

Conclusions

On the basis of the experimental data obtained in this study, we have proposed that the fragmentation of these transition metal carbonyl ions occurs by successive removal of neutral CO groups. The clastograms for both the iron and nickel carbonyls are very similar, and, as mentioned above, the peculiar nature of these clastograms appears to be characteristic of these metal carbonyls.

Significantly, no ions of the type which would result from the cleavage of the C-O bonds in these carbonyls were observed, *i.e.*, NiC⁺ and NiO⁺ were not observed.

This further supports the contention that CO groups as such are removed in the successive steps of the fragmentation processes.

We are currently performing the appropriate calculations based on the improved quasi-equilibrium theory¹⁵ in order to test further the proposal concerning the successive loss of CO groups in the anticipation that this approach will either give additional strength to these ideas or show up any fallacy in these contentions.

(15) M. Vestal, A. L. Wahrhaftig, and W. H. Johnston, *J. Chem. Phys.*, **37**, 1276 (1962).

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Vibrational Spectra and Bonding in Metal Carbonyls. III. Force Constants and Assignments of CO Stretching Modes in Various Molecules; Evaluation of CO Bond Orders^{1a}

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Data from the literature for a large number of substituted group VI carbonyls and for some manganese carbonyl halides and their derivatives are treated by the methods described in earlier papers in this series. It is shown how the method can eliminate incorrect assignments in certain cases. A relationship between CO bond orders and CO force constants is delineated and used to deduce, from differences in the calculated CO stretching constants, the changes in CO bond orders. It is also shown that absolute values of the bond orders may be estimated. The relative π acceptor strengths of various ligands are discussed semiquantitatively and it is shown, *inter alia*, that PF₃ is a stronger π -accepting ligand than CO, while ligands such as dimethylformamide and methylformamide are actually π -donors. The relationship of the CO stretching force constants used in this series of papers to more rigorous values is discussed.

I. Introduction

In earlier papers in this series,^{2,3} a method for analyzing and assigning the spectra of CO stretching vibrations in octahedral metal carbonyls has been proposed, tested, and applied to a limited number of substituted group VI carbonyls. The present paper extends the study in the following ways:

(1) Using the method, data from the literature for a large number of diverse compounds are treated. It is shown how the method can eliminate incorrect assignments in certain cases.

(2) A relationship between CO bond orders and CO force constants is delineated and used to deduce, from differences in the calculated CO stretching constants, the changes in CO bond orders. It is also shown that absolute values of the bond orders may be estimated.

(3) The relative π -acceptor strengths of various ligands are discussed semiquantitatively and it is shown, *inter alia*, that PF₃ is a stronger π -accepting ligand

than CO, while ligands such as dimethylformamide and methylformamide are actually π -donors.

(4) The relationship of the CO stretching force constants used in this series of papers to more rigorous values is discussed.

II. Group VI Carbonyls

Sources of Data.—Poilblanc and Bigorgne⁴ have reported data for a great many substituted molybdenum carbonyls in which the substituents are phosphorus(III) compounds. Schmutzler⁵ has prepared, in small quantities, *cis*-Mo(PF₃)₃(CO)₃ and recorded its CO stretching frequencies in KBr. Data for still other compounds containing P(III) compounds as ligands have been reported by Magee, *et al.*,⁶ Chatt and Watson,⁷ Abel, Bennett, and Wilkinson,⁸ and in part I of this series. Data for molecules with sulfur(II) molecules as substituents have been reported by

(4) R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962).

(5) R. Schmutzler, Explosives Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Del., private communication.

(6) T. A. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *J. Am. Chem. Soc.*, **83**, 3200 (1961).

(7) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961).

(8) E. W. Abel, M. A. Bennett, and G. Wilkinson, *ibid.*, 2323 (1959).

(1) (a) Supported by the U. S. Atomic Energy Commission; (b) Fellow of the Alfred P. Sloan Foundation.

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

(3) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

TABLE I
 CO STRETCHING FREQUENCIES AND FORCE CONSTANTS IN $ML(CO)_5$ MOLECULES

Compound	Frequencies, cm^{-1}				Data ref.	Force constants, $mdynes/\text{\AA}$.		
	$A_1^{(2)}$	$A_1^{(1)}$	B_1	E		k_1	k_2	k_i
Mo(PCI ₃)(CO) ₅	2095	2001	...	1987	4	16.38	16.46	0.26
Mo(PCI ₂ OC ₂ H ₅)(CO) ₅	2091	1987	2012	1975	4	16.15	16.33	0.28
Mo[P(OC ₆ H ₅) ₃](CO) ₅	2083	1975	...	1963	4	15.97	16.14	0.29
Mo[P(OCH ₃) ₃](CO) ₅	2080	1967	1995	1950	4	15.62	16.02	0.30
Cr[P(C ₆ H ₅) ₃](CO) ₅	2070	~1944	1989	1944	2	15.50	15.88	0.33
Mo[P(C ₆ H ₅) ₃](CO) ₅	2078	~1951	1990	1951	2, 4	15.57	15.99	0.31
W[P(C ₆ H ₅) ₃](CO) ₅	2074	~1943	1981	1943	2	15.58	15.85	0.30
Mo[P(C ₂ H ₅) ₃](CO) ₅	2070	1941	1980	1948	4	15.40	15.88	0.30
Mo[P(CH ₃) ₃](CO) ₅	2071	1952	...	1943	4	15.61	15.87	0.31
Cr(C ₆ H ₁₁ NH ₂)(CO) ₅	2067	1890	1980	1935	3	14.59	15.77	0.32
Mo(C ₆ H ₁₁ NH ₂)(CO) ₅	2072	1895	1983	1938	3	14.65	15.83	0.32
W(C ₆ H ₁₁ NH ₂)(CO) ₅	2071	1894	1974	1929	3	14.65	15.74	0.35
W[(C ₂ H ₅) ₂ O](CO) ₅	2074	1908	...	1931	12	14.90	15.76	0.35
Mo[(<i>n</i> -C ₃ H ₇) ₂ O](CO) ₅	2079	1893	...	1940	12	14.65	15.90	0.35
W(C ₂ H ₅ OH)(CO) ₅	2078	1885	...	1929	12	14.53	15.73	0.35
Mo(<i>n</i> -C ₆ H ₁₃ OH)(CO) ₅	2080	1895	...	1940	12	14.68	15.90	0.35
Cr(CH ₃ CN)(CO) ₅	2080	1930	...	1954	13	15.21	16.04	0.31
W(CH ₃ CN)(CO) ₅	2083	1931	...	1948	11, 13	15.22	16.00	0.31
W(DMF)(CO) ₅	2067	1847	...	1917	12	13.93	15.58	0.36
Mo(DMF)(CO) ₅	2068	1847	...	1924	12	13.93	15.67	0.36
Mo(MF)(CO) ₅	2072	1862	...	1932	12	14.15	15.77	0.35

