Discussion

The reaction between $V(CO)_6$, $V(C_5H_5)_2$, and CO can be interpreted straightforwardly in terms of an electron transfer from $V(C_5H_5)_2$ to $V(CO)_6$. This fact allowed us to look more deeply into the details of the above mentioned mechanism of formation of $[V(C_7H_7)(C_7H_8)][V(CO)_6]$ from $V(CO)_6$ and C_7H_8. In that case the postulated hydride elimination from an intermediate $V(C_7H_8)(CO)_3$ could be conceived as a two-step process involving a hydrogen elimination and an electron abstraction; the first step being either a hydrogen transfer to $V(CO)_6$ to form the unstable[3] vanadium hexacarbonyl hydride $HV(CO)_6$ or an electron transfer to $V(CO)_6$.

The successful reaction between $V(CO)_6$ and $V(C_5H_5)_2$ seems to suggest that the intermediate formation of the unstable $HV(CO)_6$ is not necessarily required during the reaction of $V(CO)_6$ with C_7H_8.

The cation $[V(C_5H_5)_2(CO)_2]^+$ has not been described so far, whereas the uncharged $V(C_5H_5)(CO)_4$ and the anion $[V(C_5H_5)(CO)_3]^{2-}$ have been reported.[7,9]

The diamagnetic $[V(C_5H_5)_2(CO)_2]^+$ is isoelectronic with $Ti(C_5H_5)_2(CO)_2$ described some years ago by Murray.[10] The latter compound was reported to have two infrared carbonyl stretching bands at about 1965 and 1885 cm.$^{-1}$, to be compared with the bands at about 2050 and 2010 cm.$^{-1}$ for the related vanadium complex. In the latter case, the shift of the carbonyl stretching bands toward higher frequencies must be attributed to the increased positive charge on the metal.

At least one other case of oxidation–reduction reaction involving a metal carbonyl and a metal π-complex is known in the literature. As a matter of fact, Hein and Reinert,[11] in an attempt to prepare $Cr(CO)_6$, treated iron pentacarbonyl with bis-(diphenyl)-chromium(0) at 90–95° for 3–4 hr., the end product of the reaction being $[Cr(C_6H_5{-}C_6H_5)_2]_2[Fe_4(CO)_{13}]$. The mild conditions of formation of $[V(C_5H_5)_2(CO)_2][V(CO)_6]$ from $V(C_5H_5)_2$, $V(CO)_6$, and CO at atmospheric pressure and 15° clearly show the strong tendency of vanadium hexacarbonyl to act as an electron acceptor. Vanadium hexacarbonyl seems, therefore, to offer new and wider possibilities of straightforward preparation of cationic metal carbonyl species. Several complex cations have been reported recently such as $[C_5H_5Fe(CO)_3]^+$, $[C_5H_5Mo(CO)_4]^+$, $[C_5H_5W(CO)_4]^+$, $[C_5H_5Cr(CO)_4]^+$, and $[Mn(CO)_6]^+$. These cations were obtained in the presence of CO under pressure by the action of Friedel–Crafts halogen acceptors on metal carbonyl halides or cyclopentadienyl metal carbonyl halides,[12,13] or by the action[14] of $BF_3{-}O(CH_3)_2$ on the hydride $C_5H_5Cr(CO)_3H$, or, finally, by the action[15] of $NaB(C_6H_5)_4$ on $C_5H_5Fe(CO)_2Cl$. Other reactions of $V(CO)_6$ with metal complexes containing π-bonded aromatic ring systems will be investigated.

Acknowledgment.—We are greatly indebted to Professors G. Natta and R. Ercoli for their interest in this work and useful discussions, to Prof. R. Cini of the University of Florence, who carried out the magnetic susceptibility measurements, and to Dr. E. Lombardi and Dr. A. Segre for measuring the n.m.r. spectra and discussing them.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY

Infrared Spectroscopic Study of Derivatives of Cobalt Tricarbonyl Nitrosyl

BY W. D. HORROCKS, JR., AND R. CRAIG TAYLOR

Received November 24, 1962

Infrared spectra of mono- and disubstituted derivatives of $Co(CO)_3NO$ in which CO is replaced by PCl_3, $PCl_2C_6H_5$, $PCl(C_6H_5)_2$, $P(C_6H_5)_3$, *p*-tolyl isonitrile, *t*-butyl isonitrile, and *o*-phenanthroline are recorded. The π-electron accepting abilities of coördinated CO and NO are compared and a "spectrochemical series" for π-bonding ligands is proposed.

