

midal monobromo complex or the square-planar dibromide, in the ratio of approximately one paramagnetic complex to three diamagnetic entities. Calculated on this basis, the magnetic moment per octahedral nickel ion has the very rational value of 3.1 BM. Wetting the crystal serves to destroy the paramagnetism without greatly altering the crystal structure. This suggests a mechanism for weakening the bromide ion-nickel

interaction, perhaps through hydrogen bonding as suggested by Melson.¹⁸

Acknowledgment.—This investigation was supported by U. S. Public Health Service Grant GM-10040 from the National Institute of General Medical Sciences. This financial assistance is deeply appreciated.

(18) G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 4830 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF GEORGIA, ATHENS, GEORGIA

"Mixed" Complexes of Group VIb Metal Carbonyls

BY LARRY WAYNE HOUK AND GERARD R. DOBSON

Received May 4, 1966

Forty-nine new "mixed" derivatives—which contain two different noncarbonyl substituent groups—of the group VIb metal carbonyls are reported. These are of the types $M(\text{CO})_3\text{X}_2\text{Y}$ and $M(\text{CO})_2\text{X}_2\text{Y}_2$ where $M = \text{Cr, Mo, W}$; $\text{X}_2 = 2,2'$ -dipyridyl (dipy) or *o*-phenanthroline (phen); and $\text{Y} =$ various monodentate Lewis bases. Carbonyl stretching frequencies for many derivatives containing strongly π -accepting Y ligands yield complex Cotton-Kraihanzel force constants; real force constants may be obtained if the two physically different *cis*-CO-CO interactions are differentiated in a physically reasonable way. Evidence is presented that *N,N'*-dimethylformamide (DMF) and acetamide exhibit "normal" coordination through oxygen in the complexes $\text{Mo}(\text{CO})_3(\text{phen})(\text{DMF})$ and $\text{Mo}(\text{CO})_3(\text{phen})(\text{acetamide})$.

Introduction

"Mixed" derivatives—those containing two different noncarbonyl substituent groups—were among the first reported derivatives of the group VIb metal carbonyls^{1,2} but had been little further studied until rather recently. Two types are known: *cis*- $M(\text{CO})_3\text{X}_2\text{Y}$ complexes, where $M = \text{Cr, Mo, or W}$; X_2 is 2,2'-dipyridyl (dipy) or *o*-phenanthroline (phen); and Y is a monodentate Lewis base, and the more highly substituted $M(\text{CO})_2\text{X}_2\text{Y}_2$, in which the two Y ligands evidently occupy *trans* sites. Among Y ligands for which derivatives have been reported are pyridine (py),¹⁻⁵ ammonia,³ triphenylphosphine,^{4,5} and several phosphites.^{5,6} The trisubstituted complexes are of particular interest in that CO stretching spectra are readily interpretable through consideration of the differing bonding properties of the substituent groups,⁵ thus rendering possible an *internal* comparison of bonding properties for two different ligands. Further, application of the secular equations of Cotton and Kraihanzel^{7,8} to the determination of CO stretching and CO-CO interaction force constants has led, for $\text{Mo}(\text{CO})_3(\text{dipy})[\text{P}(\text{OC}_2\text{H}_5)_3]$ and $\text{Mo}(\text{CO})_3(\text{phen})[\text{P}(\text{OC}_2\text{H}_5)_3]$, to complex roots.⁵ These considerations

have prompted this more comprehensive investigation of mixed derivatives.

Experimental Section

Complexes of the types $M(\text{CO})_3\text{X}_2\text{Y}$ and $M(\text{CO})_2\text{X}_2\text{Y}_2$ were prepared through direct action of excess monodentate ligand Y on $M(\text{CO})_4\text{X}_2$ under nitrogen in a refluxing common solvent; preparative methods have been described in detail elsewhere.⁵ Physical constants for derivatives (color, CO stretching frequencies, and, where it was possible to obtain solution spectra, CO stretching and CO-CO interaction force constants) are given in Tables I and II. Also listed are the solvents in which the reactions were carried out and the reaction times. Infrared spectra were recorded on a Perkin-Elmer Model 421 grating spectrophotometer and were calibrated against the known bands of polystyrene. For certain derivatives which decomposed rapidly in solution, mull (Nujol) spectra were obtained. Because of the large number of derivatives reported here, and their similarity as to type, chemical analyses were not obtained for all; representative analyses are given in Table III. Identification of the remaining complexes was made on the basis of infrared data. The derivatives are all highly colored crystalline or microcrystalline solids, soluble in polar organic solvents (sometimes with decomposition), virtually insoluble in nonpolar organic solvents, and insoluble in water.

No evidence for complex formation was obtained for the monodentate ligands *trans*-2-butene, stilbene, urea, diphenylacetylene, chloroacetonitrile, dichloroacetonitrile, trichloroacetonitrile, and *n*-butyl ether.

