Contribution from the Department of Chemistry, North Texas State University Denton, Texas 76203, U.S.A.

Octahedral Metal Carbonyls. XXI.[1a] Carbonyl and Metal-Carbon Stretching Spectra of Monosubstituted Group VIB Metal Carbonyls[1b]

R.A. Brown and G.R. Dobson

Received April 17, 1971

The infrared spectra in solution of thirty-seven complexes of the type $LM(CO)_5$ *(L = Lewis base; M = Cr. Mo, W) have been recorded in the regions 2100-1800 and 700-300* cm^{-1}. *It has been found that the position of the metal-carbon stretching absorption (E-mode) is determined by the identity of the Lewis base donor atom, being lowest for "hard" bases. Within a series of derivatives of ligands containing the same donor atom, however, the expected "reciprocal relationship" between* νCO *and* νMC *is observed. The positions of* νMC *correlate well with complex reactivity* via *rate-determining dissociation of CO. The results are examined on the basis of current bonding theories.*

Introduction

Recent kinetic studies of substitution reactions of Group VIB metal carbonyls have shown that reaction rates *via* the ligand-independent path, which involves rate-determining fission of metal-carbon bonds, is strongly dependent upon the identity of the donor atom of a substituent Lewis base.[2] Angelici and Graham have observed, qualitatively, that ligands in which the atom bonded to the metal is either a first row element or a halogen labilize the carbonyls relative to the hexacarbonyl, while those containing second and third row elements, together with CNR, are non-labilizing.[3] Thus, in general, "hard" bases are labilizing and "soft" bases are non-labilizing.[4]

Inferences as to metal-carbon bond strengths have often been made on the basis of carbonyl stretching data. Lower carbonyl stretching frequencies are generally held to be indicative of more extensive metal-to-carbonyl π–bonding, which, in terms of two limiting valence bond structures,

$$:\overset{-}{M}-C\equiv\overset{+}{O}:\longleftrightarrow M=C=\ddot{O}: \qquad (1)$$

should also suggest stronger metal-carbon bonds.[5] Stronger metal-carbon bonds could thus be expected in complexes containing a first row element bonded to the transition metal, for which carbonyl stretching frequencies are significantly lower than are those observed in analogous complexes containing heavier donor atoms.

On this basis, exactly the opposite trends in kinetic behavior as are observed would be expected. This "anomalous" reactivity has been interpreted both in terms of stabilization of the transition state by "hard" bases,[6] and destabilization of the ground state, which results from decreased CO-to-metal bond strengths.[7] Although metal-carbon stretching frequencies for substituted metal carbonyls would more directly bear on the question of ground state destabilization by hard base substituents than do carbonyl stretching frequencies, relatively little such data are available.[8] Accordingly, a general investigation of metal-carbon stretching frequencies as a function of the metal atom, the nature of the substituent, the degree of substitution and molecular stereochemistry has been undertaken. As part of this study, the infrared spectra of some thirty-seven complexes of the type $LM(CO)_5$ (L = Lewis base bonded through N, P, As, Sb, Bi, O or S donor atom; M = Cr, Mo W) have been obtained in solution in the 2100-1800 cm^{-1} and 700-300 cm^{-1} regions of the infrared, and are reported and discussed here.

Experimental Section

General. The metal carbonyls and ligands were obtained from commercial sources and were used without further purification. All reaction procedures were carried out under an atmosphere of prepurified nitrogen; the complexes containing ligands bonding through N, Bi, O or S are unstable to oxygen in solution and require rigorous exclusion of air to prevent decomposition. The purity of the complexes was checked by comparing their carbonyl stretching spectra to those previously reported in the literature, or by elemental analysis.

---

(1) a. Part. XX: Ross E.P., Jernigan R.T. and Dobson G.R. *J., Inorg. Nucl Chem.* 33, 3375 (1971); b. Presented in part at the III Inorganica Chimica Acta Symposium, Venice, Sept. 1970.

(2) For the most recent reviews of kinetics of substitution reactions of carbonylmetal complexes, see, Werner H., *Angew. Chem. Intern. Ed.*, 7, 930 (1968) and Angelici R.J., *Organometal Chem. Rev.*, 3, 273 (1968); the latter reference contains a compilation of relevant rate data.

(3) Angelici R.J. and Graham J.R., *Inorg. Chem.*, 6, 988 (1967).

(4) Pearson R.G., *J. Amer. Chem. Soc.*, *85*, 3533 (1963).

(5) See, *e. g.*, Cotton F.A., *Inorg. Chem.*, 3, 702 (1964).

(6) Angelici R.J., Jacobson S.E., and Ingemanson C.M., *Inorg. Chem.*, 7, 2466, (1968), and references cited therein.

(7) Dobson G.R. and Houk L.W., *Inorg. Chim. Acta*, *1*, 287 (1967).

(8) See, *e. g.*, Table III.

