way in explaining the large separation between the ground and first excited state which is observed spectrally and implied magnetically.

Experimental Section

Tris(o-phenylenebisdimethylarsine)nickel(II) Perchlorate. Nickel chloride hexahydrate (1.2 g) and o-phenylenebisdimethylarsine (3.5 ml, 4.5 g) were mixed in warm diethylene glycol (30 ml). The resulting deep red-brown solution was refluxed for 1 hr, filtered in 100°, and diluted with ethanol (100 ml). Sodium tetraphenylborate (3 g) in acetone (10 ml) was added to the dark brown filtrate; thereupon a pink precipitate was formed. The mixture was warmed and stirred on a steam bath for a few minutes, and the precipitate was filtered and washed with successive portions of hot ethanol (total 500 ml) to remove any of the brown tervalent nickel bis-(ditertiary arsine) complex. The solid was recrystallized from acetone–diethyl ether (yield 1.5 g). The tetraphenylborate salt (1.5 g) was taken up in acetone (400 ml) containing dilute perchloric acid (50 ml) and digested on a steam bath for 1 hr. The residue was filtered and dissolved in water (500 ml) and the solution heated for 2 hr. On cooling the solution deposited deep maroon crystals which were filtered and washed with cold water. A further crop of crystals was obtained by evaporating the filtrate to a small volume. Two recrystallizations from hot water containing a few drops of perchloric acid gave the pure salt (1.0 g).

Anal. Calcd for $C_{30}H_{48}O_8Cl_2As_6Ni$: C, 32.3; H, 4.3; Cl, 6.4; As, 40.3. Found: C, 32.4; H, 4.2; Cl, 6.3; As, 39.7.

The nuclear magnetic resonance of the nickel complex was measured by means of a 60-Mc/sec Perkin-Elmer R10 instrument, and that of the cobalt complex was measured with a 100-Mc/sec converted Varian (V-4300B) spectrometer.

Kinetics and Mechanism of Substitution Reactions of Nitrosyltricarbonylcobalt(0)

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Abstract: Nitrosyltricarbonylcobalt(0) undergoes carbonyl substitution in the presence of phosphines, phosphites, arsines, pyridine and its derivatives, and isonitriles to give the monosubstituted derivatives, $CoNO(CO)_2L$. The preparation and spectra of several mono- and disubstituted derivatives are reported. The rates of these reactions depend on the concentration and nature of the nucleophile. For the phosphines and phosphites the reactions proceed at intermediate to fast rates, and for the arsines and pyridines the rates are slow. These results are in accordance with the substrate being a class b or soft metal. There is little effect on the rates of these reactions with changes in dielectric constant or coordinating ability of the solvent. For nucleophiles with the same ligand atom the rates of the reactions increase with increasing basicity (or polarizability) of the reagents. Triphenylarsine reacts at a rate which is both zero and first order in its concentration. Carbon monoxide exchange experiments indicate that the rate of exchange is independent of the CO concentration. However, the rate of CO substitution by $As(C_6H_5)_3$ at the extrapolated zero concentration of arsine is approximately 50-fold slower than the rate of CO exchange. The results obtained for the substitution reactions support a bimolecular displacement mechanism, and this is discussed in terms of the nature of the chemical bonding in $CoNO(CO)_3$.

Nitrosyltricarbonylcobalt(0) is a member of a family of neutral and anionic compounds which are both isostructural and isoelectronic with tetracarbonylnickel(0). Most of these compounds have been known for quite some time, and all of them form derivatives with appropriate reagents.[2] However, only during the last few years have kinetics studies been made on some of these reactions.[3]

Recently, there has been discussion concerning the anomalous behavior of $Ni(CO)_4$ in CO substitution and CO exchange reactions.[3c] Both reactions are first order in $Ni(CO)_4$ and independent of the concentration of the other reagent. However, the two reactions apparently take place by two different mechanisms since they proceed at different rates and are not competitive.

Heck[3b] has reported briefly on the reaction of CoNO-$(CO)_3$ with $P(C_6H_5)_3$ in ether solutions. He found that the rate of reaction was first order in both substrate and nucleophile concentrations. Thus, although this carbonyl is structurally and electronically like $Ni(CO)_4$, the two are dissimilar in their kinetic behavior. Furthermore, the cobalt compound is apparently one of the few simple metal carbonyls that undergoes CO substitution by a process which is dependent upon the nature and concentration of the nucleophile.[3b] Therefore, it offers a unique opportunity to study the properties influencing nucleophilicity toward metals in low oxidation states. This paper reports the kinetic data concerning the first step of CO substitution of CoNO-$(CO)_3$

$$CoNO(CO)_3 + L \longrightarrow CoNO(CO)_2L + CO \qquad (1)$$

where L = PR_3, $P(OR)_3$, AsR_3, pyridine and its deriva-

(1) Taken in part from the Ph.D. Thesis of E. M. T., Northwestern University, 1966.

(2) J. Chatt, P. L. Pauson, and L. M. Venanzi, "Organometallic Chemistry," H. H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 468.

(3) (a) F. Basolo and A. Wojcicki, *J. Am. Chem. Soc.*, **83**, 520 (1961); (b) R. F. Heck, *ibid.*, **85**, 657 (1963); (c) L. R. Kangas, R. F. Heck, P. M. Henry, S. Breitschaft, E. M. Thorsteinson, and F. Basolo, *ibid.*, **88**, 2334 (1966).

Table I. Analytical Data for CoNO(CO)₂L

L	Isolated as	Mp, °C^a	Calcd, % C	H	N	Found, % C	H	N	Mol wt Calcd	Found
P(C₆H₁₁)₃^b	Orange solid	120–122	56.46	7.82	3.29	56.88	7.88	3.66	425.4	426
P(C₆H₅)₃^b	Red solid	130	59.10	3.71	...	59.08	4.01	...	...	...
P(p-CH₃OC₆H₄)₃	Orange-red solid	173–175	55.54	4.26	2.82	55.24	4.52	3.03	497.3	485
P(OC₆H₅)₃^b	Orange solid	50	53.18	3.32	...	52.22	3.58	...	...	...
P(OCH₂)₃CCH₃	Yellow-orange solid	150	28.69	3.10	4.78	29.02	3.12	5.13	293.1	292
P(OCH₃)₃	Dark red liquid	...	22.32	3.37	5.21	22.78	3.40	5.68	269.0	275
P(C₂H₅)₃	Dark red liquid	...	36.52	5.75	5.32	36.10	5.78	5.30	263.1	267
As(C₆H₅)₃^b	Red solid	110	53.33	3.36	...	53.53	3.35	...	...	...
CNC₆H₁₁	Dark red solid	...	42.53	4.36	11.03	43.36	4.46	10.58	254.1	257
P(p-CH₃OC₆H₄)₃	Brown solid	179–180	62.85	5.15	1.74	62.17	5.15	1.84	821.7	831
P(OCH₂)₃CCH₃	Yellow solid	∼250	31.98	4.39	3.39	32.04	4.57	3.12	...	...

