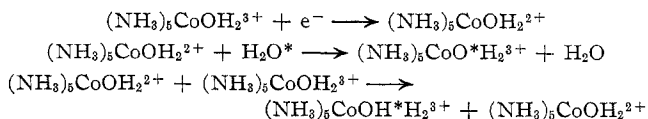


cobalt(III) complexes at the dropping-Hg electrode and by outer-sphere reducing agents has already been pointed out.^{16,17} The results in Table I suggest that the similarity extends, at least for $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ as oxidant, to the metals Pt, Cu, Ag, and possibly Cr acting as cathode. For Cu f is independent of the current density, and in this case at least it is fairly certain that f is characteristic of the electrode process rather than of the diffusion step. When diffusion to the electrode is rate limiting, a value of f very close to 1.000 is expected. The data for Cr in fact show a variation of f with current density and suggest that at the higher current densities, diffusion to the electrode becomes rate limiting. It is difficult to understand why the limiting diffusion current at the Cr electrode is less than at Pt, Cu (and apparently Ag), and we can only suppose that there was a difference in experimental arrangement, perhaps having to do with the rate of stirring. This value is fairly close to that observed for the reductants $\text{Ru}(\text{NH}_3)_6^{2+}$, V^{2+} , and Eu^{2+} which we take to react by outer-sphere activated complexes. The Ni cathode appears to behave differently from the others. We have no reason to set aside this result but, since only a single experiment with

Ni was done, are not prepared to assert that this electrode is really different.

Metallic iron reduces the aquopentaamminecobalt(III) complex directly and at a rate so great that the reaction must be diffusion controlled. The value of f is observed to be close to 1.00, as would be expected for a diffusion-controlled process.

The most significant of the results reported by us may well be those contained in Table II. As has already been mentioned, they suggest that the electron-transfer reactions induce exchange between $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ and solvent. This implies that the cobalt(II) complex which is formed on electron transfer lasts long enough to undergo water exchange with the solvent and electron transfer with Co(III) .



The effect merits further investigation and we plan to work on this aspect of the subject.

Acknowledgments.—Financial support by the Office of Naval Research, Contract Nonr 225(63), is gratefully acknowledged. Acknowledgment is also made to the Deutschen Akademischen Austauschdienstes for a NATO postdoctoral fellowship in support of the research of P. D.

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Kinetics of Substitution Reactions of Some Monosubstituted Derivatives of Nitrosyltricarboxylcobalt(0)¹

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Compounds of the type $\text{CoNO}(\text{CO})_2\text{L}$, where $\text{L} = \text{CO}$, $\text{CNC}_6\text{H}_{11}$, $\text{As}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$, $\text{P}(\text{OCH}_3)_3$, and $\text{P}(\text{C}_6\text{H}_5)_3$, undergo L group substitution in the presence of phosphines to give $\text{CoNO}(\text{CO})_2\text{L}'$. The reactions at 40.4° proceed at slow to moderate rates and are dependent upon the nature and concentration of L' . For the same substrate $\text{CoNO}(\text{CO})_2\text{L}$, the rates of reaction increase with changes in reagent L' in the order: $\text{P}(\text{OC}_6\text{H}_5)_3 < \text{P}(\text{C}_6\text{H}_5)_3 < \text{P}(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5 < \text{P}(n\text{-C}_4\text{H}_9)_3$. For the same reagent but different substrates the rates of reaction increase with changes in L in the order: $\text{P}(\text{C}_6\text{H}_5)_3 < \text{P}(\text{OCH}_3)_3 < \text{P}(\text{OC}_6\text{H}_5)_3 < \text{As}(\text{C}_6\text{H}_5)_3 \sim \text{P}(\text{OCH}_2)_3\text{CCH}_3 < \text{CNC}_6\text{H}_{11} < \text{CO}$. The reaction of $\text{CoNO}(\text{CO})_2\text{L}$ with L to give $\text{CoNO}(\text{CO})\text{L}_2$ and CO at 40.4° proceeds more slowly than L group exchange and is also dependent upon the nature and concentration of L. The results are compared and contrasted to the $\text{Ni}(\text{CO})_2\text{L}_2$ system,² and the nature of the bonding between metal and L group in both systems is discussed.