Introduction

Considerable interest has been shown recently in the infrared spectra of transition metal carbonyl compounds and their derivatives in the C–O stretching region. Several studies have dealt with the effect on the observed C–O frequencies of replacing some of the CO groups by other ligands.[1–8] In the present work we have studied the N–O frequencies as well as the C–O frequencies in mono- and disubstituted derivatives of cobalt tricarbonyl nitrosyl. A number of investigations have been made concerning the infrared absorp-

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tion of molecules containing coördinated nitric oxide.[9-12] These studies indicate that an absorption band in the region of 1575 to 1950 cm.$^{-1}$ is diagnostic of NO acting as a three-electron donor and coördinating as an NO^+ ion. The NO stretching frequency in gaseous $Co(CO)_3NO$ occurs at 1822 cm.$^{-1}$,[13] which falls in the above mentioned region. The NO^+ ion is isoelectronic with neutral CO and it is of interest to compare the behavior of these two groups when they are both coördinated to the same central metal atom. A previous study[9] seemed to show that varying the electronegativity of other ligands had little effect on the observed NO frequencies in substituted nitrosyl carbonyl compounds. We find this not to be the case. $Co(CO)_3NO$ is a pseudotetrahedral molecule with C_{3v} symmetry. The complete infrared spectrum of this compound has been analyzed[13] and is well understood. When two of the CO groups in the above molecule are replaced by other ligands, such as substituted phosphines, we have a situation where the remaining CO and NO moieties are competing with each other for electron density to be back-donated from filled cobalt orbitals into the vacant antibonding π-orbitals on the ligands. We have studied a number of molecules of this type. The ligands were chosen so as to have quite different electron accepting abilities. The C–O and N–O frequencies are sensitive indicators of the amount of charge back-donated into their antibonding π-orbitals. The greater the back-donation, the lower the observed CO or NO frequency. Increasing the charge density on the central metal atom by replacing CO groups by other ligands therefore lowers the frequency of the remaining coördinated CO and NO groups.

Combining the results of the present research with data available in the literature we propose a sort of "spectrochemical series" for π-bonding ligands, arrangement being in order of decreasing ability to withdraw charge from the central metal either by an inductive or π-electron accepting mechanism.

Experimental

Materials.—$Co(CO)_3NO$ was prepared by the dithionite method of Bor and Mohai.[14] An additional trap containing water inserted just prior to the described $CaCl_2$–P_2O_5 drying system effectively removed NH_3 from the gaseous product. The $Co(CO)_3NO$ obtained by this method was used directly without further purification. $Co(CO)_3NO$ was stored at −25° in a sealed tube.

Triphenylphosphine ($P(C_6H_5)_3$), chlorodiphenylphosphine ($PCl(C_6H_5)_2$), and dichlorophenylphosphine ($PCl_2C_6H_5$) were reagent grade chemicals obtained from Aldrich Chemical Co. Phosphorus trichloride (PCl_3) was reagent grade obtained from Allied Chemical Co.

o-Phenanthroline monohydrate was obtained from the G. Frederick Smith Chemical Co.

t-Butyl and *p*-tolyl isonitriles were prepared and purified according to the procedure of Ugi and Meyr.[15]

Preparation of Complexes. $Co(CO)_2(NO)(PCl_3)$ and $Co(CO)(NO)(PCl_3)_2$.—$Co(CO)_3(NO)$ (4.3 g., 0.025 mole) was pipetted into a reaction tube equipped with a stopcock. The tube and its contents were then cooled to −78° and 6.8 g. (0.05 mole) of PCl_3 was added. The reaction tube was evacuated and then allowed to warm to room temperature. The liquids were thoroughly mixed, cooled to −78°, evacuated, and then heated at 60° for 20–24 hr. After evacuation at −78°, the dark red liquid was warmed to room temperature and any unreacted $Co(CO)_3NO$ and PCl_3 were removed by application of a vacuum for at least 10 hr. Based on the infrared data, the dark red liquid contains both the mono- and disubstituted derivatives. Thus far, all attempts to isolate and purify these derivatives have resulted in decomposition.