^{a} All solid compounds melt with decomposition. ^{b} These compounds have been reported elsewhere. See ref 10.

tives, CNC₆H₁₁, and CO. Also, the synthesis and characterization of some of the simple mono- and disubstituted derivatives of CoNO(CO)₃ are described.

Experimental Section

Compounds and Solvents. The CoNO(CO)₃ was prepared by the method of Seel[4] and identified by its infrared spectrum.

The reagents P(C₆H₅)₃, As(C₆H₅)₃, and P(OC₆H₅)₃ were Eastman Organic Chemicals and were used without further purification. Pyridine, P(O-n-C₄H₉), and P(OCH₃)₃ were also obtained from Eastman Organic Chemicals, but these were distilled under nitrogen before use. The phosphines P(n-C₄H₉)₃ and P(C₆H₅)₂Cl were obtained from Aldrich Chemical Co. and were also distilled under nitrogen before use. The compounds 4-picoline and 3-chloropyridine were obtained from Matheson Coleman and Bell and were distilled under nitrogen before use. The phosphines[5] P(C₂H₅)₃, P(C₆H₅)(C₂H₅)₂, P(C₆H₅)₂(C₂H₅), P(C₆H₅)₂(n-C₄H₉), P(C₆H₁₁)₃, P(p-CH₃OC₆H₄)₃, as well as P(OCH₂)₃CCH₃,[6] P[N(CH₃)₂]₃,[7] As(n-C₄H₉)₃,[8] and the isonitrile CNC₆H₁₁,[9] were prepared by methods described in the literature.

All of the solvents were distilled under nitrogen. Toluene was distilled over calcium hydride. The tetrahydrofuran was refluxed with sodium and benzophenone until the solution turned blue and then distilled. The nitromethane, Spectrograde from Eastman Organic Chemicals, was distilled over phosphorus pentoxide.

Stock solutions of CoNO(CO)₃ of known concentration were prepared by distilling weighed amounts of the material into appropriate solvents contained in airtight flasks. Portions of a stock solution were withdrawn from the flask with syringes as needed through serum caps. This technique made handling of the very volatile material quite simple and rapid. The stock solutions were found to exist in the dark at 0° for months with only very slight decomposition.

Preparation of Complexes. The preparation of some of the complexes reported here have been previously described by other workers[10] (see Table I). Since all the complexes were prepared in the same manner, we present here only a general method for their preparation.

All the complexes were prepared under an atmosphere of nitrogen. However, owing to their stability in air they were chromatographed and isolated with no further precautions. Yields of the complexes were 70% or better. The analytical data for these complexes are presented in Table I.

The monosubstituted derivatives, CoNO(CO)₂L, were prepared in tetrahydrofuran, since this solvent could be easily removed under reduced pressure before chromatography. The proportions of the reactants were found to be not very crucial, since excess ligand could be removed by means of judicious recrystallization, and excess CoNO(CO)₃ could be removed at reduced pressure. The reactions were carried out at room temperature or only slightly elevated temperatures, since CoNO(CO)₃ undergoes thermal decomposition in solution at about 55°. At reactant concentrations of ca. 0.5 M or greater, a reaction time of ca. 6 hr was found to be sufficient for most reagents except As(C₆H₅)₃ and P(OC₆H₅)₃. These two compounds are very poor reagents toward CoNO(CO)₃ and, therefore, more rigorous reaction conditions were required. The compound CoNO(CO)₂As(C₆H₅)₃ was prepared by adding As(C₆H₅)₃ (1.20 g, 3.9 mmoles) to CoNO(CO)₃ (0.52 g, 3.0 mmoles) in toluene (5 ml) and allowing the reaction mixture to stand at 50° for 1 week. The compound CoNO(CO)₂P(OC₆H₅)₃ was prepared by adding P(OC₆H₅)₃ (0.99 g, 3.2 mmoles) to CoNO(CO)₃ (0.52 g, 3.0 mmoles) in toluene (5 ml) and allowing the reaction mixture to stand at room temperature for 3 days.

The disubstituted derivatives, CoNO(CO)L₂, were prepared in toluene. Initially, the reaction mixtures were allowed to stand for several hours at room temperature to allow time for the formation of the monosubstituted derivative. The mixtures were then heated to about 65°. It was found that heating the reaction mixtures as high as 80° caused the monosubstituted derivatives to undergo thermal decomposition. Since the rates of these reactions vary widely with various reagents, occasional infrared spectra were taken to observe the progress of the reaction.

The products of these reactions were purified by means of chromatography over silica. Separation of mono- and disubstituted derivatives was effectively carried out with appropriate eluents. For phosphite derivatives chromatography over silica even with a very polar eluent such as dichloromethane perfected good separation between the mono- and disubstituted derivatives. For phosphine derivatives hexane–dichloromethane mixtures were used, and for the isonitrile derivatives 100% hexane gave good separation. In all cases the monosubstituted derivative is the faster moving of the two species on the chromatographic column. Decomposition products remained at the top of the column.

Most of the solid derivatives reported here were crystallized from concentrated hexane–dichloromethane mixtures except for the monosubstituted As(C₆H₅)₃ and P(OC₆H₅)₃ derivatives which were crystallized from cold concentrated solutions in absolute methanol.[10] All the complexes were dried under high vacuum for several hours.