Introduction

The monosubstituted derivatives of $\text{CoNO}(\text{CO})_3$ might be expected to exhibit kinetic behavior similar to that of the disubstituted derivatives of $\text{Ni}(\text{CO})_4$, since the two systems are structurally and electronically similar. Meriwether and Fiene² have found that com-

pounds of the type $\text{Ni}(\text{CO})_2\text{L}_2$ in the presence of a phosphine undergo ligand exchange more rapidly than additional CO substitution. Furthermore, all reactions involving derivatives of $\text{Ni}(\text{CO})_4$ were found to be first order in complex and independent of the added phosphine. Work has also been reported on the reaction of $\text{Ni}(\text{CO})_4$ with L to give $\text{Ni}(\text{CO})_3\text{L}^3$ and thence

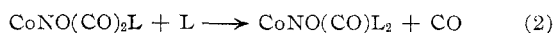
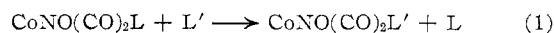
(1) Taken in part from the Ph.D. Thesis of E. M. T., Northwestern University, 1966.

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(3) (a) F. Basolo and A. Wojcicki, *ibid.*, **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).

$\text{Ni}(\text{CO})_2\text{L}_2$.² These reactions are also first order in complex and independent of L.

By contrast it has been shown^{3b,4} that $\text{CoNO}(\text{CO})_3$, which is isoelectronic and isostructural with $\text{Ni}(\text{CO})_4$, undergoes CO substitution to give $\text{CoNO}(\text{CO})_2\text{L}$ by a process which is both first order in substrate and nucleophile concentrations. This paper reports the kinetic behavior of various monosubstituted derivatives of $\text{CoNO}(\text{CO})_3$ in ligand-exchange reactions of type 1 and CO substitution of type 2.



Experimental Section

Materials.—The solvent and reagents were prepared and/or purified as previously described.⁴

Preparation of Complexes.—The preparation and characterization of the complexes used in this study have also been previously described.⁴ The monosubstituted derivatives of $\text{CoNO}(\text{CO})_3$ which were used in the kinetic studies leading to the disubstituted derivatives were prepared *in situ* under the kinetic conditions listed in Table III. The initial concentration of $\text{CoNO}(\text{CO})_3$ in these solutions was *ca.* $5 \times 10^{-3} M$ or less. Owing to the large disparity in rates between the reactions leading to the mono- and disubstituted derivatives, no kinetic complications arose, except in the case of $\text{CNC}_6\text{H}_{11}$ where both rates appear to be of the same order of magnitude.

Kinetic Data.—The rates of both the ligand exchange and CO substitution reactions were followed by observing the disappearance of the highest energy carbonyl band of the starting material. Measuring the rate of the carbonyl substitution reactions by observing the rate of evolution of CO is not a convenient method in these cases because the reactions are quite slow. All of the kinetic studies reported herein were performed in a manner completely analogous to that previously described.⁴ The concentration of the substrate was always *ca.* $5 \times 10^{-3} M$ or less while that of the reagent was at least in tenfold excess. The infrared spectra of the monosubstituted derivatives of $\text{CoNO}(\text{CO})_3$ discussed in this work have been presented previously.⁴

Figure 1 shows the infrared spectral changes which take place in the metal carbonyl and nitrosyl regions during the ligand-exchange reaction of $\text{CoNO}(\text{CO})_2\text{P}(\text{OCH}_2)_3\text{CCH}_3$ and $\text{P}(n\text{-C}_4\text{H}_9)_3$. In going from the phosphite to the phosphine derivative, the shift of the three bands is to lower frequencies. In a few instances (see Table II) the overlap of the reactant and product bands was large and this resulted in a pronounced curvature of the pseudo-first-order kinetic plot. In such cases the rate constant was determined from the initial slope of the curve and should be considered only approximate.

Most of the exchange reactions reported here are of the phosphite derivative leading to the phosphine. It is difficult to study the reactions proceeding in the opposite direction, since the equilibrium is on the phosphine derivative side. Furthermore, phosphites at 0.1 M concentration or larger absorb noticeably in the carbonyl region of the infrared spectrum and thus interfere with the kinetics. Nevertheless, we report here two reactions of the $\text{P}(\text{C}_6\text{H}_5)_3$ derivative with phosphites. These rate constants also should be considered approximate. The same is true for the CO substitution reactions with trimethyl phosphite as the reagent. For the reactions where more than one run was carried out, the average deviation of the calculated rate constant was 10%.

