$(C_5H_5)_2Mo_2(CO)_5[(C_6H_5)_3P]$ are both shifted from that of $[C_5H_5Mo(CO)_3]_2$; the doublet at τ 5.28 is assigned as arising from the cyclopentadienyl protons on the ring attached to the molybdenum atom which also bears the triphenylphosphine moiety. This conclusion is drawn from both the multiplicity and position of this absorption. The fact that the other resonance is also slightly shifted is probably a reflection of both electronic and steric factors.

The compound $[C_5H_5Mo(CO)_2COCH_3]_2$-μ-diphos decomposes very rapidly in deuteriochloroform solution, precluding a detailed analysis of the nmr spectrum.

Acknowledgment.—The authors are indebted to Mr. Larry Sims for his assistance in obtaining the nmr spectra. We are pleased to acknowledge partial support of this work through National Science Foundation Grants GP 4667 and GP 5966.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLORIDA

Metal Carbonyl–Phosphorus Trifluoride Systems. IV.[1] Cobalt Nitrosyl Tricarbonyl

BY RONALD J. CLARK

Received May 23, 1966

Cobalt nitrosyl tricarbonyl reacts readily with phosphorus trifluoride to yield all possible substitution products of the type $Co(NO)(CO)_x(PF_3)_{3-x}$. This reaction, which can be induced either thermally or by ultraviolet irradiation, always yields mixtures of species which can be separated in high purity by gas–liquid partition chromatography. The pure compounds are reddish liquids that disproportionate slowly at room temperature. The stepwise replacement constants K_1, K_2, and K_3 for the reactions illustrated by the equation

$$Co(NO)(CO)_{4-n}(PF_3)_{n-1} + PF_3 \longrightarrow Co(NO)(CO)_{3-n}(PF_3)_n + CO$$

are 2.7, 0.69, and 0.25. The values are close to the random substitution values of 3.00, 1.00, and 0.33. Both infrared studies and equilibration studies strongly indicate that PF_3 π bonds to about the same degree as carbon monoxide.

Introduction

Cobalt nitrosyl tricarbonyl has been studied as part of a continuing investigation into the interaction of phosphorus trifluoride with metal carbonyls. The remarkable similarity between the ligands carbon monoxide and phosphorus trifluoride has been clearly demonstrated several times. This similarity is shown in both the intermediate compounds[1] and the totally substituted trifluorophosphine complexes which are analogs of metal carbonyls.[1-4]

The use of a compound like $Co(NO)(CO)_3$ provides an opportunity to study not only the remaining carbonyl groups but also the nitrosyl group as the carbon monoxide is being displaced. The isoelectronic similarity between the nitrosyl group and the carbonyl ligand makes an infrared comparison quite reasonable. In addition, the possibility of the replacement of a ligand other than CO can be examined. The substitution of nitrosyl is not, in general, to be expected, but the possibility cannot *a priori* be eliminated.

During the progress of the work, it developed that cobalt nitrosyl tricarbonyl presents an ideal case for an exact study of the distribution of the various $Co(NO)(CO)_x(PF_3)_{3-x}$ species at various $CO:PF_3$ ratios. Cobalt nitrosyl carbonyl yields intermediate substitution compounds readily, and, in addition, these compounds are more clearly separable than the species in systems such as iron, nickel, and molybdenum. Further, the cobalt nitrosyl carbonyl substituents are much less subject to disproportionation than the labile nickel complexes. These advantages make possible a study of the species using vapor–liquid partition chromatography as the analytical tool.

A short report on the preparation of the cobalt nitrosyl complex totally substituted by PF_3 has been published by Kruck[5] but there is no previous information on the intermediates.

The data obtained during the preparation, isolation, and characterization of the compounds in this carbonyl–trifluorophosphine system are reported.