These compounds are soluble in most organic solvents. However, the triphenylarsine and crystalline phosphite derivatives are more soluble in alcohols and ethers, and less soluble in alkane and aromatic solvents than the crytalline phosphine derivatives. They can all be stored indefinitely under a nitrogen atmosphere. The carbonyl and nitrosyl stretching frequencies for the monosubstituted derivatives described here and others for which we studied the rates of formation are given in Table II. The corresponding data for the disubstituted derivatives are given elsewhere.[11]

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Table II. Carbonyl and Nitrosyl Stretching Frequencies for
Compounds CoNO(CO)₂L in Toluene[a]

L	ν_{CO}, cm⁻¹		ν_{NO}, cm⁻¹
CO	2110	2042	1802
P(OC₆H₅)₃	2061	2004	1776
P(OCH₂)₃CCH₃	2061	2004	1773
P(C₆H₅)₂Cl	2055	2004	1767
P[N(CH₃)₂]₃	2052	1995	1764
P(OCH₃)₃	2050	1996	1764
CNC₆H₁₁	2050	1995	1762
P(O-n-C₄H₉)₃	2050	1988	1760
As(C₆H₅)₃	2047	1986	1756
3-Chloropyridine	2041	1969	1739
Pyridine	2041	1969	1733
4-Picoline	2041	1966	1733
P(C₆H₅)₃	2038	1981	1750
P(C₆H₅)₂(C₂H₅)	2038	1981	1752
P(C₆H₅)₂(n-C₄H₉)	2038	1981	1752
P(p-CH₃OC₆H₄)₃	2038	1977	1748
As(n-C₄H₉)₃	2035	1975	1753
P(C₆H₅)(n-C₄H₉)₂	2032	1975	1756
P(n-C₄H₉)₃	2032	1973	1744
P(C₂H₅)₃	2032	1969	1747
P(C₆H₁₁)₃	2027	1965	1741

[a] All solutions contained an excess of ligand.

The analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill. The molecular weight determinations were carried out by Miss H. Beck of this department. They were performed with approximately 5 × 10⁻² M benzene solutions, using a Mechrolab Inc. Model 302 osmometer.

Reactions of Substituted Compounds with Carbon Monoxide. Some qualitative observations have been made on the reversibility of the reactions in these systems. Solutions of the substituted compounds were saturated with CO at atmospheric pressure, and any changes in the infrared spectra of the solutions with time were observed.

Carbon monoxide under a pressure of slightly greater than 1 atm was in contact with a 0.005 M solution of CoNO(CO)₂As-(C₆H₅)₃ in toluene for 21 hr at room temperature. During this time there was evidence for the formation of only a very slight amount of CoNO(CO)₃. It was identified by its high-energy carbonyl band at 2110 cm⁻¹.

Similar treatment with CO of a kinetic solution of 0.003 M CoNO(CO)₃, 0.002 M CoNO(CO)₂-pyridine, and 0.75 M pyridine in nitromethane resulted in an appreciable increase in intensity of the absorption band at 2110 cm⁻¹ after the space of only 1 hr.

Kinetic Studies. The rates of the substitution reactions were followed by observing changes in the infrared spectra of the reaction mixtures and also by the rate of CO evolution. Both methods have been previously described.[12] It was not possible to follow the rates of these reactions by observing changes in the absorption spectra in the visible region, since the differences in spectra between starting material and product are only slight.

All the kinetic studies were carried out under pseudo-first-order conditions, using at least a tenfold excess of reagent. The concentration of the substrate was ca. 5 × 10⁻³ M. It was found that CoNO(CO)₃ obeys the Beer-Lambert law in the metal carbonyl region of the infrared, the molar absorptivity of the carbonyl band at 2110 cm⁻¹ being 1.3 × 10² M^{-1} mm⁻¹. In most cases this was the band that was under observation during a reaction. The reactions were carried out in foil-wrapped, nitrogen-filled flasks kept in constant-temperature baths. Aliquots were withdrawn from the flasks through a serum cap, and transferred to 1.0-mm NaCl cells; their infrared spectra were measured against that of a reference solution containing no metal complex. The infrared data were obtained with a Perkin-Elmer Model 337 infrared spectrophotometer equipped with an external recorder.

A few reactions were too fast to follow by the conventional point-by-point method, and they had to be observed continuously. In such instances, the reactants were first thermostated at 25° for a sufficient length of time and rapidly mixed, and then an aliquot was

transferred to a 1.0-mm NaCl cell. With the frequency set on the instrument at that corresponding to the high-energy carbonyl band of CoNO(CO)₃, the change in transmittance at this frequency was observed continuously with time by means of the variable speed external recorder. The reactions followed by this method were complete in 3 min or less. Since the reaction mixtures were not thermostated throughout the entire length of reaction, the resulting rate constants should be considered approximate.

The reactions of CoNO(CO)₃ with pyridine and its derivatives yielded kinetic data that gave pseudo-first-order kinetic log plots having some curvature. This is due to the fact that these reactions at these conditions do not go to completion, as described above. The rate constants, therefore, were determined from the initial slope of the curve. The products of these reactions are quite easily oxidized. In order to determine if the reactions were complicated by small amounts of oxygen, they were also carried out in an atmosphere of air, instead of nitrogen. By deliberately decomposing the product in this manner, good straight-line log plots of the kinetic data were obtained. Under the same experimental conditions, but in the absence of pyridine, there is only a slight oxidation of CoNO(CO)₃ over a 3-day period. There was always satisfactory agreement in the rate constants obtained from data by running the kinetic reactions under an atmosphere of nitrogen and from data obtained from decomposition of the product in the presence of air.

The reaction of CoNO(CO)₃ with As(C₆H₅)₃ is quite slow and, therefore, it presented experimental difficulties. Some of the kinetic mixtures became cloudy during the course of the reaction, meaning that decomposition must have taken place. Such a result is hardly unexpected in view of the low thermal stability of CoNO-(CO)₃ and slowness of these reactions. Also, some of these reactions yielded kinetic data which gave curved pseudo-first-order kinetic plots. Owing to these difficulties the kinetic data for the reaction of CoNO(CO)₃ with As(C₆H₅)₃ should be considered less reliable than those for the other substitution reactions.

The CO evolution data were obtained using the gasometric apparatus described earlier.[13] The experimental infinite time volume was always in good agreement with the calculated volume corresponding to the release of 1 mole of CO per mole of CoNO-(CO)₃.

The rate constants obtained by the infrared and the CO evolution methods were in good agreement and were reproducible to within 10% or better. The values of ΔH^* and ΔS^* are estimated to be ±1 kcal/mole and ±2 eu, respectively.

The method used to investigate the rate of ¹⁴CO exchange with CoNO(CO)₃ was similar to that described earlier,[3a] the chief modification being the apparatus used to measure the radioactivity of the gas phase. This was done with a 100-ml DCF ion chamber and electrometer system "Dynacon" Model 6010 obtained from Nuclear Chicago.