Preparative. $Ph_3EM(CO)_5$ (E = As, Sb, P; M = Cr, Mo) and related complexes: Although these complexes had been prepared previously,[9-11] the procedure described below was found to give cleaner products and better yields. The appropriate hexacarbonyl (13.7 mmole), and 11.3 mmole of the ligand in 100 ml of 2,2,5-trimethylhexane (b.p., 124°) were heated at reflux until 11.3 mmole of carbon monoxide had evolved, or until the rate of gas evolution was less than 20 ml per hour. The reaction flask was stoppered and cooled overnight at —10°, after which the product was collected by suction filtration. It was then dried at 50° and 0.1 mm for two hr to remove any excess hexacarbonyl. The residue was dissolved in acetone, immediately reprecipitated by addition of water, collected, dried *in vacuo,* and then recrystallized from *n*-hexane until pure. Yields ranged from 60 to 90 per cent. Similarly were prepared $Ph_3EW(CO)_5$ (E = P, As, Sb), employing a 2:1 mixture of *n*-decane and 2,2,5-trimethylhexane as refluxing solvent. $Ph_3BiM(CO)_5$ (M = Cr, Mo, W) were prepared by the literature method.[12]

$LW(CO)_5$ (L = $(BuO)Ph_2P$, $(BuO)_2PhP$, $(BuO)_3P$, $(PhO)_3P$, Bu_3Sb): These complexes are liquids at room temperature and are more difficult to purify than are solid products since the high boiling solvent used in their preparation tends to remain dissolved in the product. Accordingly, the method of Strohmeier and Müller[13] involving uv irradiation (see below) of the hexacarbonyl in tetrahydrofuran (THF) and subsequent addition of the ligand to the $(THF)W(CO)_5$ product was employed. After reaction and removal of the THF *in vacuo,* the blue or green oily residue was chromatographed on silica (*n*-heptane eluant) to give a clear yellow solution. The solvent was removed *in vacuo* to yield the pure product.

$(Am)W(CO)_5$ (Am = amines, pyridines and acetonitrile) complexes were prepared by the method of Angelici and Malone.[14]

$LW(CO)_5$ (L=tetrahydrofuran, *n*-propanol, tetrahydrothiophene, thiophenol): These complexes are highly unstable in solution, and could not be isolated. They were prepared through irradiation of a solution of 13.7 mmoles of $W(CO)_6$, 100 ml of the appropriate ligand and 300 ml of 2,2,4-trimethylpentane employing an immersion reaction vessel and a 450 watt Hanovia medium pressure Hg lamp. After 30 min irradiation, the infrared spectra of the solutions were immediately recorded.

Infrared Spectra. All infrared spectra were recorded a Perkin Elmer 621 grating spectrophotometer employing a wavelength expansion of 5x and spectral slit widths of 2.4 – 1.7 cm^{-1} (2100 – 1800 cm^{-1}) and 2.1–3.2 cm^{-1} (700–300 cm^{-1}) and were calibrated against water vapor bands at 1869.36[15] and 303.0[16] cm^{-1}. Spectra were recorded, except where noted, employing 2,2,4-trimethylpentane solutions in 0.1 mm NaCl cells for the 2100–1800 cm^{-1} spectral region, and dichloromethane solutions and 0.2 or 0.5 mm CsI cells between 700 and 300 cm^{-1}. While it would have been desirable to obtain both M-C and C-O stretching data in a common solvent, relative band intensities and solvent transparencies in these spectral regions dictated the choices made. Band positions were determined by measuring the midpoint at half-intensity for isolated bands, or at 70–90 per cent intensity for overlapping bands. All positions are believed accurate to ± 1 cm^{-1}.

Results and Discussion

Carbonyl Stretching Spectra. The carbonyl stretching spectra of $LM(CO)_5$ complexes have been the subject of several investigations. Angelici and Malone have studied the spectra of pentacarbonyltungsten complexes containing phosphine, pyridine, and amine ligands,[14] while Darensbourg and Brown have studied a variety of derivatives of $Mo(CO)_6$.[17] The data of these last workers have also been employed by Graham in an attempt to separate σ– and π–bonding effects in these molecules.[18] In view of the extensive series of $LM(CO)_5$ complexes prepared for the study of metal-carbon stretching spectra, it was also of interest to compare carbonyl stretching spectra to results previosly obtained. Carbonyl stretching data, and Cotton-Kraihanzel force constants[19] for selected $LW(CO)_5$ complexes are given in Table I. Of particular interest is the series of twelve $LW(CO)_5$

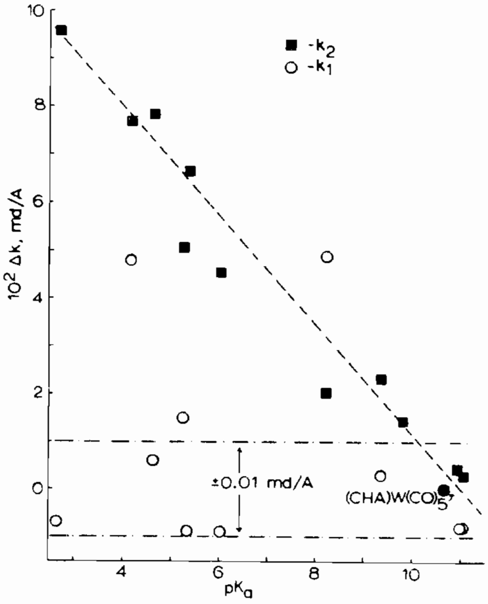

Figure 1. Changes in carbonyl stretching force constants as a function of ligand basicity for (amine)($W(CO)_5$ complexes.