 TABLE II
 CO STRETCHING FREQUENCIES AND FORCE CONSTANTS FOR *cis*-ML₂(CO)₄ MOLECULES

Compound	Frequencies, cm^{-1}				Data ref.	Force constants, $mdynes/\text{\AA}$.		
	$A_1^{(2)}$	$A_1^{(1)}$	B_1	B_2		k_1	k_2	k_i
Mo(PCI ₃) ₂ (CO) ₄	2072	2004	1994	1986	4	16.30	16.44	0.27
Mo(PCI ₂ OC ₂ H ₅) ₂ (CO) ₄	2063	1988	1977	1968	4	15.92	16.34	0.28
Mo[P(OCH ₃) ₃] ₂ (CO) ₄	2037	1946	1926	1921	4	15.35	15.60	0.38
Mo[P(C ₆ H ₅) ₃] ₂ (CO) ₄	2023	1929	1911	1899	4	14.64	15.41	0.35
Cr[C ₂ H ₄ (P(C ₆ H ₅) ₂) ₂](CO) ₄	2009	1914	1899	1877	7	14.49	15.32	0.36
Mo[C ₂ H ₄ (P(C ₆ H ₅) ₂) ₂](CO) ₄	2020	1919	1907	1881	7	14.64	15.41	0.36
W[C ₂ H ₄ (P(C ₆ H ₅) ₂) ₂](CO) ₄	2016	1912	1901	1876	7	14.58	15.32	0.32
Mo[P(C ₂ H ₅) ₃] ₂ (CO) ₄	2016	1915	1900	1890	4	14.81	15.32	0.36
Mo[P(CH ₃) ₃] ₂ (CO) ₄	2019	1920	1903	1893	4	14.82	15.33	0.36
Cr[(CH ₃ SCH ₂) ₂](CO) ₄	2020	1914	1898	1869	9	14.73	15.38	0.36
Mo[(CH ₃ SCH ₂) ₂](CO) ₄	2030	1919	1905	1868	9	14.75	14.49	0.37
W[(CH ₃ SCH ₂) ₂](CO) ₄	2023	1910	1896	1867	9	14.72	15.37	0.37
Cr(CH ₃ CN) ₂ (CO) ₄	2019	1882	1908	1843	13	14.10	15.46	0.38
Mo(CH ₃ CN) ₂ (CO) ₄	2023	1881	1912	1833	13	13.95	15.52	0.38
W(CH ₃ CN) ₂ (CO) ₄	2023	1880	1900	1840	11, 13	14.08	15.40	0.41
Cr(en)(CO) ₄	2004	1855	1873	1810	3	13.68	15.07	0.45
Mo(en)(CO) ₄	2015	1864	1890	1818	3	13.76	15.25	0.42
W(en)(CO) ₄	2006	1852	1867	1809	3	13.68	15.01	0.47
W(DMF) ₂ (CO) ₄	1997	1832	1858	1791	11	13.40	14.84	0.45

 TABLE III
 CO STRETCHING FREQUENCIES AND FORCE CONSTANTS FOR
trans-ML₂(CO)₄ MOLECULES

Molecule	Frequencies, cm^{-1}			Force constants, $mdynes/\text{\AA}$.	
	A_{1g}	B_{1g}	E_u	k_2	k_i
Mo(PCI ₃) ₂ (CO) ₄	1896	16.45	(0.28)
Mo[P(OC ₆ H ₅) ₃] ₂ (CO) ₄	1940	15.78	(0.29)
Mo[P(OCH ₃) ₃] ₂ (CO) ₄	2035	1969	1921	15.55	0.30
Cr[P(C ₆ H ₅) ₃] ₂ (CO) ₄	...	1945?	1889	15.20	(0.34)
Mo[P(C ₆ H ₅) ₃] ₂ (CO) ₄	...	1955?	1902	15.30	(0.34)
Mo[P(CH ₃) ₃] ₂ (CO) ₄	1893	15.23	(0.34)
Mo[P(C ₂ H ₅) ₃] ₂ (CO) ₄	2018	1937	1889	15.15	0.34

Mannerskantz and Wilkinson⁹ and by Cotton and Zingales.¹⁰ Sheline and co-workers^{11,12} have recently

(9) H. C. E. Mannerskantz and G. Wilkinson, *J. Chem. Soc.*, 4454 (1962).

(10) F. A. Cotton and F. Zingales, *Inorg. Chem.*, **1**, 145 (1962).

(11) G. R. Dobson, M. F. Amr El Sayed, I. W. Stolz, and R. K. Sheline, *ibid.*, **1**, 526 (1962).

(12) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *ibid.*, **2**, 323 (1963).

reported data for compounds containing acetonitrile, acetone, alcohols, ethers, dimethylformamide (DMF), and methylformamide (MF) as substituents, while a very recent paper gives further data for acetonitrile compounds.¹³ Additional data are to be found in other places, but the references cited give a body of data which appears to be entirely representative and sufficiently large and varied for our purposes.

Using data from the sources cited, Tables I-V were compiled. In general, the criteria for making the assignments and methods for computing the force constants were just those discussed in the earlier papers.^{2,3} It may be noted that for $ML(CO)_5$ species, the assignments previously proposed^{2,3} and verified in one instance² by Raman data are now confirmed in

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

TABLE IV
CO STRETCHING FREQUENCIES AND FORCE CONSTANTS FOR
cis-ML₃(CO)₃ MOLECULES

Compound	Frequencies, cm. ⁻¹		Data ref.	Force constants, mdynes/Å.	
	A ₁	E		k ₁	k _i
Mo(PF ₃) ₃ (CO) ₃	2090	2055	5	16.98	0.33
Mo(PCI ₃) ₃ (CO) ₃	2040	1991	4, 8	16.27	0.27
Mo(AsCl ₃) ₃ (CO) ₃	2031	1992	8	16.23	0.21
Mo(SbCl ₃) ₃ (CO) ₃	2045	1991	8	16.31	0.29
Mo(PCI ₂ OC ₂ H ₅) ₃ (CO) ₃	2027	1969	4	15.97	0.31
Mo(PCI ₂ C ₆ H ₅) ₃ (CO) ₃	2016	1943	8	15.64	0.39
Mo[P(OC ₆ H ₅) ₃] ₂ (CO) ₃	1994	1922	4	15.31	0.38
Cr[P(OC ₆ H ₅) ₃] ₃ (CO) ₃	2008	1912	6	15.26	0.50
Mo[P(OC ₂ H ₅) ₃] ₃ (CO) ₃	1971	1885	4	14.80	0.45
Mo[P(OCH ₃) ₃] ₃ (CO) ₃	1977	1888	4	14.85	0.46
Mo[PCI(C ₆ H ₅) ₂] ₃ (CO) ₃	1977	1885	8	14.83	0.48
Mo[P(CH ₃) ₃] ₃ (CO) ₃	1945	1854	4	14.35	0.47
Mo[P(C ₂ H ₅) ₃] ₃ (CO) ₃	1937	1841	4	14.18	0.49
Mo[P(C ₆ H ₅) ₃] ₃ (CO) ₃	1934 ^a	1835 ^a	4, 8	14.10 ^a	0.50
Mo[S(CH ₃) ₂] ₃ (CO) ₃	1925	1799	10	13.70	0.63
Mo[S(C ₂ H ₅) ₂] ₃ (CO) ₃	1930	1826	10	13.99	0.53
Mo(SC ₆ H ₅) ₃ (CO) ₃	1925	1821	10	13.91	0.52
Mo(S ₃ C ₃ H ₁₃) ₃ (CO) ₃	1932	1812	9	13.86	0.61
Cr(S ₃ C ₃ H ₁₃) ₃ (CO) ₃	1932	1818	9	13.92	0.59
Cr(CH ₃ CN) ₃ (CO) ₃	1910	1782	13	13.45	0.64
Mo(CH ₃ CN) ₃ (CO) ₃	1915	1783	13	13.50	0.66
W(CH ₃ CN) ₃ (CO) ₃	1885	1778	13	13.30	0.53
Cr(dien)(CO) ₃	1895	1759	3	13.10	0.70
Mo(dien)(CO) ₃	1898	1758	3	13.13	0.73
W(dien)(CO) ₃	1888	1751	3	13.05	0.67

^a Frequencies from mull spectra due to insolubility of the compound; frequencies in solution would probably be 10–20 cm.⁻¹ higher and hence *k*₁ is probably ~14.25 mdynes/Å.

the solid line at low *k*_i values is such as to make it reach an extrapolated *k*_i of zero when the number of π-electrons per CO reaches an extrapolated value of zero.

trans-ML₃(CO)₃ Molecules.—The secular equations for these species have not been presented before; they are given in Table VI. *trans*-ML₃(CO)₃ molecules have apparently not yet been isolated or even obtained in solution essentially free of the corresponding *cis* isomers and other ML_x(CO)_{6-x} species. Therefore uncertainties arise even in the process of determining which absorption bands may be attributed to *trans*-MoL₃(CO)₃ species, in addition to the uncertainties which may subsequently occur in deciding how the observed frequencies are to be assigned to the normal modes. Poilblanc and Bigorgne⁴ have reported data (see Table V) which may be used in an attempt to make correct assignments, and these data form the basis for the following discussion.