All of the exchange reactions investigated were found to follow the McKay[14] equation and give satisfactory linear plots of log (V_t — V_∞) vs. time where V_t is the voltage of the gas phase recorded at time t, and V_∞ is the voltage at equilibrium. From these plots the half-lives for exchange were determined and used to estimate the values of k_{true} by eq 2, where $t_{1/2}$ is the half-life for exchange, a

$$k_{true} = \frac{0.69xa^{1-\alpha}yb^{1-\beta}}{(xa + yb)t_{1/2}} \quad (2)$$

is the concentration of metal carbonyl, b is the concentration of CO in solution, x is the number of exchangeable CO's in the metal carbonyl, y is the ratio of total moles of CO in the enclosed system to the moles of CO in solution, and α represents the order in a and β the order in b. If α equals 1 and β equals 0, then the rate of exchange is first order and the specific rate constant k_{true} is designated by k_1 (sec⁻¹) whereas if α and β each equal 1, the rate is second order and its constant is represented as k_2 (M^{-1} sec⁻¹). The solubility of CO in toluene is known.[3a,15]

We found that with our present apparatus it was almost impossible to collect reliable data on the CoNO(CO)₃ system at temperatures other than about 25°. At temperatures higher than 25° the CoNO(CO)₃ would condense in the ion chamber and drastically

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(12) H. G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.*, **88**, 1657 (1966).

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(14) H. A. C. McKay, *Nature*, **142**, 997 (1938).

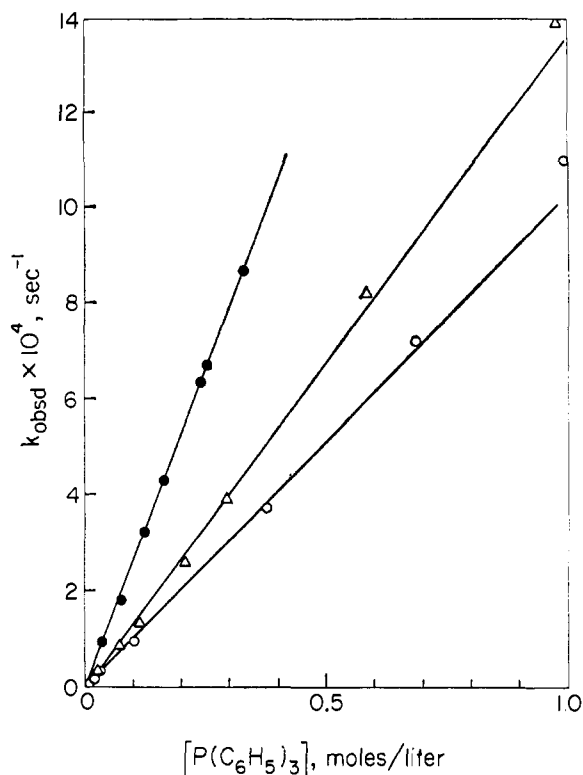(15) "International Critical Tables," Vol. III, E. W. Washburn, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1926, p 265.

Figure 1. Plot of k_{obsd} vs. [P(C₆H₅)₃] for the reaction of CoNO(CO)₃ with P(C₆H₅)₃ in nitromethane (●), tetrahydrofuran (△), and toluene (○) at 25°.

alter its resistance. At temperatures lower than 25° the exchange reaction became so slow that decomposition of the CoNO(CO)₃ became a problem. However, it was possible to collect satisfactory data at 25°, but unfortunately temperature dependence studies could not be made.

Since the exchange reactions were very slow, none of them were allowed to go to equilibrium. The infinite time voltage for each run was calculated from the amount of free CO and CoNO(CO)₃ introduced into the apparatus and from the initial voltage recorded. The calculations were based on the exchange of all three of the CO molecules in the compound. The concentration of the CoNO(CO)₃ in the solution was determined from the amount of stock solution and solvent which were introduced into the apparatus. Fresh stock solutions of known concentrations were always used. The concentration was checked at the termination of the experiment by taking the infrared spectrum of the reaction solution in the carbonyl region and determining the absorbance at 2110 cm⁻¹. Knowing the molar absorptivity of this band, the concentration of the solution could be calculated. The two calculations were always in good agreement. Therefore, very little decomposition took place during the time of the experiment.

Results

Some of the mono- and disubstituted derivatives of CoNO(CO)₃ were prepared and characterized by means of analyses and molecular weights. These compounds and the analytical data are given in Table I. The infinite-time infrared spectra in the carbonyl and nitrosyl regions of the reaction products from the kinetic runs are given in Table II. In cases where the product had been separately isolated, its infrared spectrum was in good agreement with the infinite-time infrared spectrum of the reaction mixture containing the same reagent as that in the separately isolated derivative. Reaction mixtures for which the product was not isolated gave infrared spectra analogous to either the mono- or disubstituted derivatives.

The dependence of the rate of reaction (1) on the concentration of reagent L in toluene, tetrahydrofuran, and nitromethane is shown by the data in Table III for

Table III. Rate Constants for the Reaction
CoNO(CO)₃ + P(C₆H₅)₃ → CoNO(CO)₂P(C₆H₅)₃ + CO at
25° with Changes in Solvent and Concentration of P(C₆H₅)₃

[P(C₆H₅)₃], M	10⁴k_{obsd}, sec⁻¹	10³k, M⁻¹ sec⁻¹
In Toluene		
0.0089	0.085	0.96
0.018	0.18	1.0
0.035	0.33	0.94
0.101	0.93	0.92
0.376	3.7	0.98
0.682	7.2	1.1
0.993	11	1.1
In Tetrahydrofuran		
0.029	0.38	1.3
0.072	0.84	1.2
0.116	1.3	1.1
0.027	2.6	1.3
0.291	3.9	1.3
0.583	8.2	1.4
0.979	14	1.4
In Nitromethane		
0.038	0.90	2.4
0.073	1.8	2.5
0.124	3.2	2.6
0.163	4.3	2.6
0.235	6.3	2.7
0.256	6.7	2.6
0.329	8.7	2.6

L = P(C₆H₅)₃. Figure 1 shows a plot of the data in Table III for the reaction in the three solvents. Table IV contains kinetic data for the reaction of the substrate with various reagents and also gives the relative basicities of some of the reagents.[16] Under these conditions CoNO(CO)₃ appears not to react, or it reacts only extremely slowly, with N(C₆H₅)₃ and N(n-C₄H₉)₃. It does react more rapidly with H₂NC₆H₁₁ and NCCH₃ at rates comparable to those of the reactions with pyridine and its derivatives. However, no kinetic studies were carried out on the reactions with H₂NC₆H₁₁ and NCCH₃. Data on the activation parameters in two different solvents are given in Table V.

Nitrosyltricarbonylcobalt(0) reacts very slowly with As(C₆H₅)₃ in toluene, and the rate of reaction follows a two-term rate law (3)

$$\text{rate} = \{k_1 + k_2[\text{As}(\text{C}_6\text{H}_5)_3]\}[\text{CoNO(CO)}_3] \quad (3)$$

The kinetic data and activation parameters gathered on this reaction are presented in Table VI. This substrate also undergoes ¹⁴CO exchange very slowly in toluene, and the rate of exchange appears to be first order in CoNO(CO)₃ and zero order in CO concentrations. The kinetic exchange data are presented in Table VII.