Discussion

$M(\text{CO})_3\text{X}_2\text{Y}$ Derivatives. Solution Spectra.—Assignments of CO stretching modes for mixed derivatives have been discussed elsewhere.⁵ For three ligands of equivalent bonding properties, on the basis of the local symmetry of the carbonyl groups (C_{3v}), two bands, $A_1 + E$, the *E* mode being the stronger, low-energy

- (1) W. Hieber and F. Mühlbauer, *Z. Anorg. Allgem. Chem.*, **221**, 337 (1935).
- (2) W. Hieber and E. Romberg, *ibid.*, **221**, 349 (1935).
- (3) H. Behrens and N. Harder, *Chem. Ber.*, **97**, 433 (1964).
- (4) M. H. B. Stiddard, *J. Chem. Soc.*, 756 (1963).
- (5) L. W. Houk and G. R. Dobson, *ibid.*, 317 (1966).
- (6) R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **87**, 5568 (1965); J. R. Graham and R. J. Angelici, *ibid.*, **87**, 5590 (1965).
- (7) F. A. Cotton and C. S. Kraihanzel, *ibid.*, **84**, 4432 (1962).
- (8) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

TABLE I
 MIXED TRISUBSTITUTED DERIVATIVES OF $M(\text{CO})_5$

Compound	Color	Preparation			CO stretching frequencies, cm^{-1}				Force constants, mdynes/A		
		Solvent	Time	Medium	A'(2)	A'(1)	E	A''	k_1	k_2 (c)	k_3
$\text{Cr}(\text{CO})_5(\text{dipy})(\text{C}_6\text{H}_5\text{N})$	Green-black	$\text{C}_6\text{H}_5\text{N}$	4 hr	$\text{C}_6\text{H}_5\text{N}$	1897		1781		13.38		0.58
$\text{Cr}(\text{CO})_5(\text{phen})(\text{C}_6\text{H}_5\text{N})^1$	Black	$\text{C}_6\text{H}_5\text{N}$	2 hr	$\text{C}_6\text{H}_5\text{N}$	1898		1780		13.38		0.58
$\text{Cr}(\text{CO})_5(\text{dipy})[(\text{C}_6\text{H}_5)_3\text{P}]$	Purple-black	Xylene	2 hr	CHCl_3	1912	1824		1786		(0.91)	
$\text{Cr}(\text{CO})_5(\text{phen})[(\text{C}_6\text{H}_5)_3\text{P}]$	Purple-black	Xylene	2 hr	CHCl_3	1916	1826		1788		(0.93)	
$\text{Cr}(\text{CO})_5(\text{phen})[(\text{C}_2\text{H}_5\text{O})_3\text{P}]$	Purple-black	Toluene	20 min	CHCl_3	1921	1829		1785		(0.86)	
$\text{Cr}(\text{CO})_5(\text{dipy})[(\text{C}_2\text{H}_5\text{O})_3\text{P}]$	Purple-black	Toluene	20 min	CHCl_3	1922	1830		1786		(0.86)	
$\text{Mo}(\text{CO})_5(\text{phen})(\text{C}_6\text{H}_{11}\text{NH}_2)$	Purple-black	Xylene	2 hr	CH_3NO_2	1901		1770		13.30		0.65
$\text{Mo}(\text{CO})_5(\text{dipy})(\text{CH}_3\text{CN})$	Purple-black	CH_3CN	2 hr	CH_3CN	1910		1787		13.51		0.61
$\text{Mo}(\text{CO})_5(\text{phen})(\text{CH}_3\text{CN})$	Purple-black	CH_3CN	2 hr	CH_3CN	1910		1787		13.51		0.61
$\text{Mo}(\text{CO})_5(\text{phen})[(\text{C}_6\text{H}_{17})_3\text{P}]$	Red-black	Xylene	1 hr	CHCl_3	1912	1813		1786	14.11	13.40	0.52
$\text{Mo}(\text{CO})_5(\text{phen})[(n\text{-C}_4\text{H}_9)_3\text{P}]$	Red-black	Xylene	1 hr	CHCl_3	1913	1813		1786	14.11	13.40	0.52
$\text{Mo}(\text{CO})_5(\text{phen})[(\text{C}_6\text{H}_5)_3\text{P}]^5$	Violet	Xylene	1 hr	CHCl_3	1919	1820		1788	14.31	13.42	0.51
$\text{Mo}(\text{CO})_5(\text{phen})[(\text{C}_6\text{H}_5)_3\text{As}]$	Purple-black	Xylene	2 hr	CHCl_3	1917	1816		1788	14.19	13.44	0.53
$\text{Mo}(\text{CO})_5(\text{phen})[(i\text{-C}_4\text{H}_7\text{O})_3\text{P}]$	Purple-black	Xylene	1 hr	CHCl_3	1925	1825		1787		(0.99)	