Experimental Section

Cobalt nitrosyl tricarbonyl was prepared several ways using low-pressure synthesis methods. The best approach employed some variations of the method by Gilmont and Blanchard.[6]

The main variations were mechanical ones dealing with the manner of gas absorption and the scale of the reaction. The reaction was carried out in a 3-l., three-neck flask. The center

---

(1) Please consider the following references as the previous papers in the series: (a) I. R. J. Clark, *Inorg. Chem.*, **3**, 1395 (1964); (b) II. R. J. Clark and E. O. Brimm, *ibid.*, **4**, 651 (1965); (c) III. R. J. Clark and P. I. Hoberman, *ibid.*, **4**, 1771 (1965).

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

(3) Th. Kruck, *Chem. Ber.*, **97**, 2018 (1964); Th. Kruck and A. Prasch., *Z. Naturforsch.*, **19b**, 669 (1964).

(4) Th. Kruck, *Angew. Chem.*, **76**, 593, 892 (1964); Th. Kruck, *ibid.*, **77**, 132 (1965).

(5) Th. Kruck and W. Lang, *ibid.*, **76**, 787 (1964).

(6) P. Gilmont and A. A. Blanchard, *Inorg. Syn.*, **2**, 239 (1946).

neck was equipped with an adaptor containing a stirring gland and an extension which had a Teflon washer to act as a second bearing support. Stirring was provided by means of a Teflon spray agitator produced by Nester–Faust. At moderate stirrings speeds, large volumes of solution or suspension were sprayed onto the sides of the flask resulting in very efficient gas–liquid contact. The other necks were equipped for gas inlet, solution admission, and gas outlet.

Careful purging of the flask prior to the addition of the solution was accomplished most simply by filling the flask with water and then allowing it to be drained through a stopcock on the bottom while admitting carbon monoxide. It was found that the best yields were obtained by using purified carbon monoxide, but it was only necessary to pass reagent grade carbon monoxide over a tube containing copper heated to about 700°.

Cobalt chloride, potassium hydroxide, and potassium cyanide were used in the same relative proportion as by Gilmont and Blanchard[6] but increased by a factor of 5. The water was increased by a factor of 7–8. The resulting suspension was stirred for 24–36 hr until the rate of carbon monoxide uptake decreased to a small fraction of the original rate. At the conclusion of this time, concentrated hydrochloric acid was added slowly with some cooling until the solution was nearly neutral. Commercial nitric oxide, purified by passing it through a $-78°$ trap, and carbon monoxide were passed through the flask for several hours until the evolution of yellow fumes ceased. The yield of the material dried over 4-A molecular sieves was 14.0 g or 65%.

The substitution reaction between PF_3 and $Co(NO)(CO)_3$ resulted from both the high-pressure–high-temperature and the low-pressure–ultraviolet methods that have been used for other systems.[1] For general work, the irradiation method was most convenient. In a typical reaction, about 0.5 g of $Co(NO)(CO)_3$ was distilled *in vacuo* into a 300-ml flask. Phosphorus trifluoride was admitted to a pressure of about 400 torr. Irradiation of the contents for about 2 hr yielded an equilibrium mixture containing about equal quantities of the mixed carbonyl–trifluorophosphines and lesser quantities of the two end members. A higher ratio of PF_3 to $Co(NO)(CO)_3$ resulted in higher concentrations of the PF_3-rich products. Similarly, removal of carbon monoxide by vacuum at $-195°$ followed by further irradiation at room temperature pushed the reaction toward the higher phosphines.

The various species were separated by gas–liquid partition chromatography under conditions described earlier.[1] A 25 ft × $^1/_4$ in. 15% silicone oil column on Kromat FB was used at 60° with helium as the carrier gas. The compounds are separated slightly better than other carbonyl–phosphines so that injections of 20–30 µl of the neat liquids were made. A somewhat larger injection was made if only the dicarbonyl was to be isolated. The samples were trapped at $-78°$ and the water that was inevitably trapped at the same time was removed by distilling the samples *in vacuo* through 4-A molecular sieves. For the monophosphine, this had to be done quickly to prevent the sample from disproportionating.

