1:1 mixture of water and acetonitrile. The analysis indicated a composition of $[(CH_3)_4N]_2B_{11}Br_9H_2$. *Anal.* Calcd. for $[(CH_3)_4N]_2$-$B_{11}Br_9H_2$: C, 9.7; H, 2.7; N, 2.8; B, 12.0; Br, 72.8. Found: C, 9.7; H, 3.0: N, 2.9; B, 11.8; Br, 72.5. The infrared spectrum of this compound showed a weak B–H absorption at 2580 cm^{-1}; cage bands occurred at 1150 (w), 1120 (m), 1010 (m), 990 (m), 960 (s), 845 (s), 820 (sh), and 720 cm^{-1}. The compound had ultraviolet absorption at 2360 A (ϵ 4350) and a shoulder at 2860 A (ϵ 108). The B^{11} nmr spectrum consisted of a broad peak at +30.7 ppm with a shoulder at +20.8 ppm.

Polarographic Data.—A polarographic oxidation reduction study on $Cs(CH_3)_4NB_{11}H_{11}$ in acetonitrile solution in the potential range +0.6 to −2.0 v, with $(C_4H_9)_4NClO_4$ as supporting electrolyte, showed a well-defined oxidation wave at $E_{1/2} = 0.20$ v corresponding to approximately a two-electron oxidation. The reduction observed at $E_{1/2} = -1.9$ v was less well defined and probably represented a many-electron step. In an aqueous 0.5 M K_2SO_4 solution, the $B_9H_9^{2-}$ anion was oxidized at −0.15 v. The process was diffusion controlled at a platinum surface, and the oxidation might have been autocatalytic in nature. The use of a phosphate buffer solution did not significantly alter the results obtained in K_2SO_4 solution.

X-Ray Data.—As an additional characterization of some of the salts described in this article, lattice constants were determined from precession and Weissenberg photographs. The results are as follows (the experimentally determined density (by flotation)

is abbreviated d_E, the calculated density is designated d_X): $Rb_2B_9H_9$: tetragonal, $a = 6.33$, $c = 11.51$, $Z = 2$, $d_X = 1.98$, $d_E = 1.99$; $Cs_2B_9H_9$: tetragonal, $a = 6.50$, $c = 12.06$; $Z = 2$, $d_X = 2.43$, $d_E = 2.43$; $Cs(CH_3)_4NB_{10}H_{10}$: orthorhombic, $a = 27.72$, $b = 7.47$, $c = 7.42$, $Z = 4$, $d_X = 1.406$, $d_E = 1.390$; $Cs(CH_3)_4NB_{11}H_{13}$: orthorhombic, $a = 5.715$, $b = 5.779$, $c = 12.370$, $Z = 1$, $d_X = 1.378$, $d_E = 1.382$; $Cs(CH_3)_4NB_{11}H_{11}$: monoclinic, $a = 12.59$, $b = 5.69$, $c = 5.68$, $\beta = 96.62°$, $Z = 1$, $d_X = 1.385$, $d_E = 1.368$; $Zn(NH_3)_4B_{11}H_{11}$: hexagonal, $a = 7.46$, $c = 14.40$, $Z = 2$, $d_X = 1.26$, $d_E = 1.29$.[29]

(29) Note Added in Proof.—A recent experiment with the tetra-*n*-butylammonium salt of $B_9H_9^{2-}$ in dimethyl sulfoxide has established a minimum lifetime for the ground state (D_{3h}) geometry *at 200°* of ~10^{-4} sec. The characteristic B^{11} spectrum of $B_9H_9^{2-}$ is unperturbed at 200° and 32 Mc. We would estimate from this information that the barrier to polyhedral rearrangement in unsubstituted (*exo* or skeletal polyhedral) $B_9H_9^{2-}$ is at least 30 kcal. This experiment was performed with the cooperation of Professor M. F. Hawthorne and Phillip Garrett and with their 32-Mc radiofrequency unit. (*Caution:* Mixtures of $B_9H_9^{2-}$ salts and dimethyl sulfoxide react irreversibly and explosively fast after relatively long (minutes) induction periods at 200° and above.)

Contribution from the Frick Chemical Laboratory,
Princeton University, Princeton, New Jersey

Approximate Force Constants for Tetrahedral Metal Carbonyls and Nitrosyls

By GERALD R. VAN HECKE and WILLIAM DeW. HORROCKS, JR.

Approximate carbonyl and nitrosyl force constants have been calculated for the molecules in the tetrahedral isoelectronic series $Mn(NO)_3(CO)$, $Fe(NO)_2(CO)_2$, $Co(NO)(CO)_3$, $Ni(CO)_4$, and their substituted derivatives. The required secular equations are given for species having two different oscillators. These force constants provide a quantitative means for comparing relative π-acceptor strengths of the substituent ligands. Explicit inclusion of the CN oscillator of isonitriles is shown to be important in derivatives of ligands of this type. Empirical relationships have been determined which allow the prediction of force constants and frequencies in substituted derivatives provided information on a related molecule is available.

Introduction

In a recent series of articles[1-3] Cotton demonstrated the usefulness of easily calculated "nonrigorous" force constants for carbonyl complexes. In this method force constants are calculated from secular equations in which only the CO oscillators and their interactions are considered. Couplings between the CO vibrations and other deformations of the molecule are not included. Observed frequencies, uncorrected for anharmonicity, for molecules in solution are used, and so long as a similar procedure is employed for a series of compounds, meaningful comparisons of the calculated force constants may be made. We have extended this type of treatment to the tetrahedral isoelectronic series $Mn(NO)_3(CO)$, $Fe(NO)_2(CO)_2$, Co-

$(NO)(CO)_3$, $Ni(CO)_4$, and their substituted derivatives. Quite recently Beck and Lottes[4] reported such calculations for a large number of carbonyl, nitrosyl, and halogen compounds of manganese, iron, and cobalt. We incorporate their data with ours and with that culled from the literature by us for cobalt and nickel carbonyl and nitrosyl compounds to present a fairly complete summary of all known tetrahedral molecules of this general type. The appropriate secular equations are presented explicitly here for future use and reference.

Experimental Section

Materials.—$Co(CO)_3(NO)$ was prepared as described by Horrocks and Taylor.[5] The ditertiary phosphines 1,1-bis(diphenylphosphino)methane (dpm), 1,2-bis(diphenylphosphino)ethane (dpe), and 1,3-bis(diphenylphosphino)propane (dpp) were prepared using the method of Hewertson and Watson.[6] 1,3-Bis-

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

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

(3) F. A. Cotton, *ibid.*, **3**, 702 (1964). One of the secular equations for $Ni(CO)_4$ given in ref 3 is in error and should read, in Cotton's notation, $\lambda_{T_2} = \mu(k - k_i)$.

(4) W. Beck and K. Lottes, *Chem. Ber.*, **98**, 2657 (1965).

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

(6) W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1490 (1962).

(diphenylphosphino)propane has not been previously reported and represents a new ligand. The tertiary phosphines *n*-butyl-diphenylphosphine and di(*n*-butyl)phenylphosphine were prepared as described by Davis and Jones.[7] The Ni(CO)₄ was used from a lecture bottle supplied by A. D. McKay, Inc.

1,3-Bis(diphenylphosphino)propane.—To a solution of sodium (17.18 g, 0.746 g-atom) in 900 ml of liquid ammonia contained in a three-necked flask fitted with a stirring rod, a calcium chloride drying tube, and a stopcock was added triphenylphosphine (97.82 g, 0.372 mole). After 1 hr ammonium bromide (36.61 g, 0.377 mole) was added to the deep red solution with a resulting paling of the color to orange. One-half hour later 1,3-dibromopropane (37.56 g, 0.186 mole) in 10 ml of ether was added from a side-armed dropping funnel dropwise but rapidly. The reaction was allowed to continue 1.5 hr, at which time the Dry Ice–acetone bath was removed and the ammonia allowed to evaporate. The workup consisted of washing with 500 ml of water, followed by washing with portions of methanol until a white powder was obtained. Recrystallization was from methanol, yielding 26.5 g (30%). *Anal.* Calcd for C₂₇H₂₆P₂: C, 78.64; H, 6.31. Found: C, 78.40; H, 6.51.

