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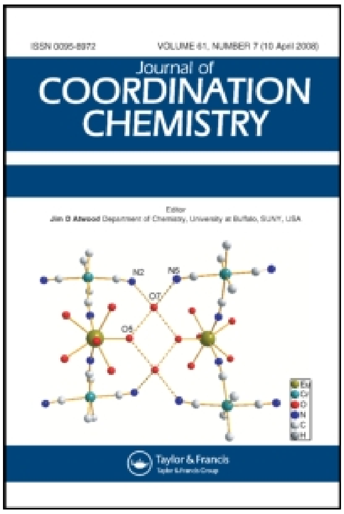

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OCTAHEDRAL METAL CARBONYLS: XXVI Carbonyl Stretching Spectra and Force Constants for cis-Disubstituted Derivatives of the Group VI-B Metal Carbonyls

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OCTAHEDRAL METAL CARBONYLS: XXVI[1]

Carbonyl Stretching Spectra and Force Constants for cis-Disubstituted Derivatives of the Group VI-B Metal Carbonyls

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The carbonyl stretching spectra (CS_2 solution) of twenty-six *cis*-$L_2M(CO)_4$ complexes (L_2 = bidentate chelating ligand bonding through N, P, As or S donor atoms; M = Cr, Mo, W) have been obtained. Two carbonyl stretching force constants and three CO—CO stretch-stretch interaction constants have been determined from the four carbonyl stretching frequencies through an iterative procedure: no relationships among the interaction constants have been assumed. The results are in excellent agreement with force constant data previously derived through isotopic enrichment studies. An approach to the separation of π-bonding and Fenske-DeKock "direct donation" effects in these systems is presented.

INTRODUCTION

Literally hundreds of papers have employed the Cotton-Kraihanzel[2] force field to evaluate carbonyl stretching force constants in substituted octahedral metal carbonyl complexes.[3] However, in many systems the limited number of observed carbonyl stretching absorptions has necessitated the use of approximations relating the various interaction constants. An alternative, but experimentally more demanding approach has been to employ isotopically enriched derivatives to obtain additional carbonyl stretching frequencies; these data can then be fitted to the carbonyl stretching force constants and interaction constants (F, IC) through use of iterative procedures.‡

In *cis*-$L_2M(CO)_4$ complexes, for example, there are two carbonyl stretching force constants (k_1, *cis* carbonyls, and k_2, *trans* carbonyls), and three physically different CO—CO stretch-stretch interaction constants, k_t, k_c and k_c', Figure 1, and only four carbonyl stretching frequencies from which to calculate them. In the absence of enrichment data, it has been necessary to employ relationships among the interaction constants to solve the secular equations. These relationships have included those proposed by Cotton and Kraihanzel ($k_t/k_c = 2$; $k_c = k_c'$)[2] and by Stone and coworkers($k_t/k_c' = 1.4$; $k_c/k_c' = x$, where x is varied).[4,5] More recently, Delbeke and associates have employed the ratios $k_t/k_c' = 1.4$ and $k_t/k_c' = 2$ to calculate "exact" force constants for a variety of *cis*-$L_2M(CO)_4$ and related complexes.[6] While the ratios given above have been derived from orbital overlap theories,[2,7] available isotopic enrichment data for $XM(CO)_5$ complexes (X = Cl, Br, I, CH_3, H, D; M = Mn, Re)[8–10] indicate these ratios to vary with X. From similar data for *cis*-$X_2Fe(CO)_4$ complexes (X = Br, I)[11, 12] (Table III) it is also evident that these ratios are not applicable.

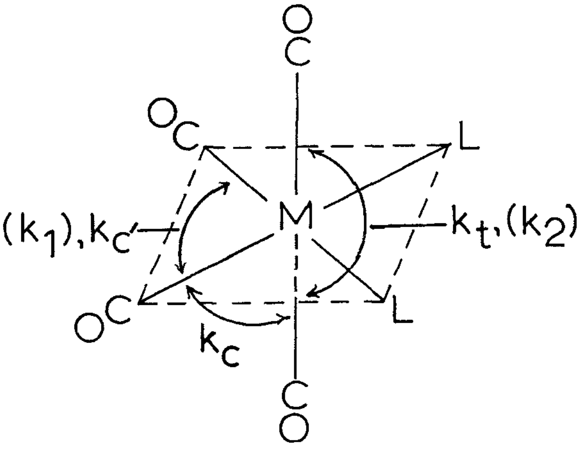

FIGURE 1 Definition of carbonyl stretching force constants and interaction constants for *cis*-$L_2M(CO)_4$ molecules.