Results

Tables I and II present evidence for the second-order nature of the ligand-exchange reactions. The leaving group is displaced from the $\text{CoNO}(\text{CO})_2$ moiety at a

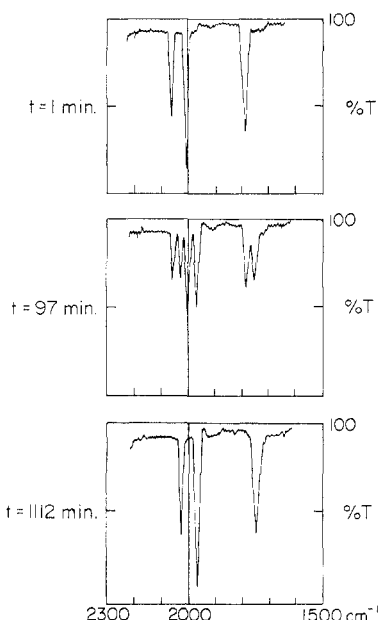


Figure 1.—Infrared spectra of the reaction of $\text{CoNO}(\text{CO})_2\text{P}(\text{OCH}_2)_3\text{CCH}_3$ with $\text{P}(n\text{-C}_4\text{H}_9)_3$ in toluene at 40.4° .

TABLE I
RATE CONSTANTS FOR THE REACTIONS
 $\text{CoNO}(\text{CO})_2\text{L} + \text{P}(n\text{-C}_4\text{H}_9)_3 \longrightarrow \text{CoNO}(\text{CO})_2\text{P}(n\text{-C}_4\text{H}_9)_3 + \text{L}$
IN TOLUENE AT 40.4°

$[\text{P}(n\text{-C}_4\text{H}_9)_3], M$	$k_{\text{obsd}}, \text{sec}^{-1}$	$k, M^{-1} \text{sec}^{-1}$
L = $\text{P}(\text{OCH}_2)_3\text{CCH}_3$		
0.024	1.1×10^{-4}	4.6×10^{-3}
0.029	1.3×10^{-4}	4.5×10^{-3}
0.213	8.9×10^{-4}	4.2×10^{-3}
0.388	1.6×10^{-3}	4.1×10^{-3}
0.683	2.5×10^{-3}	3.7×10^{-3}
1.12	4.0×10^{-3}	3.6×10^{-3}
0.371 ^a	5.2×10^{-4}	1.4×10^{-3}
L = $\text{P}(\text{OCH}_3)_3$		
0.026	1.5×10^{-5}	5.8×10^{-4}
0.111	5.4×10^{-5}	4.9×10^{-4}
0.378	2.1×10^{-4}	5.6×10^{-4}
0.762	4.0×10^{-4}	5.3×10^{-4}
1.14	5.4×10^{-4}	4.7×10^{-4}
0.381 ^b	6.7×10^{-5}	1.8×10^{-4}

^a This reaction was performed at 25.0° and allows an estimate of $\Delta H^* = 12 \text{ kcal/mole}$; $\Delta S^* = -30 \text{ eu}$. ^b This reaction was performed at 25.0° and allows an estimate of $\Delta H^* = 12 \text{ kcal/mole}$; $\Delta S^* = -34 \text{ eu}$.

rate which is dependent upon the concentration and nature of the entering nucleophile. The data at 40.4° for CO as the leaving group, *i.e.*, $\text{CoNO}(\text{CO})_3$ as the substrate, have been previously presented.⁴

Table III presents the kinetic data concerning the second step of CO substitution. As in the case of the ligand-exchange reactions these are also second order, first order in substrate and first order in nucleophile concentrations. However, except for the reaction with $\text{CNC}_6\text{H}_{11}$, these reactions are much slower than the ligand-exchange reactions. The carbonyl and nitrosyl vibrational frequencies for the disubstituted derivatives of $\text{CoNO}(\text{CO})_3$ are given in Table IV.