Preparation of the Complexes. Co(NO)(CO)[(C₆H₅)₂P(CH₂)₃-P(C₆H₅)₂].—Co(NO)(CO)₃ (1.56 g, 9.03 mmoles) was weighed out in a cold room and placed in a solution of 100 ml of diglyme contained in a 500-ml three-necked flask. The flask was fitted with a N₂ inlet tube, reflux condenser, and side-armed dropping funnel. The ditertiary phosphine, dpp (3.68 g, 8.94 mmoles), dissolved in 20 ml of diglyme was added dropwise to the solution, which was stirred *via* a magnetic stirrer. During the course of the reaction a small, constant stream of nitrogen was maintained over the solution. After refluxing for 4 hr, when no more gas evolution was observed, the solution was cooled to room temperature. Its color was a very deep red, darker than the initial Co-(NO)(CO)₃ solution. Workup proceeded first by filtration of the fine purple powder from the solution and then crystallization from the hot diglyme solution by addition of hot water. The reddish brown microcrystals obtained were air stable indefinitely. *Anal.* Calcd for CoC₂₈H₂₆O₂NP₂: C, 63.52; H, 4.91. Found: C, 62.50; H, 5.23.

Co(NO)(CO)[(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂].—Co(NO)(CO)₃ (1.00 ml, 7.63 mmoles) pipetted as a liquid at room temperature into 50 ml of diglyme (the amount needed determined from the density, assumed to be approximately that of Ni(CO)₄, 1.32 g/ml) and dpe (3.01 g, 7.46 mmoles) in 40 ml of diglyme were treated in the manner above. Air-stable reddish brown microcrystals were obtained. *Anal.* Calcd for CoC₂₇H₂₄O₂NP₂: C, 62.91; H, 4.65. Found: C, 62.91; H, 4.79.

Co(NO)(CO)[(C₆H₅)₂P(CH₂)P(C₆H₅)₂].—Co(NO)(CO)₃ (0.45 ml, 3.4 mmoles) and dpm (1.29 g, 3.45 mmoles) were treated as above. Reddish orange microcrystals were obtained. These were air stable for a period of a few weeks but after that decomposition seemed to occur as indicated by the color change to brown. *Anal.* Calcd for CoC₂₆H₂₂O₂NP₂: C, 62.28; H, 4.39. Found: C, 62.29; H, 4.51.

Co(NO)(CO)[C₄H₉P(C₆H₅)₂]₂ and Co(NO)(CO)₂[C₄H₉P(C₆H₅)₂].—Co(NO)(CO)₃ (0.75 ml, 5.7 mmoles) and the phosphine (2.78 g, 1.15 mmoles) were treated as above except for the workup. Two products were obtained from the hot water crystallization: small brown crystals and deep red part oil–part crystalline material. Analysis and spectra indicate the brown crystals to be the disubstituted product, and the oily mass a mixture of the di- and monosubstituted compounds. *Anal.* Calcd for CoC₂₉-H₂₉O₂NP₂: C, 65.89; H, 6.32. Found: C, 65.75; H, 6.16.

Co(NO)(CO)[(C₄H₉)₂P(C₆H₅)]₂.—Co(NO)(CO)₃ (0.59 ml, 4.5 mmoles) and the phosphine (1.67 g, 7.17 mmoles) were treated as above again except for the workup. The product is a deep red oil which was not isolable; however, the infrared spectrum indicated the oil contained only the disubstituted product.

Ni(CO)₂[(C₆H₅)₂P(CH₂)₃P(C₆H₅)₂].—The same experimental setup as used with the cobalt compounds was employed except

the Ni(CO)₄ was placed into a modified buret, and then the amount required, as calculated from the density, was added to benzene in a side-armed dropping funnel. The carbonyl (1.03 ml, 7.9 mmoles) was then added dropwise to the solution containing dpp (2.92 g, 7.07 mmoles) in 80 ml of benzene. The reaction was allowed to proceed at room temperature, and only when no more gas evolution was observed was the solution gently heated; additional gas evolution was observed and a fine white precipitate formed. After 2 hr of heating the solvent was removed on a rotary evaporator. The pale yellow residue washed with methanol gave a white powder that was the product. *Anal.* Calcd for NiC₂₉H₂₆O₂P₂: C, 66.03; H, 4.93. Found: C, 65.77; H, 5.07.

Ni(CO)₂[(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂].[8]—Ni(CO)₄ (1.10 ml, 8.5 mmoles) in 20 ml of benzene was added dropwise to a solution of dpe (3.29 g, 8.26 mmoles) in 70 ml of benzene and the reaction allowed to proceed 8 hr at room temperature. Solvent was taken off then and the residue washed with methanol, yielding 3.59 g of white powder (84% yield). *Anal.* Calcd for NiC₂₈-H₂₄O₂P₂: C, 65.50; H, 4.72. Found: C, 65.73; H, 4.62.

Ni(CO)₂[(C₆H₅)₂P(CH₂)P(C₆H₅)₂].—Ni(CO)₄ (1.05 ml, 8.1 mmoles) in 30 ml of benzene and dpm (2.94 g, 7.65 mmoles) in 60 ml of benzene were treated as above for 2 hr. Evaporation of solvent left a pale yellow residue which when washed with methanol retained its color. The pale yellow powder, 3.49 g, was collected, dried *in vacuo*, and is the product (91% yield). The compound is air stable the order of 2–3 weeks but turns a dull ochre color indicating decomposition after 1 month. *Anal.* Calcd for NiC₂₇H₂₂O₂P₂: C, 64.92; H, 4.41. Found: C, 65.01; H, 4.64.

Ni(CO)₂[C₄H₉P(C₆H₅)₂]₂.—Ni(CO)₄ (0.65 ml, 5.1 mmoles) in 20 ml of benzene and the phosphine (2.47 g, 10.2 mmoles) in 80 ml of benzene were treated as above except gentle heating was employed. The solution turned yellowish with heat and after 1 hr was allowed to cool. The yellow residue, left after solvent removal, was washed with methanol and yielded a white powder which was dried *in vacuo* at room temperature. *Anal.* Calcd for NiC₃₀H₂₉O₂P₂: C, 68.11; H, 6.34. Found: C, 67.96; H, 6.35.

Ni(CO)₂[(C₄H₉)₂P(C₆H₅)]₂.—Ni(CO)₄ (0.36 ml, 2.8 mmoles) in 30 ml of benzene and the phosphine (1.00 g, 4.63 moles) in 60 ml of benzene were treated as above, except when no more gas evolution could be seen at room temperature, the solution was heated to reflux for 15 min and allowed to cool. Evaporation of solvent left a yellow oil which did not precipitate on addition of methanol and has not been isolated.

The microanalyses were done by either George I. Robertson, Jr., Florham Park, N. J., or Galbraith Laboratories, Inc., Knoxville, Tenn.

Infrared Measurements.—All infrared spectra reported for these new compounds were recorded on a Beckman IR-12 grating spectrometer.

Procedure

The secular equations for the known types of tetracoordinate carbonyl and nitrosyl molecules were generated by standard procedures[9] utilizing Cotton and Kraihanzel's assumptions.[1] The appropriate secular equations for tetracoordinate molecules containing a single type of oscillator are given in footnote 22 of ref 3. Those applicable to molecules containing two different types of oscillator are presented in Table I. The principal stretching force constants are f_{XO}, f_{ZO}; stretch–stretch interaction force constants between the same type of oscillator are designated f'_X,

(7) W. C. Davis and W. J. Jones, *J. Chem. Soc.*, 33 (1929).

(8) J. Chatt and F. A. Hart, *ibid.*, 1378 (1960), first prepared this complex. Their method differs in heating the solution and recrystallization from ethanol with great loss of product.