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‡ While this method affords accurate values for F, IC, caveats with respect to the significance of Cotton-Kraihanzel F, IC, which have been briefly summarized in Ref. 12, should be observed.

The availability of carbonyl F, IC determined through use of isotopic data allows various methods of calculation to be tested. A "good" method would be one which yields F, IC in close agreement with those calculated through use of isotopically enriched derivatives. The present report describes a method of calculation which makes no assumptions with regard to relationships among interaction constants and which utilizes only $^{12}C^{16}O$ stretching frequencies, and its application to a number of *cis*-$L_2M(CO)_4$ complexes (L = phen, tmen, diphos, P-en, dpae, diars, dto, dth and tmpa‡; M = Cr, Mo, W).

EXPERIMENTAL

The preparations of the *cis*-$L_2M(CO)_4$ complexes have been discussed elsewhere.[13] Carbonyl stretching spectra were obtained in CS_2 solution employing 0.1 mm NaCl cells on a Perkin Elmer Model 621 grating spectrophotometer, and were calibrated against a band of water vapor at 1869.4 cm^{-1} [14] and a band of carbon monoxide at 2139.4 cm^{-1}.[15] It is important to note that all spectra were run in the same non-polar solvent (CS_2) and thus possible solvent influences on (νCO) were minimized. A wavelength expansion scale of 5x and spectral slit widths of 2.4–1.7 cm^{-1} were employed. Band positions were determined by finding the mid-point at half intensity for isolated bands, or at 70–90 per cent intensity for overlapping bands. In several instances four bands were not observed, apparently as the result of accidental degeneracy of absorptions; in these cases the position of the missing band was estimated. Where band positions were not estimated, they are believed accurate to ± 1 cm^{-1}; estimated frequencies are believed accurate to ± 3 cm^{-1}. Carbonyl stretching data are presented in Table I.

All computations were performed at the North Texas State University Computing Center on an IBM 360, model 50 computer.

RESULTS AND DISCUSSION

(a) *Assignment of carbonyl stretching absorptions*

For *cis*-$L_2M(CO)_4$ complexes, under the C_{2v} local symmetry of the carbonyls, four infrared-active carbonyl stretching absorptions are expected, $2A_1 + B_1 + B_2$. The assignments of these follow the position and intensity arguments advanced by Orgel,[16] and are given in Table I.

TABLE I

Carbonyl stretching frequencies in CS_2 solution and band assignments for *cis*-$L_2M(CO)_4$ complexes

Compound[a]	Carbonyl Stretching Frequencies, cm^{-1}			
	$A_1{}^2$	$A_1{}^1$	B_1	B_2
(phen)Cr(CO)$_4$	2005	1893	1901	1844
(tmen)Cr(CO)$_4$	2005	1879	1868	1839
(diphos)Cr(CO)$_4$	2009	1918	1903	1887
(P-en)Cr(CO)$_4$	2018	1932	1907	1907
(dpae)Cr(CO)$_4$	2008	1918	1902	1885
(diars)Cr(CO)$_4$	2005	1914	1894	1885
(dto)Cr(CO)$_4$	2013	1902	1893	1867
(dth)Cr(CO)$_4$	2015	1911	1894	1874
(phen)Mo(CO)$_4$	2009	1889	1903	1846
(tmen)Mo(CO)$_4$	2012	1880	1880	1843
(diphos)Mo(CO)$_4$	2020	1925	1912	1894
(P-en)Mo(Co)$_4$	2028	1937	1915	1915
(dpae)Mo(CO)$_4$	2022	1925	1912	1894
(diars)Mo(CO)$_4$	2018	1922	1907	1894
(dto)Mo(CO)$_4$	2021	1905	1905	1872
(dth)Mo(CO)$_4$	2023	1911	1903	1878
(tmpa)Mo(CO)$_4$	2013	1881	1881	1837
(phen)W(CO)$_4$	2003	1886	1892	1840
(tmen)W(CO)$_4$	2005	1872	1864	1838
(diphos)W(CO)$_4$	2017	1918	1903	1888
(P-en)W(CO)$_4$	2024	1930	1907	1907
(dpae)W(CO)$_4$	2017	1918	1903	1887
(diars)W(CO)$_4$	2013	1914	1896	1887
(dto)W(CO)$_4$	2016	1897	1892	1868
(dth)W(CO)$_4$	2016	1906	1891	1874
(tmpa)W(CO)$_4$	2006	1873	1866	1832

[a] See footnote for abbreviations for ligands.

