explained in terms of a steric effect as a result of the large π electron density population between the metal and axial CO group. However, it might better be explained considering electronic effects. Fenske and Dekock[12] have recently shown in $Mn(CO)_5X$ compounds, where X = Cl, Br, I, and H, that there is significant donation from the σ_z orbitals of the X groups into the $2\pi_y$ (cis) orbitals of the carbonyl groups. A bending of the *cis* CO groups towards the substituted ligand should increase this type of inte-

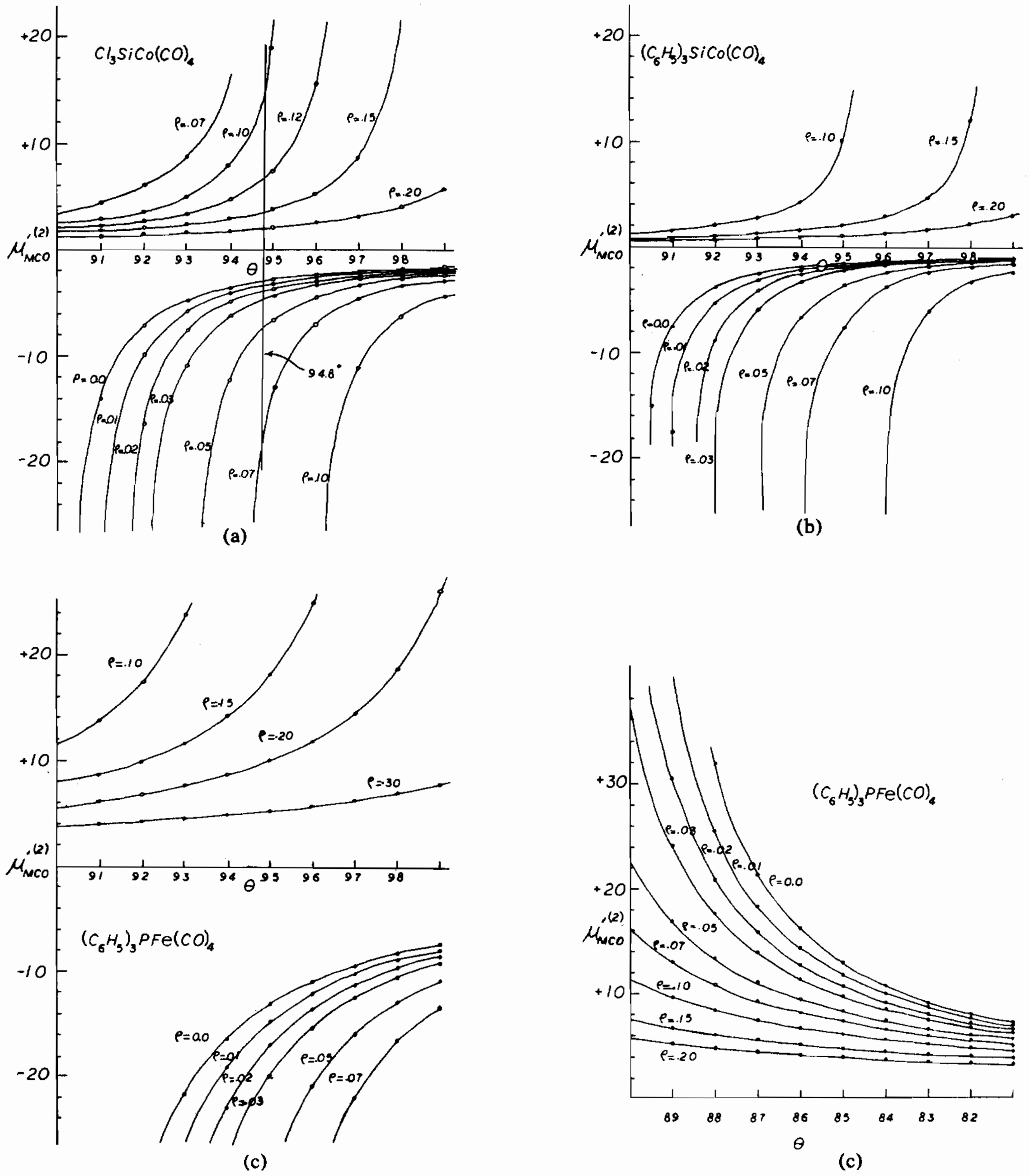

Figure 2. a) Plot of $\mu'_{MCO}{}^{(2)}$ versus θ and ρ for $Cl_3SiCo(CO)_4$; b) Plot of $\mu'_{MCO}{}^{(2)}$ versus θ and ρ for $(C_6H_5)_3SiCo(CO)_4$; c) Plot of $\mu'_{MCO}{}^{(2)}$ versus θ and ρ for $(C_6H_5)_3PFe(CO)_4$.

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(8) It should be noted from the form of equations (1) and (2) that as the difference between cos θ and ρ goes to zero $\mu'_{MCO}{}^{(2)}$ becomes increasing large in value and eventually becomes mathematically undefined at cos θ = ρ.

(9) A. G. Robiette, G. M. Sheldinck, R. N. F Simpson, B. J. Aylett, and J. A. Campbell, *J. Organometal. Chem.* (Amsterdam), 14, 279 (1968).

(10) K. Emerson, P. R. Ireland, and W. T. Robinson, *Inorg. Chem.*, 9, 436 (1970).

(11) W. T. Robinson and J. A. Ibers, *ibid.*, 6, 1208 (1967).

(12) R. F. Fenske and R. L. DeKock, *ibid.*, 9, 1053 (1970).

(13) The CO group may be viewed alternatively as a bridging ligand. Contribution of electron density from the ligand's ($(C_6H_5)_3Si$—, Cl,— Br—, or H—) σ_z orbital to the π^* orbitals of the *cis* carbonyls constitutes the weak bridging link.

raction.[13] Therefore, this directive donation plus the steric requirements of the X group versus the axial CO group most likely determine the angle (θ) between axial and equatorial carbonyl groups. For example, θ is found to be 93° in $Mn(CO)_5Br$[14] and 98° in $Mn(CO)_5H$.[15] This difference probably illustrates the greater steric repulsion of Br as compared to H.