(9) See E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

TABLE I

SECULAR EQUATIONS FOR TETRACOORDINATE MOLECULES
CONTAINING TWO TYPES OF OSCILLATOR[a]

Type of molecule or ion (molecular symmetry)	Vibrational symmetry species	Secular Equations
$M(XO)(ZO)_3$ (C_{3v})	A_1	$\begin{vmatrix} \mu_{ZO}(f_{ZO} + 2f'_Z) - \lambda & 3^{1/2}\mu_{ZO}f'_{XZ} \\ 3^{1/2}\mu_{XO}f'_{XZ} & \mu_{XO}f_{XO} - \lambda \end{vmatrix} = 0$
	E	$\lambda = \mu_{ZO}(f_{ZO} - f'_Z)$
$M(XO)_2(ZO)_2$ (C_{2v})	A_1	$\begin{vmatrix} \mu_{XO}(f_{XO} + f'_X) - \lambda & 2\mu_{XO}f'_{XZ} \\ 2\mu_{ZO}f'_{XZ} & \mu_{ZO}(f_{ZO} + f'_Z) - \lambda \end{vmatrix} = 0$
	B_1	$\lambda = \mu_{XO}(f_{XO} - f'_X)$
	B_2	$\lambda = \mu_{ZO}(f_{ZO} - f'_Z)$
$ML(XO)_2(ZO)$ (C_s)	A'	$\begin{vmatrix} \mu_{XO}(f_{XO} + f'_X) - \lambda & 2^{1/2}\mu_{XO}f'_{XZ} \\ 2^{1/2}\mu_{ZO}f'_{XZ} & \mu_{ZO}f_{ZO} - \lambda \end{vmatrix} = 0$
	A''	$\lambda = \mu_{XO}(f_{XO} - f'_X)$
$ML_2(XO)(ZO)$ (C_s)	A'	$\begin{vmatrix} \mu_{XO}f_{XO} - \lambda & \mu_{XO}f'_{XZ} \\ \mu_{ZO}f'_{XZ} & \mu_{ZO}f_{ZO} - \lambda \end{vmatrix} = 0$

[a] μ_{XO} is the reciprocal reduced mass of the XO oscillator, etc.; $\lambda = 4\pi^2\nu^2$ where ν is the vibrational frequency.

f'_Z, while the stretch–stretch interaction force constant between different types of oscillators is designated f'_{XZ}. The secular equations for hexacoordinate carbonyl compounds containing ligands themselves with stretching frequencies close to the carbonyl region (*i.e.*, isonitriles) were constructed in a like manner and are available from the authors. Following Cotton[1] the *cis* and *trans* interaction force constants in the hexacoordinate molecules are assumed to have the relationships: $f''_{XZ} \approx 2f'_{XZ} = f_{XZ}$ and $f''_X \approx 2f'_X = f_X$, where the double prime refers to a *trans* situation and single prime to a *cis*. In the tetracoordinate molecules with two types of oscillators, more unknown force constants appear than there are observed frequencies. In these cases the secular equations were solved by making some reasonable assumption about the value of the stretch–stretch interaction force constant, f'_{XZ}, between the different oscillators. The principal force constants are then functions of f'_{XZ}, although, fortunately, not very sensitive ones. The many calculations herein presented were facilitated by use of a computer program written to cover all tetracoordinate cases although this is not necessary or even desirable in individual instances. The force constant values given in the tables below are those for which all stretch–stretch interaction constants are set approximately equal.

Results and Discussion

The calculated force constants for the $Ni(CO)_{4-n}L_n$ tetracoordinate molecules are presented in Tables II, III, and IV. The ligands have been ordered according to the values of the principal CO stretching force constants in the substituted molecules. For any particular isosymmetric series of compounds these orderings parallel those obtained from raw frequency data and, as well discussed in the literature, provide a measure of π-acceptor abilities of the various ligands. The ligand order is essentially independent of the

TABLE II

OBSERVED FREQUENCIES AND CALCULATED FORCE CONSTANTS
FOR $M(XO)_3L$ MOLECULES[e]

$Ni(CO)_3L$

Ligand	f_{CO}	f'_C	A_1	E	Solv	Ref
PF_3	17.26	0.35	2109	2046.5	a	f
$P(CF_3)_3$	17.25	0.34	2107.0	2046.0	a	g
PCl_3	17.19	0.33	2103	2043	a	f
$PCl_2(OC_4H_9)$	17.06	0.36	2097.5	2033.5	a	h
$PCl_2(C_6H_5)$	16.96	0.36	2092.7	2027.5	a	h
$As(OCH_3)_3$	16.90	0.39	2093	2022	a	i
$As(OC_2H_5)_3$	16.87	0.40	2092	2019.5	a	i
$PCl(OC_4H_9)_2$	16.85	0.38	2088.7	2019.5	a	h
$P(OC_6H_5)_3$	16.79	0.38	2070	1997	a	f
$SbCl(C_2H_5)_2$	16.76	0.37	2082	2014.5	a	j
$PCl(C_6H_5)_2$	16.74	0.38	2082	2012.5	a	h
$P(C\equiv C(C_6H_5))_3$	16.73	0.37	2079.6	2013.2	a	g
$P(OCH_3)_3$	16.65	0.40	2079	2006	a	f
$P(OC_4H_9)_3$	16.62	0.40	2077.0	2004	a	h
$P(C_6H_5)$-$(C\equiv CC(CH_3)_2OH)$	16.61	0.38	2073.8	2004.6	a	f
$Sb(C_6H_5)_3$	16.61	0.38	2074	2004.5	a	j
$As(NC_5H_{10})_3$	16.55	0.41	2074	1999	a	i
$As(C_6H_5)_3$	16.54	0.40	2072	1999	a	i
$Bi(C_2H_5)_3$	16.52	0.41	2072	1997.5	a	j
$P(C_6H_5)_3$	16.50	0.40	2070	1997	a	h
$Sb(C_2H_5)_3$	16.48	0.39	2067.4	1996	a	j
$P(CH_3)_3$	16.46	0.41	2068.5	1993.5	a	f
$As(C_2H_5)_3$	16.41	0.40	2067	1990	a	i
$P(C_2H_5)_3$	16.41	0.41	2066.0	1991.0	a	f
C_5H_5N	16.23	0.51	2067	1973	d	l

$Mn(NO)_3L$

Ligand	f_{NO}	f'_N	A_1	E	Solv	Ref
$P(p\text{-}OC_6H_4Cl)_3$	13.35	0.49	1805.0	1709.5	b	4
$P(OC_6H_5)_3$	13.31	0.49	1802.0	1707.5	b	4
$Te(C_6H_5)_2$	13.22	0.47	1794	1703	c	k
$P(SC_6H_5)_3$	13.20	0.46	1792	1702.0	b	4
$P(OC_2H_5)_3$	13.13	0.50	1792.0	1695.0	b	4
$P(OC_{10}H_{21})_3$	13.13	0.50	1792.0	1694.5	b	4
$P(OC_6H_5)(OC_{10}H_{21})_2$	13.16	0.49	1792.5	1697.5	b	4
$Sb(C_6H_5)_3$	13.13	0.47	1788.0	1696.5	b	4
$As(C_6H_5)_3$	13.09	0.48	1787.0	1693.5	b	4
C_6H_5CN	13.07	0.53	1792.0	1688.5	b	4
$(C_6H_5)CH_2CN$	13.07	0.53	1792.5	1688.0	b	4
$As(p\text{-}C_6H_4OCH_3)_3$	13.07	0.46	1783.0	1690.5	b	4
$P(C_6H_5)_3$	13.04	0.46	1781.5	1691.5	b	4
$P(C_2H_5)_3$	12.96	0.47	1778.5	1685.0	b	4
C_6H_5N	12.95	0.52	1784.0	1681.0	b	4
NH_3	12.90	0.51	1778.5	1678.5	b	4
$P(C_6H_{11})_3$	12.89	0.48	1774.0	1680.5	b	4
$C_6H_{11}N$	12.88	0.52	1778.5	1676.0	b	4

[a] Hexadecane. [b] Cyclohexane. [c] Tetrahydrofuran. [d] Pyridine. [e] In this and all subsequent tables frequencies are given in cm^{-1} and force constants in mdynes/A. [f] M. Bigorgne, *Bull. Soc. Chim. France*, 1986 (1960). [g] M. Bigorgne, *J. Inorg. Nucl. Chem.*, **26**, 107 (1964). [h] M. Bigorgne in S. Kirschner, Ed., "Advances in the Chemistry of Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, p 199. [i] G. Bouquet and M. Bigorgne, *Bull. Soc. Chim. France*, 433 (1962). [j] D. Benlian and M. Bigorgne, *ibid.*, 1583 (1963). [k] W. Hieber and R. Kramolowsky, *Z. Anorg. Allgem. Chem.*, **321**, 94 (1963). [l] W. Hieber, J. Ellermann, and E. Zahn, *Z. Naturforsch.*, **18b**, 589 (1963).

type of molecule; approximate force constants for substituted hexacoordinated group VI carbonyls yield substantially similar results.[1-3] A general decrease of f_{CO} and increase of the stretch–stretch interaction force constant, f'_C, on increased carbonyl substitution is evident. Exceptions to this general trend are the ligands PF_3 and $P(CF_3)_3$,[10] where f_{CO} and f'_C show the opposite behavior. This suggests that these ligands are stronger π-acceptors than CO.