The gas chromatography apparatus was contained entirely within a hood which had good circulation as the compounds were expected to be quite toxic.

Infrared spectra on the pure species were run in hexane on a Perkin-Elmer grating 521. The 4000–650-cm^{-1} region was covered in 0.1-mm NaCl cells, and the 650–250-cm^{-1} region, in 1.0-mm cells constructed of polyethylene. Alternately, this latter region was covered in 10-cm gas cells with windows made of polyethylene film. The gas cells were purged with dry nitrogen and the compounds injected into the cells through septums and allowed to vaporize.

Ultraviolet and visible spectra were recorded on a Beckman DB.

The new compounds were analyzed for cobalt and nitrogen. For the cobalt analysis, a weighed sample was dissolved by nitric acid in a closed container to prevent loss and then analyzed by standard EDTA methods.[7] For the nitrogen analysis, a weighed sample was slowly swept into the combustion tube of a Dumas nitrogen analyzer and the nitrogen collected.

Anal. Calcd for $Co(NO)(CO)_2(PF_3)$: N, 6.01; Co, 25.3. Found: N, 5.93; Co, 25.0. Calcd for $Co(NO)(CO)(PF_3)_2$: N, 4.78; Co, 20.1. Found: N, 4.87; Co, 19.8.

Other data such as solvent stability and density were determined as before.[1]

Equilibrium data on the $Co(NO)(CO)_x(PF_3)_{3-x}$ species were obtained by gas–liquid partition chromatographic analysis of the equilibrated species. The analyses were run under conditions such that the equilibrium was not disturbed by the process of separating the species.

When efforts were made to equilibrate the end members or to disproportionate one of the intermediates to an equilibrium mixture of all four species, some decomposition always took place. This was indicated by the presence of a blackish product on the reaction vessel walls. This decomposition was prevented by performing the equilibration studies in the presence of 700 torr of ligand gas.

In a typical run, CO and PF_3 were admitted into a 200-ml evacuated flask so that each had the desired partial pressures. Next, about 100 µl of $Co(NO)(CO)_3$ was injected into the vessel through a silicone rubber septum. The vessel was irradiated in front of an AH-6 lamp for 3 hr although it was shown that no further change occurred after 1 hr. To check further on the attainment of true equilibrium, $Co(NO)(PF_3)_3$ was used and it was found that the data were consistent between the two approaches.

The analysis of the mixtures of six species was performed in two stages. In analyzing the mixture for carbon monoxide and phosphorus trifluoride, the sample was cooled to $-78°$ in order to remove the $Co(NO)(CO)_x(PF_3)_{3-x}$ species from the gas phase. Gas samples of about 1–2 ml were injected onto an 8-ft silica column at 45° using helium as a carrier gas, yielding wide separation between the PF_3 and CO peaks and an acceptable separation between the CO and air peaks. The analysis was calibrated with mixtures of CO and PF_3 made up to known partial pressures.

The $Co(NO)(CO)_x(PF_3)_{3-x}$ species were analyzed on the 25-ft silicone column using 200–400-µl gas-phase samples at room temperature. On this column, the CO and PF_3 occurred at the same time as the air peak. The analysis was calibrated by mixtures made from known volumes of the four isolated species. As the densities of the pure compounds were known, the relative weights or mole fractions of the species in the mixtures were calculated.

The relative concentrations of the ligand gas species and volatile metal complex species were determined over the entire range of composition.

Results

The reaction of $Co(NO)(CO)_3$ with PF_3 under either irradiation or pressure conditions produces three substitution products representing the sequential replacement of the carbonyl groups. No evidence for the replacement of the nitrosyl group was ever found.