---

[9] Magee T., Mathews C.N., Wang T.S., and Wotiz J.H., *J. Amer. Chem. Soc., 83,* 2300 (1961).

[10] Poilblanc R. and Bigorgne M., *Compt. rend., 250,* 1064 (1960).

[11] Poilblanc R. and Bigorgne M., *ibid., 252,* 3054 (1961).

[12] Brown R.A. and Dobson G.R., *J. Inorg. Nucl. Chem., 33,* 892 (1971).

[13] Strohmeier W. and Müller F.J., *Chem. Ber., 102,* 3608 (1969).

[14] Angelici R. J., and Malone M.D., *Inorg. Chem., 6,* 1731 (1967).

[15] Plyler E.K., Danti A., Blaine L.R., and Tidwell E.D. *J. Res. Nat. Bur. Standards, 64A,* 29 (1960).

[16] Bentley F.F., Smithson L.D., and Rozek R.L., « Infrared Spectra and Characteristic Frequencies ~ 700-300 cm^{-1} », Interscience Publishers, New York, 1968, p. 13.

[17] Darensbourg D.J. and Brown T.L., *Inorg. Chem., 7,* 959 (1968).

[18] Graham W.A.G., *Inorg. Chem., 7,* 315 (1968).

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

Table I. Carbonyl Stretching Frequencies and Force Constants for $LM(CO)_5$ Complexes[a]

Complex		$\nu CO(cm^{-1})$[b]			$F_{CO}(md/A)$	
	A_1^2	E	A_1^1	k_1	k_2	k_i
$Cr(CO)_5(AsPh_3)$	2068m	1946.5vs	1946.5vs	15.55	15.87	0.29
$Cr(CO)_5(SbPh_3)$	2065m	1948vs	1948vs	15.57	15.88	0.28
$Cr(CO)_5(C_6H_{11}NH_2)$	2068w	1935.5vs	1917ms	15.07	15.77	0.32
$W(CO)_5(PBu_3)$	2068.5w	1935.5vs	1943m	15.52	15.75	0.31
$W(CO)_5(PPh_3)$	2075m	1944vs	1944vs	15.52	15.88	0.31
$W(CO)_5[PPh_2(OBu)]$[c]	2074.5mw	1944s	1954.5m	15.71	15.87	0.31
$W(CO)_5[PPh(OBu)_2]$[c]	2077mw	1947s	1957m	15.75	15.92	0.31
$W(CO)_5[P(OBu)_3]$	2079w	1946.5vs	1960.5mw	15.81	15.92	0.31
$W(CO)_5(SbBu_3)$[c]	2068mw	1940vs	1940vs	15.45	15.80	0.30
$W(CO)_5(BiPh_3)$	2077mw	1951vs	1946msh	15.54	15.97	0.30
$W(CO)_5(C_4H_8S)$	2075mw	1941.5vs	1930.5ms	15.29	15.86	0.32
$W(CO)_5(PhSH)$	2080w	1948vs	1935.5m	15.37	15.96	0.32
$W(CO)_5$(piperidine)	2072.5w	1930vs	1919m	15.12	15.73	0.34
$W(CO)_5(C_6H_{11}NH_2)$	2072w	1930vs	1919.5m	15.13	15.72	0.34
$W(CO)_5$(piperazine)[c]	2072.5w	1931vs	1920mw	15.14	15.74	0.34
$W(CO)_5(PhCH_2NH_2)$[c]	2072w	1932s	1920msh	15.13	15.75	0.34
$W(CO)_5$(morpholine)	2073.5vw	1931.5vs	1922.5mwsh	15.18	15.75	0.34
$W(CO)_5(Et_2NH)$[c]	2073w	1930vs	1919m	15.12	15.73	0.34
$W(CO)_5$(4-picoline)	2073w	1933.5vs	1919.5m	15.12	15.77	0.34
$W(CO)_5(C_5H_5N)$	2073w	1934vs	1921m	15.15	15.77	0.33
$W(CO)_5(PhNH_2)$	2074w	1936s	1920msh	15.13	15.80	0.33
$W(CO)_5$(*p*-anisidine)	2075w	1934.5vs	1919.5m	15.12	15.79	0.34
$W(CO)_5$(*p*-chloroaniline)[c]	2075w	1935.5vs	1923m	15.18	15.80	0.34
$W(CO)_5$(*o*-chloroaniline)[c]	2075w	1937vs	1920mw	15.12	15.82	0.33
$W(CO)_5(NCCH_3)$	2078w	1944.5s	1927m	15.22	15.91	0.32
$W(CO)_5(n\text{-}C_3H_7OH)$	2075w	1930s	1914msh	15.04	15.74	0.35

[a] All complexes for which carbonyl stretching spectra have been obtained are listed in Table II. Where carbonyl stretching spectra of comparable quality have previously been reported (see references in Table III) or where spectra are not specifically mentioned in the text, they are not given here. Data not reported are available from the authors upon request. [b] 2,2,4-trimethylpentane solvent; relative band intensities: s = strong; m = medium; w = weak; v = very. sh = shoulder. [c] Previously unreported complex.