(b) *Calculation of force constants and interaction constants*

The secular equations derived by Cotton and Kraihanzel employing an energy-factored force field are given in Table II. The various k are defined in Figure 1. Since there are five constants to be calculated and only four carbonyl stretching frequencies, the two generalized substitutions,

$$\left.\begin{aligned} k_c &= Xk_{c'} \\ k_t &= Yk_{c'} \end{aligned}\right\} \qquad (1)$$

were employed to reduce the number of unknowns to three. The five constants were calculated from three carbonyl stretching frequencies (one A_1, B_1, B_2) and the parameters X and Y. The latter were

---

‡ Abbreviations: phen = *o*-phenanthroline; tmen = *N,N,N′,N′*-tetramethylethylenediamine; diphos = 1,2-bis (diphenylphosphino)ethane; P-en = ethylenediphosphine; dpae = 1,2-bis(diphenylarsino)ethane; diars = *o*-phenylenebis(dimethylarsine); dto = 2,2,7,7,-tetramethyl-3,6-dithiaoctane; dth = 2,5-dithiahexane; tmpa = *N,N,N′,N′*-tetramethyl-1,3-diaminopropane.

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TABLE II

Secular equations for *cis*-$L_2M(CO)_4$ complexes

Symmetry species	Secular equations[a]
$A_1{}^1$ $A_1{}^2$	$0 = \begin{vmatrix} \mu(k_2 + k_t) - \lambda & 2\mu k_c \\ 2\mu k_c & \mu(k_1 + k_c') - \lambda \end{vmatrix}$
B_1	$\lambda = \mu(k_2 - k_t)$
B_2	$\lambda = \mu(k_1 - k_c')$

[a] Force constants in dynes cm^{-1}; μ represents the reciprocal of the reduced mass, *viz.*, $(16.00 + 12.01)/(16.00 \times 12.01) = 0.14583$; $\lambda = (5.8890 \times 10^{-2})v^2$, where v is the appropriate carbonyl stretching frequency in cm^{-1}.

varied by small increments and the constants were calculated employing an iterative procedure. The parameter X was allowed to vary from 0.4 to 1.4, while the values of Y ranged from 0.7 to 3.0. The A_1 carbonyl stretching frequency not employed in the calculation was then determined from the force constants. The A_1 frequencies were then interchanged, and the process was repeated. Plots of the calculated A_1 frequencies for (diphos)$W(CO)_4$ as a function of Y for various constant values of X are given in Figure 2. It can be seen from these plots that for only a very limited range of values of X (ca. $0.75 < X < 0.81$) are the A_1 frequencies produced for reasonable values of Y. Figure 3 demonstrates that corresponding to a maximum value of X ($\cong 0.81$) is a unique solution to the equations, although it can also be seen that an infinite number of solution pairs are also possible. To ascertain whether or not the unique solution was a "good" solution, the program was employed to calculate F, IC for *cis*-$X_2Fe(CO)_4$ complexes,[11, 12] the only ones for which isotopic data have allowed direct F, IC calculation. These values, together with those obtained through the isotopic investigations are presented in Table III. It can be seen that with the exception of the *cis*-$Br_2Fe(CO)_4$ F, IC calculated by Johnson and coworkers,[11] the results are very satisfying. However, these F, IC, alone of all those reported in Table III, were determined from the natural abundance of ^{13}CO rather than from enrichment data, and the positions of the ^{13}CO absorptions differ from those reported by Butler and Spendjian,[12] which were obtained from enrichment data. Further, both sets of F, IC for