We turn first to the compound *trans*-Mo[P(OC₂H₅)₃]₃(CO)₃, for which three distinct frequencies were observed in both the infrared and the Raman spectra and the following assignments were suggested.

$$\begin{array}{l}
 A_1 \left\{ \begin{array}{l} 1988 \text{ (weak); } \\ 1909 \text{ (medium); } \end{array} \right. \quad \begin{array}{l} 1990 \text{ (strong) cm.}^{-1} \\ 1915 \text{ (medium) cm.}^{-1} \end{array} \\
 B_1 \quad 1883 \text{ (medium); } 1870 \text{ (very weak) cm.}^{-1}
 \end{array}$$

Upon solving the secular equations with these assignments, and using for the frequencies the average

TABLE V
CO STRETCHING FREQUENCIES AND FORCE CONSTANTS FOR *trans*-ML₃(CO)₃ MOLECULES^a

Compound	Frequencies, cm. ⁻¹			Force constants, mdynes/Å.		
	A ₁ ⁽²⁾	A ₁ ⁽¹⁾	B ₁	k ₁	k ₂	k _i
Mo(PCI ₃) ₃ (CO) ₃	2056	~1980	~1980	15.96	16.38	0.27
Mo(PCI ₂ OC ₂ H ₅) ₃ (CO) ₃	2042	~1963	~1963	15.70	16.12	0.28
Mo[P(OC ₆ H ₅) ₃] ₃ (CO) ₃	2017	1932	1924	15.22	15.61	0.33
Mo[P(OC ₂ H ₅) ₃] ₃ (CO) ₃	2017	1924	1932	15.09	15.67	0.30
Mo[P(OCH ₃) ₃] ₃ (CO) ₃	1993	1890	1919	14.53	15.41	0.27
Mo[P(OC ₂ H ₅) ₃] ₃ (CO) ₃	1989	1912	1877	15.05	14.97	0.37
Mo[P(OC ₂ H ₅) ₃] ₃ (CO) ₃	1989	1877	1912	14.32	15.32	0.28
Mo[P(C ₆ H ₅) ₃] ₃ (CO) ₃	1952	1846	"~1887"	13.86	14.70	0.27
Mo[P(CH ₃) ₃] ₃ (CO) ₃	1961	1854	(1890?)	(13.95)	(14.85)	(0.27)

^a All frequencies from ref. 4.

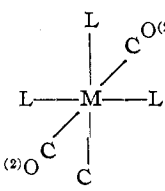
several other cases by the Raman data supplied by Poilblanc and Bigorgne.⁴

In part I,² it was suggested that "stretch-stretch interaction constants should probably increase with increasing replacement of CO by ligands of lower π-bonding ability." As an obvious corollary to this, one might propose also the rule that in compounds of a given type, as the π-acceptor ability of the substituents decreases, making more dπ-electrons available to the CO groups, the stretch-stretch interaction constants should increase. The data in Table IV for *cis*-ML₃(CO)₃ molecules are sufficiently extensive to provide a stringent check on this proposal. Figure 1 shows a plot of *k*_i values for the *cis*-MoL₃(CO)₃ compounds, which demonstrates that this rule is very well fulfilled indeed. (The origin of the lower abscissa scale will be explained later.) The limiting slope of

values 1989, 1912, and 1877 cm.⁻¹, the following force constants are obtained: *k*₁ = 15.05, *k*₂ = 14.97, and *k*_i = 0.37 mdynes/Å. Since, as shown previously, we must expect *k*₁ < *k*₂, these simple computations tell us at once that this assignment is incorrect, in the sense of being inconsistent with the generally accepted, qualitative ideas as to the nature of M to CO bonds. There do not appear to be any experimental criteria supporting the above assignment; we therefore accept the conclusion that it is incorrect and search for a new one. The form of the secular equations, together with the conditions *k*₁ < *k*₂ and *k*_i > 0, requires that the band of highest frequency be due to an A₁ mode, and, specifically, to the one arising mainly in the *trans* pair of CO groups (A₁⁽²⁾). As shown by Orgel,¹⁴ the fact that this band is the

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

TABLE VI
SECULAR EQUATIONS AND RELATED INFORMATION ON CO STRETCHING MODES IN *trans*-ML₃(CO)₃

Type of molecule	Molecular sym.	Sym. species of CO stretching modes	Activities	Secular equations	
				"Exact"	"Approximate"
	C _{2v}	$\left. \begin{array}{l} A_1 \\ A_1 \\ B_1 \end{array} \right\}$	Raman and infrared	$\begin{vmatrix} \mu k_1 - \lambda & \sqrt{2\mu k_i} \\ \sqrt{2\mu k_1} & \mu(k_2 + k_t) - \lambda \end{vmatrix} = 0$ $\lambda = \mu(k_2 - k_t)$	$\begin{vmatrix} \mu k_1 - \lambda & \sqrt{2\mu k_i} \\ \sqrt{2\mu k_1} & \mu(k_2 + 2k_t) - \lambda \end{vmatrix} = 0$ $\lambda = \mu(k_2 - 2k_t)$

weakest of the three also suggests the same assignment for it. Therefore the only other assignment which may be considered is: A₁⁽²⁾, 1989; A₁⁽¹⁾, 1877; B₁, 1912 cm.⁻¹. With this assignment we obtain the following force constants: $k_1 = 14.32$; $k_2 = 15.32$; $k_i = 0.28$ mdynes/Å. Since these are well in accord with the requirement $k_1 < k_2$, and k_i has a reasonable value, we conclude that this is the correct assignment.

In an exactly similar way, we also conclude that for Mo[P(OCH₃)₃]₃(CO)₃ the assignment A₁⁽¹⁾, 1890; A₁⁽²⁾, 1993; B₁, 1919 cm.⁻¹, which leads to the force constants $k_1 = 14.53$; $k_2 = 15.41$; $k_i = 0.27$ mdynes/Å. is correct, rather than the one previously suggested⁴ in which the frequencies of the A₁⁽¹⁾ and B₁ modes are reversed.

Now, following arguments similar to those previously used³ for ML(CO)₃ molecules, it may be expected that the frequency of the A₁⁽¹⁾ mode will vary more rapidly with the π-acceptor strength of L than will the frequency of the B₁ mode. Hence, as the π-acceptor strength of L increases, $\nu_{A_1^{(1)}}$ will rise closer to, and possibly become equal to or even greater than, ν_{B_1} , while a decrease in the π-acceptor strength of L will cause $\nu_{A_1^{(1)}}$ to move even further below ν_{B_1} . With these considerations in mind, assignment of the spectra of the *trans*-MoL₃(CO)₃ molecules with L = P(C₂H₅)₃, P(CH₃)₃, P(OC₆H₅)₃, PCl₂(OC₂H₅)₃, and PCl₃ may be considered.

For *trans*-Mo[P(OC₆H₅)₃]₃(CO)₃, Poilblanc and Bigorgne report A₁, 2017; A₁, 1932; B₁, 1924 cm.⁻¹. Since, as shown later, P(OC₆H₅)₃ generally behaves as a stronger π-acceptor than do P(O-alkyl)₃ groups, we expect $\nu_{B_1} - \nu_{A_1^{(1)}}$ to be smaller than in the above P(OC₂H₅)₃ and P(OCH₃)₃ compounds, and, perhaps, even negative as in the above assignment. However, the alternative in which the assignments of the 1932 and 1924 cm.⁻¹ bands are interchanged cannot be ruled out. Table II shows the set of force constants obtained with each of these possible assignments; they appear about equally acceptable.