$Co(CO)_2(NO)PCl_2C_6H_5$ and $Co(CO)(NO)(PCl_2C_6H_5)_2$.—$Co(CO)_3NO$ (1.7 g., 0.01 mole) and 3.6 g. (0.02 mole) of $PCl_2C_6H_5$ were treated as above with the exception that this reaction mixture was heated at 80° for 18 hr. The dark red liquid contained both mono- and disubstituted products. Attempts to isolate and purify again led to decomposition.

$Co(CO)_2(NO)PCl(C_6H_5)_2$ and $Co(CO)(NO)[PCl(C_6H_5)_2]_2$.—A 1:1 mole mixture of $Co(CO)_3NO$ and $PCl(C_6H_5)_2$ treated in the same manner at 100° for 5 hr. resulted in a dark red liquid, which, based on infrared data, contained some $PCl(C_6H_5)_2$ as well as a large amount of $Co(CO)_2(NO)PCl(C_6H_5)_2$. Attempts to purify led to decomposition.

A 1:2 mole mixture treated in the same manner gave reddish black platelets. The crude material, $Co(CO)(NO)[PCl(C_6H_5)_2]_2$, melts at ~95–100°.

Anal. Calcd. for $Co(CO)(NO)[PCl(C_6H_5)_2]_2$: C, 53.80; H, 3.61. Found: C, 54.17; H, 3.80.

$Co(CO)_2(NO)P(C_6H_5)_3$ and $Co(CO)(NO)[P(C_6H_5)_3]_2$.—$Co(CO)_2(NO)P(C_6H_5)_3$ was prepared as a side product by the method of Malatesta and Araneo.[16] On allowing the toluene solution of $Co(CO)_3NO$ and $P(C_6H_5)_3$ to stand, the monosubstituted product crystallized along with the excess $P(C_6H_5)_3$. The well formed red crystals could be easily picked out; m.p. of $Co(CO)_2(NO)P(C_6H_5)_3$ 74–76°.

Anal. Calcd. for $Co(CO)_2(NO)P(C_6H_5)_3$: C, 58.98; H, 3.71. Found: C, 60.58; H, 3.99.

The disubstituted derivative was prepared by the preceding method of Malatesta, except that the solvent used was bis-(β-methoxyethyl) ether as in the method of Matthews, Magee, and Wotiz.[17] The reaction was quite vigorous, when warmed, and red-brown platelets crystallized out as CO was evolved. The product was removed by filtration and washed with boiling methanol; m.p. of $Co(CO)(NO)[P(C_6H_5)_3]_2$ 175–178° (lit.[16] 130°).

Anal. Calcd. for $Co(CO)(NO)[P(C_6H_5)_3]_2$: C, 69.27; H, 4.71. Found: C, 69.31; H, 5.09.

$Co(CO)(NO)(CH_3C_6H_4NC)_2$ was prepared by the method of Malatesta and Sacco[18]; m.p. 133–136° (lit.[18] 156–159°).

Anal. Calcd. for $Co(CO)(NO)(CH_3C_6H_4NC)_2$: C, 58.13; H, 4.02. Found: C, 55.28; H, 4.04.

$Co(CO)(NO)((CH_3)_3CNC)_2$ was prepared by adding a solution of 1.8 g. of *t*-butyl isonitrile in 5 ml. of petroleum ether (30–60°) to a solution of 1 g. of $Co(CO)_3NO$ in 10 ml. of petroleum ether.

Evolution of carbon monoxide began immediately. The reaction mixture was allowed to stand for 10 hr., during which time orange-red crystals separated out. The complex was washed thoroughly with cold (−78°) petroleum ether. The solid was allowed to air dry and then stored at −25° in a sealed vial.