The composition of the species is confirmed in several ways. The obvious assumption that the carbonyl groups are replaced sequentially serves in itself to give almost certain identification of the peaks that appear gas chromatographically. Cobalt nitrosyl tricarbonyl has the longest retention time of the various species observed. As the reaction of the tricarbonyl with PF_3 proceeds, the first new species to be produced has somewhat lower retention time and should be dicarbonylnitrosyltrifluorophosphinecobalt. Later in time, the third and fourth peaks appear successively at progressively shorter retention times and should be

---

[7] F. J. Welcher, "The Analytical Uses of Ethylenediamine Tetraacetic Acid," D. Van Nostrand Co., Inc., New York, N. Y., 1957.

carbonylnitrosylbis(trifluorophosphine)cobalt and nitrosyltris(trifluorophosphine)cobalt.

These peaks were trapped individually, purified, and subjected to further identification. The infrared analyses serve very nicely to confirm the assignments made thus far. These infrared data are shown in Table I. In the carbonyl stretching region, the absorptions are as expected for the three proposed species. The compounds assigned as $Co(NO)(CO)_2(PF_3)$, $Co(NO)(CO)(PF_3)_2$, and $Co(NO)(PF_3)_3$ have, respectively, two, one, and zero bands. Other than a shift to higher frequencies, the spectra of the first two species compare well with values found by Horrocks and Taylor[8] for related species. All three trifluorophosphine compounds have a single intense nitrosyl stretching frequency in the 1830-cm^{-1} region at a value only slightly shifted from that of the parent compound. This clearly shows that only the carbonyl groups are being replaced. Finally the frequencies for the PF_3 and NO groups for the compound assigned as $CO(NO)(PF_3)_3$ agree fairly closely with those reported by Kruck[5] for this compound.

TABLE I

INFRARED DATA ON $Co(NO)(CO)_x(PF_3)_{3-x}$ SPECIES (CM^{-1})

Species	CO str	NO str	PF str	Far-infrared region	
$Co(NO)(CO)_3$	2100 s	1806 s	. . .	595 w	440 s
	2033 s			560 s	390 w
				480 s	310 w
				465 s	
$Co(NO)(CO)_2(PF_3)$	2083 s	1817 s	875	610 vw	484 w
	2037 s			562 ms	462 m
				534 w	427 m
				509 vs	
$Co(NO)(CO)(PF_3)_2$	2059 s	1822 s	900 s	613 vw	504 vs
			853 s	560 m	456 ms
				535 sh	408 ms
				515 vs	386 vw
$Co(NO)(PF_3)_3$	. . .	1832 s	924 s	627 vw	388 ms
			891 s	590 vw	264mw
			882 sh	525 s	
			856 s	505 vs	
				446 w	

The peaks in the 650–250-cm^{-1} region are not particularly useful in determining the nature of the species. The region contains frequencies corresponding to vibrations such as M–C stretch, M–C–O bend, M–N stretch, etc. The assignment of the frequencies to various modes is not always clear, but some arguments will be made later.

As final confirmation, some cobalt and nitrogen analyses were made which agree well with the expected values. The values for the two new intermediate compounds are shown in the Experimental Section.

The gas chromatographic isolation of these species results rather simply in view of the extreme sharpness of the peaks. The separation of the peaks as indicated by the relative retention times shown in Table II is better than for any metal carbonyl–trifluorophosphine system studied before. The compounds are trapped easily and are found to be chromatographically pure. No sign of disproportionation on the column is noted under the conditions sited, although the monophosphine disproportionates quite readily and would probably do so under slightly different conditions.

As was noted for the nickel carbonyl system,[1b] carbon monoxide suppresses the disproportionation of the mixed carbonyl species. In this system the use of carbon monoxide as a carrier gas does not noticeably change the analytical results obtained for a mixture of species. It is also possible to obtain a pure sample of the most labile compound, $Co(NO)(CO)_2(PF_3)$, without the aid of carbon monoxide as a carrier gas. Still an atmosphere of CO helps suppress the room temperature disproportionation of the monophosphine and in the process it does not cause particularly fast substitution in the absence of irradiation.