For the *trans*-MoL₃(CO)₃ molecules in which L = P(C₂H₅)₃ and P(CH₃)₃, Poilblanc and Bigorgne⁴ report only two bands, the higher ones at 1953 and 1962 cm.⁻¹, respectively, and the lower ones at 1846 and 1854 cm.⁻¹, respectively. The upper ones must certainly be due to the A₁⁽²⁾ modes. The postulate that the lower ones represent superposed A₁⁽¹⁾ and B₁ bands

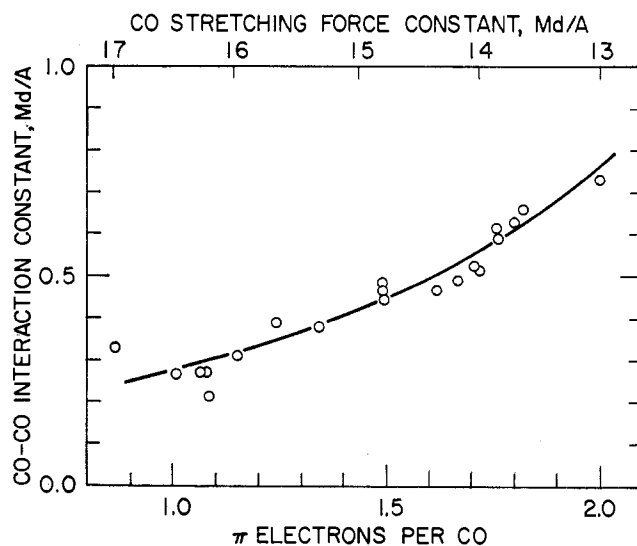


Fig. 1.—Graphical demonstration of the proposition that the greater the π-electron population in the M-C bonds, the greater the CO-CO stretching interaction constant. Data for *cis*-ML₃(CO)₃ molecules from Table IV.

is inadmissible, since in these molecules $\nu_{B_1} - \nu_{A_1^{(2)}}$ must be even greater than in the molecules with L = P(O-alkyl)₃. Poilblanc and Bigorgne assign the lower frequency bands to the A₁⁽¹⁾ modes and give no frequencies for the B₁ bands which ought, by analogy with the results for other compounds, to be of comparable intensity. Using the frequencies 1953 cm.⁻¹ for A₁⁽²⁾ and 1846 cm.⁻¹ for A₁⁽¹⁾ in the P(C₂H₅)₃ compound and assuming $k_i = 0.27$ mdyne/Å., we can calculate k_1 and k_2 and then a frequency for the B₁ mode. The result is ~1887 cm.⁻¹. We believe that Fig. 3 of Poilblanc and Bigorgne's paper⁴ shows a definite indication of the presence of this band, although they do not record such an absorption in their Table VIIA. Analogously, for the P(CH₃)₃ complex, we would predict a B₁ band at ~1890 cm.⁻¹, but in this case, the spectrum is not depicted so that the prediction cannot be checked.

For *trans*-Mo(PCl₃)₃(CO)₃ and *trans*-Mo(PCl₂OC₂H₅)₃(CO)₃, Poilblanc and Bigorgne⁴ report only two frequencies, which they assign to A₁ and B₁ modes, leaving blanks for the remaining A₁ modes. On the basis of earlier considerations, it seems plausible that the lower frequencies correspond to superposed A₁⁽¹⁾ and B₁ bands. When such an assignment is made in each of

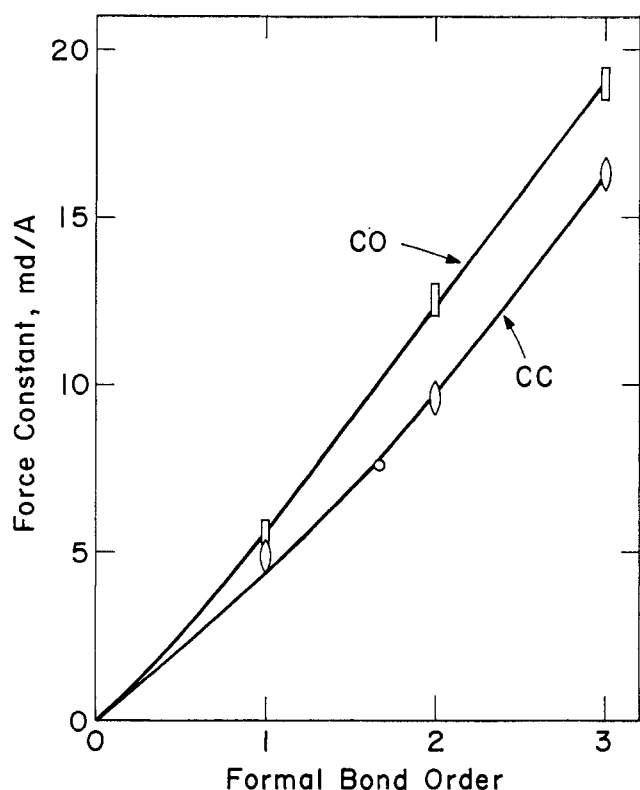


Fig. 2.—Variation of CO and CC stretching force constants with formal bond order, n . Data taken from ref. 15.

these molecules, very reasonable force constants are obtained, as shown in Table V.

Other Compounds.—For all other compounds, the assignments and computations were made using the previously published secular equations² and reasoning analogous to that discussed fully in the earlier papers.^{2,3}

III. Correlation of Changes in Force Constants with Changes in CO Bond Orders

As will be discussed in detail in section VI, the CO stretching constants obtained by the method used here are not *rigorous*. However, *differences* between these force constants in a series of compounds of the same stoichiometric and structural type, $ML_n(CO)_{6-n}$, should have rigorous significance, at least to a good approximation. These differences should therefore bear a direct relation to the actual numbers of π -electrons involved in the M–C and C–O bonds and to the bond orders.

In order to establish such a relationship, data were taken from an existing compilation¹⁵ of CO stretching force constants in some simple molecules and also, for comparison, for some CC force constants. In Fig. 2 these are plotted against the formal CO and CC bond orders. It will be noted that in both cases, the relationship is essentially linear between bond orders (n) of ~ 1.5 and 3.0 , with a slope $\Delta k/\Delta n$ of ~ 6.8 mdynes/ \AA . per unit of bond order for CO bonds.

For $M(CO)_6$ there are six metal $d\pi$ -electrons avail-

able for M–C π -bonding, that is, one per M–C bond. In a *cis*-triamminetricarbonyl, *cis*- $M(R_3N)_3(CO)_3$, there are six metal $d\pi$ -electrons for only three M–C bonds, assuming as before³ that the M–N bonds are pure σ -bonds. Thus, in going from $M(CO)_6$ to *cis*- $M(R_3N)_3(CO)_3$, the M–C bond order should increase by 0.5 if the available $d\pi$ -electrons tend to be fully used. If we assume that the sum of bond orders to carbon is a constant, an increase of 0.5 in the M–C bond order implies a drop of 0.5 in the C–O bond order, and according to the approximately linear relationship between C–O stretching force constant and C–O bond order there should be a decrease of $0.5 \times 6.8 = 3.4$ mdynes/ \AA . in the CO force constant. According to the results in Table IV of ref. 2, the decreases in CO stretching constants on going from $M(CO)_6$ molecules to the corresponding $M(\text{dien})(CO)_3$ molecules are 3.39, 3.39, and 3.36 mdynes/ \AA . for $M = \text{Cr}, \text{Mo},$ and W , respectively. This excellent agreement we take as evidence for the essential correctness of the assumptions which are made in this series of papers about the manner and degree of multiple bonding in the compounds under discussion. It is necessary to point out, however, that the validity of the correlation could be defended on the basis of less exact agreement, since the force constants probably have uncertainties of at least ± 0.1 mdynes/ \AA .

IV. Assessment of π -Acceptor (and π -Donor) Abilities of Various Ligands

Qualitative ordering of ligands in terms of relative π -acceptor strengths in metal carbonyls is not a new procedure.^{4,8,16,17} To the extent that such orderings as can be inferred from each of the Tables I–V are comparable to one another, they agree and, moreover, they all agree with the fairly extensive series recently given by Horrocks and Taylor.¹⁶ However, this limited sort of result could have been obtained from the frequencies alone without recourse to the force constants. In the following paragraphs of this section, it will be apparent that the force constants permit comparisons and (at least rough) quantitative estimates which cannot be made using only the frequencies.