It is proposed here that a similar mechanism is responsible for the observed angles in the silyl derivatives of cobalt tetracarbonyl (Figure 3). Unfortunately, there are no corresponding crystal structure data for $LFe(CO)_4$ compounds, but they too would be expected to have a CO_{ax}–Fe–CO_{eq} angle greater than 90°.

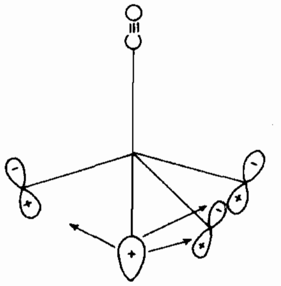

Figure 3. Direct donation from ligand's σ_z orbital into the $2\pi_y(cis)$CO orbitals in $M(CO)_4L$ molecules.

Electronic Effects on the μ'_{MCO}'s. It has previously been shown that the infrared intensities of the CO vibrations in metal carbonyls is largely determined by π-electronic charge migration in the M–C–O grouping during the CO stretch.[7] This would in turn be a function of the demand made for π-electronic charge during the various CO symmetry vibrations. The demand increases as the CO bond stretches, since the π*-orbitals of the CO group decrease in energy. The $A_1^{(2)}$ vibration makes a large demand for the π electrons whereas the $A_1^{(1)}$'s demand is small. In the E mode vibration, the demand made by the CO groups is zero. This is illustrated in Figure 4 and is analogous to the arguments made in the $M(CO)_5L$ molecules.[5] However, in the C_{3v} molecules, because of the large degree of mixing of the CO coordinates in the two A_1 vibrational modes, the $A_1^{(1)}$ vibration makes less of a demand for π electron density than the corresponding vibration in the C_{4v} case. Force constant analyses in L $Co(CO)_4$ and L $Fe(CO)_4$ molecules indicate greater M–C–O π electron delocalization in the *cis* carbonyls as compared with the *trans* CO group. Therefore, on the basis of both these considerations, $\mu'_{MCO}{}^{(3)}$ should be greater than $\mu'_{MCO}{}^{(1)}$ or $\mu'_{MCO}{}^{(2)}$. The ordering of the latter two derivatives is somewhat dubious from these arguments alone.