complexes containing pyridine and amine ligands, similar to that investigated by Angelici and Malone.[14] The variation of Cotton-Kraihanzel force constants, k_1 (axial carbonyl) and k_2 (equatorial carbonyls) as a function of the pk_a[20] of the amine is exhibited in Fig. 1, which shows differences in k_1 and k_2 from the corresponding values for an arbitrarily selected member for the series, (cyclohexylamine)$W(CO)_5$. The data indicate that while the value of k_2 decreases regularly with increasing amine pK_a, k_1 remains essentially constant; k_1 values for nine of the twelve complexes fall within the range 15.13 ± 0.01 md/A. A close examination of the results of Angelici and Malone[14] also reveals no trend in k_1 as a function of pk_a. These workers interpreted their data on the basis of such a trend, a limiting ability of ligands to affect carbonyl stretching frequencies *via* σ–donation at high pK_a's, and steric effects exerted by secondary and tertiary amines. However, the fact that the latter two effects are not exhibited in their plots of k_2 *vs.* pK_a (or in that shown in Fig. 1) would seem to be inconsistent with these proposals. Further, it is generally observed in substitution products of Group VIB metal carbonyls that k_1 changes more than does k_2 as the bonding properties of π-accepting ligands are varied; such a trend is expected on the basis of the directional properties of the metallic d_π orbitals.[19] The fact that k_1 is invariant to pk_a in the present study is strong evidence that there is a negligible change in CO-to-metal π–bonding in this series of complexes. This would seemingly indicate that the separation of σ– and π–bonding, expected on the basis of symmetry only for the octahedral complexes $M(CO)_6$, also holds for this series of $W(CO)_5L$ complexes.

The apparent lack of a σ–bonding influence at the position *trans* to the ligand requires a reexamination of the conclusion of Angelici and Malone[14] that changes in carbonyl stretching force constants for phosphine complexes may be interpreted in terms of σ–bonding alone. For three of the five (phosphine)$W(CO)_5$ complexes studied by these workers it was not possible to resolve the A_1^1 and E bands of the carbonyl stretching spectra. It was thus necessary to estimate the position of the A_1^1 band, of critical importance to the values obtained for the carbonyl stretching force constants. The estimates were based on the assumption that the position of the A_1^1 band was shifted from its position in (phosphine)$W(CO)_5$ complexes for which the A_1^1 band is resolved by an amount equal to the average of shifts of the A_1^2 and E bands (involving respectively the symmetrical and antisymmetrical stretch of the equatorial carbonyls). This assumption is without theoretical justification, and further, it should be evident that a combination of σ– and π–bonding which could produce the effect as required by this assumption would be fortuitous indeed. Moreover, the separation of the A_1^1 and E bands, based on the estimated position of the former, is 5.5 cm^{-1} in $Ph_3PW(CO)_5$, and should be observable. This may be inferred from a comparison of the carbonyl stretching spectra of $Ph_3PW(CO)_5$ and $Ph_3BiW(CO)_5$ and selected for comparison on the basis of similar band widths at half intensity (13 cm^{-1} *vs.* 14 cm^{-1}) and band separation (5.5 cm^{-1} *vs.* 5 cm^{-1}. While the

---

(20) Weast R.C., Ed. « Handbook of Chemistry and Physics » 50th Ed., Chemical Rubber Co., Cleveland (1969) p. D115.

E mode for $Ph_3PW(CO)_5$ appears to be symmetrical, the A_1^1 band appears as a distinct shoulder in $Ph_3BiW(CO)_5$. Thus the evidence strongly indicates that the positions of A_1^1 modes as estimated by Angelici and Malone are in error, and that any conclusions drawn on the basis of those estimated frequencies are suspect. Indeed, it follows from the observation that k_1 is invariant for ligands which cannot enter into π—bonding that where variations of k_1 with the identity of the ligand are noted, changes in ligand-metal π—bonding are involved.[21] One obvious contrast to be noted in the carbonyl stretching force constant data in Table I is that while k_1 is invariant and k_2 changes with pK_a for the series of (amine)$W(CO)_5$ complexes, k_1 varies much more than does k_2 for the series of complexes $[P(Ph)_{3-x}(OBu)_x]W(CO)_5$ ($x = 0$–3), as is expected on the basis of the well-documented directional nature of π—bonding.[19]

It is also important to note that the values of the carbonyl stretching force constants obtained for the three (pyridine)$W(CO)_5$ complexes do not differ significantly from those of the other nine (amine)-$W(CO)_5$ complexes. Thus there would not appear to be appreciable π—bonding between pyridines and the metal in monosubstituted derivatives, a conclusion also reached by Kraihanzel and Cotton based on spectra obtained in $CHCl_3$ solution.[22]

While the fact that the carbonyl stretching force constants for the equatorial carbnyls vary with pK_a while those for the axial (*trans*) carbonyl are essentially constant for (amine)$W(CO)_5$ complexes is inconsistent with π—bonding influences, it would appear to be consistent with a proposal advanced by Fenske and DeKock to explain a similar variation of k_1 and k_2 in the series of complexes $Mn(CO)_5X$ ($X =$ Cl, Br, I), in which direct overlap of the σ_z bonding orbital of X and the π* orbitals of CO (equatorial) is postulated.[23] The magnitude of such overlap would be expected to increase with increasing ligand basicity, consistent with the observed trend in k_2 values. This interpretation successfully explains the observed trend in carbonyl stretching force constants with changes in amine pK_a. It implies that there is little effect of changes in ligand σ—bonding on carbonyl stretching frequencies either through interaction with the metallic π—system or directly through changes in carbonyl-to-metal σ—bonding, since both of these mechanisms would be expected to influence k_1.[24]