An example of the value of these constants is afforded by the coordinated isonitrile systems, $Ni(CO)_{4-n}$-

(10) M. Bigorgne, *J. Inorg. Nucl. Chem.*, **26**, 107 (1964).

TABLE III
Observed Frequencies and Calculated Force Constants for $M(XO)_2L_2$ Molecules

$Ni(CO)_2L_2$

Ligand	f_{CO}	f'_C	A_1	B_1	Solv	Ref
PF$_3$	17.32	0.38	2093.5	2049	a	i
P(CF$_3$)$_3$	17.27	0.33	2088	2048	a	j
(CF$_3$)$_2$P(CH$_2$)$_2$P(CF$_3$)$_2$	17.23	0.34	2085	2045	b	k
PCl$_3$	17.18	0.32	2081	2043	a	i
PCl$_2$(OC$_4$H$_9$)	16.91	0.37	2068.2	2023.5	a	l
PCl$_2$(C$_6$H$_5$)	16.72	0.38	2057.5	2011.5	a	l
As(OCH$_3$)$_3$	16.60	0.45	2054	2000	a	m
PCl(OC$_4$H$_9$)$_2$	16.51	0.43	2047.5	1995.5	a	l
As(OC$_2$H$_5$)$_3$	16.50	0.43	2047	1995	a	m
P(OC$_6$H$_5$)$_3$	16.49	0.40	2045	1996	a	i
SbCl(C$_6$H$_5$)$_2$	16.31	0.41	2034	1984	a	n
P(C≡C(C$_6$H$_5$))$_3$	16.29	0.39	2032.5	1984.2	a	k
PCl(C$_6$H$_5$)$_2$	16.24	0.42	2031.3	1979.5	a	l
P(OCH$_3$)$_3$	16.11	0.44	2024	1970	a	i
P(OC$_4$H$_9$)$_3$	16.02	0.45	2019	1963.5	a	l
Sb(C$_6$H$_5$)$_3$	15.99	0.43	2016	1963	a	n
P(C$_6$H$_5$)$_2$-(C≡CC(CH$_3$)$_2$OH)	15.95	0.46	2015.8	1959.0	a	k
As(C$_6$H$_5$)$_3$	15.86	0.47	2010	1952	a	m
P(C$_6$H$_5$)$_3$	15.84	0.45	2007.6	1952.4	c	l
Sb(C$_2$H$_5$)$_3$	15.78	0.45	2004	1948.5	a	n
dpe	15.76	0.48	2005.6	1944.9	d	
P(CH$_3$)$_3$	15.69	0.48	2001.0	1940.2	a	k
dpp	15.66	0.51	2000.2	1937.0	d	
dpm	15.65	0.46	1997.4	1939.3	d	
As(C$_2$H$_5$)$_3$	15.62	0.48	1996	1936	a	m
P(C$_4$H$_9$)(C$_6$H$_5$)$_2$	15.61	0.51	1998.2	1934	d	
P(C$_2$H$_5$)$_3$	15.60	0.48	1995.0	1935.0	a	k
tdp	15.33	0.50	1992	1929	e	o
ophen	15.27	0.58	1981	1907	f	p

$Fe(NO)_2L_2$

Ligand	f_{NO}	f'_N	A_1	B_1	Solv	Ref
PF$_3$	14.46	0.40	1838.0	1788.0	g	4
P(OC$_6$H$_5$)$_3$	13.39	0.39	1769.5	1719	g	4
As(C$_6$H$_5$)$_3$	12.82	0.34	1730	1684.5	g	4
P(C$_6$H$_5$)$_3$	12.73	0.33	1723	1679	g	4
dpe	12.75	0.35	1726	1679	h	q
Te(C$_6$H$_5$)$_5$	12.38	0.32	1699.5	1656	g	4

^{a} Hexadecane. ^{b} Frequencies corrected to hydrocarbon solvent. ^{c} Cyclohexane. ^{d} Chloroform. ^{e} Halocarbon mull. ^{f} Benzene. ^{g} Carbon tetrachloride. ^{h} Tetrachloroethylene. ^{i} Table II, footnote f. ^{j} Table II, footnote k. ^{k} M. Bigorgne, *J. Organometal. Chem.* (Amsterdam), **1**, 101 (1963). ^{l} Table II, footnote h. ^{m} Table II, footnote i. ^{n} Table I, footnote j. ^{o} R. B. King, *Inorg. Chem.*, **2**, 936 (1963). ^{p} Table II, footnote l. ^{q} W. Hieber and J. Ellermann, *Ber.*, **96**, 1643 (1963).

TABLE IV
Observed Frequencies and Calculated Force Constants for $M(XO)L_3$ Molecules

$Ni(CO)L_3$

Ligand	f_{CO}	A_1	Solv	Ref
PF$_3$	17.35	2073	a	c
PCl$_3$	17.12	2059	a	c
PCl$_2$(OC$_4$H$_9$)	16.76	2037	a	d
PCl$_2$(C$_6$H$_5$)	16.45	2018.5	a	d
PCl(OC$_4$H$_9$)$_2$	16.22	2004	a	d
P(OC$_6$H$_5$)$_3$	16.22	2004	a	c
PCl(C$_6$H$_5$)$_2$	15.76	1975.7	a	d
P(OCH$_3$)$_3$	15.56	1963	a	c
P(OC$_4$H$_9$)$_3$	15.42	1954.3	a	d
P(CH$_3$)$_3$	14.84	1917	a	c

$Co(NO)L_3$

Ligand	f_{NO}	A_1	Solv	Ref
PF$_3$	14.90	1844	b	4
P(OC$_6$H$_5$)$_3$	13.29	1738	b	4
P(C$_6$H$_5$)$_3$	11.83	1640	b	4

^{a} Hexadecane. ^{b} Carbon tetrachloride. ^{c} Table II, footnote f. ^{d} Table II, footnote h.

$(CNR)_n$, with $R = CH_3$, C_2H_5, C_4H_9, C_6H_5; $n = 1, 2, 3, 4$. In Table V are given the force constants for molecules of this type calculated from two points of view: (i) considering the isonitrile group to be a noninteracting ligand, L; (ii) considering the CN stretch to be coupled to the carbonyl stretch. It is reasonable to require that the values of f_{CO} and f'_C fall near the locus of points shown in Figure 1. For the "complete" calculation the stretch–stretch interaction constant between a CO and the CN of the isonitrile, f'_{CRNC}, was taken such that $f'_{RNC} \approx f'_{CRNC}$, where f'_{RNC} is the interaction constant between CN stretches of two coordinated isonitriles and f'_{CRNC} is the CO–isonitrile interaction constant. The f_{CO} and f'_C values obtained considering the CN and CO oscillators fall nicely within the points in Figure 1, while the values obtained taking CNR = L and noninteracting are in poor agreement. Similar results obtain for the $Mo(CO)_{6-n}(CNR)_n$ systems.
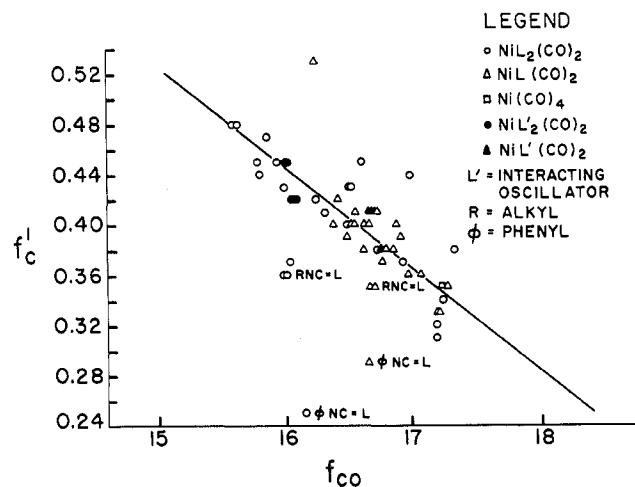

Figure 1.—Stretch–stretch interaction force constants *vs.* the principal force constants for substituted $Ni(CO)_4$ derivatives.