P(III) Ligands.—It may be seen in all of the Tables I–V that these ligands span a considerable range of π -acceptor strength depending on the identity of the three groups attached to the phosphorus atom.

The complex $\text{Mo}(\text{PF}_3)_3(\text{CO})_3$ is unusually interesting. The idea that PF_3 should be a very potent acceptor of π -electrons, comparable in this respect to CO itself, was advanced many years ago,^{18–20} and qualitative confirmation was provided.²⁰ From the force constant in Table IV, it can be seen that PF_3 is actually a

(16) W. D. Horrocks, Jr., and R. C. Taylor, *Inorg. Chem.*, **2**, 723 (1963).

(17) L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959).

(18) A. A. Blanchard, Massachusetts Institute of Technology, personal communication to J. W. Irvine; see J. W. Irvine, Jr., and G. Wilkinson, *Science*, **113**, 742 (1951).

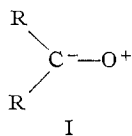
(19) J. Chatt, *Nature*, **165**, 637 (1950).

(20) G. Wilkinson, *J. Am. Chem. Soc.*, **73**, 5501 (1951).

(15) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955, p. 175, Table 8-1.

noticeably stronger π -acceptor than CO.²¹ This follows from the fact that the comparable force constant for Mo(CO)₆, as reported earlier,² is 16.52 mdyne/Å. It is to be noted that from observed frequencies alone, without recourse to force constants, a comparison such as this could not have been made. It is possible to go a little further and state that since the CO force constant in Mo(PF₃)₃(CO)₃ is ~ 0.5 mdyne/Å. higher than that in Mo(CO)₆, the CO bond orders are $\sim 0.5/6.8$ or 0.07 higher. This in turn means that each CO is obtaining some 0.14 electron less in Mo(PF₃)₃(CO)₃ than in Mo(CO)₆ and, therefore, of the six d π -electrons available, the CO groups are getting $3 - 3(0.014) = 2.58$ while the PF₃ groups are presumably getting 3.42. PF₃ is thus about $3.42/2.58 = 1.32$ times stronger a π -electron acceptor than CO. Naturally, this figure should not be taken too literally, but it probably represents an estimate which is reliable within limits of, say, 20%. Qualitatively, the same general conclusion about PF₃ can be reached from data for Ni(PF₃)_n(CO)_{4-n} species.²²

Molecules with Alcohols, Ethers, and Ketones as Substituents.—The assumption made earlier that amines are ligands with π -acceptor strength of zero, due to the absence of any vacant low-lying π -orbitals on the nitrogen, would have as an obvious corollary that alcohols, ethers, and, to the extent that the canonical form I is unimportant, ketones also have π -acceptor



strengths of zero. This is confirmed by the fact that for all of the complexes in which such ligands occur, the frequencies and force constants do not differ signifi-

(21) Since the force constant was calculated from frequencies measured on a spectrum of the solid compound, it is to be considered a lower limit, and might well be 0.1–0.2 unit higher if obtained from data for a solution.

(22) M. Bigorgne, *Bull. Soc. Chim. France*, 1986 (1960), reports CO stretching frequencies for these molecules, while H. Stammreich, *et al.*, *J. Chem. Phys.*, **35**, 2168 (1961), give the frequencies of the A₁ and T₂ CO stretching modes of Ni(CO)₄. From these data, using the equations

$$\begin{array}{l} \text{Ni(CO)}_4 \quad \begin{cases} \lambda_{A_1} = \mu(k + 3k_i) \\ \lambda_{T_2} = \mu k \end{cases} \\ \text{NiL(CO)}_3 \quad \begin{cases} \lambda_A = \mu(k + 2k_i) \\ \lambda_E = \mu(k - k_i) \end{cases} \\ \text{NiL}_2(\text{CO})_2 \quad \begin{cases} \lambda_{A_1} = \mu(k + k_i) \\ \lambda_{E_1} = \mu(k - k_i) \end{cases} \\ \text{NiL}_3(\text{CO}) \quad \lambda = \mu k \end{array}$$

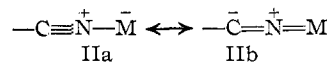
one obtains the following values for k and k_i

$$\begin{array}{ll} \text{Ni(CO)}_4 & k = 16.67; k_i = 0.51 \\ \text{Ni(PF}_3)_3(\text{CO)}_3 & k = 17.27; k_i = 0.35 \\ \text{Ni(PF}_3)_2(\text{CO)}_2 & k = 17.32; k_i = 0.37 \\ \text{Ni(PF}_3)_3(\text{CO)} & k = 17.35 \end{array}$$

Thus, an effect of similar magnitude to that in Mo(PF₃)₃(CO)₃ is evident, but due to the mixing of π and σ character of some d-orbitals, there is no secure way to attempt a more quantitative interpretation for these molecules.

cantly from those for the analogous amine complexes.²³

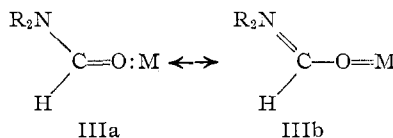
Nitrile Complexes.—The data for several of these, of different stoichiometric types, clearly indicate that acetonitrile possesses a small but real ability to accept π -electrons in competition with CO groups. In resonance terms, we may say that the canonical form IIb makes a finite contribution. Using, for simplicity,



the data on the *cis*-ML₃(CO)₃ compounds, and noting that k in the CH₃CN compounds is ~ 0.35 mdyne/Å. higher than in the M(dien)(CO)₃ compounds, we may, by an argument analogous to that used above for the PF₃ complex, conclude that in the M(CH₃CN)₃(CO)₃ complexes, the CO groups are getting only 1.9 π -electrons apiece as compared to 2.0 in M(dien)(CO)₃ and thus assign canonical forms IIa and IIb relative weights of 0.95 and 0.05 in a resonance hybrid description of the bonding.

Dimethylformamide and Methylformamide Complexes.—A feature of extreme interest in Tables I and II is the data for substituted carbonyls containing dimethylformamide and methylformamide. In these molecules the CO frequencies and force constants are lower than those for analogous amine-, alcohol-, or ether-containing molecules, implying that the formamides have less than zero π -acceptor strength. Physically, this can only mean that these molecules are, in fact, π -donors. So far as is known to the author, this is the first explicit postulation of π -donor substituents in metal carbonyls.

The π -donor capacity of the formamides can be understood by considering the bonding in terms of the hybridization of the canonical forms (III). As before,



an estimate of the relative importance of the contributions of these canonical structures to the resonance hybrid can be made using the force constants. Here, however, we are forced to deal with the less simple ML(CO)₅ and *cis*-ML₂(CO)₄ cases, with the added complication, which has arisen before in the pyridine and bipyridyl compounds, that the π -bonding is not cylindrically symmetrical.

For the ML(CO)₅ species, we may assume, as in the pyridine compound, that the orientation of the ligand is such as to π -bond equally to all the *cis*-CO groups. It then interacts with two d π -orbitals, both of which also interact with the *one trans*-CO (CO⁽¹⁾) and both

(23) It has been reported [A. Werner and T. H. Coffield, *Chem. Ind.* (London), 936 (1960)], that Mo(diglyme)(CO)₃ has frequencies appreciably lower than those for Mo(dien)(CO)₃ and this has led E. W. Abel [*Quart. Rev.* (London), **17**, 133 (1963)] to suggest that the CO force constants must be quite sensitive to the electronegativity of the ligand atoms. However, this compound has been examined only in the solid state and, curiously, it is very insoluble in all the usual organic solvents with which it does not react. Attempts are currently being made to reinvestigate its spectrum under conditions more suited to making a comparison with other data.