$\text{Mo}(\text{CO})_5(\text{phen})[(n\text{-C}_4\text{H}_9\text{O})_3\text{P}]$	Purple-black	Xylene	1 hr	CHCl_3	1927	1829		1789		(0.95)	
$\text{Mo}(\text{CO})_5(\text{phen})[(\text{C}_2\text{H}_5\text{O})_3\text{P}]^5$	Red	Xylene	30 min	CHCl_3	1928	1831		1791		(0.94)	
$\text{Mo}(\text{CO})_5(\text{phen})[(\text{CH}_3\text{O})_3\text{P}]$	Red	Xylene	15 min	CHCl_3	1931	1838		1795		(0.88)	
$\text{Mo}(\text{CO})_5(\text{phen})[(\text{C}_6\text{H}_5\text{O})_3\text{P}]$	Red	Toluene	20 min	CHCl_3	1944	1855		1810		(0.83)	
$\text{Mo}(\text{CO})_5(\text{phen})[(\text{C}_6\text{H}_5\text{O})_2\text{HOP}]$	Red	Xylene	1 hr	CHCl_3	1943	1855		1809		(0.81)	
$\text{Mo}(\text{CO})_5(\text{dipy})[(i\text{-C}_4\text{H}_7\text{O})_3\text{P}]$	Red	Xylene	20 min	CHCl_3	1923	1824		1787	14.54	13.36	0.47
$\text{Mo}(\text{CO})_5(\text{dipy})[(n\text{-C}_4\text{H}_9\text{O})_3\text{P}]$	Purple	Xylene	30 min	CHCl_3	1926	1829		1789		(0.94)	
$\text{Mo}(\text{CO})_5(\text{dipy})[(\text{CH}_3\text{O})_3\text{P}]$	Red	Xylene	15 min	CHCl_3	1930	1836		1793		(0.88)	
$\text{Mo}(\text{CO})_5(\text{dipy})[(\text{C}_6\text{H}_5\text{O})_3\text{P}]$	Red	Xylene	15 min	CHCl_3	1943	1855		1809		(0.81)	
$\text{Mo}(\text{CO})_5(\text{dipy})[(\text{C}_6\text{H}_5\text{O})_2\text{HOP}]$	Red	Xylene	1 hr	CHCl_3	1944	1855		1807		(0.79)	
$\text{Mo}(\text{CO})_5(\text{phen})(n\text{-C}_4\text{H}_9\text{NH}_2)$	Purple-black	Xylene	3 hr	Mull	1885	1765		1743			
$\text{Mo}(\text{CO})_5(\text{phen})[(\text{C}_2\text{H}_5)_2\text{NH}]$	Purple-black	Mesitylene	3 hr	Mull	1891	1769		1742			
$\text{Mo}(\text{CO})_5(\text{phen})[(\text{C}_6\text{H}_5)_3\text{Sb}]$	Purple-black	Xylene	2 hr	Mull	1914	1814		1792			
$\text{Mo}(\text{CO})_5(\text{phen})[(\text{C}_6\text{H}_5)_3\text{Bi}]$	Black	Xylene	2 hr	Mull	1889	1826		1770			
$\text{Mo}(\text{CO})_5(\text{phen})[(\text{C}_6\text{H}_5)_2\text{Se}]$	Red	Mesitylene	1 hr	Mull	1887	1824		1760			
$\text{Mo}(\text{CO})_5(\text{phen})(\text{DMF})$	Purple-black	Xylene	2 hr	Mull	1898	1782		1749			
$\text{Mo}(\text{CO})_5(\text{phen})[\text{CH}_3\text{CONH}_2]$	Purple-black	Xylene	2 hr	Mull	1901	1769		1739			
$\text{Mo}(\text{CO})_5(\text{phen})[\text{CH}_3\text{CSNH}_2]$	Violet	Xylene	4 hr	Mull	1901	1793		1760			
$\text{Mo}(\text{CO})_5(\text{phen})[(\text{NH}_2)_2\text{CS}]$	Red-brown	Xylene	4 hr	Mull	1905	1781		1760			
$\text{W}(\text{CO})_5(\text{dipy})(\text{C}_6\text{H}_5\text{N})^3$	Black	$\text{C}_6\text{H}_5\text{N}$	2 hr	$\text{C}_6\text{H}_5\text{N}$	1892		1773		13.28		0.59
$\text{W}(\text{CO})_5(\text{phen})(\text{C}_6\text{H}_5\text{N})^2$	Black	$\text{C}_6\text{H}_5\text{N}$	2 hr	$\text{C}_6\text{H}_5\text{N}$	1894		1780		13.36		0.56
$\text{W}(\text{CO})_5(\text{dipy})[(\text{C}_6\text{H}_5)_3\text{P}]$	Purple-black	Xylene	2 hr	CHCl_3	1911	1817		1783	14.31	13.30	0.46
$\text{W}(\text{CO})_5(\text{phen})[(\text{C}_6\text{H}_5)_3\text{P}]$	Purple-black	Xylene	2 hr	CHCl_3	1912	1818		1783	14.38	13.28	0.45
$\text{W}(\text{CO})_5(\text{dipy})[(\text{C}_2\text{H}_5\text{O})_3\text{P}]$	Purple-black	Xylene	3 hr	CHCl_3	1917	1824		1785		(0.93)	
$\text{W}(\text{CO})_5(\text{phen})[(\text{C}_2\text{H}_5\text{O})_3\text{P}]$	Purple-black	Xylene	2 hr	CHCl_3	1921	1828		1787		(0.90)	