A potential problem one encounters while working with metal carbonyls in a gas chromatograph is that of metal plating the filaments of the thermal conductivity cells. The trouble one encounters ranges from an abrupt shift in the base line following a peak to the complete imbalancing of the filaments. The latter case can result fairly readily with $Ni(CO)_4$. Favoring this decomposition are high filament currents, high detector temperatures, and large samples. Opposing the decomposition is the reverse of the above plus the use of carbon monoxide as a carrier gas.

In the cobalt series, trouble has been encountered only with $Co(NO)(CO)_3$. When large quantities (about 40 μl) of mixtures which are carbonyl rich are used, a small base-line shift is frequently encountered after the parent carbonyl peak. The trouble can be eliminated by turning the filaments off while that peak is being eluted. No trouble has ever been encountered during small-scale analytical runs. None of the other species have given any sign of decomposition.

Filaments have been cleaned successfully using dilute hydrochloric acid to dissolve their metal coating.

The phosphine substituents are all volatile liquids whose vapor pressures appear higher than that of the parent carbonyl. All three compounds are liquids below −78° and freeze in the range of −92° reported by Kruck[5] for $Co(NO)(PF_3)_3$. Some difficulty was encountered in attempting to obtain sharp melting points, owing perhaps to supercooling.

These compounds are mildly stable in air and moisture. They can be manipulated quickly in air with no apparent attack, but extensive oxidation or hydrolysis occurs in 24 hr. Only disproportionation takes place for samples stored in sealed, evacuated ampoules and storage at −78° will prevent this reaction.

The densities of the liquids increase regularly as the degree of PF_3 substitution increases. These data are shown in Table II.

The liquids are deep red, but the intensity decreases noticeably as the degree of PF_3 substitution increases. The visible and ultraviolet spectra of all compounds are similar. A band occurs between 370 and 350 mμ and a very intense tail starts about 280 mμ which

---

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

TABLE II

PHYSICAL DATA ON $Co(NO)(CO)_x(PF_3)_{3-x}$ SPECIES

Species	Density, g/ml	Rel retention time	Absorption max, mμ	Extinction coefficient, M^{-1} cm^{-1}
$Co(NO)(CO)_3$	1.46	1.00	374	640
$Co(NO)(CO)_2(PF_3)$	1.63	0.64	370	680
$Co(NO)(CO)(PF_3)_2$	1.77	0.45	360	590
$Co(NO)(PF_3)_3$	1.83	0.36	355	610

appears characteristic of a charge-transfer absorption. The data are given in Table II.

The species are stable in solvents like hydrocarbons but undergo extensive reactions in alcohols and acetone. The solvolysis reactions in alcohols will be the subject of a subsequent communication.

Attempts to study equilibration reactions which can be illustrated by disproportionation in the equation

$$2Co(NO)(CO)_2(PF_3) \longrightarrow Co(NO)(CO)_3 + Co(NO)(CO)(PF_3)_2$$

were discarded. This approach has been used quite profitably by Van Wazer and co-workers[9] in other types of systems. However, when attempts were made to utilize their approach in this system equilibrating either a single compound or a combination of the two end members in the absence of ligand gas, decomposition always occurred. This decomposition was indicated by the presence of a black product which formed to the extent of at least 1%.

The blackening never occurs when ligand gas is present so it seems reasonable to assume that the rearrangement must take place through a mechanism which includes ligand gas under moderate pressures. When that gas is not present initially, then the compounds must decompose to yield the needed gas plus other products.

Since the ligand gas is required, it was decided to have it present initially and look at the stepwise equilibrium illustrated by the equation

$$Co(NO)(CO)_{4-x}(PF_3)_{x-1} + PF_3 \longrightarrow Co(NO)(CO)_{3-x}(PF_3)_x + CO$$

Three equations of this sort exist with corresponding equilibrium constants. The concentration of the cobalt compounds is kept low enough so that all species are in the gas phase.

The analysis of the three equilibrium constants entails the determination of the concentrations of the four complex species and the two ligand gases. The constants can be determined from only one mixture, but it was decided to use a series of mixtures over the composition range. For any given constant, the mole ratio of two complex species and the mole ratio of the free ligands are needed. Since only two ratios are needed, the relative amounts of ligand gas and cobalt species were not determined.