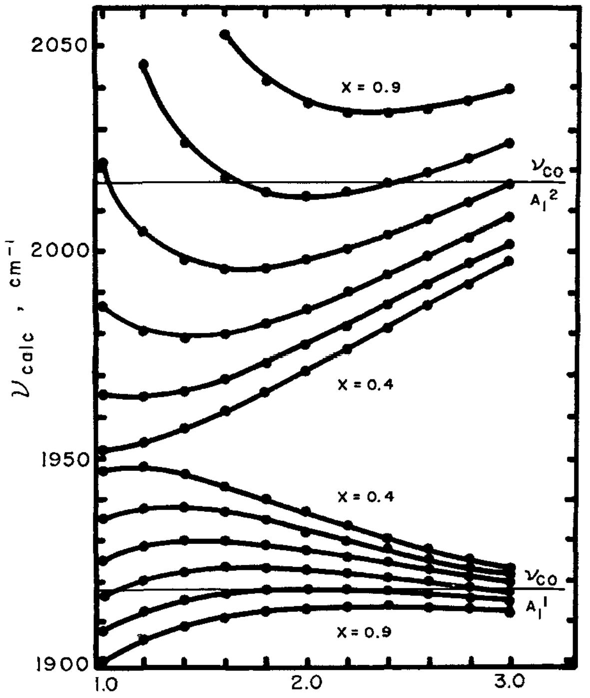

FIGURE 2 Plots of carbonyl stretching frequencies (A_1 modes) *vs.* Y parameter for various values of X parameter for (diphos)$W(CO)_4$.

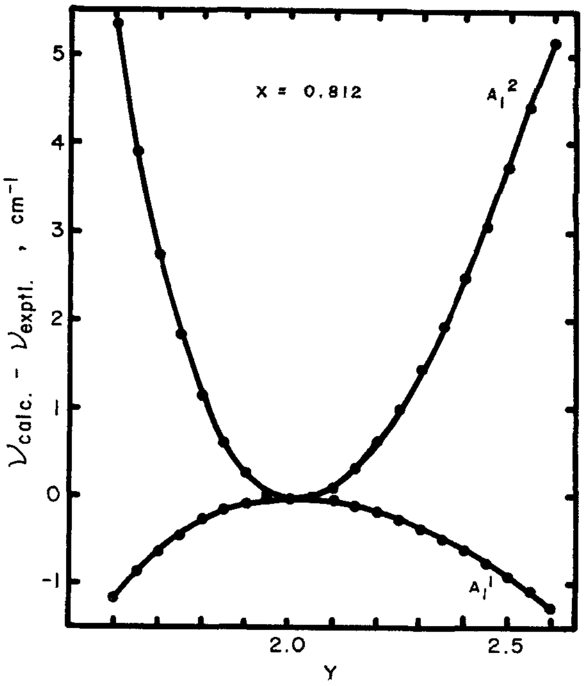

FIGURE 3 Plots of differences between calculated and observed carbonyl stretching frequencies (A_1) *vs.* Y parameter at a value of X parameter = 0.812 for (diphos)$W(CO)_4$.

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TABLE III

Experimental and calculated force constants for iron tetracarbonyls

Compound	Ref.	Method	Force constants (mdyn/Å)				
			k_1	k_2	k_c'	k_c	k_t
cis-$I_2Fe(CO)_4$	11	Exptl.	17.451	17.860	0.280	0.160	0.300
		Calc.	17.432	17.820	0.290	0.167	0.290
cis-$Br_2Fe(CO)_4$	11	Exptl.	17.617	18.290	0.220	0.098	0.337
		Calc.	17.668	18.178	0.300	0.186	0.256
cis-$I_2Fe(CO)_4$	12	Exptl.	17.407	17.813	0.273	0.174	0.283
		Calc.	17.426	17.819	0.289	0.163	0.289
cis-$Br_2Fe(CO)_4$	12	Exptl.	17.652	18.212	0.295	0.172	0.261
		Calc.	17.682	18.197	0.306	0.182	0.241

cis-$Br_2Fe(CO)_4$ calculated through use of the procedure reported here are in excellent agreement with the "exact" F, IC of Butler and Spendjian.[12] It is also to be noted that this procedure correctly determines k_c' to be larger than k_t for this molecule, also in agreement with the calculations of Butler and Spendjian, but contrary to those of Johnson, *et al.* Thus the procedure given here very closely reproduces force constants determined through isotopic enrichment studies, and yet eliminates the necessity of arbitrary relationships among the interaction constants. The carbonyl stretching force