However, the enhancement observed of the A_1 vibration moment derivatives over that of the E vibration can be thought to arise from a vibronic contribution.[5] This results from a transfer of π-electronic charge from the silicon or phosphorus ligands through the metal to the carbonyl groups as the CO groups stretch. It is possible to conclude from the greater value of $\mu'_{MCO}{}^{(1)}$ over $\mu'_{MCO}{}^{(3)}$ that there is a considerable amount of π bonding in the silicon or phosphorus-metal bond.

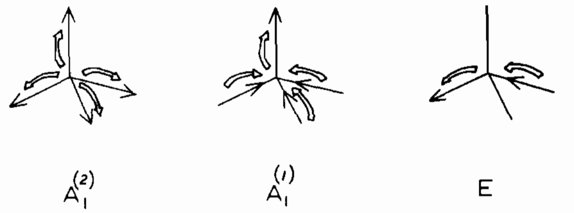

Figure 4. Schematic illustration of the flow of π-electronic charge between the metal d_π and CO π* orbitals during the CO symmetry stretching modes.

At this point, it is worth noting that the vibronic contribution is highly dependent on both the ability of the substituent to hold onto its electron density and the demand made for these electrons during the A_1 symmetry CO vibrations. This is exemplified in the smaller vibronic contribution in the $-SiCl_3$ derivative where the chlorine atoms are extremely electron withdrawing. Since the demand made for electronic charge during the two A_1 vibrations is quite different, there is no *a priori* reason for assuming that $\mu'_{MCO}{}^{(1)}$ and $\mu'_{MCO}{}^{(2)}$ will be equal in magnitude.[16] The one fact which should be fairly obvious from this discussion is that infrared intensities cannot be used to determine θ.

In the $LM(CO)_4$ molecules, the molecular dipole moment derivative in the E vibrational mode is polarized perpendicular to the M–L bond. Therefore, there can be no transfer of charge along the M–L bond axis during the asymmetric vibration.

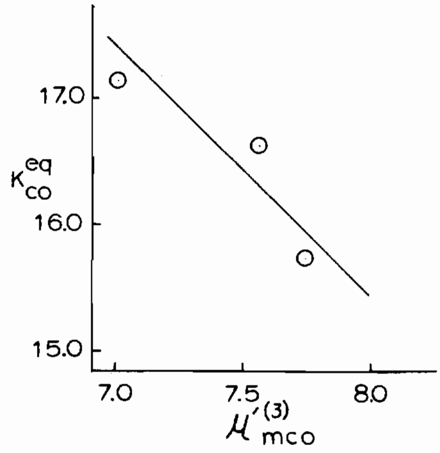

Figure 5. Plot of k_{CO}^{eq} versus $\mu'_{MCO}{}^{(3)}$ in $M(CO)_4L$ compounds.

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[14] R. F. Bryan, reported in paper by T. L. Brown, *ibid.*, *7*, 2673 (1968).

[15] S. J. LaPlaca, J. A. Ibers, and W. C. Hamilton, *J. Am. Chem. Soc.*, *86*, 2288 (1966).

[16] However, these would not be expected to differ widely, thereby eliminating many of the possibilities shown graphically in Figure 2. For example, where θ is known in the $Cl_3SiCo(CO)_4$ molecule, in order for $\mu'_{MCO}{}^{(2)} = +\mu'^{(1)}$ ρ must be 0.05 or 0.12. That is, the vibronic contribution would be on the order of 5-12%. Figure 2c shows that for $\mu'_{MCO}{}^{(1)} = +\mu'_{MCO}{}^{(2)}$ in the $(C_6H_5)_3PFe(CO)_4$ molecule ρ has to be rather large, (approximately 0.25), for a θ value similar to that found in the silyl derivatives. Alternatively, one may assume ρ to be relatively small and θ fairly large (90+8°) and achieve $\mu'_{MCO}{}^{(1)} = +\mu'_{MCO}{}^{(2)}$ for $(C_6H_5)_3PFe(CO)_4$ This latter assumption would appear to be the less probable.