Discussion

Recent studies[3] on Ni(CO)₄ have shown that it undergoes CO substitution very rapidly at 25° at a rate which

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Table IV. Rate Constants for the Reactions $CoNO(CO)_3 + L \rightarrow CoNO(CO)_2L + CO$ at 25° with Changes in the Nature of L[a]

L	In toluene	In tetra-hydrofuran	In nitro-methane	ΔHNP[b]
		k, M^{-1} sec^{-1}		
$P(C_2H_5)_3$	3×10^{-1}[c]	2×10^{-1}[c]	3×10^{-1}[c]	111
$P(n\text{-}C_4H_9)_3$	9×10^{-2}[c]	8×10^{-2}[c]	3×10^{-1}[c]	131
$P(C_6H_5)(C_2H_5)_2$	3.3×10^{-2d}	6×10^{-2}[c]	9.9×10^{-2}	300
$P(C_6H_{11})_3$	9.5×10^{-3}	1.4×10^{-2}	...	33
$P(C_6H_5)_2(C_2H_5)$	5.9×10^{-3}	7.4×10^{-3}	1.6×10^{-2}	400[e]
$P(C_6H_5)_2(n\text{-}C_4H_9)$	4.6×10^{-3d}	5.2×10^{-3d}	1.3×10^{-2}	400[e]
$P(p\text{-}CH_3OC_6H_4)_3$	...	...	7.7×10^{-3}	439
$P(O\text{-}n\text{-}C_4H_9)_3$	2.9×10^{-3}	2.5×10^{-3d}	3.1×10^{-3}	520[f]
$P(OCH_3)_3$	1.8×10^{-3}	1.9×10^{-3}	2.0×10^{-3}	520[f]
$P(C_6H_5)_3$	1.0×10^{-3}	1.3×10^{-3}	2.6×10^{-3}	573
$P(OCH_2)_3CCH_3$	6.5×10^{-4}	8.0×10^{-4}	6.3×10^{-4}	665
$P(C_6H_5)_2Cl$	8.9×10^{-5}	...	...	...
$P(OC_6H_5)_3$	3.4×10^{-5}	3.0×10^{-5}	5.8×10^{-5}	875
$P[N(CH_3)_2]_3$	3.2×10^{-5}	...	...	...
CNC_6H_{11}	7.2×10^{-3}	7.8×10^{-3}	3.0×10^{-3}	...
$As(n\text{-}C_4H_9)_3$	9.0×10^{-5}	...	...	...
$As(C_6H_5)_3$	2.3×10^{-6}	...	...	...
4-Picoline	8×10^{-5g}	1×10^{-4g}	8×10^{-5g}	220[e]
Pyridine	4×10^{-5g}	6×10^{-5g}	5×10^{-5g}	286
3-Chloropyridine	1×10^{-5g}	1×10^{-5g}	9×10^{-6g}	466[e]

[a] A more detailed form of this table has been deposited as Document No. 8920 with the ADI Auxiliary Publications Project, Photo-duplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document no. and remitting $1.25 for photoprints, or $1.25 for 25-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress. [b] Difference in half-neutralization potential between L and N,N'-diphenylguanidine in nitromethane. The smaller ΔHNP, the more basic is L.[16] [c] Reaction was followed continuously using unthermostated NaCl infrared cells by observing the disappearance of the high-energy carbonyl band of $CoNO(CO)_3$ at 2110 cm^{-1} (see Experimental Section). [d] Reaction was followed by observing the evolution of CO. [e] This value has been estimated from the information contained in ref 16 and other references cited therein. [f] This is the value for $P(O\text{-}n\text{-}C_4H_9)_3$. [g] Owing to curvature of the kinetic plot this value was obtained from the initial slope of the curve (see Experimental Section).

Table V. Activation Parameters for the Reaction $CoNO(CO)_3 + L \rightarrow CoNO(CO)_2L + CO$

Solvent	L	Temp,[a] °C	k_1, M^{-1} sec^{-1}	ΔH^*, kcal/ mole	ΔS^* (298°), eu
Toluene	$P(C_6H_5)_2C_2H_5$	40.4	2.1×10^{-2}	15	-19
Toluene	$P(C_6H_5)_3$	40.4	3.5×10^{-3}	15	-24
Toluene	$P(OC_6H_5)_3$	40.4	1.8×10^{-4}	19	-14
Toluene	$P(C_6H_5)_2Cl$	35.0	2.4×10^{-4}	17	-19
Toluene	$P(C_6H_5)_2Cl$	15.0	3.1×10^{-5}		
CH_3NO_2	$P(C_6H_5)_3$	35.0	5.5×10^{-3}	14	-23
CH_3NO_2	$P(C_6H_5)_3$	15.0	9.9×10^{-4}		
CH_3NO_2	$P(OC_6H_5)_3$	35.0	1.6×10^{-4}	17	-22
CH_3NO_2	$P(OC_6H_5)_3$	15.2	2.3×10^{-5}		

[a] For the data at 25° see Table IV.

Table VI. Rate Constants for the Reaction $CoNO(CO)_3 + As(C_6H_5)_3 \rightarrow CoNO(CO)_2As(C_6H_5)_3 + CO$ in Toluene with Changes in the Concentration of $As(C_6H_5)_3$[a]

$$k_{obsd} = k_1 + k_2[As(C_6H_5)_3]$$

$[As(C_6H_5)_3]$, M	Temp, °C	$10^6 k_{obsd}$, sec^{-1}	$10^7 k_1$, sec^{-1}	$10^6 k_2$, M^{-1} sec^{-1}
0.014[b]	25	0.12		
0.103	25	0.30		
0.435	25	1.1	~0.75	2.3
1.13[c]	25	2.7		
0.014[c]	35	0.46		
0.103	35	1.1	~4.0	7.0
0.480[b]	35	3.7		
0.014[b]	45	2.3		
0.098[b]	45	3.9		
0.525	45	12	~20	24
1.02[c]	45	23		

[a] These data allow the following estimates of the activation parameters: for k_1, $\Delta H^* = 30$ kcal/mole, ΔS^* (289°) $= +10$ eu; for k_2, $\Delta H^* = 21$ kcal/mole, ΔS^* (289°) $= -13$ eu. [b] Reaction mixture turned slightly cloudy. [c] Kinetic plot curves and the observed rate constant was calculated from the initial slope of the line.