The calculated equilibrium constants at various $CO:PF_3$ mole ratios are shown in Table III. These values were calculated from each set of analytical data for which the concentrations were large enough to allow the calculated constant to have some meaning. The average values of the constants for the successive replacement of the carbonyl groups are 2.7, 0.69, and 0.25. These are to be compared with values of 3.00, 1.00, and 0.33 for random distribution.

TABLE III

CALCULATED SUCCESSIVE EQUILIBRIUM CONSTANTS[a] FOR $Co(NO)(CO)_3 + PF_3$

$CO:PF_3$ ratio	K_1	K_2	K_3
0.79	2.4	0.62	...
0.71	3.2	0.74	0.24
0.59	3.0	0.64	0.20
0.59	2.2	0.60	0.23
0.52	3.1	0.79	0.28
0.39	2.5	0.74	0.26
0.33	2.5	0.71	0.28

[a] Conditions of equilibration: 700 torr of ligand gas, 25°, 3-hr irradiation by an AH-6 lamp.

Discussion

Cobalt nitrosyl tricarbonyl conforms to the general pattern shown with nickel tetracarbonyl, iron pentacarbonyl, and molybdenum hexacarbonyl.[1] Phosphorus trifluoride replaces the carbonyl groups, successively yielding as mixtures all possible compositions. These compounds can be isolated and fully characterized.

In this nitrosyl carbonyl, there is no indication of the displacement of the nitrosyl group. Although one can envision a PF_3 group replacing the NO group followed by the dimerization of the compound, there is no indication that this ever takes place. The dimer would be expected to be considerably less volatile than the monomeric nitrosyl compounds. There is a total lack of any evidence for lower volatility compounds as indicated either by their behavior under vacuum or in their glpc behavior. Also, the lack of a glpc peak that could reasonably be attributed to nitric oxide is a further confirmation.

The observation that a neutral group does not replace a group with a formal charge is, of course, quite general in the substitution reactions of metal carbonyls.

The effect of the PF_3 group on the CO stretching frequencies is again such as to mark the PF_3 as an excellent π-bonding ligand. The fairly large shift in carbonyl frequency to lower values that usually occurs as the carbonyl groups are being replaced by ligands is attributed by most workers[10] to the poor π-bonding ability of those ligands. The lack of a strong trend in the PF_3 compounds can be cited as evidence in favor of the strong π-bonding ability of that ligand. This conclusion is consistent with other work on the ligand.[1] It is also in agreement with the substitution data. The fact that the ligand substitution is nearly random indicates that the character of a given bond to the central metal is essentially unaffected by the presence of varying amounts of the other substituent.

When the infrared data of this system are compared with the data found by Horrocks and Taylor,[8] some

---

(9) See, for example, J. R. Van Wazer and S. Norval, *Inorg. Chem.*, **4**, 1294 (1965), and earlier papers.

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

interesting differences are observed. In all of the compounds that they studied, which included phosphorus trichloride, both the CO and the NO stretching frequencies decreased as the substituent replaced one or more CO groups. Further, the decrease was greater as either the degree of substitution increased or the π-bonding ability of the ligand decreased. A reversal occurs when phosphorus trifluoride is included in the series. The carbonyl frequencies still decrease slightly as the degree of substitution increases, although to a lesser degree than any other phosphine studied.[8] However, the nitrosyl stretching frequencies increase slightly as one goes through the series to the triphosphine.

If one were to judge the relative π-bonding abilities of CO and PF_3 on the basis of NO frequencies, PF_3 would be better. A similar comparison of these two ligands on the basis of CO frequencies would place CO slightly better. A similar degree of confusion would exist when judging the position of NO in the "spectrochemical" series which has been proposed by Horrocks and Taylor.[8] One can argue that PF_3 is better at π bonding than NO. Since all of these changes are small ones, the best conclusion is that all three have strong π-bonding abilities.