TABLE VII
 OBSERVED CO STRETCHING FREQUENCIES AND CALCULATED FORCE CONSTANTS FOR $MnX(CO)_5$ MOLECULES

X	Observed frequencies, cm^{-1}			Solvent	Source	Force constants, $mdynes/\text{\AA}$		
	$A_1^{(2)}$	$A_1^{(1)}$	E			k_1	k_2	k_3
Cl	2148	2002	2063	CCl_4	<i>a</i>	16.27	17.63	0.22
	2138	1999	2054	CCl_4	<i>b</i>	16.23	17.49	0.22
Br	2144	2004	2056	CCl_4	<i>a</i>	16.31	17.53	0.23
	2133	2001	2050	CCl_4	<i>b</i>	16.24	17.41	0.22
I	2133	2005	2048	CCl_4	<i>a</i>	16.33	17.41	0.22
	2125	2003	2044	CCl_4	<i>b</i>	16.28	17.31	0.22
CH_3	2116	1991	2015	CCl_4	<i>a</i>	16.14	16.92	0.26
	2108	1989	2010	$C_2H_2Cl_4$	<i>c</i>	16.12	16.82	0.25
C_2F_5	2130	2023	2038	$C_2H_2Cl_4$	<i>c</i>	16.67	17.25	0.24

^a Unpublished measurements by Dr. C. S. Kraihanzel. ^b J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **1**, 933 (1962). ^c E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **18**, 585 (1963).

of which also interact with all four of the *cis*-CO ($CO^{(2)}$) groups. Thus, any π -electron density injected by L into $M(CO)_5$ will go $4/5$ to $CO^{(1)}$ and $1/5$ to each $CO^{(2)}$. We might then expect k_1 to be lowered four times as much as is k_2 on going from $M(R_2NH)(CO)_5$ to $M(DMP)(CO)_5$, and in fact $\Delta k_1 = -0.73$, while $\Delta k_2 = -0.16$, a ratio of 4.5. It should be remembered, however, that estimating the uncertainty in each force constant, somewhat conservatively, perhaps, as ± 0.1 $mdyne/\text{\AA}$, this ratio might actually be anything in the range 1.5–100. From the shift in k_1 , which is larger and hence more reliable, we might deduce that the dimethylformamide injects $(5/4)(0.73/6.8)$ or 0.14 electron pair into $M(CO)_5$, whence we may say that the relative weights of IIIa and IIIb in the resonance hybrid must be about 0.86 and 0.14, respectively. For $W(DMF)_2(CO)_4$ the shifts are so small and the uncertainty as to what should be assumed about the orientation of the ligand π -system relative to the $d\pi$ -orbitals of the metal is so great as to render a quantitative discussion unprofitable. It may also be noted that the shifts in $Mo(MF)(CO)_5$ are smaller than those in $Mo(DMF)(CO)_5$. This might be expected because of the inductive effect of methyl groups which is exemplified in the decrease in the ν_{CO} or "amide I" bands as one goes from secondary (1700–1670 cm^{-1}) to tertiary (1670–1630 cm^{-1}) amides.²⁴

V. Manganese Carbonyl Compounds

$XMn(CO)_5$ Compounds.—Table VII records data for several different compounds of this type taken partly from the literature and partly from work done here. Following the arguments used previously^{1,2} for the monosubstituted group VI carbonyls, the bands can be assigned as shown and with these assignments the three force constants can be calculated. A much more thorough investigation of these and other, new $XMn(CO)_5$ compounds is in progress, so that discussion here will be curtailed. A few qualitative observations are the following.

The over-all variation of the force constants is not large. If both CH_3 and C_2F_5 are assumed to be incapable of any π -interaction with Mn, the differences

here give a measure of inductive effects; both k_1 and k_2 should have the same dependence on this factor and, within experimental error, they do. For compounds of the three halogens, which have inductive effects lying between those of CH_3 and C_2F_5 , the force constants are very similar in magnitude; they do not, however, lie between those of the CH_3 and C_2F_5 compounds in the case of k_2 . It is at present uncertain whether this discrepancy is meaningful, but at least it can be said that the *net* π -electron-withdrawing (or donating) powers of the halogen atoms are not greatly different from zero.^{24a}

$[Mn(CO)_4X]_2$ Compounds.—The compound in which $X = Br$ has been studied²⁵ by X-ray diffraction and shown to have two Br bridges and idealized molecular symmetry D_{2h} . The molecule thus consists of two *cis*- $MnX_2(CO)_4$ units fused together on the X–X line and it may certainly be expected that coupling between the CO stretching modes in one unit and those in the other will be negligible. Therefore, the B_{1u} , B_{2u} , and $2B_{3u}$ CO stretching fundamentals of the dimer may be treated as identical with the B_1 , B_2 , and $2A_1$ CO stretching modes of a *cis*- $ML_2(CO)_4$ molecule and the secular equations presented previously² may be used. El-Sayed and Kaesz²⁶ have recently reported the four frequencies for the molecules containing Cl, Br, and I. Table VIII shows the observed frequencies, the assignments here proposed, the force constants obtained from these data, and the frequencies calculated from the force constants. Since there are four frequencies and only three constants to be determined, it is possible to choose various sets of constants, none of which, in general, exactly reproduces all of the observed frequencies. The constants reported in Table VIII give frequencies with the least mean square deviation from those observed, and in each case the agreement is satisfactory considering the probable uncertainties in the data and the approximate nature of the secular equations used. The justification for the assignments used and the method of obtaining the force constants will now be explained.²⁷

(24a) NOTE ADDED IN PROOF.—Further work, in cooperation with Dr. J. A. McCleverty, has led to the conclusion that CF_3 (and thus, presumably, also C_2F_5) possesses a small, but appreciable, π -acceptor capacity in such molecules.

(25) L. F. Dahl and C.-H. Wei, *Acta Cryst.*, **16**, 611 (1963).

(26) M. A. El-Sayed and H. D. Kaesz, *Inorg. Chem.*, **2**, 158 (1963).

(24) Cf. L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 205, Table 12.

TABLE VIII
OBSERVED CO STRETCHING FREQUENCIES, ASSIGNMENTS, FORCE CONSTANTS,
AND CALCULATED FREQUENCIES FOR $[\text{MnX}(\text{CO})_4]_2$ MOLECULES

X	Observed frequencies ^a (cm. ⁻¹) and assignments ^b				Force constants, mdynes/Å.			Calculated frequencies, cm. ⁻¹			
	A ₁ ⁽²⁾ (B _{3u})	A ₁ ⁽¹⁾ (B _{3u})	B ₁ (B _{1u})	B ₂ (B _{2u})	k ₁	k ₂	k _i	A ₁ ⁽²⁾	A ₁ ⁽¹⁾	B ₁	B ₂
Cl	2104	2012	1045	1977	16.06	17.24	0.20	2098	1999	2042	1982
Br	2099	2011	2042	1975	16.07	17.23	0.20	2097	2000	2042	1982
I	2087	2009	2033	1976	16.10	17.10	0.21	2090	2001	2032	1983

^a From ref. 26. ^b Notation appropriate to $\text{MnX}_2(\text{CO})_4$ with C_{2v} symmetry with that for the dimer of D_{2h} symmetry in parentheses

TABLE IX

THE SIX POSSIBLE ASSIGNMENTS OF THE CO STRETCHING
FREQUENCIES (CM.⁻¹) IN $[\text{MnCl}(\text{CO})_4]_2$

	1	2	3	4	5	6
A ₁ ⁽²⁾	2104	2104	2104	2104	2104	2104
A ₁ ⁽¹⁾	2045	2045	2012	2012	1977	1977
B ₁	1977	2012	2045	1977	2045	2012
B ₂	2012	1977	1977	2045	2012	2045

As we have noted earlier, the form of the secular equations, coupled with the assumptions (1) that $k_i > 0$ and (2) $k_1 < k_2$ require the A₁ mode, A₁⁽²⁾, which is localized mainly in the CO groups *cis* to the substituents (the CO⁽²⁾ groups) to have the highest frequency. The assignments of the other three modes are not subject to any general restrictions and thus six assignments have to be considered as possible ones at the outset. For $[\text{MnCl}(\text{CO})_4]_2$, these are indicated in Table IX. It can be seen from Table VIII that the pattern of CO stretching frequencies is so nearly independent of whether X is Cl, Br, or I that fixing the assignment in the chloro compound will fix it for all of them.