The results also dictate revision of the Graham equations for separation of σ— and π—bonding effects in these systems.[18] Following Graham, but assuming a direct ligand to ligand donation cffect, dependent upon ligand basicity but exerted only at the four radial carbonyls, the equations,

$$\Delta k_1 = 2\Delta\pi$$
$$\Delta k_2 = \Delta d + \Delta\pi \qquad \text{(II)}$$

are applicable.[25] Using the carbonyl stretching force constants for (cyclohexylamine)$W(CO)_5$ as the standard, the modified parameters given in Table II for selected LW)CO)$_5$ complexes are obtained.

Table II. Bonding Parameters for Selected $LW(CO)_5$ Complexes.

L	d	π
	(md/A)	
CO [a]	0.05	0.64
$P(OPh)_3$	—0.05	0.38
$P(OBu)_3$	—0.14	0.34
$PPh(OBu)_2$	—0.11	0.31
$PPh_2(OBu)$	—0.15	0.29
PPh_3	—0.03_5	0.19_5
PBu_3	—0.16_5	0.19_5
CH_3CN	0.13_5	0.04_5
$C_6H_{11}NH_2$ [b]	0.00	0.00
$PhCH_2NH_2$	0.03	0.00
$PhNH_2$	0.08	0.00
o-$ClC_6H_4NH_2$	0.10_5	—0.00_5
no substituent [c]	0.44	0.07

[a] Calculated from force constants given in Ref. 19. [b] Arbitrarily selected standard. [c] Calculated from force constants for $W(CO)_5$ in argon matrix at 20° K; Ref. 28.

There are several important features to be noted with regard to these parameters. First, the trend in the π—parameter obtained for phosphorus-containing ligands is more reasonable than that obtained by Graham[18] in that it parallels the π—accepting abilities of ligands as would be inferred from inductive effects of substituents bonded to phosphorus. Second, ligands bonded through phosphorus are observed to exert a greater "direct donation" effect than do ligands bonded through nitrogen. This is also to be expected on the basis of the greater diffuseness of the requisite orbital on phosphorus, which should results in greater p_z—pπ* interaction; a similar trend was noted by Fenske and DeKock for $XMn(CO)_5$ complexes ($X =$ Cl, Br, I).[23] Third, these parameters indicate acetonitrile to be a π—acceptor, while Graham parameters show it to be a π donor. There is ample evidence to support the first interpretation in that the CN stretching frequency in $CH_3CNW(CO)_5$[26] is lower than is that reported for $CH_3CN{:}BF_3$,[27] in which there can be no π—bonding, and that the CN stretching frequencies exhibit further decrease in the complexes cis–$(CH_3CN)_2W(CO)_4$ and cis–$(CH_3CN)_3W(CO)_3$.[26] Exactly this sort of evidence has been taken as indicative of d_π—p_π* bonding for carbon monoxide in its complexes. Finally, the bonding parameters obtained for $W(CO)_5$, the infrared spectrum for which has been obtained in an argon matrix at 20° K,[28] agree amazin-

---

(21) The possibility that opposing σ- and π-effects can result in an invariant k_1 would appear to be implausible, since increased amine basicity (more charge denated to the metal) would lead to increased metal-to-CO π-bonding and decreased CO-to-metal σ-bonding: both effects would be expected to lower k_1.

(22) Kraihanzel C.S. and Cotton F.A., *Inorg. Chem.*, *2*, 533 (1963); $CHCl_3$ is a less desirable solvent for carbonyl stretching spectral determinations because of its polarity.

(23) Fenske R.F. and DeKock R.J., *Inorg. Chem.*, *9*, 1053 (1970); Fenske R.F., personal communication.

(24) This is not to say that amine-to-metal or CO-to-metal σ-bonding to not change with amine basicity, but rather that such changes are not manifested to an observable extent in carbonyl stretching frequencies and force constants.

(25) « d » is used in these equations rather than the « σ » employed by Graham to distinguish between Fenske's « direct donation » effect and the through-metal σ-inductive effect.

(26) Ross B.L., Grasselli J.G., Ritchey W.M., and Kaesz H.D., *Inorg. Chem.*, *2*, 1023 (1963).

(27) Coerver H.J., and Curran A.C., *J. Amer. Chem. Soc.*, **80**, 3522 (1958).

(28) Graham M.A., Poliakoff M., and Turner J.J., *J. Chem. Soc. A.*, 2939 (1971).

Table III. Far Infrared Spectra of Monosubstitution Products of the Group VIB Metal Carbonyls[a].