To determine the effect of two dissimilar oscillators in hexacoordinate compounds, the series $Mo(CO)_{6-n}$-$(CNR)_n$ was investigated. The results of the calculations are presented in Table VI. The same relationship between *cis* and *trans* force constants assumed by Cotton[1] is also employed here. The "complete" calculation was made tractable without recourse to a computer by neglecting all off-diagonal elements. It is seen from Table VI that as expected $f_{CO}(trans) > f_{CO}(cis)$ when isonitrile oscillators are included. For the $Mo(CO)_3(CNR)_3$ *cis* system there is no difference in Cotton's secular equations where CNR = L and those obtained from the "complete" equation with neglect of off-diagonal elements; to the first approximation, then, the consideration of the CN oscillator of the isonitrile ligands in such a system affords no advantage. It is in the $Mo(CO)_5(CNR)$ system that the "complete" equations prove their worth, for the RNC = L $f_{CO}(cis) > f_{CO}(trans)$, which is not in agreement with previous results.[1-3] However, the expected order obtains when the calculations

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TABLE V

OBSERVED FREQUENCIES AND CALCULATED FORCE CONSTANTS FOR SOME $M(XO)_2(ZO)_2$ AND $M(XO)(ZO)_3$ MOLECULES

$Ni(CO)_2(CNR)_2$

</div>

	Cotton		"Complete"										Solv	Ref
	f_{CO}	f'_C	f_{CO}	f'_C	f_{RNC}	f'_{RNC}	f'_{CRNC}	A_1	A_1	B_1	B_2		Solv	Ref
$CNCH_3$	16.03	0.37	16.08	0.42	17.67	0.26	0.25	2176.0	2015.5	1969.0	2138.5		a	e
CNC_2H_5	16.00	0.36	16.06	0.42	17.53	0.24	0.25	2166.5	2013.0	1968.0	2131.0		a	e
CNC_4H_9	15.99	0.36	16.04	0.42	17.45	0.24	0.25	2163.7	2012.0	1967.0	2125.0		a	e
CNC_6H_5	16.15	0.25	16.05	0.49	16.94	0.40	0.25	2142.0	2016.0	1963.0	2085.0		b	f

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$Fe(NO)_2(CO)_2$

</div>

	f_{CO}	f'_C	f_{NO}	f'_N	f'_{NC}	A_1	A_1	B_1	B_2	Solv	Ref
	17.06	0.35	14.12	0.40	0.35	2083	1810	2034	1766	c	g

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$Ni(CNR)(CO)_3$

</div>

	Cotton		"Complete"							Solv	Ref
	f_{CO}	f'_C	f_{CO}	f'_C	f_{RNC}	f'_{CRNC}	A_1^{CN}	A_1^{CO}	E^{CO}	Solv	Ref
CNC_6H_5	16.65	0.29	16.74	0.38	17.31	0.30	2147	2066	2013	a	f
$CNCH_3$	16.65	0.36	16.70	0.41	18.07	0.30	2187.5	2073.2	2008.5	a	e
CNC_2H_5	16.63	0.35	16.69	0.41	17.89	0.30	2178	2071.5	2007.8	a	e
CNC_4H_9	16.62	0.35	16.68	0.41	17.83	0.30	2174.3	2071.3	2007.0	a	e

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$Co(CO)_3(NO)$

</div>

	f_{CO}	f'_C	f_{NO}	f'_{NC}	A_1	A_1	E	Solv	Ref
	17.04	0.35	14.44	0.35	2100.2	1807.0	2033.2	d	h

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$Ni(CO)(CNR)_3$

</div>

	Cotton		"Complete"							Solv	Ref
	f_{CO}	f'_C	f_{CO}	f_{RNC}	f_{RNC}	f'_{CRNC}	A_1^{CN}	A_1^{CO}	E^{CN}	Solv	Ref
CNC_6H_5	15.69	...	15.83	16.65	0.34	0.35	2142	1971	2070	a	f
$CNCH_3$	15.39	...	15.47	17.16	0.30	0.30	2165	1952	2104	a	e
CNC_2H_5	15.36	...	15.44	17.01	0.29	0.30	2155	1950	2096	a	e
CNC_4H_9	15.36	...	15.44	16.94	0.31	0.30	2153	1950	2090	a	e

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$Mn(CO)(NO)_3$

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	f_{CO}	f_{NO}	f'_N	f'_{NC}	A_1^{CO}	A_1^{NO}	E^{NO}	Solv	Ref
	17.43	13.75	0.53	0.50	2088	1823	1734	d	i, j

^{a} Hexadecane. ^{b} Chloroform. ^{c} Tetrachloroethylene. ^{d} Cyclohexane. ^{e} Table III, footnote k. ^{f} M. Bigorgne, *Bull. Soc. Chim. France*, 295 (1963). ^{g} D. W. McBride, S. L. Stafford, and F. G. A. Stone, *Inorg. Chem.*, **1**, 386 (1962). ^{h} W. D. Horrocks, Jr., and R. H. Mann, *Spectrochim. Acta*, **21**, 399 (1965). ^{i} C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2582 (1961). ^{j} W. Hieber and T. Krum, *Chem. Ber.*, **94**, 1214 (1961).

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TABLE VI

OBSERVED FREQUENCIES AND CALCULATED FORCE CONSTANTS FOR SOME
SUBSTITUTED ISONITRILE MOLYBDENUM HEXACARBONYLS^a

$Mo(CO)_5(CNR)$

</div>

Ligand	Cotton				Present											Solv	Ref
	f_{CO}^t	f'^t_C	f_{CO}^c	f'^c_C	f_{CN}	f_{CO}^t	f'^t_C	f_{CO}^c	f'^c_C	A_1^{CN}	A_1^{CO}	A_1^{CO}	E			Solv	Ref
CH_3NC	15.72	0.22	16.67	0.11	18.06	16.11	0.58	15.51	0.29	2178	2070.8	1959.9	1959.7			b	c
C_2H_5NC	15.70	0.22	16.65	0.11	17.84	16.09	0.60	15.49	0.30	2165	2069	1958.5	1958.5			b	c
C_6H_5NC	16.03	0.23	15.73	0.12	18.41	16.08	0.51	15.58	0.26	2135	2057.5	1964	1964			b	d

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cis-$Mo(CO)_4(CNR)_2$

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Ligand	Cotton				Present												Solv	Ref
	f_{CO}^t	f'^t_C	f_{CO}^c	f'^c_C	f_{CN}	f'_N	f_{CO}^t	f'^t_C	f_{CO}^c	f'^c_C	A_1^{CN}	B_1^{CN}	A_1^{CO}	A_2^{CO}	B_2^{CO}	B_1^{CO}	Solv	Ref
CH_3NC	15.47	0.84	15.04	0.42	17.73	0.30	15.79	0.73	15.09	0.16	2176	2140	2022.5	1943.4	1930.7	1923.0	b	c
C_2H_5NC	15.45	0.82	14.99	0.41	17.56	0.28	15.69	0.70	15.07	0.16	2165	2131	2018	1941.5	1930	1921.5	b	c
C_6H_5NC	15.47	0.48	15.69	0.24	16.34	0.44	15.81	0.58	15.32	0.096	2135	2078	2015	1954	1942	1942	b	d

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cis-$Mo(CO)_3(CNR)_3$

</div>

Ligand	Cotton				Present							Solv	Ref
	f_{CO}	f'_C	f_{CN}	f'_N	f_{CO}	f'_C	A_1^{CN}	E^{CN}	A_1^{CO}	E^{CO}		Solv	Ref
CH_3NC	14.83	0.31	17.54	0.22	14.83	0.31	2174	2133	1957	1896		b	c
C_2H_5NC	14.80	0.29	17.35	0.21	14.80	0.29	2160	2122	1952	1895		b	c
C_6H_5NC	15.09	0.15	16.63	0.36	15.09	0.15	2135	2068	1953	1823.5		b	d