From the frequencies of the B₁ and B₂ modes, one can calculate k_1 and k_2 for any assumed value of k_i . From the two A₁ frequencies one can also calculate k_1 and k_2 , but only for assumed k_i values between 0 and some upper limit beyond which the stretching constants become complex numbers. Such calculations have been carried out for each of the six assignments, and the results are presented graphically in Fig. 3. In each case, the highest value of k_i is the limiting one in the A₁ quadratic equation.

Five of the six assignments can be rejected on the basis of the force constants they give, namely, numbers 1, 2, 4, 5, and 6. Assignment 1, for example,²⁸ has two serious difficulties: (1) throughout the entire range of k_i , the B₁ and B₂ frequencies lead to $k_1 < k_2$, and (2) nowhere in the range of k_i do the two values of k_1 and, *a fortiori*, of k_2 come at all close together. In short, there is no way to choose a reasonable value of k_i and real values of k_1 and k_2 and get an acceptable fit to the observed frequencies when they are identified as in assignment 1. Assignment 2 is satisfactory in giving $k_2 > k_1$, when these are obtained from the

(27) The method used here is different from that used previously²⁻⁴ in treating *cis*-ML₂(CO)₄ molecules, because in the present cases all four bands are well resolved and their frequencies equally reliable. In previous cases, one band has been poorly resolved or unresolved and the treatment was such as to permit the maximum disagreement between calculated and observed frequencies to occur with this particular band, while securing the best agreement for the remaining three.

(28) This is the assignment proposed by El-Sayed and Kaesz. Professor Kaesz (private communication) has expressed a preference for the assignment proposed here over the one suggested earlier

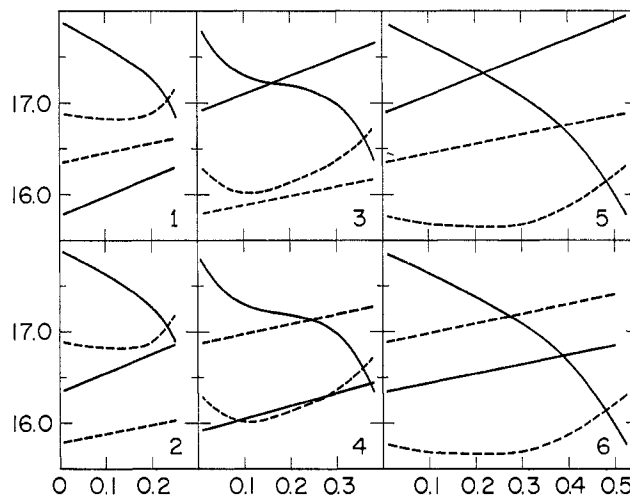


Fig. 3.—Force constants, k_1 and k_2 , for $[\text{MnCl}(\text{CO})_4]_2$, calculated as functions of k_i for the six possible assignments as listed in Table IX. Solid lines are for k_2 values and dashed lines for k_1 values. Straight lines are k values obtained from the B₁ and B₂ frequencies; curves lines are k values obtained from the A₁ frequencies.

frequencies of the B₁ and B₂ modes, but fails insofar as the force constants obtained from the A₁ modes are greatly different from those from the B₁ and B₂ modes for all acceptable values of k_i . Much the same criticisms may be made of the force constants given by assignments 4, 5, and 6.

Assignment 3 alone produces acceptable force constants. For k_i values between ~ 0.1 and ~ 0.25 , the two values of k_1 differ by 0.20 or less, as do those for k_2 , and all k_1 values are less than k_2 values. For $k_i \approx 0.165$, the agreements between the k_1 values and between the k_2 values are simultaneously best, and the mean values of k_1 and k_2 at $k_i = 0.165$ produce a set of frequencies which agree with those observed to within the expected limits of the data and the probable reliability of the approximations used in setting up the secular equations.^{28a}

trans- $\text{MnBrL}_2(\text{CO})_4$.—For these species, Angelici, Basolo, and Poë²⁹ have recently reported CO stretching frequencies and assignments. The latter were based on intensity considerations (for A₁⁽²⁾) and on the assumption that since Br is a poorer π -acceptor than

(28a) NOTE ADDED IN PROOF.—Orgel (*Inorg. Chem.*, **3**, 303 (1964)) has also proposed this assignment using his qualitative method. However, the methods used here do not support his further suggestion that assignment 4 is "just possible" if the interaction constants have values "very different" from the usual ones, because the required "very different" values either would be negative or would lead to imaginary stretching constants, and we do not believe that either of these situations merits consideration.

(29) R. J. Angelici, F. Basolo, and A. J. Poë, *J. Am. Chem. Soc.*, **85**, 2215 (1963).

TABLE X
CO STRETCHING FREQUENCIES AND FORCE CONSTANTS IN
trans-MnBrL₂(CO)₃ MOLECULES^a

L	Frequencies observed, cm. ⁻¹			Force constants, mdynes/Å.		
	A ₁ ⁽²⁾	A ₁ ⁽¹⁾	B ₁	k ₁	k ₂	k _i
PC ₆ H ₅ Cl ₂	2075	1953	2004	15.48	16.78	0.28
P(OC ₆ H ₅) ₃	2070	1949	2000	15.42	16.71	0.28
P(OC ₄ H ₉) ₃	2049	1927	1969	15.10	16.26	0.30
P(C ₄ H ₉) ₃	2020	1894	1938	14.59	15.77	0.30

TABLE XI
SECULAR EQUATIONS AND RELATED INFORMATION ON CO STRETCHING MODES IN *cis*-MXY₂(CO)₃ MOLECULES

Structure	Point symmetry	Sym. species of CO stretching modes	Activities	Secular equations
	C _s	$\left. \begin{array}{l} A^{(1)} \\ A^{(2)} \\ B \end{array} \right\}$	Infrared and Raman	$\begin{cases} \mu k_1 - \lambda \\ \sqrt{2} k_i \end{cases} \begin{cases} \sqrt{2} k_i \\ \mu(k_2 + k_i) - \lambda_1 \end{cases} = 0$ $\lambda = \mu(k_2 - k_i)$

TABLE XII
CO STRETCHING FREQUENCIES, ASSIGNMENTS, AND FORCE CONSTANTS FOR *cis*-MnBrL₂(CO)₃ MOLECULES

L	Observed frequencies (cm. ⁻¹) and assignment			Force constants, mdynes/Å.		
	A ⁽²⁾	A ⁽¹⁾	B	k ₁	k ₂	k _i
PC _{1/2} C ₆ H ₅	2058	1953	2004	15.56	16.58	0.36
P(OC ₆ H ₅) ₃	2053	1949	2000	15.50	16.50	0.35
P(OC ₄ H ₉) ₃	2037	1927	1969	15.24	16.09	0.43
P(C ₄ H ₉) ₃	2008	1894	1938	14.73	15.60	0.43

the ligands, L, occurring in their compounds, $\nu_{A_1^{(2)}}$ should be less than ν_{B_1} . Their assignments of the A₁⁽²⁾ modes is of course the only acceptable one from the nature of the secular equations (if $k_1 < k_2$) and, as shown in Table X, the force constants obtained with this assignment fulfill the requirement $k_1 < k_2$. Reversal of the assignments for A₁⁽¹⁾ and B₁ leads to a violation of this requirement. Thus, the proposed assignments receive support from the calculations reported here.