It is expected that if both the force constant k_{CO}^{eq} (k_2) and the dipole moment derivative ($\mu'_{MCO}{}^{(3')}$) are related to the extent of π electron delocalization, there will be a relationship between these two independently determined quantities. The evidence indicates that this is indeed the case, for as k_{CO}^{eq} increases, indicating a decrease in M–C π bonding, $\mu'_{MCO}{}^{(3)}$ decreases (Figure 5). The increase in M–C π bonding in the series $Cl_3SiCo(CO)_4$, $(C_6H_5)_3SiCo(CO)_4$, and $(C_6H_5)_3PFe(CO)_4$ may arise from either a decrease in the ligand's π-acceptor or an increase in the ligand's σ donor strengths. Undoubtedly, both these factors are important.

Experimental Section

Preparation of (trichlorosilyl)Co(CO)₄. An excess of trichlorosilane and $Co_2(CO)_8$ were stirred together under nitrogen. After evolution of H_2 had ceased, the excess Cl_3SiH was removed by passing nitrogen over the solution at room temperature. The dark gray residue which remained was sublimed under vacuum at 25 °C to give a yellow product. *Anal.* Calcd for $Cl_3SiCo(CO)_4$: C, 15.72; Cl, 34.83. Found: C, 15.92; Cl, 35.05.

Preparation of (triphenylsilyl)Co(CO)₄. 3.40 g of $Co_2(CO)_8$ and 2.40 g of $(C_6H_5)_3SiH$ in 15 ml of hexane were stirred together under N_2 at room temperature for 1.2 hours. The solvent was removed under reduced pressure and the remaining solid was heated at 60-70° under vacuum during which time a black material (probably $Co_4(CO)_{12}$) sublimed. The product was recrystallized from hexane to give white crystals. *Anal.* Calcd. for $(C_6H_5)_3SiCo(CO)_4$: C, 61.40; H, 3.51. Found: C, 62.24; H, 3.56.

Preparation of (triphenylphosphine) Fe(CO)₄. 2.0 g of $(C_6H_5)_3P$ and 1.14 g of $Fe_3(CO)_{12}$ in 100 ml of benzene were refluxed with stirring under nitrogen. Solvent was removed at 25° and reduced pressure. The solid isolated was chromatographed on a 12 inch silica gel column in a manner similar to that described by G. Bor.[2] $Fe_3(CO)_{12}$ was eluted by hexane; $(C_6H_5)_3PFe(CO)_4$ by 1:4 benzene-hexane mixture. The disubstituted $(C_6H_5)_3P$ compound essentially remained on the top of the column under these conditions. Solvent was removed *in vacuo* and $(C_6H_5)_3PFe(CO)_4$ was recrystallized from hexane at −77 °C. The yellow crystals melted at 201° with decomposition. *Anal.* Calcd for $(C_6H_5)_3PFe(CO)_4$: C, 61.40; H, 3.51. Found: C, 62.81; H, 3.83.

Infrared Spectra. Infrared spectral measurements were made on either a Beckman IR-7 or a Perkin-Elmer 521 Spectrophotometer. Both spectrophotomethers were equipped with a linear absorbance potentiometer. The spectral slit width of the instruments were set at 1.5-1.8 cm^{-1}. Recordings were made on an expanded scale and areas under bands were determined by planimeter or the weighing method. Calibrated 1 mm sodium chloride cells were employed in the measurements. Intensities were determined at a number of concentrations and extrapolated to zero concentration. All data wre analyzed by the linear least-squares method.

Calculations. The force constants and L matrix elements were calculated using ^{13}CO frequency data with an iterative computer program. The program based on the work of Schachtschneider and Snyder,[17] adjusts a set of force constants common to a group of related molecules to give simultaneously a least-squares fit between observed and calculated frequencies for all molcules. Calculations were performed using an energy-factored block matrix for the carbonyl stretching modes, but without any other predetermined constraints on the force field.

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(17) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, *19*, 85, 117 (1963).