TABLE II
RATE CONSTANTS FOR THE REACTIONS
 $\text{CoNO}(\text{CO})_2\text{L} + \text{L}' \longrightarrow \text{CoNO}(\text{CO})_2\text{L}' + \text{L}$
IN TOLUENE AT 40.4°

L	L'	[L'], M	k_{obsd} , sec ⁻¹	k , M ⁻¹ sec ⁻¹
CNC ₆ H ₁₁	P(<i>n</i> -C ₄ H ₉) ₃	0.117	7.3×10^{-4}	6.2×10^{-3}
CNC ₆ H ₁₁	P(C ₆ H ₅) ₃ C ₂ H ₅	0.473	2.8×10^{-4}	5.9×10^{-4}
CNC ₆ H ₁₁	P(C ₆ H ₅) ₃	0.456	4.1×10^{-5}	9.0×10^{-5}
P(OCH ₃) ₃ CCH ₃	P(C ₆ H ₅) ₃	0.144	3.5×10^{-5}	2.4×10^{-4}
P(OCH ₃) ₃ CCH ₃	P(C ₆ H ₅) ₃ C ₂ H ₅	0.383	6.7×10^{-5}	1.7×10^{-4}
P(OCH ₃) ₃ CCH ₃	P(C ₆ H ₅) ₃	0.488	8.2×10^{-5}	1.7×10^{-5}
As(C ₆ H ₅) ₃	P(<i>n</i> -C ₄ H ₉) ₃ ^a	0.114	4×10^{-4}	4×10^{-3}
P(OC ₆ H ₅) ₃	P(<i>n</i> -C ₄ H ₉) ₃	0.115	1.6×10^{-4}	1.4×10^{-3}
P(OC ₆ H ₅) ₃	P(C ₆ H ₅) ₃ C ₂ H ₅	0.456	3.1×10^{-5}	6.8×10^{-5}
P(OC ₆ H ₅) ₃	P(C ₆ H ₅) ₃	0.131	6.5×10^{-7}	5.0×10^{-6}
P(OCH ₃) ₃	P(C ₆ H ₅) ₃ C ₂ H ₅	0.680	1.1×10^{-5}	1.6×10^{-5}
P(OCH ₃) ₃	P(C ₆ H ₅) ₃ ^a	0.898	1×10^{-6}	1×10^{-6}
P(C ₆ H ₅) ₃	P(<i>n</i> -C ₄ H ₉) ₃	...	...	3×10^{-4b}
P(C ₆ H ₅) ₃	P(OCH ₃) ₃ ^a	0.833	7×10^{-6}	8×10^{-6}
P(C ₆ H ₅) ₃	P(OC ₆ H ₅) ₃ ^a	0.661	4×10^{-7}	6×10^{-7}

^a Owing to partial overlap of the reactant and product carbonyl bands, the kinetic plot showed pronounced curvature. The rate constant was obtained from the initial slope of the curve.

^b This value was obtained by extrapolation from the other data for this substrate assuming a linear free energy relationship between log k and ΔH_{NP} . ^c The kinetic plot showed pronounced curvature. The rate constant was determined from the initial slope of the line.

TABLE III
RATE CONSTANTS FOR THE REACTIONS
 $\text{CoNO}(\text{CO})_2\text{L} + \text{L} \longrightarrow \text{CoNO}(\text{CO})\text{L}_2 + \text{CO}$
IN TOLUENE AT 40.4°

L	[L], M	k_{obsd} , sec ⁻¹	k , M ⁻¹ sec ⁻¹
CNC ₆ H ₁₁	0.635	Reaction complete in 1 day	
P(OCH ₃) ₃ ^a	0.343	2×10^{-6}	6×10^{-6}
P(OCH ₃) ₃ ^a	0.672	4×10^{-6}	6×10^{-6}
P(OCH ₃) ₃ ^a	1.24	8×10^{-6}	6×10^{-6}
P(OCH ₃) ₃ CCH ₃	0.569	2.3×10^{-6}	4.0×10^{-6}
P(<i>n</i> -C ₄ H ₉) ₃	0.452	2.1×10^{-7}	4.9×10^{-7}
P(<i>n</i> -C ₄ H ₉) ₃	0.583	2.7×10^{-7}	4.6×10^{-7}
P(OC ₆ H ₅) ₃	0.555	Very slow	
P(C ₆ H ₅) ₃	0.535	Very slow	

^a Trimethyl phosphite absorbs in the metal carbonyl region of the infrared spectrum and the kinetic plots showed a pronounced curvature. The rates of these reactions were determined from the initial slopes of the curves.