TABLE IV

Calculated force constants for *cis*-$L_2M(CO)_4$ complexes

Compound	Force constants (mdyn/Å)					k_c/k_c'	k_t/k_c'
	k_c'	k_c	k_t	k_1	k_2		
(phen)$Cr(CO)_4$	0.57	0.37	0.62	14.30	15.22	0.65	1.1
(tmen)$Cr(CO)_4$	0.49	0.39	0.88	14.15	14.97	0.79	1.8
(diphos)$Cr(CO)_4$	0.38	0.29	0.69	14.76	15.32	0.76	1.8
(P-en)$Cr(CO)_4$	0.32	0.26	0.76	15.00	15.44	0.83	2.4
(dpae)$Cr(CO)_4$	0.40	0.29	0.69	14.75	15.30	0.72	1.7
(diars)$Cr(CO)_4$	0.36	0.28	0.74	14.71	15.22	0.79	2.1
(dto)$Cr(CO)_4$	0.43	0.35	0.80	14.51	15.27	0.81	1.8
(dth)$Cr(CO)_4$	0.45	0.33	0.79	14.63	15.27	0.74	1.8
(phen)$Mo(CO)_4$	0.52	0.38	0.65	14.28	15.27	0.74	1.2
(tmen)$Mo(CO)_4$	0.46	0.38	0.86	14.17	15.13	0.86	1.9
(diphos)$Mo(CO)_4$	0.38	0.30	0.71	14.87	15.47	0.78	1.8
(P-en)$Mo(CO)_4$	0.29	0.27	0.78	15.10	15.59	0.93	2.7
(dpae)$Mo(CO)_4$	0.39	0.30	0.73	14.87	15.49	0.79	1.9
(diars)$Mo(CO)_4$	0.35	0.29	0.74	14.84	15.43	0.83	2.1
(dto)$Mo(CO)_4$	0.41	0.35	0.76	14.56	15.42	0.85	1.8
(dth)$Mo(CO)_4$	0.42	0.34	0.79	14.66	15.41	0.83	1.9
(tmpa)$Mo(CO)_4$	0.53	0.41	0.84	14.16	15.12	0.77	1.6
(phen)$W(CO)_4$	0.54	0.38	0.68	14.21	15.13	0.69	1.2
(tmen)$W(CO)_4$	0.42	0.38	0.93	14.07	14.96	0.91	2.2
(diphos)$W(CO)_4$	0.38	0.31	0.76	14.77	15.38	0.81	2.0
(P-en)$W(CO)_4$	0.30	0.28	0.81	14.98	15.49	0.92	2.7
(dpae)$W(CO)_4$	0.39	0.31	0.75	14.77	15.38	0.80	2.0
(diars)$W(CO)_4$	0.34	0.30	0.79	14.72	15.30	0.87	2.3
(dto)$W(CO)_4$	0.37	0.34	0.83	14.46	15.29	0.93	2.2
(dth)$W(CO)_4$	0.40	0.33	0.83	14.58	15.27	0.83	2.1
(tmpa)$W(CO)_4$	0.50	0.41	0.90	14.05	14.96	0.81	1.8

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constants and interaction constants for twenty-six *cis*-$L_2M(CO)_4$ complexes are given in Table IV. Based upon the estimated uncertainties in the carbonyl stretching frequencies, average deviations in k_1 and k_2 were calculated to be < 0.02 mdyn/Å for k_1 and k_2, and < 0.01 mdyn/Å for k_c, k_c' and k_t.

Attempts to calculate force constants for $LM(CO)_5$ complexes through a similar procedure were unsuccessful in that maxima and minima were not obtained for plots similar to those shown in Figure 2 and Figure 3, and thus unique solutions were not obtained.