$Co(CO)(NO)((CH_3)_3CNC)_2$ is extremely soluble in most common organic solvents. These solutions are somewhat air sensitive, decomposing on standing or heating. The dry solid can be

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stored indefinitely at −25°; m.p. of $Co(CO)(NO)((CH_3)_3CNC)_2$ 70–72°.

Anal. Calcd. for $Co(CO)(NO)((CH_3)_3CNC)_2$: C, 46.65; H, 6.41. Found: C, 44.74; H, 6.42.

$Co(CO)(NO)(C_{12}H_8N_2)$ was prepared by the method of Hieber and Anderson[19] by mixing equimolar quantities of $Co(CO)_3NO$ and *o*-phenanthroline monohydrate in pyridine; m.p. ~190° dec.

Anal. Calcd. for $Co(CO)(NO)(C_{12}H_8N_2)$: C, 52.54; H, 2.72. Found: C, 50.20; H, 2.94.

All microanalyses were performed by George I. Robertson, Jr., Florham Park, N. J.

Infrared Measurements.—All infrared measurements were recorded on a Perkin-Elmer 421 grating spectrophotometer equipped with a dual grating interchange.

The scanning rate was 33 cm.$^{-1}$/min. in the 2150–2000 cm.$^{-1}$ region and 21 cm.$^{-1}$/min. in the 2000–1650 cm.$^{-1}$ region. Each cm. on the chart paper represented 10 cm.$^{-1}$. Peak positions were determined by the method of Plyler, *et al.*[20] The accurate location of the peak position was aided by the use of a Bausch and Lomb measuring magnifier with a lens calibrated in tenths of a mm. Frequencies are believed accurate to ±0.6 cm.$^{-1}$.

All complexes with the exception of $Co(CO)(NO)(C_{12}H_8N_2)$ were run in cyclohexane in 0.1-mm. NaCl liquid cells.

In the case of $Co(CO)(NO)[P(C_6H_5)_3]_2$ the pen expansion factor was changed to 5× and the slit width was doubled. This procedure was necessitated because of the low solubility of the complex in cyclohexane.

All spectra were calibrated with CO and water vapor using the wave number values of Plyler, *et al.*[20]

Results

The carbonyl and nitrosyl frequencies of the mono- and disubstituted phosphine derivatives of $Co(CO)_3NO$ taken in cyclohexane solution are shown in Table I. As expected the monosubstituted compounds show two CO stretching bands attributable to the symmetric and antisymmetric stretch in a molecule of pseudo C_s symmetry (neglecting the asymmetry of the phosphine ligand). The disubstituted compounds have only one CO and one NO group remaining and one stretching frequency is observed for each. The molecular symmetry is also pseudo C_s.

TABLE I

DATA FOR PHOSPHINE DERIVATIVES OF $Co(CO)_3NO$

	ν_{CO} sym., cm.$^{-1}$	ν_{CO} antisym., cm.$^{-1}$	ν_{NO}, cm.$^{-1}$
$Co(CO)_3NO$	2100.3	2033.0	1806.2
	One ligand		
PCl_3	2073.1	2029.6	1805.7
$PCl_2C_6H_5$	2061.4	2014.4	1785.6
$PCl(C_6H_5)_2$	2048.5	1996.0	1772.5
$P(C_6H_5)_3$	2035.0	1981.2	1761.0
	Two ligands		
PCl_3	2044.5		1793.2
$PCl_2C_6H_5$	2023.6		1771.7
$PCl(C_6H_5)_2$	1987.3		1747.2
$P(C_6H_5)_3$	1956.7		1717.0

In Table II are listed the infrared bands for $Co(CO)(NO)$(*p*-tolyl isonitrile)$_2$, $Co(CO)(NO)$(*t*-butyl isonitrile)$_2$, and $Co(CO)(NO)$(*o*-phenanthroline). The spectra of the first two compounds were recorded in cyclohexane solution, that of the *o*-phenanthroline compound could only be obtained on a halocarbon oil mull due to its insolubility in organic solvents. The bands due to the NC frequencies of the two coördinated isonitrile compounds are reported. These correspond to the symmetric and antisymmetric stretches under pseudo C_s symmetry. The values for the free isonitrile ligand in cyclohexane solution also are presented for comparison purposes.