 TABLE II
 MIXED TETRASUBSTITUTED DERIVATIVES OF $M(\text{CO})_5$

Compound	Color	Preparation		Frequencies (CHCl_3), cm^{-1}		Force constants, mdynes/A	
		Solvent	Reflux time, hr	A_1	B_1	k_1	k_2
$\text{Mo}(\text{CO})_2(\text{phen})[(\text{C}_6\text{H}_{17})_3\text{P}]_2$	Blue-black	Mesitylene	30	1802	1722	12.54	0.57
$\text{Mo}(\text{CO})_2(\text{phen})[(\text{C}_4\text{H}_9)_3\text{P}]_2$	Blue-black	Mesitylene	36	1804	1724	12.57	0.57
$\text{Mo}(\text{CO})_2(\text{phen})[(i\text{-C}_4\text{H}_7\text{O})_3\text{P}]_2$	Purple-black	Xylene	3	1822	1739	12.81	0.60
$\text{Mo}(\text{CO})_2(\text{phen})[(n\text{-C}_4\text{H}_9\text{O})_3\text{P}]_2$	Purple-black	Xylene	3	1829	1745	12.90	0.61
$\text{Mo}(\text{CO})_2(\text{phen})[(\text{CH}_3\text{O})_3\text{P}]_2$	Purple-black	Xylene	8	1837	1755	13.03	0.60
$\text{Mo}(\text{CO})_2(\text{phen})[(\text{C}_6\text{H}_5\text{O})_3\text{P}]_2$	Purple	Xylene	4	1872	1790	13.54	0.61
$\text{Mo}(\text{CO})_2(\text{dipy})[(i\text{-C}_4\text{H}_7\text{O})_3\text{P}]_2$	Purple-black	Xylene	2	1821	1739	12.80	0.59
$\text{Mo}(\text{CO})_2(\text{dipy})[(n\text{-C}_4\text{H}_9\text{O})_3\text{P}]_2$	Purple-black	Xylene	3	1827	1746	12.90	0.58
$\text{Mo}(\text{CO})_2(\text{dipy})[(\text{CH}_3\text{O})_3\text{P}]_2$	Purple-black	Xylene	4	1838	1755	13.04	0.61
$\text{Mo}(\text{CO})_2(\text{dipy})[(\text{C}_6\text{H}_5\text{O})_2\text{HOP}]_2$	Dark red	Xylene	8	1870	1788	13.52	0.60
$\text{Mo}(\text{CO})_2(\text{dipy})[(\text{C}_6\text{H}_5\text{O})_3\text{P}]_2$	Purple	Xylene	4	1871	1788	13.52	0.62
$\text{Cr}(\text{CO})_2(\text{phen})[(\text{C}_2\text{H}_5\text{O})_3\text{P}]_2$	Purple-black	Xylene	3	1827	1743	12.87	0.61
$\text{Cr}(\text{CO})_2(\text{dipy})[(\text{C}_2\text{H}_5\text{O})_3\text{P}]_2$	Purple-black	Mesitylene	8	1827	1743	12.87	0.61
$\text{Cr}(\text{CO})_2(\text{dipy})[(\text{C}_6\text{H}_5)_3\text{P}]_2$	Green-brown	Mesitylene	8	1785	1720	12.41	0.46
$\text{W}(\text{CO})_2(\text{phen})[(\text{C}_2\text{H}_5\text{O})_3\text{P}]_2$	Purple-black	Mesitylene	4	1825	1740	12.83	0.62

mode, are expected. For $M(\text{CO})_5\text{X}_2\text{Y}$ complexes in which the bidentate ligand is phen or dipy, the net charge-releasing ability of the ligands is usually in the

order $\text{X}_2 > \text{Y}$, and the low-energy E bond when split is split into two components, $A' + A''$ (C_s symmetry), of which the latter is of lower energy.⁵ As is generally