^{a} $f^t = f^{trans}$; $f^c = f^{cis}$. ^{b} Hexadecane. ^{c} Table III, footnote k. ^{d} Table V, footnote f.

include the CN oscillator. Further, treating coordinated isonitrile as a noninteracting ligand L in complexes of the type $Mo(CO)_5L$ produces values of the interaction constants $f'_C(cis)$ and $f'_C(trans)$ which do not fall anywhere near the locus of points generally found in plots of these quantities *vs.* $f_{CO}(cis)$ and $f_{CO}(trans)$ in molecules of this general type. However, when a RCN–CO interaction constant is introduced quite reasonable values of $f'_C(cis)$ and $f'_C(trans)$ are obtained. Although quite approximate, the ease with

TABLE VII

OBSERVED FREQUENCIES AND CALCULATED FORCE CONSTANTS FOR $M(XO)_2(ZO)L$ MOLECULES

Ligand	f_{CO}	f'_C	f'_{NC}	f_{NO}	A'_{CO}	A'_{NO}	A''_{CO}	Solv	Ref	f_{CO}	f'_N	f_{NO}	f'_{NC}	A'_{CO}	A'_{NO}	A''_{NO}	Solv	Ref
					Co(NO)(CO)$_2$L								Fe(CO)(NO)$_2$L					
PCl$_3$	16.97	0.33	0.35	14.39	2073.1	1805.2	2029.6	a	5									
PCl$_2$(C$_6$H$_5$)	16.75	0.36	0.35	14.08	2061.4	1785.6	2014.4	a	5									
P(OC$_6$H$_5$)$_3$	16.65	0.42	0.40	14.06	2060	1783	2005	b	c	16.55	0.41	13.71	0.40	2029.5	1786.5	1739.0	b	4
PCl(C$_6$H$_5$)$_2$	16.48	0.39	0.40	13.90	2048.5	1772.5	1996.0	a	5									
Sb(C$_6$H$_5$)$_3$										16.27	0.36	13.53	0.35	2011.0	1772.5	1730.0	b	4
As(C$_6$H$_5$)$_3$	16.36	0.43	0.45	13.80	2044	1765	1986	b	c									
P(C$_6$H$_5$)$_3$	16.25	0.40	0.40	13.72	2035	1761.0	1981.2	a	5	16.23	0.39	13.42	0.40	2010	1766	1764	b	4
Te(C$_6$H$_5$)$_2$										16.14	0.40	13.24	0.20	2012	1721	1727	a	c
P(C$_6$H$_{11}$)$_3$	16.14	0.43	0.45	13.54	2031	1748	1972	b	c	16.04	0.36	13.24	0.35	1997	1753.5	1711	b	4

^{a} Cyclohexane. ^{b} Carbon tetrachloride. ^{c} Table III, footnote q.

TABLE VIII

OBSERVED FREQUENCIES AND CALCULATED FORCE CONSTANTS FOR Co(NO)(CO)L$_2$ MOLECULES^a

Ligand	f_{CO}	f_{NO}	A_1^{CO}	A_1^{NO}	Solv	Ref
PCl$_3$	16.86	14.17	2044.5	1793.2	b	5
PCl$_2$(C$_6$H$_5$)	16.52	13.83	2023.6	1771.7	b	5
P(OC$_6$H$_5$)$_3$	16.26	13.71	2008	1764	c	h
PCl(C$_6$H$_5$)$_2$	15.93	13.45	1987.3	1747.2	b	5
C$_5$H$_5$N	15.60	13.42	1967	1745	d	h
Sb(C$_5$H$_5$)$_3$	15.52	13.02	1962	1719	e	h
dpe	15.47	12.82	1958.8	1705.3	f	
As(C$_6$H$_5$)$_3$	15.47	13.07	1959	1722	c	h
As(C$_6$H$_5$)$_3$P(C$_6$H$_5$)$_3$	15.46	12.99	1958	1717	c	h
P(C$_6$H$_5$)$_3$	15.42	13.01	1956.7	1717.0	b	5
dpm	15.37	13.12	1952.4	1725.2	f	
dpp	15.30	12.76	1947.8	1701.7	f	
P(C$_4$H$_9$)(C$_6$H$_5$)$_2$	15.20	12.71	1942.2	1697.3	f	
P(C$_6$H$_{11}$)$_3$	15.03	12.66	1931	1695	c	h
C$_{12}$H$_8$N	14.77	12.19	1914	1663	c	h
o-phenan	14.71	12.12	1909.8	1658.1	g	5

^{a} f'_{NC} = 0.30 for all compounds. ^{b} Cyclohexane. ^{c} Carbon tetrachloride. ^{d} Petroleum ether. ^{e} KBr pellet. ^{f} Chloroform.
^{g} Nujol mull. ^{h} Table III, footnote q.

which these numbers may be obtained through the neglect of off-diagonal terms recommends this application of the "complete" equations.

The force constants calculated for derivatives of Co(NO)(CO)$_3$ are presented in Tables IV, VII, and VIII. Since in the Co(NO)(CO)$_3$ derivatives there are more force constants than observed frequencies, the solution of the secular equations requires the choice of a parameter. The CoL$_2$(NO)(CO) system (see Table VIII) is unique in that it is described by only one interaction constant, a value for which must be assumed, and no criterion for choice is available, such as assuming that all interaction constants are equal. An upper limit may be assigned to f'_{NC}, however. The solution of the secular equation has f'_{NC} appearing in the discriminant of general solution of a quadratic equation. The upper limit is then

$$f'_{NC} \leqq (4\mu_{CO}\mu_{NO})^{-1/2}(\lambda_1 - \lambda_2)$$

where λ_1 and λ_2 are calculated from the observed A' frequencies by $\lambda_i = 4\pi^2\nu_i^2$. For PCl$_3$ ($\lambda_1 - \lambda_2$) is the largest so that $f'_{NC} = 1.31 \times 0.5679 = 0.634$. It is evident from the calculations that regardless of the f'_{NC} value, the trend of decreasing both f_{CO} and f_{NO} with substitution of carbonyl groups by those of lesser π-bonding ability still obtains. Figure 2 demonstrates this trend in f_{CO} and f_{NO} for a fixed value of f'_{NC}. The slope of a plot of f_{NO} vs. f_{CO} is less than 1.0, indicating that f_{CO} is slightly more sensitive to
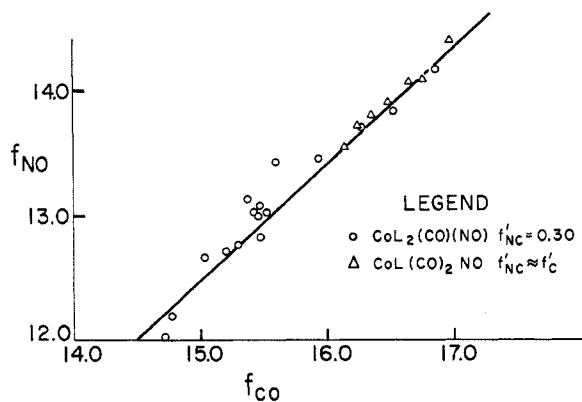
Figure 2.—Principal NO force constant *vs.* the principal CO force constant for Co(NO)(CO)$_{3-n}$L$_n$ derivatives: Co(NO)-(CO)$_2$L values of f_{NO}, f_{CO} for which $f'_{NC} \approx f'_C$; Co(NO)(CO)L$_2$ values of f_{NO}, f_{CO} for f'_{NC} = 0.30.

change in ligand than f_{NO}. Tables IV, VII, and VIII present the calculated force constants arranged in order of decreasing f_{CO} values. Once again the correlation between π-bond acceptor ability and the magnitude of the main force constants f_{CO} and f_{NO} is manifest. There are, however, some puzzles. It has so far been observed that f_{NO} follows f_{CO} in any given trend, but in the CoL$_2$(NO)(CO) molecules for the ligands Sb(C$_6$H$_5$)$_3$, As(C$_5$H$_5$)$_3$, P(C$_6$H$_5$)$_3$, dpm, dpe, dpp (recall the definition of dpm, dpe, dpp in the Experimental Section) this is not true. Here f_{NO}