TABLE II

DATA FOR SOME DISUBSTITUTED DERIVATIVES OF $Co(CO)_3NO$ (CM.$^{-1}$)

L	Free ligand in C_6H_{12} ν_{C-N} band	Coördinated C–N bands		ν_{C-O}	ν_{N-O}
p-Tolyl isonitrile	2120.4	2135.4	2085.9	1987.1	1745.7
		Av. = 2110.7			
-Butyl isonitrile	2131.3	2141.8	2108.4	1975.5	1733.3
		Av. = 2125.1			
o-Phenanthroline	. . .	. . .		1909.8	1658.1

Discussion

The carbonyl and nitrosyl stretching frequencies for the mono- and disubstituted derivatives of cobalt tricarbonyl nitrosyl with the series of ligands: phosphorus trichloride, dichlorophenylphosphine, chlorodiphenylphosphine, and triphenylphosphine are shown graphically in Fig. 1. The phosphines, being poorer electron acceptors than the carbonyl or nitrosyl groups, cause the electron density around the cobalt to be higher in the substituted compounds than in the parent molecule. This allows more charge to be back-donated into antibonding pπ orbitals on the remaining carbonyl and nitrosyl groups, decreasing the C–O and N–O force constants and thereby lowering the observed frequencies. The order for the different ligands is as expected. The phosphorus trichloride derivatives have the highest frequency since this ligand readily accepts charge into its vacant low lying d-orbitals due to the inductive effect of the electronegative chlorines; substituting phenyl groups for chlorines on the phosphorus makes the ligand less able to accept charge and lowers the observed CO and NO stretching frequencies. For a given ligand, the disubstituted compound has lower CO and NO frequencies than the monosubstituted molecule, which is certainly to be expected. Two phosphines will cause a higher electron density around the central metal than will one.

In Fig. 2 are plotted the single carbonyl and single nitrosyl frequencies for the compounds of the type $Co(CO)(NO)L_2$. The position of any ligand on the ordinate scale can be considered as a rough measure of the electron density accepting ability of that molecule when coördinated. It should be noted that the nitrosyl and carbonyl frequencies show approximately the same behavior on substitution of various ligands. Using this kind of graph we are able to arrange the ligands in a sort of "spectrochemical series" for π-bond-