Complex	νMC, cm⁻¹ A₁	A₁	E	δMCO, cm⁻¹				Other bands, cm⁻¹			
$Cr(CO)_5(PPh_3)$*[b,-c]	—	543w	466m	670s	654vs	616vw	—[d]	520s	512m	497mw	420w
$Cr(CO)_5(AsPh_3)$	—	546mw	466s	671s	655vs	615vw	—[d]	476vs	419w	324m	—
$Cr(CO)_5(SbPh_3)$	—	545mw	465s	670vs	653vs	614vw	—[d]	457ms	—	—	—
$Cr(CO)_5(BiPh_3)$*[d]	—	545mw	456vs	662s	647vs	612vw	—[d]	448ms	—	—	—
$Cr(CO)_5(C_6H_{11}NH_2)$	—	556m	444.5s	675s	658vs	—	—[d]	586w	413m	383w	—
$Mo(CO)_5(PPh_3)$*[b,-ef]	446w	387sh	378s	606vs	584vs	—	—	519vs	512m	493m	417m
$Mo(CO)_5(AsPh_3)$*[g,-h]	436vw	395m	378.5s	607vs	586vs	—	—	527vw	475s	327m	—
$Mo(CO)_5(SbPh_3)$*[g,-h]	436vw	398s	379.5s	606vs	582vs	—	—	454ms	—	—	—
$Mo(CO)_5(BiPh_3)$*[e]	418vw	390m	377s	605s	580vs	—	—[i]	448ms	—	—	—
$Mo(CO)_5(C_6H_{11}NH_2)$*[g]	—	376sh	364s	608vs	599s	572mw	550w	538mw	—	—	—
$W(CO)_5(PPh_3)$	450w	418mw	383s	597s	576vs	—	521vs	510m	495m	—	—
$W(CO)_5[PPh_2(OBu)]$	428mw	410w	384s	595s	574vs	547m	529ms	506w	490w	—	—
$W(CO)_5[PPh(OBu)_2]$	420mw	—	385.5s	595s	574vs	556s	534vw	—	—	—	—
$W(CO)_5[P(OBu)_3]$	435wsh	421mw	385.5s	595vs	572vs	552m	—	—	—	—	—
$W(CO)_5[P(OPh)_3]$*[j]	432sh	415m	381.5s	589vs	570s	—	—	—	615mw	499m	478mw
$W(CO)_5(PBu_3)$*[bj]	430mw	414w	387s	—	572vs	—	—	—	—	—	—
$W(CO)_5(AsPh_3)$*[e]	429vw	410w	384s	598vs	577vs	—	—	475ms	327m	—	—
$W(CO)_5(SbPh_3)$*[e]	431vw	411m	386.5s	597vs	574vs	—	—	453m	—	—	—
$W(CO)_5(SbBu_3)$	434vw	413w	388s	600vs	576vs	—	—	512vw	454vw	—	—
$W(CO)_5(BiPh_3)$	—	406w	383s	596vs	574vs	—	—	447ms	—	—	—
$W(CO)_5(C_4H_8S)$	427w	408w	378.5vs		not examined				not examined		
$W(CO)_5(PhSH)$	417w	395w	374vs		not examined				not examined		
$W(CO)_5$(piperidine)	429w	403w	371vs	601vs	584s	—	547	—	—	—	—
$W(CO)_5(C_6H_{11}NH_2)$	429w	406w	370s	602vs	590s	576ms	549m	475wbr	—	—	—
$W(CO)_5$(piperazine)	429w	404w	371s	600vs	585s	—	545m	620m	—	—	—
$W(CO)_5(PhCH_2NH_2)$	430vw	405vw	371s	598vs	580vs	568ssh	546m	—	—	—	—
$W(CO)_5$(morpholine)	430vw		371vs	600vs	586vs	—	546m	—	—	—	—
$W(CO)_5(Et_2NH)$	429vw	403vw	373vs	601s	588ssh	581vs	548m	—	—	—	—
$W(CO)_5$(4-picoline)	428vw	407w	369.5vs	597vs	586vs	—	546m	492ms	—	—	—
$W(CO)_5(C_5H_5N)$	428vw	403vw	368.5vs	600vs	588vs	—	547m	468wbr	627w	—	—
$W(CO)_5PhNH_2)$	428vw	402vw	371vs	598vs	592ms	567mw	547w	519mw	—	—	—
$W(CO)_5$(*p*-anisidne)	427w	399mw	369vs	597vs	588ssh	564m	546mw	528mw	478vwbr	—	—
$W(CO)_5$(*p*-chloroaniline)	425vw	381sh	371vs	597vs	582vs	565m	546w	515m	497mw	—	—
$W(CO)_5$(*o*-chloroaniline)	440w	403w	371vs	596vs	580s	569m	546mw	614wbr	590sh	—	—
$W(CO)_5(NCCH_3)$[k,-l]	428w	388m	371vs	592s	582s	—	545w	620w	—	—	—
$W(CO)_5(THF)$*[m]	—	403mw	364vs		not examined				not examined		
$W(CO)_5(n\text{-}C_3H_7OH)$	—	402w	363vs		not examined				not examined		