(*c*) *Separation of bonding effects on* (νCO)

Graham has proposed a method for the separation of σ- and π-bonding effects in $LM(CO)_5$ complexes from carbonyl stretching force constant data through a consideration of the directional nature of π-bonding and the isotropic nature of σ-bonding effects.[17]

The Graham relationships are,

$$\begin{aligned} \Delta k_1 &= \Delta\sigma + 2\Delta\pi \\ \Delta k_2 &= \Delta\sigma + \Delta\pi \end{aligned} \qquad (2)$$

where Δk_1 and Δk_2 are the differences in the respective force constants for the complex of interest from those of an arbitrarily chosen standard complex. Recently, however, a study of the carbonyl stretching spectra of (amine)$W(CO)_5$ complexes as a function of the pK_a of the amine has indicated that the effects of amine basicity are evident only at the four radial carbonyls, and are not isotropic.[18] The variation of the radial carbonyl stretching force constant (k_2) with amine pK_a, while not consistent with an isotropic σ-bonding effect, is consistent with theoretical results by Fenske and DeKock for $XMn(CO)_5$ complexes ($X = $ Cl, Br, I) which indicate an appreciable "direct" donation of electron density from the p_z orbital of X to the π^* orbitals of the radial (adjacent) carbonyls.[19] More recently, Keeling, Kettle and Paul have invoked this bonding mechanism in the interpretation of the absolute intensities of carbonyl stretching absorptions in these complexes.[20] In a manner analogous to that employed in the formulation of the Graham parameters, equations separating "direct" and π-bonding effects were developed for $LM(CO)_5$ complexes, and applied to a variety of tungsten derivatives.[19] Similarly the equations,

$$\begin{aligned} \Delta k_1 &= \Delta d + 3\Delta\pi \\ \Delta k_2 &= 2\Delta d + 2\Delta\pi \end{aligned} \qquad (3)$$

are appropriate for *cis*-$L_2M(CO)_4$ complexes, where d reflects the influence of direct ligand interaction with the π^* orbitals of the adjacent carbonyls or other such anisotropic effects, and π represents the directional influence of metal-to-CO π-bonding; this latter parameter is identical to the π-parameter employed by Graham.[17] Table V exhibits the d and π parameters calculated through use of (tmen)$M(CO)_4$ as the arbitrarily selected standard.

TABLE V

Bonding Parameters for *cis*-$L_2M(CO)_4$ complexes

M	L_2	(L)	Δd (mdyn/Å)		$\Delta\pi$ (mdyn/Å)	
Cr	tmen[a]		0.00		0.00	
Cr	phen		0.11		0.01	
Cr	diphos		−0.04		0.22	
Cr	P-en		−0.07		0.31	
Cr	dpae		−0.05		0.22	
Cr	diars		−0.09		0.22	
Cr	dth		−0.02		0.16	
Cr	dto		0.04		0.10	
Cr	CO[b]		−0.03		0.79	
Mo	tmen[a]		0.00		0.00	
Mo	tmpa		0.00		0.00	
Mo	phen		0.05		0.02	
Mo	diphos		−0.10		0.26	
Mo	P-en		−0.12		0.35	
Mo	dpae		−0.08		0.26	
Mo	diars		−0.11		0.26	
Mo	dth		−0.04		0.18	
Mo	dto		−0.02		0.12	
Mo	CO[b]		−0.13		0.83	
W	tmen[a]	(CHA)[c]	0.00	(0.00)[d]	0.00	(0.00)[d]
W	tmpa		0.01		0.01	
W	phen		0.06		0.03	
W	diphos	(PPh_3)[c]	−0.04	(-0.03_5)[d]	0.24	(0.16_5)[d]
W	P-en		−0.06		0.32	
W	dpae		−0.04		0.24	
W	diars		−0.07		0.24	
W	dth		−0.02		0.18	
W	dto		0.05		0.11	
W	CO[b]	(CO)	−0.08	(0.05)[d]	0.81	(0.64)[d]

[a] Arbitrarily selected standard.

[b] Ref. 2.

[c] CHA = cyclohexylamine; PPh_3 triphenylphosphine.

[d] Data given in Ref. 17.