TABLE III
ANALYSES

Compound	—% carbon—		—% hydrogen—	
	Calcd	Found	Calcd	Found
Mo(CO) ₃ (phen)[(<i>i</i> -C ₃ H ₇ O) ₃ P]	50.70	50.68	5.15	5.31
Mo(CO) ₃ (phen)[(<i>n</i> -C ₄ H ₉ O) ₃ P]	53.11	53.10	5.79	5.94
Mo(CO) ₃ (phen)[(CH ₃ O) ₃ P]	44.54	44.18	3.54	3.65
Mo(CO) ₃ (dipy)[(<i>i</i> -C ₃ H ₇ O) ₃ P]	48.53	48.67	5.38	5.28
Mo(CO) ₃ (dipy)[(C ₆ H ₅ O) ₃ P]	57.59	57.51	3.59	3.95
Mo(CO) ₃ (dipy)[(<i>n</i> -C ₄ H ₉ O) ₃ P]	51.19	52.08	6.03	6.20
Cr(CO) ₃ (phen)[(C ₆ H ₅) ₃ P]	68.50	68.22	4.02	4.12
W(CO) ₃ (phen)[(C ₆ H ₅) ₃ P]	55.79	55.91	3.27	3.44
W(CO) ₃ (dipy)[(C ₆ H ₅) ₃ P]	54.24	54.37	3.38	3.53
Cr(CO) ₃ (dipy)[(C ₂ H ₅ O) ₃ P]	49.78	49.54	5.07	5.00
Cr(CO) ₃ (phen)[(C ₂ H ₅ O) ₃ P]	52.28	53.05	4.82	4.75
Mo(CO) ₃ (phen)[C ₆ H ₁₁ NH ₂]	54.90	54.89	4.62	4.64
Mo(CO) ₃ (phen)[<i>n</i> -C ₄ H ₉ NH ₂]	52.66	52.81	4.43	4.63
Mo(CO) ₃ (phen)[DMF]	49.89	50.16	3.50	3.84
Mo(CO) ₃ (phen)[(NH ₂) ₂ CS]	44.04	44.28	2.78	2.93
Mo(CO) ₃ (phen)[(C ₆ H ₅) ₃ Sb]	55.56	55.37	3.26	3.40
Mo(CO) ₃ (phen)[CH ₃ CSNH ₂]	46.90	45.78	3.02	2.87
Mo(CO) ₃ (phen)[CH ₃ CN]	50.88	49.53	2.77	2.95
Mo(CO) ₃ (dipy)[CH ₃ CN]	47.75	48.10	2.95	3.80
Mo(CO) ₂ (phen)[(<i>i</i> -C ₃ H ₇ O) ₃ P] ₂	51.33	51.33	6.74	6.20
Mo(CO) ₂ (phen)[(CH ₃ O) ₃ P] ₂	41.39	40.39	4.52	5.00
Mo(CO) ₂ (phen)[(<i>n</i> -C ₄ H ₉ O) ₃ P] ₂	54.79	54.40	7.52	7.61
Mo(CO) ₂ (dipy)[(C ₆ H ₅ O) ₃ P] ₂	62.07	61.11	4.13	4.13
Mo(CO) ₂ (phen)[(C ₆ H ₅ O) ₃ P] ₂	63.02	61.44	4.03	4.06
Mo(CO) ₂ (dipy)[(C ₆ H ₅ O) ₂ (HO)P] ₂	55.67	55.79	3.90	4.02
Mo(CO) ₂ (dipy)[(<i>i</i> -C ₃ H ₇ O) ₃ P] ₂	49.72	50.45	6.97	7.38
Mo(CO) ₂ (dipy)[(<i>n</i> -C ₄ H ₉ O) ₃ P] ₂	53.45	52.88	7.74	7.70
Mo(CO) ₂ (dipy)[(CH ₃ O) ₃ P] ₂	38.86	39.11	4.72	4.93
Cr(CO) ₂ (phen)[(C ₂ H ₅ O) ₃ P] ₂	50.31	50.57	6.18	6.14
Cr(CO) ₂ (dipy)[(C ₂ H ₅ O) ₃ P] ₂	48.31	48.11	6.43	6.53

seen (Table I), the more dissimilar the bonding properties of X₂ and Y,⁹ the greater the splitting of the E mode and the higher the CO stretching frequencies and force constants. For phosphite derivatives, changes in force constants and splitting of the E mode are in accord with the inductive influences of R groups bonded to oxygen. It has already been shown⁵ that in dipy-py and phen-py mixed complexes the E mode is unsplit, and thus it has been inferred that dipy, phen, and py have similar bonding characteristics. For mixed derivatives reported here the same observations may be made and conclusions drawn for dipy and phen mixed complexes containing acetonitrile and cyclohexylamine (Table I). For the cyclohexylamine complex it is possible, however, that two close-lying bands were unresolvable owing to solvent band broadening. The spectrum of a typical M(CO)₃X₂Y complex, showing splitting of the E mode, is given in Figure 1.

Application of the secular equations of Cotton and Kraihanzel^{7,8} toward the determination of force constants for the mixed trisubstituted derivatives leads, for ligands commonly regarded as strong π acceptors, *e.g.*, some phosphines and most phosphites, to complex roots, whereas real roots are obtained for ligands closely approaching dipy and phen in their bonding properties. This observation suggests that the failure of the secular equations may, at least in part, be due to

(9) W. D. Horrocks, Jr., and R. C. Taylor (*Inorg. Chem.*, **2**, 723 (1963)) list Lewis base ligands in qualitative order of charge-releasing ability; this list was compiled from CO stretching frequencies for similar derivatives; the order of charge-releasing ability obtained here, internally, is in agreement with the "spectrochemical series" of Horrocks and Taylor.

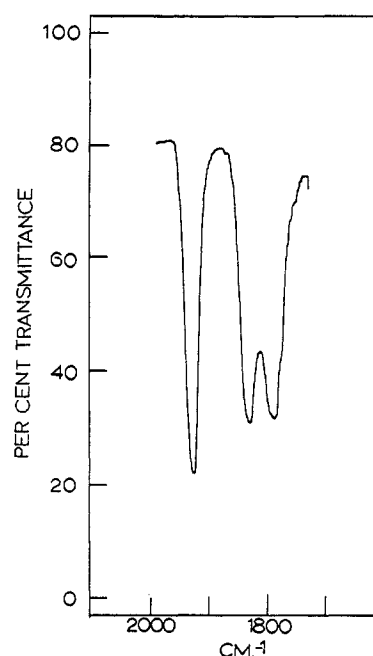


Figure 1.—Infrared spectrum, CO stretching region, for Mo(CO)₃(dipy)[P(C₆H₅)₃] in CHCl₃.