**Table VII.** Rate of ^{14}CO Exchange with $CoNO(CO)_3$ in Toluene at 25.5°

$[CoNO\text{-}(CO)_3]$[a]	$[CO]_s$[a]	$[CO]_t$[a]	$t_{1/2}$, hr	$10^6 k_1$, sec^{-1}[b]	$10^2 k_2$, M^{-1} sec^{-1}[b]
6.23	0.091	0.13	21	4.9	5.4
20.2	0.16	0.23	33	1.9	1.2
3.16	0.16	0.22	68	3.6	2.2
6.44	0.36	0.50	62	4.2	1.2
22.2	1.3	1.8	94	3.0	0.23
34.3	2.5	3.6	120	3.2	0.13

[a] Concentrations, mM; $[CO]_s$ = dissolved CO; $[CO]_t$ = total CO in mmoles in enclosed system. [b] True first-, k_1, and second-, k_2, order rate constants calculated from the observed half-life for exchange by eq 2. Note the variation in k_2 with changes in concentration of CO, whereas the values of k_1 are reasonably constant supporting a first-order exchange.

is first order in the concentration of $Ni(CO)_4$ and zero order in the concentration of the entering reagent. It might be expected that $CoNO(CO)_3$ would behave in a similar fashion, since the two compounds have a tetrahedral arrangement of the ligands about the metal atom and are isoelectronic. However, the data in Tables III and IV show that the CO substitution of $CoNO(CO)_3$ follows a second-order rate law (eq 4).
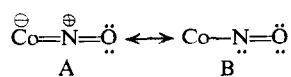
$$\text{rate} = k_2[CoNO(CO)_3][L] \quad (4)$$

This rate law holds for good nucleophiles, as is shown by a plot (Figure 1) of the pseudo-first-order rate constants vs. the concentration of $P(C_6H_5)_3$ for its reaction with $CoNO(CO)_3$. These results suggest that substitution involves a bimolecular displacement mechanism perhaps of the type shown by eq 5. There is no requirement

$$(5)$$
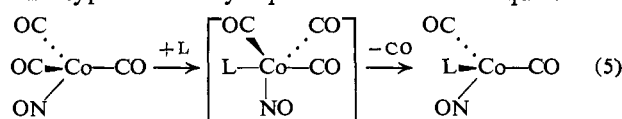
that the five-coordinated species have a trigonal-bipyramidal structure, but there is considerable precedence for such a structure in these systems containing π-bonding ligands, *e.g.*, Fe(CO)₅. Furthermore, for the compound Fe(CO)₄P(C₆H₅)₃ the phosphine occupies an apical position and the CO *trans* to it undergoes ¹⁴CO exchange quite slowly, while the three CO's in the plane undergo exchange more rapidly.[17] This is a general behavior of compounds in which a carbonyl group is *trans* to a basic L group. For example, for the compounds Mn(CO)₅X, where X = Cl, Br, and I, four CO's undergo ¹⁴CO exchange rapidly whereas one is slow.[18] These compounds also react with L to give *cis*-Mn(CO)₄XL.[19] Analogously, if [CoNO(CO)₃L] is trigonal bipyramidal, then the group *trans* to L may be held more firmly than those *cis* to L. On this basis the leaving CO is expected to be located *cis* to the entering group and not *trans* to it. It may be possible to test this hypothesis someday providing one can resolve an optically active compound of the type CoNO(CO)-LL′.[10b]

The difference between NO and CO is perhaps largely responsible for the difference in behavior of the compounds Ni(CO)₄ and CoNO(CO)₃. In terms of the effective atomic number concept, NO is believed to act as a three-electron donor to the metal. This gives the metal a formal negative charge, whereas NO takes on a formal positive charge. Because of the smaller nuclear charge on cobalt and its formal negative charge, the extent of π bonding of the type M = CO is greater than it is in the nickel system. This is supported by the fact that the infrared spectra of the compounds show a C–O stretching frequency that is higher for Ni(CO)₄ than it is for CoNO(CO)₃.[2] It follows that the Co–C bond strength is greater than that for Ni–C, and a first-order process that involves primarily the M–C bond is expected to take place more readily in the nickel system than in that of cobalt. Thus, the cobalt system in its reactions needs more assistance from the entering nucleophile which may account for its reactions being second order.

Another reason that nitrosyl metal carbonyls undergo bimolecular displacement reactions may be due to the ease with which nitric oxide can occur in metal complexes in the forms NO⁺, NO, and NO⁻.[20] With reference to carbon monoxide being a two-electron donor in these systems, nitric oxide is a three-electron donor and can be thought of as being initially present as NO²⁺. However, the infrared spectra of these compounds in the N–O stretching region suggest there is extensive M–N π bonding[20] and, thus, a better approximation of the ground-state existence of this ligand would be the nitrosonium ion, NO⁺. Viewing only Co–NO in the compound CoNO(CO)₃, these considerations support a major contribution from canonical structure (A) to the Co–NO bonding.

$$\overset{\ominus}{Co}=\overset{\oplus}{N}=\overset{..}{\overset{..}{O}} \longleftrightarrow Co-N=\overset{..}{\overset{..}{O}}$$

$$\quad A \qquad\qquad\qquad B$$

In this structure cobalt has a low-spin d¹⁰ electronic structure, the same as does nickel in Ni(CO)₄. Ca-

nonical structure B shows nitric oxide behaving as a one-electron donor and being present in the compound as the neutral ligand NO. In this structure cobalt has a low-spin d⁸ electronic structure, the same as does nickel(II) in Ni(CN)₄²⁻.

Although for the ground state of CoNO(CO)₃, structure B does not appear to make much of a contribution, it may become important in the transition state. Its formation here would make available a vacant orbital of low energy on the metal which can then readily accept a pair of electrons from an entering nucleophile and facilitate a bimolecular displacement process. Such a process would be much less likely for the analogous Ni(CO)₄, where if we consider only one Ni–CO this would involve the canonical structures C and D.

$$Ni=C=\overset{..}{\overset{..}{O}} \longleftrightarrow \overset{\oplus}{Ni}-\overset{\ominus}{C}=\overset{..}{\overset{..}{O}}$$

$$\quad C \qquad\qquad\qquad D$$
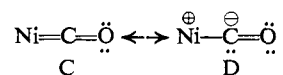
Structure C is believed to make the major contribution to the ground state of Ni(CO)₄, and structure D almost certainly must be of higher energy than is the corresponding structure B. This is because nitrogen is more electronegative than carbon and because in these systems the nitrogen atom has a formal positive charge which would further enhance its electron affinity over that of carbon which is present with a formal charge of zero.