* See footnote *a*, Table I. - Far infrared spectrum previously investigated, see reference cited here. [a] Dichloromethane solution, unless otherwise noted; relative band intensities: s = strong; m = medium; w = weak; v = very; sh = shoulder; br = broad. These bands are considerably weaker than are carbonyl stretching bands. [b] S. O. Grim, D.A. Wheatland and W. McFarlane, *J. Amer.-Chem. Soc.*, *89*, 5573 (1967). [c] A.A. Chalmers, J. Lewis, and R. Whyman, *J. Chem. Soc.* (A), 1817 (1967). [d] Solvent absorption above *ca.* 675 cm⁻¹ may mask one δMCO absorption. [e] Ref. 12. [f] C. Barbeau and J. Turcotte, *Can. J. Chem.*, *48*, 3583 (1970). [g] D.J. Darensbourg and T.L. Brown, *Inorg. Chem.*, *7*, 959 (1968). [h] S. Singh, P.P. Singh and R. Rivest, *Inorg. Chem.*, *7*, 1236 (1968). [i] δMCO region examined as nujol mull. [j] R.L. Keiter and J.G. Verkade, *Inorg. Chem.*, *8*, 2115 (1969). [k] Ref. 26. [l] M.F. Farona, J.G. Grasclli and B.L. Ross, *Spectrochim. Acta*, *23A*, 1875 (1967). [m] I.W. Stolz, H. Haas and R.K. Sheline, *J. Amer. Chem. Soc.*, *87*, 716 (1965).

gly well with those expected, taking into consideration the fact that carbonyl stretching intensity data support a somewhat altered geometry for the $W(CO)_5$ moiety from that in $LW(CO)_5$ complexes.[28] It is seen that "π—bonding" at the vacant site very closely approximates that of cyclohexylamine (*i. e.*, none) while the value of the d parameter is large and positive, indicating a minimal "direct donation" effect. Thus the parameters calculated on the basis of the model presente here lend strong support to this interpretation.

Metal-Carbon Stretching Spectra. Bands observed in the region 700—300 cm⁻¹ are exhibited in Table III. That thirty-seven complexes of the same (local C_{4v}) symmetry have been studied, has allowed the assignment of metal-carbon stretching and metal-carbon-oxygen deformation bands with considerable confidence, since bands attributable to ligand vibrations will differ from complex to complex. The further fact that the M-C stretches and M-C-O deformation absorptions in $LCr(CO_5$ complexes are observed to occur some 70 to 80 cm⁻¹ higher than in the corresponding Mo and W complexes also aids in band assignments. Since the M-C-O linkage in these complexes is linear, the numbers and symmetries of the M-C absorptions are identical to those of the carbonyl stretching vibrations ($2A_1 + E$).

The metal-carbon stretching spectrum is characterized by a strong absorption which, on the basis of its intensity, is most probably the E mode. This assignment is identical to that made by Poilblanc and Bigorgne for $LMo(CO)_5$ complexes in which L contain phosphorus donor atoms.[29] The assignments of the other two bands, of A_1 symmetry, are less certain, although two other weak metal-carbon stretching bands are observed for Mo and W complexes. It is fortunate that the band for which assignment appears unequivocal involves the stretch of equatorial carbonyls, which as has been observed earlier, are also most affected by changes in ligand basicity in (amine)-$W(CO)_5$ complexes and which have the greater likelihood to dissociate in substitution reactions which proceed *via* ligand-independent rate laws.[30]

Changes in frequency as a function of the nature of the ligand are illustrated in Figure 2, in which νCO(E) is plotted *vs.* νMC(E) for twenty-seven

(29) Poilblanc R. and Bigorgne M., *Bull. Soc. Chim. France*, 1301 (1962).
(30) Dokiya M., Johnston R.D., and Basolo F., *Inorg. Chem.*, 9, 996 (1970).

complexes of the type $LW(CO)_5$. It is seen that the frequency of the M-C strech is strongly related to the identity of the donor atom in L, and that the expected reciprocal relationship between νCO expected on the basis of a dominant π–bonding influence on νMC is observed only within series of complex containing the same donor atom. If it is assumed that changes in M-C stretching frequencies reflect changes in the strengths of metal-carbon bonds (see later discussion), these results clearly are at variance with a "π–bonding only" interpretation.

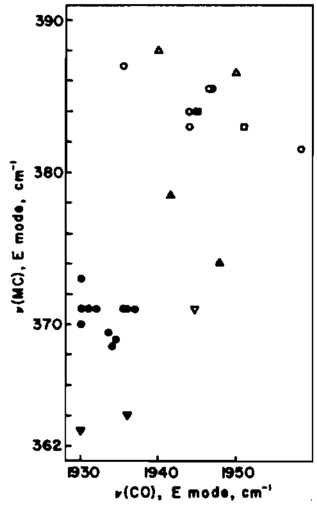

Figure 2. Plot of metal-carbon stretching frequencies (E-mode) *vs.* carbonyl stretching frequencies (E-mode) for various $LW(CO)_5$ complexes.

Donor atoms: nitrogen ● phosphorus ○ arsenic ■ antimony △ bismuth □ oxygen ▼ (acetonitrile ▽)

Table IV. Effect on ν(CO) and ν(MC) of an Increasing Ligand Bonding Interaction.