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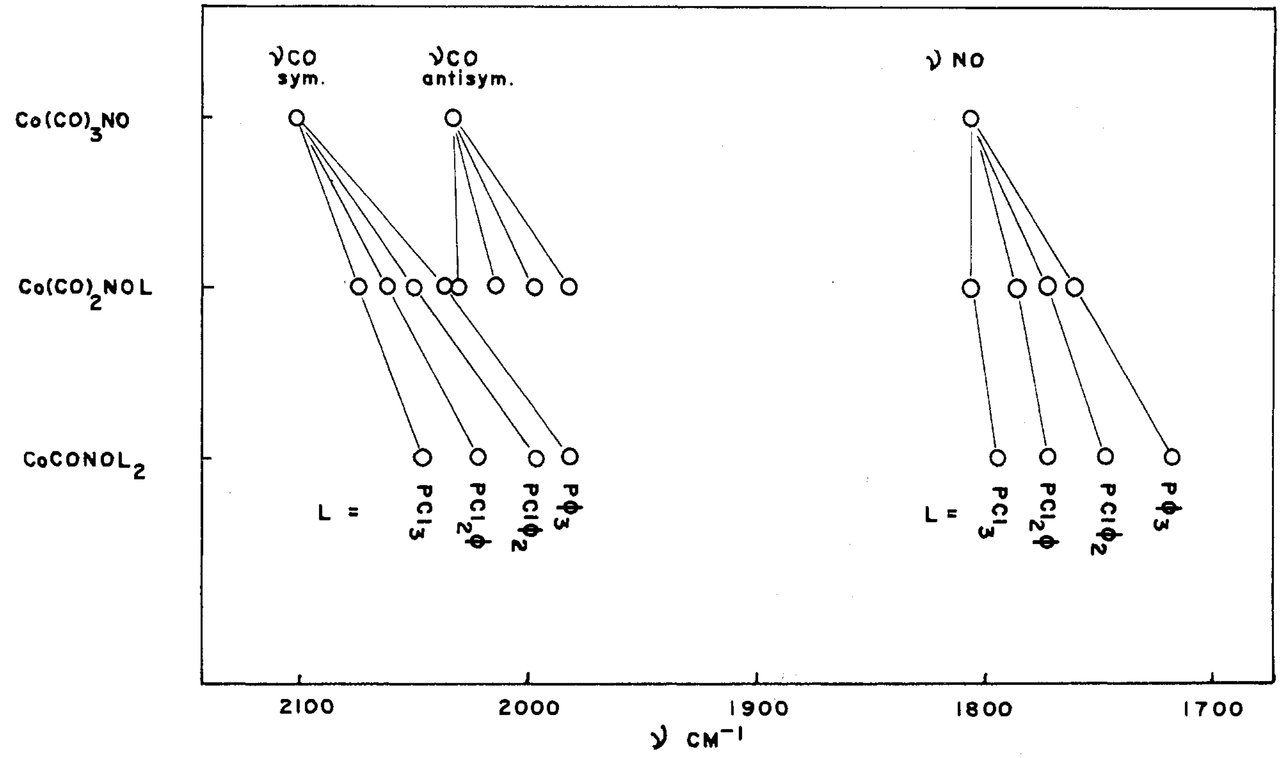

Fig. 1.—Frequencies of CO and NO bands in $Co(CO)_3NO$ and mono- and disubstituted derivatives recorded in cyclohexane solution; ϕ = phenyl.

ing ligands. The substituted phosphines fall in the expected order with decreasing electron attracting ability as phenyl groups are added. According to our data, *p*-tolyl isonitrile has almost the same electron withdrawing ability as chlorodiphenylphosphine, while the *t*-butyl compound is slightly less electronegative in behavior. This is consistent with the accepted inductive effects of aryl and alkyl groups. Our data for the isonitrile complexes are consistent with those of Cotton and Zingales[21] for some other isonitrile complexes. Two effects are expected upon coördination of an isonitrile. The mechanical coupling of the N–C and C–Co oscillators tends to raise the observed N–C stretching frequency, and back-donation from filled metal atom orbitals into vacant pπ antibonding levels on the ligand tends to lower the observed frequency. In the present case the slight lowering of the average N–C frequency, 10 cm.$^{-1}$ in the case of the *p*-tolyl compound and 6 cm.$^{-1}$ in the case of the *t*-butyl compound, over that of the free ligand, indicates that some back-donation to the coördinated isonitrile molecules is involved. In these compounds, as in the substituted carbonyl compounds studied by Cotton and Zingales,[21] the CO and NO groups bear the greater burden of charge removal.

It was of special interest to compare the electron accepting ability of coördinated CO and NO groups. The disubstituted derivatives of $Co(CO)_3NO$ are ideal for this comparison since in this case the CO and NO groups are competing directly against each other for electron density in an otherwise identical environment. It can easily be shown that for a diatomic harmonic oscillator the fractional change in force constant, dk/k, is equal to twice the fractional change in observed frequency, $d\nu/\nu$. Table III shows a comparison of three disubstituted molecules. In going from the PCl_3 to the $P(C_6H_5)_3$ derivatives the percentage change in CO and NO frequencies, and hence in the respective force constants, is approximately equal. Comparing the triphenylphosphine and *o*-phenanthroline derivatives it appears that the NO frequency and force constant is more affected by the change in electronic environment than is the CO. This is consistent with the data of Barraclough and Lewis[22] for the isoelectronic series: $Ni(CO)_4$, $Co(CO)_3NO$, $Fe(CO)_2(NO)_2$, $MnCO(NO)_3$, which indicates that at high electron densities around the central metal, the NO group is a better acceptor of charge than the CO group. It would appear from the present work that in situations of low electron density that CO and NO are almost identical in their electron accepting power while at higher charge densities the NO group is slightly better.