One further point can be made with reference to the above suggestion that in structure B cobalt is in a low-spin d⁸ system. Complexes of such metal systems are known to have a square-planar structure and to undergo substitution reactions by means of a bimolecular displacement mechanism.[21] Thus, viewed in this manner, the reactions of CoNO(CO)₃ may be considered to have a formal analogy to the reactions of platinum(II) complexes.

Since the reactions of CoNO(CO)₃ are second order, it is possible to determine the nucleophilic strengths of different reagents toward this substrate. The data in Tables IV and V present information of this type. These data show that in general the phosphorus ligand atom donors react faster than either the arsenic or nitrogen ligand atom donors. This difference between the various kinds of ligand atom reagents is in accord with the metal in the substrate being a class b[22] or soft metal.[23] Stability data for metal complexes of class b metals show that for the group V elements, phosphorus compounds form the most stable metal complexes and the stabilities vary in the order N ≪ P > As > Sb.

The results obtained indicate that phosphines are better reagents toward CoNO(CO)₃ than are the corresponding phosphites. Since phosphites are better π bonders in these systems than are phosphines,[24] it follows that the π-bonding tendency of a reagent is not a predominant factor in determining it reactivity.

The data in Table IV also indicate that for a given family of ligand atom donors the rates of reaction with CoNO(CO)₃ increase with increasing basicity[16] of the reagent. This same behavior has been found with

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$Rh(C_5H_5)(CO)_2$[12] and $Fe(NO)_2(CO)_2$.[25] Figure 2 shows the linear free-energy relationship between the rate of reaction and basicity of reagent in nitromethane solution. Unfortunately, no basicity data are available for the arsines, but it is known that they are weak bases.[26] The relative basicities of the reagents were measured by Streuli[16] using nitromethane as a solvent and recording the difference in half-neutralization potentials, ΔHNP, from that of N,N'-diphenylguanidine taken as a standard. That tricyclohexylphosphine reacts slower than would be predicted by its basicity can be attributed to steric effects caused by the large cyclohexyl groups.

It is seen from Figure 2 that the parallelism between reagent reactivity and base strength is restricted to a given family of ligand atom compounds. It is not correct to conclude that the stronger the base strength of a nucleophile, the better reagent it will be toward CoNO-$(CO)_3$. The base strength of pyridine is stronger than that of most of the phosphorus compounds investigated, yet the phosphorus compounds are better reagents than are the pyridine compounds. This appears to be due to the difference between class a and b behavior[22] of a metal substrate. Since cobalt in $CoNO(CO)_3$ is a class b or soft metal,[23] it has a greater affinity for the soft phosphorus atom than for the hard nitrogen atom. The results suggest that for this substrate the softness or polarizability of the nucleophile is more important in determining its nucleophilic strength than is its basicity.

Edwards[27] has discussed the nucleophilic strengths of different reagents in terms of the two parameters, basicity and polarizability, and a review has been written[28] of the qualitative contributions of each of these with regards to different substrates. If data were available on the polarizability of the ligand atoms of the nucleophiles used in the reactions with $CoNO(CO)_3$, it would be of interest to make a linear free-energy relationship plot such as Figure 2, using the polarizability values instead of basicity. Since these values are not available, the basicity parameter was used, but it is believed that for similar reagents with the same ligand atom the basicity closely parallels the polarizability of the nucleophile at the reaction site. Therefore, it may seem more reasonable to think of the correlation shown in Figure 2 as one with the polarizability of the nucleophile rather than its basicity.

However, the arsenic ligand atom compounds, while being weaker bases[26] than either the nitrogen or phosphorus compounds, are certainly more polarizable. This suggests that a third factor, namely π-bonding ability, must be of at least some significance in determining reactivity. Since phosphorus ligand atom donors are better π bonders than arsenic donors which in turn are better than nitrogen donors,[24] this conclusion seems plausible. It is well known that strong π-bonding ligands stabilize five-coordination in low-spin d^8 metal systems[29] such as $Fe(CO)_5$, $Ni(CN)_5^{3-}$,[30] and $Pt(SnCl_3)_5^{3-}$.[31] Thus, the presence of the best π-bond-
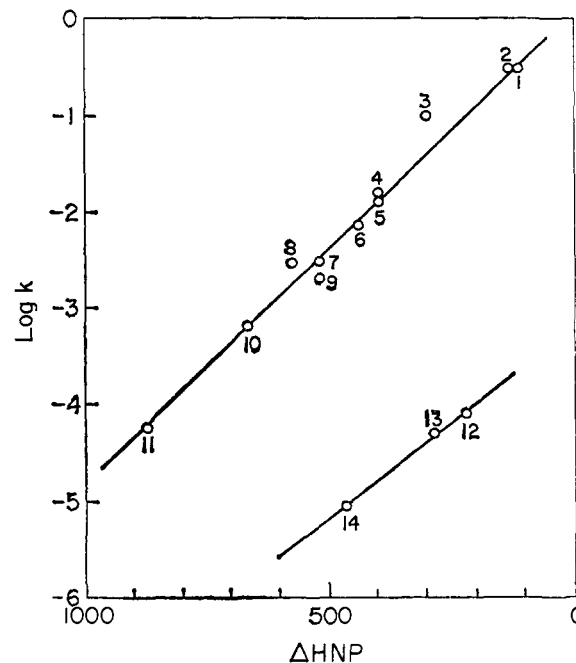

Figure 2. The linear free-energy relationships of the rate of reaction with the polarizability of the nucleophile for the reaction of CoNO-$(CO)_3$ with (1) $P(C_2H_5)_3$, (2) $P(n-C_4H_9)_3$, (3) $P(C_6H_5)(C_2H_5)_2$, (4) $P(C_2H_5)_2(C_2H_5)$, (5) $P(C_6H_5)_2(n-C_4H_9)$, (6) $P(p-CH_3OC_6H_4)_3$, (7) $P(O-n-C_4H_9)_3$, (8) $P(C_6H_5)_3$, (9) $P(OCH_3)_3$, (10) $P(OCH_2)_3CCH_3$, (11) $P(OC_6H_5)_3$, (12) 4-picoline, (13) pyridine, (14) 3-chloropyridine. See text for discussion that ΔHNP measures basicity which is believed to parallel polarizability for these compounds.

ing ligand atom, phosphorus, relative to arsenic or nitrogen will have the greatest stabilizing influence on the five-coordinated species in the displacement reactions of $CoNO(CO)_3$. This lowers the activation energy for reaction and increases the rate of reaction for the phosphorus ligand atom relative to the arsenic and nitrogen nucleophiles (Tables V and VI). Another explanation may merely be that arsines, compared with phosphines, are always weaker bases, no matter what the reference acid is. Thus arsines will form less stable complexes[22] and be poorer nucleophiles than are the corresponding phosphines.[28]