Ligand Interaction	ν(CO	ν(MC)
σ-bonding (through-metal inductive effect)	no effect	decrease
π-bonding	increase	decrease
direct donation	decrease	increase

The observed trends can, however, be reconciled through consideration of "direct donation" as well as σ– and π–bonding effects. Table IV summarizes the effects on νCO and νMC to be expected with an increase in each of these types of interaction. The observed changes are consistent with the relative influences on carbonyl stretching frequencies, π–bonding > "direct" ≫ σ–bonding, and on metal-carbon stretching frequencies, ("direct" + σ–bonding) > π–bonding. The importance of a direct donation mechanism to the observed metal-carbon stretching frequencies, suggested by the observation that those frequencies are strongly dependent upon the identity of the donor atom of L, is further demonstrated through the relationship between νMC(E) and the Allred-Rochow electronegativities[31] as exhibited in Figure 3. Allred-Rochow electronegativities would appear to be reasonable indicators of the extent of direct donation of L in that they are determined from covalent radii and effective nuclear charges of the donor atoms. However, a better linear plot (not shown) can be obtained through use of Pauling electronegativities.[32] It is also important to note that a similar relationship holds between νMC(E) and νMC-(A_1, radial) for $XMn(CO)_5$ (X = Cl, Br, I)[33] and the Allred-Rochow electronegativities for X.

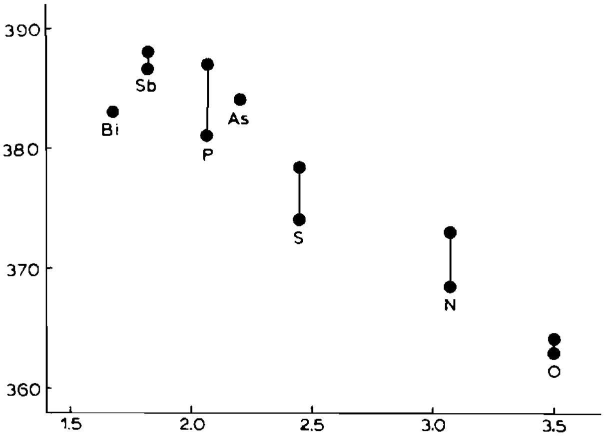

Figure 3. Plot of Metal-Carbon Stretching Frequencies (E-mode) *vs.* Allred-Rochow electronegativities of donor atoms for $LW(CO)_5$

Ordinate: Metal-Carbon stretching frequency, E-mode, cm⁻¹
Abscissa: Allred-Rochow X.

Further, no plausible combination of ligand-to-metal σ– and π–bonding can be employed to rationalize the fact that the lowest metal-carbon stretching frequencies are observed for ligands bonding through oxygen. Studies of metal-carbon stretching frequencies in various media (*e. g.*, Table V) indicate that solvent effects (see Experimental Section) are relatively unimportant and could not account for the differences observed between νMC(E) for amines and oxygen-containing L.

While consideration of the bonding effects as described in the above discussion would appear qualita-

Table V. Medium Effects on the Metal-Carbon Stretching Mode (E Symmetry) in $LW(CO)_5$ Complexes.

Medium	L=CO	Ph_3P	Ph_3Sb	$S_6H_{11}NH_2$
		νMC (cm⁻¹)		
iso-octane	374(11) [a]	384(9)	385(9)	372(10)
methylene chloride	372(21)	382(15)	386(13)	371(24)
Nujol	374(23)	383(12)	385(9)	369(19)
CsI pellet	...	383(13)	384(15)	367(19)

[a] Band widths at half intensity (cm⁻¹) given in parentheses.

---

(31) Allred A.L. and E.G. Rochow, *J. Inorg. Nucl. Chem.*, 5, 264 (1968); Little E.J. and Jones M.M., *J. Chem. Educ.*, 37, 231 (1960).

(32) Pauling L., « The Nature of the Chemical Bond », Third Ed., Cornell University Press, Ithaca, N.Y., 1960, p. 93.

(33) Butler I.S. and Spendjian H.K., *Can J. Chem.*, 47, 4117 (1969); Ugo R., Cenini S., and Bonati F., *Inorg. Chim. Acta*, *1*, 451 (1967).

tively to explain the observed trends in carbonyl and metal-carbon stretching frequencies, it must be pointed out that there is no necessary relationship between the stretching frequencies and the corresponding bond strengths.[34]

Further, there is a likelihood of strong coupling between the metal-carbon stretching mode (E) and metal-carbon-oxygen deformation modes of the same symmetry.[35] It is not possible to gauge changes in the extent of coupling as a function of changes in ligand bonding properties in the absence of Raman data to assist in the assignment of δ MCO. However, the observed reactivities *via* dissociative paths as a function of the donor atom in substitution products of the Group VIB metal carbonyls, and also in XMn(CO)$_5$ complexes (X = Cl, Br, I)[36] parallel trends in metal-carbon stretching frequencies. Thus it may reasonably be concluded that coupling effects may be neglected, and that the ground state properties of metal carbonyl derivatives exert a major influence on their reactivity *via* dissociative paths.

Acknowledgments. Support of this research by the National Science Foundation under Grant GP-16095, and the Faculty Research Fund of North Texas State University is gratefully acknowledged. We also thank Arapahoe Chemicals, Division of Syntex Corp., Boulder, Colorado for generous gifts of PPh$_2$(OBu) and PPh(OBu)$_2$, and Professor J.J. Turner for valuable discussions.

---

[34] See, *e. g.*, Basolo F. and Pearson R.G., « Mechanisms of Inorganic Reactions », Second Ed., John Wiley and Sons, Inc., New York, 1967, p. 539.

[35] On the basis of symmetry there can be no coupling between the metal-carbon stretching mode (E) and the metal-ligand vibration (of A_1 symmetry).

[36] Angelici R.J. and Basolo F., *J. Amer. Chem. Soc.*, *84*, 2495 (1962).