The spectral data of the four species in the far-infrared region have been compared with the data used in the assignment of the infrared spectrum of $Co(NO)(CO)_3$.[11] The data on the tricarbonyl shown in Table I compare favorably with that of the earlier work.[11] However, some apparent inconsistencies exist between their assignment and what would appear reasonable from data of the present study.

There is one Co–N stretch and one Co–N–O bend for all of the $Co(NO)(CO)_x(PF_3)_{3-x}$ species. One should expect that, as these frequencies are compared through the series, frequency shifts would be small and regular to either slightly higher or lower values. The prior assignment[11] indicates that in $Co(NO)(CO)_3$, the Co–N stretch occurs at 594 cm^{-1} and that the Co–N–O bend occurs at 565 cm^{-1}.

On examining the data for the phosphine series, a weak peak is found at 595 cm^{-1} for the tricarbonyl which shifts progressively to 627 cm^{-1} for the triphosphine. A stronger absorption at 560 cm^{-1} (corresponding to the earlier value at 565) remains essentially unshifted for the three carbonyls but disappears completely when the last carbonyl group is removed. There is no absorption within ±35 cm^{-1} of where the Co–N–O bend is projected to occur in the triphosphine. It would then seem that this 560-cm^{-1} absorption should belong to some Co–C or C–O mode and should not be associated with the nitrosyl group.

An absorption which occurs at 440 cm^{-1} for the tricarbonyl and shifts progressively to 388 cm^{-1} for the triphosphine seems a very likely candidate for the second absorption that should occur in this region. This frequency is labeled in the prior assignment[11] as being a degenerate C–O bend.

On the basis of this work, a reasonable assignment for the Co–N stretch and Co–N–O bend would be 595 and 440 cm^{-1}. It can also be argued that the 440-cm^{-1} frequency belongs to the Co–N stretch rather than the bend. If one assumes that when the N–O stretching frequency increases, the Co–N stretching frequency should decrease, this is a reasonable assignment which assumes a constant bond order sum for Co–N and N–O.

This reassignment of the frequencies seems consistent and reasonable within the framework of this work alone. However, since the original assignment of the 594- and 565-cm^{-1} bands was made on the basis of N^{15} substitution, a discrepancy obviously exists. The 565-cm^{-1} band shifted to 555 cm^{-1} on N^{15} substitution whereas the 442-cm^{-1} band underwent no shift. The author has no explanation for the apparent difference.

The equilibrium constant data represent, to the author's knowledge, the first time that such data have been obtained for the complete range of compounds in a metal carbonyl. The lack of such data in the past is not too surprising. Of the hundreds of Lewis bases that can substitute into metal carbonyls, few cause extensive replacement. Those that do usually require quite forcing conditions in which it is unlikely that one obtains equilibrium mixtures. In general, it is unknown whether the forcing conditions are necessary because of unfavorable equilibrium constants or because of rather high activation barriers to substitution.

In the present case, equilibration of $Co(NO)(CO)_3$ in the presence of CO and PF_3 readily yields mixtures of all possible substitution compounds. Only mild activation is needed.

The most significant feature of the data is that PF_3 and CO come fairly close to having a random distribution among the $Co(NO)(CO)_x(PF_3)_{3-x}$ species. This then means that the cobalt does not have a particularly preferential affinity for either ligand. The similarity in attraction for the two ligands is quite consistent with the view that the bonding of CO and PF_3 to transition metals is quite similar.

Finally, it should be noted that the small deviation from randomness that does exist is in the direction of a slight preference for CO over PF_3 in the complex. This could be accounted for by steric effect of the larger PF_3, but other factors could be responsible.

Acknowledgments.—The author gratefully acknowledges the financial assistance of the Atomic Energy Commission, AT(40-1)3352, during the course of the work.

---

(11) R. S. McDowell, W. H. Horrocks, and J. T. Yates, *J. Chem. Phys.*, **34**, 530 (1961).