The activation parameters for the reactions of $CoNO(CO)_3$ with various reagents in toluene and nitromethane are shown in Table V. The negative entropies of activation are in accord with a bimolecular displacement process in which there is considerable bond formation with the entering reagent in the transition state. This increase in coordination number restricts the motion in the activated complex relative to the reactant molecules, resulting in a decrease in entropy. Similar values of negative entropies of activation are found for a large number of displacement reactions of metal complexes.[32]

The results in Tables III, IV, and V show that the solvent has only a small effect on these reactions of $CoNO(CO)_3$ with reagents that are good nucleophiles. Toluene is often used as a solvent for these systems and it was the solvent of choice here. The selection of nitromethane as a solvent was made because of its relatively high dielectric constant and low coordinating ability. Tetrahydrofuran was used because its dielectric con-

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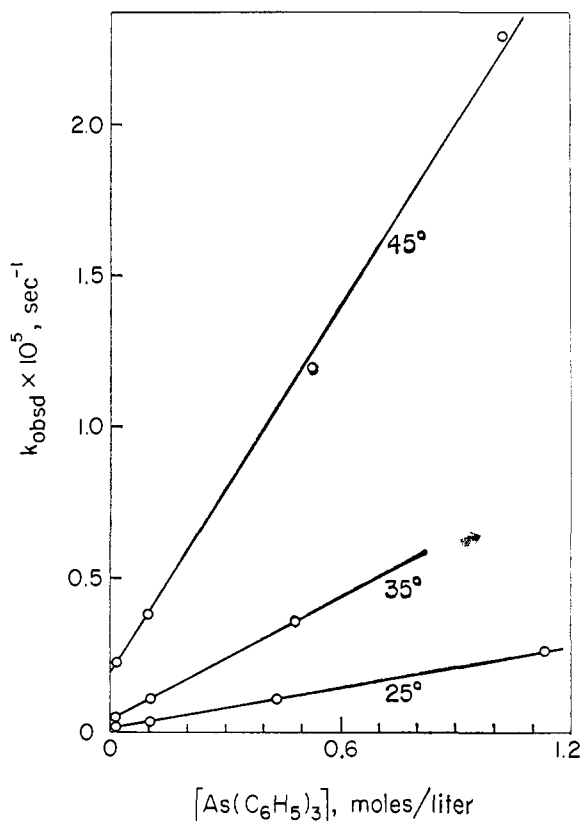(31) R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *J. Am. Chem. Soc.*, 87, 658 (1965).

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Figure 3. Plot of k_{obsd} vs. [As(C₆H₅)₃] for the reaction of CoNO-
(CO)₃ with As(C₆H₅)₃ in toluene at 25, 35, and 45°.

stant is similar to that of toluene, but has a much greater tendency to coordinate through its ether oxygen.

The data in Table VI show that the reaction of CoNO-(CO)₃ with As(C₆H₅)₃ in toluene is quite slow. Owing to the nature of this substrate it is not surprising that over a period of several weeks a small amount of decomposition occurred in some of the reaction mixtures. Another complication arises from the fact that some of the reactions yielded kinetic data which gave pseudo-first-order kinetic plots having some curvature (see Table VI). Because of these difficulties the kinetic data for the reaction of CoNO(CO)₃ with As(C₆H₅)₃ are less reliable than those for the other substitution reactions. Nevertheless, the rates of these reactions do appear to follow the two-term rate expression of eq 3, which differs from that given by eq 4. At pseudo-first-order conditions the experimentally observed rate constants, k_{obsd}, are related to the individual rate constants and the concentration of nucleophile by

$$k_{obsd} = k_1 + k_2[As(C_6H_5)_3] \qquad (6)$$

This requires that a plot of k_{obsd} vs. [As(C₆H₅)₃] be linear (Figure 3) with a nonzero intercept equal to k_1 and a

slope of k_2. The results available are in accord with this (see Table VI).

The rate-determining step leading to the decomposition of CoNO(CO)₃ might be the same as that leading to reaction by path k_1 with As(C₆H₅)₃, since both are expected to be a first-order process. Although the solvent does not make a significant contribution to the rate of reaction of CoNO(CO)₃ with good reagents such as P(C₆H₅)₃ (Figure 1), it may provide a path for reaction (or decomposition) in the presence of poor reagents. Rate law 3 is similar to the two-term rate law found for substitution reactions of square-planar metal complexes.[21] In these cases there is good evidence that the k_1 path involves a displacement process in which the solvent acts as the nucleophile and the k_2 path is the direct displacement by the reagent. It would appear that much the same mechanism is possible for the substitution reactions of CoNO(CO)₃. For good reagents such as P(C₆H₅)₃, in the solvents used, $k_1 \ll k_2$, and therefore the reaction proceeds almost entirely by the direct reagent path. For poor reagents such as As(C₆H₅)₃, $k_1 \sim k_2$ so that at the concentration of reagents used both k_1 and $k_2[L]$ contribute to the total rate of reaction.

Finally, the exchange of ¹⁴CO with CoNO(CO)₃ was investigated, and the data obtained are given in Table VII. Because exchange is slow and because of the experimental difficulties of the method used to follow the rate of exchange, these results are also less reliable than are the kinetic data for the substitution reactions. As explained in the Experimental Section, it was not possible to make temperature-dependence studies on the rates of exchange. In spite of these shortcomings the data collected are sufficiently reliable to show that exchange takes place in toluene solution by a first-order process, one that in zero order in the concentration of CO. Furthermore, this rate of exchange is approximately 50 times faster than the extrapolated rate of the first-order path for the reaction of CoNO(CO)₃ with As(C₆H₅)₃ in toluene solution. Such a result is similar to the recent results obtained for the exchange and substitution reactions of Ni(CO)₄.[3c] Here, too, the rates of CO exchange and reaction with P(C₆H₅)₃ (or P(OCH₃)₃) differ, and although both are first order they appear to take place by different reaction paths. A somewhat similar situation is found for CO exchange and substitution reactions of Hg[Co(CO)₄]₂.[33] This anomalous behavior is not understood, and little is to be gained by speculating until more information is obtained.

Acknowledgment. This research was supported in part by the National Science Foundation (GP-1471). We wish to thank Professors J. O. Edwards and R. G. Pearson for interesting discussions on the nucleophilic strengths of various reagents toward the substrate CoNO(CO)₃.

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