It may now be observed that the differences $k_2 - k_1$ are appreciably greater for the *trans*-MnBrL₂(CO)₃ species than for the *trans*-MoL₃(CO)₃ species in which the ligands, L, are the same or similar (*i.e.*, P(OC₆H₅)₃, P(O-alkyl)₃, and P(alkyl)₃). This is entirely in accord with the view that Br is a poorer π -acceptor than phosphites, or trialkylphosphines, and thus also in accord with the conclusion drawn earlier that the halogens have only weak net abilities to accept or donate π -electrons in these molecules.

cis-MnBrL₂(CO)₃.—Angelici, Basolo, and Poë¹¹ have also reported the CO stretching frequencies for molecules of this type, corresponding to the *trans* isomers of the same stoichiometry which were discussed above. The molecular symmetry, selection rules, and secular equations are given in Table XI. Since, according to the preceding discussions, Br must be a poorer acceptor of metal d π -electrons than the various phosphorus(III)

ligands, meaning that $k_1 < k_2$, and using also the relation $k_i > 0$, we can infer from the secular equations that the highest observed frequency must be that of the A⁽²⁾ mode. There are then two possible assignments. The one in which the lowest frequency is assigned to the B mode makes it impossible, using any remotely plausible value of k_i , to obtain $k_2 > k_1$. The only remaining assignment shown in Table XII, however,

leads to sets of force constants which are entirely plausible on comparison with those for related molecules.

VI. Relationship of the "Nonrigorous" Force Constants Used to "Rigorous" Ones³⁰

It is perhaps worthwhile to point out, explicitly, that the absolute values of the force constants obtained by the methods used in this and the two preceding papers of the series are not significant, nor can these force constants be directly compared with those calculated by the same method for molecules with different structures.

The first restriction may be illustrated by considering the absolute value of the CO stretching force constant in Mo(CO)₆, obtained by a full matrix normal coordinate analysis involving all modes and taking account of kinetic couplings. According to Jones,³¹ this constant has the value 18.1 mdynes/Å., whereas the value obtained in this work is 16.5 mdynes/Å.

In respect to the second restriction, we may observe that, again according to a complete normal coordinate treatment by Jones,³¹ the CO stretching force constant in Ni(CO)₄ is 17.6 mdynes/Å. Thus the best "rigorous" values for the CO stretching force constants for Mo(CO)₆ and Ni(CO)₄ decrease in that order, and, as Jones has observed, this is the order to be expected.

However, as shown earlier,²² using frequencies from a condensed phase, uncorrected for anharmonicity, one obtains for Ni(CO)₄ a force constant of 16.7 mdynes/Å., which is to be contrasted with our previously reported²

(30) Rigor in calculations of force constants is, of course, a relative matter and none are absolutely rigorous. The constants obtained in this and preceding papers are characterized as "nonrigorous" because they result from the use of a *deliberately* incomplete force field. In contrast, force constants obtained using force fields which are much more complete are, relatively speaking, "rigorous."

(31) L. H. Jones, *J. Chem. Phys.*, **36**, 2375 (1962); force constants given here include anharmonicity corrections.

comparable type of force constant, 16.5 mdynes/Å. for $\text{Mo}(\text{CO})_6$. Thus, our nonrigorous force constants are qualitatively in the wrong ratio, though quantitatively the ratios differ rather little.

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Phosphorus- and Arsenic-Bridged Complexes of Metal Carbonyls.

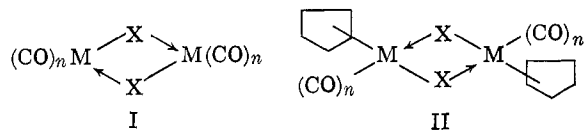
VI.^{1a} Reactions of Tetrasubstituted Biphosphines and a Biarsine with Monomeric Metal Carbonyls^{1b}

By R. G. HAYTER

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The reactions of tetramethylbiphosphine and -biarsine with the carbonyls of nickel, iron, chromium, molybdenum, and tungsten and of tetraphenylbiphosphine with nickel carbonyl have been studied and two types of binuclear complexes identified. The group VI metal carbonyls also give a third type of complex, which is apparently polymeric. The infrared and proton n.m.r. spectra of the complexes are discussed, and a few simple reactions are studied.

The reactions of tetrasubstituted biphosphines and tetramethylbiarsine with the dimeric metal carbonyls (cobalt and manganese²) and with the dimeric cyclopentadienyl metal carbonyls (iron,³ nickel,⁴ molybdenum,⁴ and tungsten⁴) have recently been found to give, in general, dimeric bridged complexes of structures I and II, respectively.



In this paper, we describe the corresponding reactions of the monomeric carbonyls of nickel, iron, chromium, molybdenum, and tungsten. It was anticipated that, if these metal carbonyls were to react to give bridged complexes of type I, metal-metal bonding would also occur in order to allow the metals to achieve an inert gas configuration. In certain complexes of this general type, the molecule is folded along the line joining the bridging atoms, and it has been proposed that the metal-metal bond is bent.⁵ One of our aims was to look for evidence of such folding using nuclear magnetic resonance spectroscopy.

While our investigation of the reactions of the group VI metal carbonyls was still incomplete, we learned that Chatt and his co-workers had prepared similar compounds.⁶ We therefore curtailed our work on group VI, although in fact our investigation appears to

complement that of Chatt, *et al.*, who used sealed tubes rather than solvents for their reactions and have in some cases isolated different products.

Experimental⁷

Infrared spectra were measured on a Beckmann IR-9 spectrophotometer. The nuclear magnetic resonance spectra were measured on a Varian Associates A-60 spectrometer, using tetramethylsilane as an internal standard. All the compounds described in this paper (except V) gave sharp n.m.r. spectra and are thus presumed to be diamagnetic. Methyl resonances were observed in the range τ 7.6–9.1 and phenyl resonances at about τ 2.65. Melting points were determined in evacuated capillaries unless otherwise stated and are uncorrected.

The phosphines and arsine were prepared as previously described.³ The metal carbonyl compounds were obtained from commercial sources, except triiron dodecacarbonyl, which was prepared from iron pentacarbonyl.⁸ All operations except the handling of the solid complexes were carried out under nitrogen. Chromatographic separations were carried out on Merck acid-washed alumina.

Preparation of the Complexes.—The complexes listed in Table I were prepared by reaction between the metal carbonyl (2 moles) and the biphosphine or biarsine ligand (1 mole). In the preparation of the iron complexes, $\text{Fe}(\text{CO})_5$ was used for the complexes of type IV, and $\text{Fe}_3(\text{CO})_{12}$ for $[\text{Fe}_2(\text{CO})_9\text{P}_2(\text{CH}_3)_4]$. The reaction conditions, purification procedures, yields, and properties of the complexes are summarized in Table I. Analytical data are given in Table II, and infrared data in Tables III and IV.

The reactions involving iron carbonyls deposited black solids, which were pyrophoric when dry and were removed by filtration before evaporation of the reaction solvent. Black metal-like solids were also formed during the reactions of the group VI metal carbonyls in diglyme, and these could only be partially re-

(1) (a) Part V: R. G. Hayter and L. F. Williams, *Inorg. Chem.*, **3**, 613 (1964); (b) presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., March 21–April 5, 1963.

(2) R. G. Hayter, *J. Am. Chem. Soc.*, **86**, 823 (1964).

(3) R. G. Hayter, *ibid.*, **85**, 3120 (1963).

(4) R. G. Hayter, *Inorg. Chem.*, **2**, 1031 (1963).

(5) (a) L. F. Dahl and C.-H. Wei, *Inorg. Chem.*, **2**, 328 (1963); (b) L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961);

(c) G. G. Sumner, H. P. Klug, and L. B. Alexander, *Acta Cryst.*, in press.

(6) J. Chatt, D. A. Thornton, and D. T. Thompson, private communications, and *J. Chem. Soc.*, in press.

(7) Microanalyses and molecular weight determinations were by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., Huffman Microanalytical Laboratories, Wheatridge, Colo., Dr. A. Bernhardt, Max-Planck Institut für Kohlenforschung, Mülheim, Germany, and Pascher Microanalytisches Laboratorium, Bonn, Germany.

(8) G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Vol. II, Ferdinand Enke Verlag, Stuttgart, 1960, p. 1510.