Table III

Comparison of Fractional Change in CO and NO Frequencies

	ν_{CO}	$\Delta\nu/\nu$	ν_{NO}	$\Delta\nu/\nu$
$Co(CO)(NO)(PCl_3)_2$	2044.5		1793.2	
		4.29%		4.24%
$Co(CO)(NO)[P(C_6H_5)_3]_2$	1956.7		1717.0	
		2.40%		3.43%
$Co(CO)(NO)$(*o*-phen)	1909.8		1658.1	

From our data on the carbonyl band of $L_2Co(CO)(NO)$ compounds and those of Bigorgne and co-workers

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[21] F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961).

[22] C. G. Barraclough and J. Lewis, *J. Chem. Soc.*, 4842 (1960); the frequencies for $Co(CO)_3NO$ reported in this reference are in error.

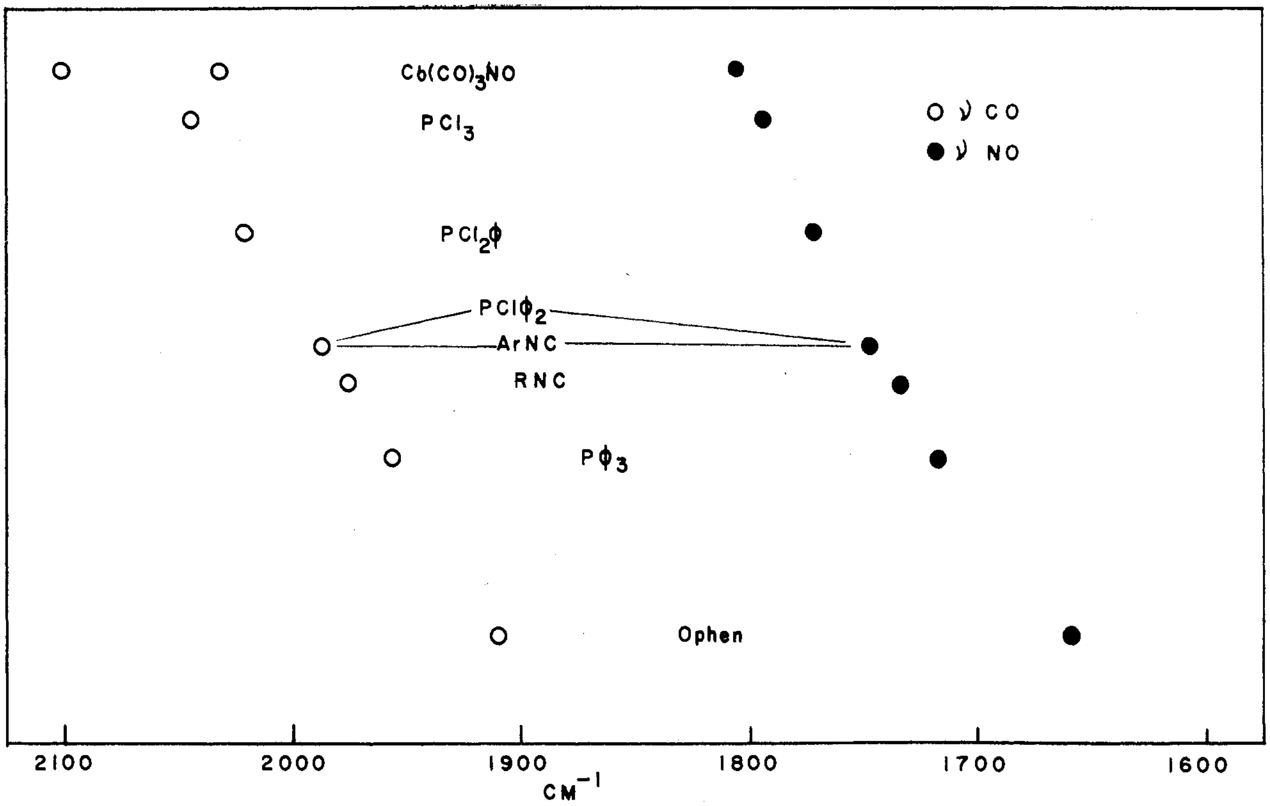

Fig. 2.—Frequencies of CO and NO bands in $Co(CO)_3NO$ and disubstituted derivatives; φ = phenyl, Ar = *p*-tolyl, R = *t*-butyl, Ophen = *o*-phenanthroline.

for the high frequency A_1 vibration in compounds of the form *cis*-$L_2Mo(CO)_4$[6,7] and for the higher frequency carbonyl band in compounds of the form $L_2Ni(CO)_2$[2] we have been able to construct a "spectrochemical series" for π-bonding neutral ligands. This is shown in Table IV. Three separate series based on data for each of the above classes of compound were formulated. These were interleaved producing no inconsistencies in ligand order. The positions of ligands not common to all three series were determined by a linear interpolation of the particular carbonyl frequency involved. The fixed points for these interpolations were the frequencies of the $L_2Co(CO)(NO)$, *cis*-$L_2Mo(CO)_4$, and $L_2Ni(CO)_2$ compounds in which L was the same in each case. All spectra here employed were of compounds in solution in saturated hydrocarbon solvents. This should minimize the solvent effect, allowing a valid comparison of frequencies.

TABLE IV

A "SPECTROCHEMICAL SERIES" FOR π-BONDING LIGANDS[a]

NO
CO
PF_3
$SbCl_3$
$AsCl_3$
PCl_3
$PCl_2(OC_4H_9)$
$PCl_2(OC_2H_5)$
$PCl_2(C_6H_5)$
PBr_2CH_3
$As(OCH_3)_3$
$PCl(OC_4H_9)_2$
$As(OC_2H_5)_3$
$P(OC_6H_5)_3$
$PCl(C_6H_5)_2$