TABLE IX

COMPARISON OF RIGOROUS AND APPROXIMATE CALCULATIONS FOR THE
PARENT NICKEL, COBALT, AND MOLYBDENUM CARBONYL COMPOUNDS

$Ni(CO)_4$

State	f_{CO}	f'_C	A_1	T	Ref
Harmonic	17.62	0.26	2135	2073.5	a
Gas	17.40	0.31	2131	2057	b
Solution	17.23	0.35	2127.5	2044.7	b, c
Rigorous	17.55	0.086			d

$Co(NO)(CO)_3$

State	f_{CO}	f'_C	f_{NO}	f'_{NC}	A_1^{CO}	A_1^{NO}	E^{CO}	Ref
Harmonic	17.60	0.30	15.06	0.17	2124	1849	2070	e
Gas	17.27	0.35	14.58	0.35	2108	1822	2047	f
Solution	17.04	0.35	14.44	0.35	2100.2	1807	2033.2	f
Rigorous	16.55	0.40	14.00					e

$Mo(CO)_6$

State	f_C	$f'_C{}^t$	$f'_C{}^c$	A_1	E	T_2	Ref
Harmonic	18.06	0.39	0.21	2186	2112	2092	d
Gas	16.68	0.46	0.27	2124	2027	2004	d
Solution	16.50	0.55	0.28	2120	2022	1987.5	f
Rigorous	18.12	0.093					d

[a] L. H. Jones, *J. Mol. Spectry.*, **5**, 133 (1960). [b] M. Bigorgne, *Bull. Soc. Chim. France*, 1986 (1960). [c] Table V, footnote f. [d] L. H. Jones, *J. Chem. Phys.*, **36**, 2375 (1962). [e] R. S. McDowell, W. D. Horrocks, Jr., and J. T. Yates, *ibid.*, **34**, 530 (1961). [f] Table V, footnote g.

does not decrease monotonically with f_{CO} but changes with a seeming arbitrariness. The solvents used in recording the infrared spectra for these were not all the same due to solubility problems, and since the force constants, *i.e.*, frequencies, fall quite close to each other, solvent effects may be responsible for the strange ordering. Although dpm, dpe, and dpp are chelating ligands capable of forming four-, five-, or six-membered rings, respectively, and thus might be expected to differ from monodentate ligands, they do not vary uniformly among themselves either in the nickel or cobalt compounds. These chelating compounds were initially prepared in view of determining the effect of chelate ring size on the carbonyl and nitrosyl frequencies. As can be seen from the tables this effect is quite small. The five- and six-membered rings are expected to be relatively little strained compared to the four-membered ring. All of these chelate compounds form readily, but the dpm complex is definitely less stable than the others. A ditertiary phosphine should show a π-acceptor ability which decreases as the aliphatic chain becomes longer and more electron releasing. This should place the ligand dpp lowest in either the nickel or cobalt series. With respect to dpe this is true; the ligand dpm does not fit into this order properly, perhaps owing to the steric strain produced by the four-membered ring. The *n*-butyldiphenylphosphine derivatives have principal force constant values lower than any of those observed for the chelating phosphines. These lower force constants demonstrate the inductive effect of the increased aliphatic chain length.

Tables III and VII present the calculated force constants for derivatives of $Fe(NO)_2(CO)_2$. The comments that have been made about the series of π-bond acceptors in the nickel and cobalt cases also apply

to these iron systems. A plot of f_{NO} *vs.* f_{CO} shows the same trend as in the cobalt systems. It can be seen from the tables that, contrary to the nickel and cobalt compounds where f'_C, the carbonyl–carbonyl stretch–stretch interaction force constant, varies inversely with f_{CO}, the nitrosyl interaction constant f'_N varies directly with f_{NO}. This is not the expected behavior, but may be a clue to the reliability of the interaction force constants.

Beck and Lottes[4] present for the $MnL(NO)_3$ system an extensive table of force constants calculated by Cotton's method omitting, however, the interaction force constants. In Table II both f_{NO} and f'_N are presented. No trend in f'_N *vs.* f_{NO} is to be found. This lack of any simple relationship between f_{NO} and f'_N is indicative of the unreliability of interaction constants calculated in this manner.

To illustrate the reliability of "nonrigorous" force constants Table IX presents the approximate force constants calculated for $Ni(CO)_4$, $Co(NO)(CO)_3$, and $Mo(CO)_6$ using observed frequencies in vapor and solution media and frequencies corrected for anharmonicity. The values obtained from the "rigorous" calculations (complete normal coordinate analyses) are included in the table for comparison. It should be pointed out that the principal force constants calculated in the present approximation from the frequencies corrected for anharmonicity in $Ni(CO)_4$ and $Mo(CO)_6$ differ from the "rigorous" values only by 0.07 and -0.06, respectively. The agreement for $Co(NO)(CO)_3$ is not as good. The lower calculated force constants based on solution data compared with those obtained using vapor-phase frequencies simply reflect the solvent-induced frequency shifts. These shifts are not necessarily identical for different types of oscillators; however, based on studies in the litera-
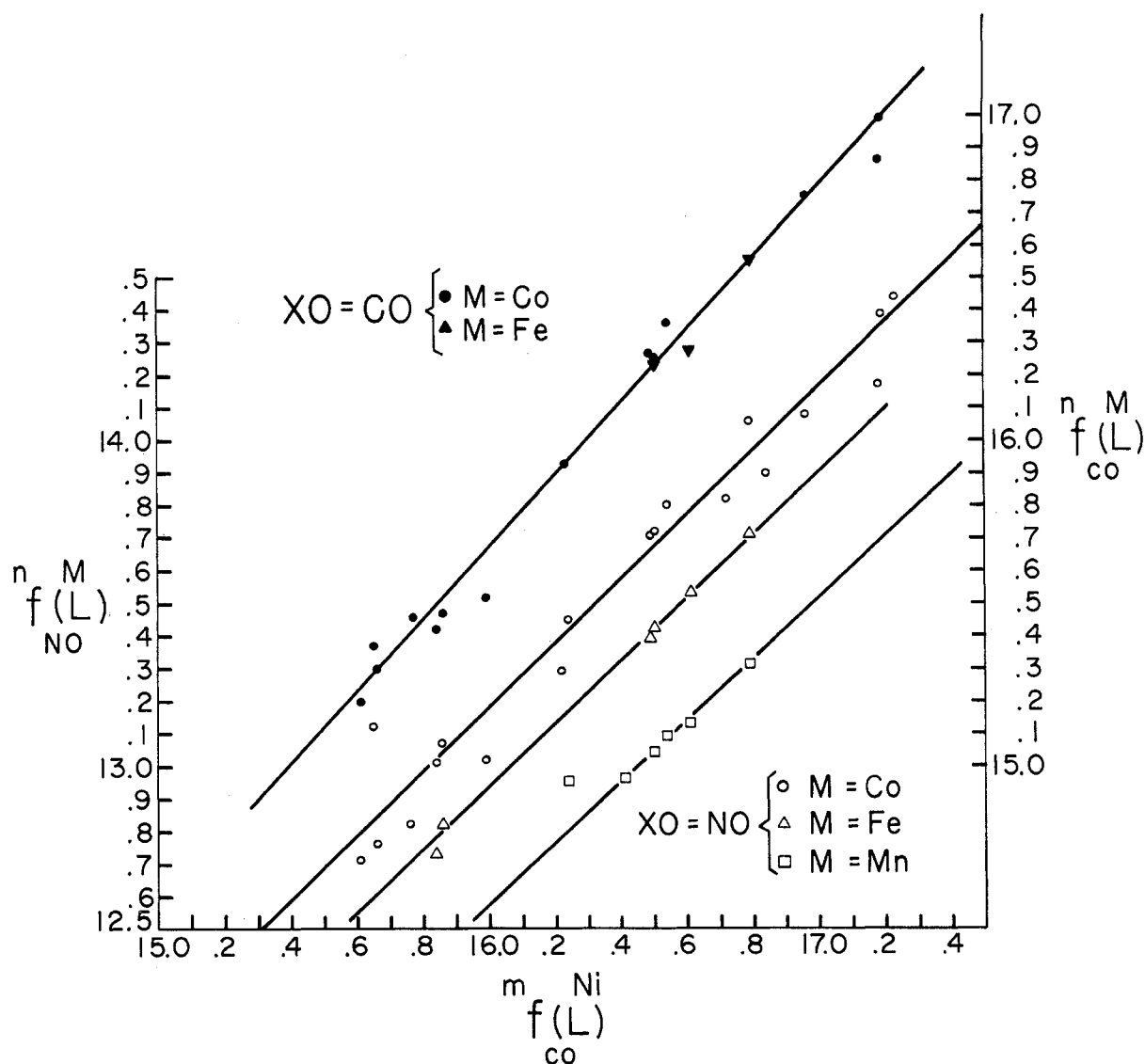
Figure 3.—Principal force constant f_{XO} for ligand L, metal M substituted to degree n vs. f_{CO} for the $Ni(CO)_4$ derivative of ligand L also substituted to degree n.