Based upon calculated average deviations for the carbonyl stretching force constants k_1 and k_2, the probable errors in the d and π parameters were calculated to be ± 0.03 mdyn/Å and ± 0.02 mdyn/Å respectively.[21]

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Several features of these parameters should be pointed out. It is to be noted that, in general, P, As and S donor atoms possess more negative values of the "*d*" parameter than do nitrogen donors. This effect, which was also observed for $LW(CO)_5$ complexes,[18] indicates that ligands bonding through the heavier donor atoms exert a greater *d* effect as would be expected on the basis of the greater extension of the p_z orbital on that atom. This is also consistent with the results of Fenske and DeKock for $X\mathrm{Mn(CO)}_5$ complexes. These workers noted a direct donation effect which varied $I > Br > Cl$[19]. Also of interest are the values for the π parameter, which, in general, indicate the π-bonding properties of various ligands to vary $P \sim As > S > N$, the generally accepted order. While direct comparisons between mono- and disubstituted complexes cannot be made because no identical ligands were employed, one interesting comparison is of the parameters for (triphenylphosphine)$W(CO)_5$[18] and (diphos)$W(CO)_4$, in which ligand bonding properties should be roughly similar. The data in Table V indicate the parameters to be comparable, with diphos the better π-accepting ligand, as might be anticipated in a more highly substituted complex. Also, consistent with this expectation, the data in Table V indicate that CO acts as a better π-accepting ligand in the disubstituted tungsten complex than in the corresponding monosubstituted complex. In general, in both $LW(CO)_5$ and *cis*-$L_2M(CO)_4$ complexes values of *d* and π are quite reasonable, lending strong support both to this qualitative and semiquantitative representation of bonding, and to the values for the force constants as determined through use of the method described here.

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REFERENCES

1. Part XXV: G. R. Dobson and A. J. Rettenmaier, *Inorg. Chim. Acta*, in press.
2. F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.* **84,** 4432 (1962).
3. For a recent and comprehensive review, see, L. M. Haines and M. H. B. Stiddard, *Adv. Inorg. Chem. Radiochem.* **12,** 53 (1969).
4. J. Dalton, I. Paul, J. G. Smith and F. G. A. Stone, *J. Chem. Soc. A*, 1195 (1968).
5. E. W. Abel, J. Dalton, I. Paul, J. G. Smith and F. G. A. Stone, *J. Chem. Soc. A*, 1203 (1968).
6. F. T. Delbeke, E. G. Claeys and G. P. van der Kelen, *J. Organometal. Chem.* **25,** 219 (1970).
7. L. H. Jones, *Advances in the Chemistry of the Coordination Compounds*, S. Kirschner, Ed., MacMillan, 1961, p. 403.
8. H. D. Kaesz, R. Bau, D. Hendrickson and J. M. Smith, *J. Amer. Chem. Soc.* **89,** 2844 (1967).
9. P. S. Braterman ,R. W. Harrill and H. D. Kaesz, *J. Amer. Chem. Soc.* **89,** 2851 (1967).
10. B. F. G. Johnson, J. Lewis, J. R. Miller, B. H. Robinson, P. W. Robinson and A. Wojcicki, *J. Chem. Soc. A*, 522 (1968).
11. B. F. G. Johnson, J. Lewis, P. W. Robinson and J. R Miller, *J. Chem. Soc. A*, 1043 (1968).
12. I. S. Butler and H. K. Spendjian, *J. Organometal. Chem.* **18,** 145 (1969).
13. R. A. Brown and G. R. Dobson, *J. Inorg. Nucl. Chem.*, in press.
14. E. K. Plyler, A. Danti, L. R. Blaine and E. D. Tidwell, *J. Res. Nat. Bur. Stand.* **64**A, 29 (1960).
15. E. K. Plyler, L. R. Blaine and W. S. Connor, *J. Opt. Soc. Amer.* **45,** 102 (1955).
16. L. E. Orgel, *Inorg. Chem.* **1,** 25 (1962).
17. W. A. G. Graham, *Inorg. Chem.* **7,** 315 (1968).
18. R. A. Brown and G. R. Dobson, *Inorg. Chim. Acta*, **6,** 65 (1972).
19. R. F. Fenske and R. L. DeKock, *Inorg. Chem.* **9,** 1053 (1970).
20. G. Keeling, S. F. A. Kettle and I. Paul, *J. Chem. Soc. A*, 3143 (1971).
21. J. N. Mellor, *Higher Mathematics for Students of Chemistry and Physics*, Dover Publications, New York, N.Y. 1955, pp. 528–529.