p-Tolyl isonitrile
$P(OCH_3)_3$
t-Butyl isonitrile
$As(NC_5H_{10})_3$
$As(C_6H_5)_3$
$P(C_6H_5)_3$
$S(C_2H_5)_2$
$As(C_2H_5)_3$
$P(CH_3)_3$
$P(C_2H_5)_3$
o-$C_6H_4[P(C_2H_5)_2]_2$
$P(NC_5H_{10})_3$
o-Phenanthroline
Diethylenetriamine

[a] Data from present work and ref. 1, 2, 6, and 7.

In the case of CO and NO the electronic environment in which the ligand finds itself determines the relative electron accepting ability to some extent. This type of behavior may very well be true for other ligands. The order of ligands is not necessarily absolute and may not hold for all molecules but this series should be a good first approximation. The ligands listed first are better acceptors of charge from the central metal than are molecules lower down the series. It should be noted that inductive effects apparently are transmitted more easily through the heavier group V ligands, probably due to their greater polarizability. The data of Abel, *et al.*,[1] indicate that aliphatic amines should be placed at the bottom of the list; these molecules have no vacant low lying orbitals suitable for accepting charge. Caution must be taken when using carbonyl and nitrosyl frequencies to place molecules in a series such as this. Orgel[8] has shown that in compounds of the type $Mo(CO)_4$(*o*-phenanthroline), the force constants of the CO groups *trans* to the *o*-phenanthroline are lowered more than are those in the *cis* position. For this reason we have not attempted to place organic dienes in our series since the same types of steric factors are involved.

Acknowledgments.—The authors wish to thank Mr. Walter A. Stark for performing some preliminary experiments and Mr. Richard Mann for assistance in recording several spectra. We are indebted to Dr. Adam Allerhand for valuable discussions concerning the preparation of the isonitriles. R. C. T. is grateful to the National Science Foundation Summer Fellowship Program for Graduate Teaching Assistants and to the Leroy McCay Fellowship Program for financial aid.