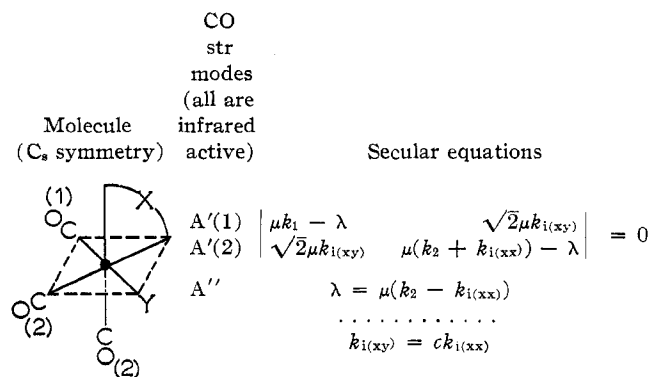


Figure 2.—Modified secular equations and related information for M(CO)₃X₂Y molecules (terms as defined in ref 7).

a failure to distinguish between two physically different *cis*-CO-CO interaction constants. These two, $k_{i(xx)}$, involving the coupling of two carbonyls each *trans* to a nitrogen, and $k_{i(xy)}$, for which one carbonyl is *trans* to a nitrogen and the second *trans* to the phosphorus,¹⁰ may differ appreciably as differences in the bonding properties of dipy or phen and the phosphine or phosphite become more pronounced, *i.e.*, with the increased π -accepting ability of the phosphorus-containing ligand. Further, it is to be expected that $k_{i(xy)} < k_{i(xx)}$ since the more strongly π -accepting phosphorus atom is better able to compete with the carbonyls for metallic $d\pi$ electrons, thus diminishing the interaction effect.

To determine if the failure to distinguish between two physically different *cis*-CO-CO interactions is a

(10) Considering only π bonding involving the t_{2g} (octahedral symmetry) metallic orbitals, two $k_{i(xy)}$ carbonyls mutually share one orbital with a phosphorus and a nitrogen, one shares an orbital with a nitrogen, a phosphorus, and a carbonyl, and the other shares an orbital with two nitrogens and a carbonyl. Two $k_{i(xx)}$ carbonyls mutually share one orbital with two nitrogens, and each shares an orbital with a nitrogen, a phosphorus, and a carbonyl.

factor in the breakdown of the Cotton secular equations, they have been modified to include the two interaction force constants $k_{i(xy)}$ and $k_{i(xx)}$ (Figure 2). As has often been the case, the number of parameters within the Cotton-Kraihanzel secular equations is limited by the number of experimental carbonyl stretching frequencies available; one would surmise that for this reason the approximation $k_{i(xx)} = k_{i(xy)}$ was explicitly adopted in the first place. To the authors' knowledge there is no way *accurately* to evaluate c ($=k_{i(xy)}/k_{i(xx)}$) within the framework of the Cotton-Kraihanzel approximations.¹¹ Therefore no values of c have been assumed, but instead the roots to the "modified" equations have been evaluated for all plausible values of c . It has been found that there is a value of c (<1) at which the roots become and remain real (Table I). Moreover, these values decrease in the expected order as the qualitative order of π -accepting ability of the phosphorus-containing ligand increases.⁹ Real force constants can thus be obtained by adjusting c in a physically reasonable way for Y ligands of varying bonding ability: this suggests that failure to distinguish between the two *cis* interaction force constants contributes in a major way to the failure of the original secular equations.

It should be noted that Cotton secular equations have been applied to representative $Mn(CO)_5Y_2X$ complexes, and in all cases real roots were obtained.⁸ This might be expected, however, since carbonyl stretching frequencies for the Mn complexes are *ca.* 150 cm^{-1} higher than for the corresponding group VIb derivatives: metal-ligand "back bonding" thus is much weaker in the Mn complexes, minimizing differences in the *cis* interaction constants.

It should also be pointed out that for octahedral derivatives of the types $M(CO)_5X$ and *cis*- $M(CO)_4X_2$, *cis* interaction force constants may be distinguished in a manner analogous to that outlined above. Thus for *cis*- $M(CO)_4X_2$ molecules three pairs of carbonyls are *trans* to a carbonyl and an X ligand, while a fourth pair is *trans* to two X ligands. For these molecules

(11) One may, considering the bonding influence of ligands *trans* to the carbonyls in question to be of primary importance, roughly estimate c from the interaction force constants for *cis*- $M(CO)_5L_3$ complexes containing the ligands X and Y or containing ligands closely approaching X and Y in bonding properties. For these molecules the carbonyls mutually share one orbital with two ligands, and each shares an orbital with a CO and two ligands (compare ref 10). Thus one might use the interaction force constants for $Mo(CO)_5(py)_3$ and $Mo(CO)_5(phosphite)_3$ to approximate c for $Mo(CO)_5(dipy)(phosphite)$ or $Mo(CO)_5(phen)(phosphite)$ through use of the relationship $c = k_{i(xy)}/k_{i(xx)} = 1/2(k_{ix} + k_{iy})/k_{ix}$, where k_{ix} and k_{iy} are the interaction force constants for $Mo(CO)_5(py)_3$ and $Mo(CO)_5(phosphite)_3$. This approximation has been applied to nine cases for which the requisite interaction force constants were available (ref 8) or could be obtained through preparation of the necessary *cis* trisubstituted derivative (through displacement of cycloheptatriene from (cycloheptatriene) $Mo(CO)_3$ by the appropriate ligand). For all nine cases real roots were obtained when the value of c was inserted into the modified secular equations. Thus this approximate evaluation of c as suggested has proven adequate for those cases in which it has been applied. Fortunately, a choice of a value of c is not extremely critical to the actual values of the real roots obtained. As an example, the effect of this modification upon the force constants for $Mo(CO)_5(dipy)P(n-C_4H_9)_3$, whose carbonyl stretching frequencies yield real roots with both the original and modified secular equations, will be given. The hitherto unreported carbonyl stretching frequencies for $Mo(CO)_5(P(n-C_4H_9)_3)_3$ are 1935 and 1837 cm^{-1} (in heptane); $k_1 = 0.49$. For $Mo(CO)_5(py)_3$, $k_1 = 0.65$ (ref 5) and thus $c = 0.88$. The calculated force constants are: original, $k_1 = 14.11$, $k_2 = 13.41$, $k_3 = 0.53$; modified, $k_1 = 13.96$, $k_2 = 13.48$, $k_{i(xx)} = 0.60$, $k_{i(xy)} = 0.53$ mdyne/A.