ture[11] an estimate of errors from this source may easily be made. For a more consistent comparison of the force constants presented earlier, all frequencies should be corrected to a standard solvent, ideally a hydrocarbon; the magnitude of such a correction to solution data may be seen from Table IX to be approximately $f_{CO}^{gas} - f_{CO}^{soln} \approx 0.15$–$0.20$. Further it is seen that the approximate interaction force constants are about four times greater than the "rigorous" ones. Jones[12] discusses the magnitude of these constants and concludes that the values obtained by the present method do not represent reality, in that they assume zero frequency for the metal–carbon stretch. Non-rigorous interaction constants essentially absorb the effects of coupling of the CO oscillator with all of the other vibrations of the molecule and cannot be expected to be in anyway comparable with the same constants derived from a complete vibrational analysis.

In addition to using these force constants to order ligands according to their π-acceptor abilities, newly derived relationships which hold with a fair degree of accuracy between force constants in different molecules allow the prediction of force constants in as yet unknown molecules. If the principal CO and NO force constants of the cobalt and iron compounds and the principal NO force constant of the manganese compounds are plotted against f_{CO} of the nickel tetracarbonyl derivative of the same degree of carbonyl substitution and for the same ligand L, reasonably good linear behavior is obtained as seen from Figure 3. The derivatives of nickel tetracarbonyl were chosen as the basis for these relationships because of the large number of compounds of this type presently known. The five sets of points have been fit by a least-squares treatment to give eq 1–5

(11) (a) W. D. Horrocks, Jr., and R. H. Mann, *Spectrochim. Acta*, **21**, 399 (1965); (b) W. Beck and K. Lottes, *Z. Naturforsch.*, **19b**, 987 (1964).
(12) L. H. Jones. *J. Mol. Spectry.*, **5**, 133 (1964).

$$^{n}f(L)^{Co}_{NO} = 0.9868^{n}f(L)^{Ni}_{CO} - 2.616 \quad \delta = \pm0.07 \quad (1)$$

$$^{n}f(L)^{Fe}_{NO} = 0.9607^{n}f(L)^{Ni}_{CO} - 2.433 \quad \delta = \pm0.02 \quad (2)$$

$$^{n}f(L)^{Mn}_{NO} = 0.9128^{n}f(L)^{Ni}_{CO} - 2.018 \quad \delta = \pm0.01 \quad (3)$$

$$^n f(L)^{Co}_{CO} = 1.1121^n f(L)^{Ni}_{CO} - 2.123 \quad \delta = \pm 0.05 \quad (4)$$

$$^n f(L)^{Fe}_{CO} = 1.1472^n f(L)^{Ni}_{CO} - 2.732 \quad \delta = \pm 0.03 \quad (5)$$

where $^n f(L)^{M}_{XO}$ indicates the principal force constant for the XO oscillator, where n CO groups have been replaced by ligand, L, and M is the metal under consideration. The average deviation δ is the difference between the force constants calculated from these equations and those presented in the tables. Equation 5, for the paucity of points (three), is the least reliable. The slopes indicate that f_{NO} is less sensitive to a change in ligand for the cobalt, iron, and manganese compounds relative to a change in the f_{CO} of nickel. In the cobalt and iron compounds, however, the f_{CO} is more sensitive to a change in

ligand relative to the same standard. These equations allow predictions of either $^n f(L)^{M}_{CO}$, $^n f(L)^{M}_{NO}$, or $^n f(L)^{Ni}_{CO}$ to be made if one of the molecules is known. For example, the molecule $Co(NO)(PCl_3)_3$ has not been reported; however, using f_{CO} for $Ni(CO)$-$(PCl_3)_3$ (Table V), f_{NO} for the cobalt derivative is predicted to be 14.29 and the NO stretching frequency at 1802 cm^{-1}. Force constants for other presently unknown molecules may be predicted in a similar manner.

Ditertiary Phosphine Complexes of Nickel.   Spectral, Magnetic, and Proton Resonance Studies.   A Planar–Tetrahedral Equilibrium[1]

By GERALD R. VAN HECKE and WILLIAM DeW. HORROCKS, Jr.

A number of complexes of nickel in oxidation states 0, II, and III with the ditertiary phosphines $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ (n = 1, 2, or 3) are reported and studied by spectral and magnetic methods. In solution in organic solvents complexes of the type $Ni[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]X_2$ where X = Br or I and n = 2 remain diamagnetic. The analogous complexes with n = 3 show a square-planar (diamagnetic)–tetrahedral (paramagnetic) equilibrium in solution. Isotropic proton magnetic resonance shifts were observed in these systems and thermodynamic parameters for the equilibrium were obtained from the temperature dependences of these shifts. The epr spectrum of polycrystalline $Ni[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]Br_3$ shows an isotropic signal at g = 2.218.

Introduction

Although there have been a great many complexes prepared from the nickel halides and tertiary phosphines,[2] relatively few complexes prepared with ditertiary phosphines have been reported. Complexes of the type $Ni[(C_6H_{11})_2P(CH_2)_nP(C_6H_{11})_2]Br_2$ (n = 3, 4, 5) have been prepared by Issleib and Hohlfeld.[3] Chatt and Hart[4] described the complexes $Ni[(C_2H_5)_2P$-$(CH_2)_2P(C_2H_5)_2]Cl_2$ and $Ni(o\text{-}C_6H_4[P(C_2H_5)_2]_2)X_2$, X = Cl, Br, I. Wymore and Bailar[5] reported $Ni[(C_2H_5)_2$-$P(CH_2)_2P(C_2H_5)_2]X_2$, $Ni[(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2](Cl$-$O_4)_2$, and $Ni[(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2]Br_3$. While the present investigation of complexes formed by nickel halides with the ditertiary phosphines $(C_6H_5)_2P$-$(CH_2)_nP(C_6H_5)_2$ (n = 1, 2, 3), abbreviated dpm, dpe, and dpp, respectively, was in progress, Booth

and Chatt[6] reported some nickel(II) complexes of these phosphines where n = 1 or 2. We report here the preparation, optical spectra, magnetic susceptibilities, and in certain cases epr and pmr measurements for the nickel(II) and nickel(III) complexes $Ni[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]_mX_2$, where for m = 1, n = 2, 3, X = Cl, Br, I and for m = 2, n = 1, 2, X = Cl, Br, I, and $Ni[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]$-$Br_3$, for n = 2, 3. The $Ni[(C_6H_5)_2P(CH_2)_3P$-$(C_6H_5)_2]X_2$ compounds exhibit a square-planar (diamagnetic) $\rightleftarrows$ tetrahedral (paramagnetic) equilibrium in solution in contrast to the corresponding compounds where the phosphorus atoms are linked by a chain of only two carbons which remain diamagnetic in solution. Isotropic pmr shifts allow thermodynamic parameters to be obtained readily. Using a new method, two zerovalent nickel complexes, $Ni[(C_6H_5)_2$-$(CH_2)_nP(C_6H_5)_2]_2$, where n = 2, 3, were prepared.

Experimental Section

The ditertiary phosphines 1,1-bis(diphenylphosphino)methane and 1,2-bis(diphenylphosphino)ethane were prepared by the

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(2) For a review see G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 1 (1964).

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(6) G. Booth and J. Chatt, *J. Chem. Soc.*, 3238 (1965).