the possibility exists that complex Cotton-Kraihanzel force constants might arise. For example, in the determination of band assignments for the (diphos)- $W(CO)_4$ molecule¹² (C_{2v} symmetry), two possible assignments differ only in the interchange of two bands *ca.* 11 cm^{-1} apart⁷

Assignment	ν_{CO}, cm^{-1}			
	A ₁ (1)	A ₁ (2)	B ₁	B ₂
(1)	2016	1901	1912	1876
(2)	2016	1912	1901	1876

Of the two assignments, assignment 1 was rejected because it yielded complex force constants; assignment 2 was thus selected as the correct one by default. Although rough band intensity or band position arguments may be cited in support of either assignment,¹³ it would appear futile to employ qualitative arguments to assign two almost accidentally degenerate bands of nearly equal intensity. It should be clear, however, that assignment 1 cannot be rejected merely because it fails to yield real roots.

Mull Spectra.—Several of the reported derivatives decompose in organic solvents transparent to infrared radiation in the region of interest, in which they are soluble. For these, mull spectra were obtained. In many mull spectra the E mode (C_{3v}) is split, even for some complexes for which the solution spectra show no splitting. Thus, splitting in the solid state may be attributed, in some instances at least, to crystal effects, and inferences as to the relative bonding properties of substituent groups from the magnitude of splitting of the E mode would be hazardous at best. Nonetheless, mull spectra for acetamide and N,N'-dimethylformamide (DMF) mixed derivatives are of particular interest inasmuch as these are the first amide derivatives of the group VIb metal carbonyls to be fully characterized.

Cotton⁸ has interpreted the anomalously low metal carbonyl CO stretching frequencies for $M(CO)_5$ -(DMF) (and analogous N-methylformamide complexes) and $W(CO)_4(DMF)_2$ (observed only in solution)¹⁴ and those for the corresponding amine derivatives as an indication that the ligands in these complexes function as π donors. Similar spectral effects may be noted for thiourea and thioacetamide derivatives as compared to R_2S ligands.¹⁵ Mull spectra for $Mo(CO)_3(phen)Y$ derivatives of DMF and amines (Table I) are, however, similar, with the frequencies of the DMF derivatives slightly higher; mull metal carbonyl CO stretching frequencies for $M(CO)_5X_2Y$ complexes appear, in general, to be rather insensitive

(12) diphos = bis(diphenylphosphino)ethane.

(13) L. E. Orgel (*Inorg. Chem.*, **1**, 25 (1962)) has cited band intensity arguments in support of assignment 2 for (diphos) $Mo(CO)_4$. We have resolved the two bands in question and find them to be very nearly of the same intensity. Greater decreases in carbonyl stretching frequencies are expected, in going from *cis*-(PF_3)₂ $Mo(CO)_4$, for which unequivocal band assignments have been made (H. Haas, Dissertation, Florida State University, Tallahassee, Fla., 1965), to (diphos) $Mo(CO)_4$, for the A₁(2) and B₂ modes, which involve the vibration of carbonyls *trans* to the phosphines, than for A₁(1) and B₁, which involve carbonyls *cis* to the phosphines. Assignment 1 is in better agreement with this expectation.

(14) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *Inorg. Chem.*, **2**, 323 (1963).

(15) F. A. Cotton and F. Zingales, *ibid.*, **1**, 145 (1962).

to the bonding properties of the Y ligand (Table I). Amide carbonyl stretching frequencies for $\text{Mo}(\text{CO})_3(\text{phen})(\text{acetamide})$ and $\text{Mo}(\text{CO})_3(\text{phen})(\text{DMF})$ are somewhat lowered from the free ligand values [1665 (mull) and 1670 (neat) cm^{-1} , respectively, for the free ligands *vs.* 1648 and 1647 cm^{-1} (mulls) in the complexes]. Such an effect in mull spectra has been cited as evidence for "normal" coordination through oxygen to the metal in complexes of DMF.^{16,17} A much larger decrease in the amide carbonyl stretching frequencies might be expected were π donation an important factor in bonding.

The diminution of the CO stretching frequencies of metal carbonyls in polar solvents is well known, and the possibility that the low frequencies for $\text{W}(\text{CO})_4(\text{DMF})_2$ in the highly polar DMF are attributable to a solvent effect must be considered. Carbonyl stretching frequencies for a typical disubstituted amine complex $\text{W}(\text{CO})_4(\text{tmen})$ (tmen = N,N,N',N'-tetramethylethylenediamine) are 2003, 1879, 1868, and 1857 cm^{-1} (heptane)¹⁸ and 2003, 1865, 1854, and 1818 cm^{-1} (DMF),¹⁹ while the frequencies for *cis*- $\text{W}(\text{CO})_4(\text{DMF})_2$ are 1997, 1858, 1832, and 1791 cm^{-1} (DMF).¹⁴ It can be seen that although solvent shifts are substantial, they do not appear to be large enough to account for the low frequencies in $\text{W}(\text{CO})_4(\text{DMF})_2$. Unless one is willing to accept two distinct types of bonding in $\text{Mo}(\text{CO})_3(\text{phen})(\text{DMF})$ and the very similar $\text{W}(\text{CO})_4(\text{DMF})_2$, the postulated π donation for amides in group VIb metal carbonyl complexes must be reassessed. The original proposal of π donation was based upon the assumption that CO stretching frequencies in octahedral carbonyl complexes reflect π bonding only and thus that the possibility that differing ligand σ -bonding strengths could result in the observed frequency changes could be discounted.⁸ This assumption was based upon the "symmetry factorability" of t_{2g} and e_g orbitals in the parent carbonyls.⁷ Kettle recently has demonstrated, however, that there can be mixing of σ and π bonding in "octahedral" metal carbonyl derivatives; thus it is entirely possible that σ -bonding properties of ligands can exert an influence on CO stretching frequencies in such complexes.²⁰ An example of such an effect is already in the literature. Abel²¹ has attributed the higher CO stretching frequencies for $\text{Mo}(\text{CO})_3(\text{diglyme})$ ²² than for $\text{Mo}(\text{CO})_3(\text{diethylenetriamine})$ ²³ to the greater electronegativity and thus lower basicity of O compared to N. Neither diglyme nor diethylenetriamine is structurally able to function as a π donor. It has

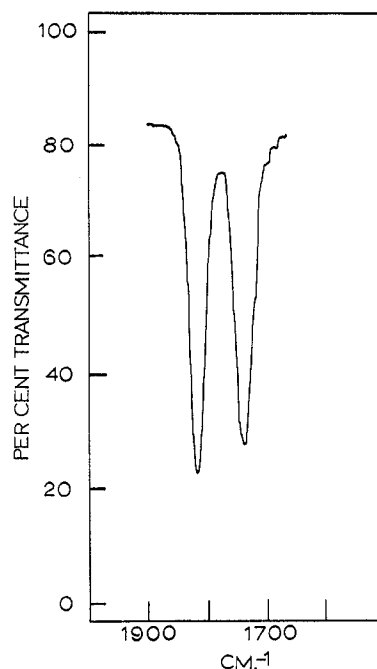


Figure 3.—Infrared spectrum, CO stretching region, for $\text{Mo}(\text{CO})_3(\text{phen})[\text{P}(\text{C}_6\text{H}_5)_3]_2$ in CHCl_3 .

also been shown for amides that partial delocalization of the lone pair of electrons on N greatly enhances the basicity of the oxygen.¹⁴ Thus it is quite reasonable to expect that simple coordinate bonding should yield low frequencies in their metal carbonyl derivatives.

$\text{M}(\text{CO})_3\text{X}_2\text{Y}_2$ Derivatives.—Physical data and preparative information for tetrasubstituted mixed derivatives are given in Table II. It has been proposed on the basis of the directive influences of substituent groups and solubility data that the phosphine and phosphite ligands occupy *trans* sites.⁵ If this is indeed the case, only one type of *cis*-CO-CO interaction is present and the secular equations of Cotton and Kraihanzel⁷ are applicable. Here again CO stretching frequencies and force constants are consistent with commonly held assessments of the bonding properties of various Y ligands. A typical spectrum in the carbonyl stretching region is shown in Figure 3. The higher energy band of the two expected CO stretching vibrations ($A_1 + B_1$, C_{2v} "local" symmetry) has been assigned as the more symmetrical A_1 mode.⁵

Acknowledgments.—Support of this research by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We also thank Diamond Alkali Co. for a gift of chromium hexacarbonyl, Carlisle Chemical Works for gifts of trioctylphosphine and tri-*n*-butylphosphine, Dr. René Poilblanc, Faculté des Sciences, Toulouse, France, for his kindness in providing the infrared spectrum of (tmen) $\text{W}(\text{CO})_4$ in DMF, and the Office of General Research, University of Georgia, for 7094 computer time.

(16) C. D. Schmulbach and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 4484 (1960).

(17) R. S. Drago, D. W. Meek, M. D. Joesten, and L. LaRoche, *Inorg. Chem.*, **2**, 124 (1963).

(18) R. Poilblanc, *Compt. Rend.*, **256**, 4910 (1963).

(19) R. Poilblanc, personal communication.

(20) S. F. A. Kettle, *Inorg. Chem.*, **4**, 1661 (1965).

(21) E. W. Abel, *Quart. Rev. (London)*, **17**, 133 (1963).

(22) R. P. M. Werner and T. H. Coffield, *Chem. Ind. (London)*, 936 (1960).

(23) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).