TABLE IV
INFRARED CARBONYL AND NITROSYL FREQUENCIES FOR SOME
COMPOUNDS OF THE TYPE $\text{CoNO}(\text{CO})\text{L}_2$ IN SOLUTION

L	Solvent ^a	ν_{CO} , cm ⁻¹	ν_{NO} , cm ⁻¹
P(OC ₆ H ₅) ₃	C	2008	1764
P(OCH ₃) ₃ CCH ₃	T	2001	1750
P(OCH ₃) ₃	T	1983	1727
CNC ₆ H ₁₁	T	1978	1721
P(C ₆ H ₅) ₃	C	1958	1714
P(<i>p</i> -CH ₃ OC ₆ H ₄) ₃	D	1943	1687
P(<i>n</i> -C ₄ H ₉) ₃	T	1957	1693

^a C refers to a carbon tetrachloride solution of the compound (W. Hieber and J. Ellermann, *Chem. Ber.*, **96**, 1643 (1963)); T refers to toluene solutions containing an excess of ligand, from the kinetic studies of this work; D refers to a dichloromethane solution of the compound.

Discussion

The compounds $\text{CoNO}(\text{CO})_2\text{L}$ and $\text{Ni}(\text{CO})_2\text{L}_2$ are analogous in that they have two carbonyl groups and two other groups tetrahedrally arranged about the

metal atom and are derived from parent compounds which are isoelectronic. They behave similarly in solution in the presence of a nucleophile in that they undergo ligand exchange more readily than CO substitution.² However, they apparently undergo reactions by processes which are fundamentally different, since the rate of reaction of $\text{Ni}(\text{CO})_2\text{L}_2$ is first-order, whereas that of $\text{CoNO}(\text{CO})_2\text{L}$ is second-order. Therefore, unimolecular dissociative and bimolecular displacement types of processes are postulated for the nickel² and cobalt systems, respectively. However, recent studies indicate that reactions of the parent compound $\text{Ni}(\text{CO})_4$ may not proceed by a simple dissociative process.^{3c}

That the two systems react by different mechanistic processes has been attributed to the presence of NO in the cobalt substrate.⁴ Since NO is a free radical, it forms complexes in which it is present in essentially one of the three forms:⁵ NO⁺, NO, or NO⁻. In order to satisfy the effective atomic number rule, so often obeyed in metal carbonyls, it is believed that NO contributes three electrons to the metal in these systems. The metal then back donates electron density through π bonding, thereby creating a strong double bond with the nitric oxide group. This gives the metal a formal negative charge, whereas NO takes on a formal positive charge. In the transition state there can be a transfer of a bonding pair of electrons to the electronegative NO⁺ group, thus resulting in the net change of $\text{Co}=\text{N}=\text{O}$ into $\text{Co}-\text{N}=\text{O}$. For the cobalt

compound under discussion this means the metal in the transition state has a low-spin d⁸ electronic structure which makes available a vacant orbital of low energy and permits the attack by a pair of electrons of the entering nucleophile. Assuming this low-spin d⁸ system has a square-planar structure, it is well known that such systems undergo bimolecular displacement reactions.⁶ A compound containing only CO ligands such as $\text{Ni}(\text{CO})_4$ does not appear to behave in this manner, perhaps because carbon is less electronegative than nitrogen and delocalization of electron density to carbon takes place less readily than it does to nitrogen.

The rates of ligand replacement of $\text{Ni}(\text{CO})_2\text{L}_2$ depend on the nature of the ligand and decrease with changes in L in the order:² PCl_3 (>300) > CO (~240)⁷ >> $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ (19) > $\text{P}(\text{C}_6\text{H}_5)_3$ (17) > $\text{P}(\text{n-C}_4\text{H}_9)_3$ (1.0) >> $\text{P}(\text{OC}_2\text{H}_5)_3$ (<0.003) ~ $\text{P}(\text{OC}_6\text{H}_5)_3$ (<0.003), where the numbers in parentheses are the rates relative to that of the $\text{P}(\text{n-C}_4\text{H}_9)_3$ derivative. It was pointed out that the rates closely parallel the order of increasing basicity of the phosphines with the exception of the two phosphite compounds. No explanation was given for the anomalous behavior of the phosphite ligands, but it was concluded that in these systems the Ni-P bond strengths are largely governed by σ -bonding properties. Thus, for phosphine ligands the most

(5) J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 32, 38 (1958).

(6) F. Basolo, *Advances in Chemistry Series*, No. 49, American Chemical Society, Washington, D. C., 1965, p 81.

(7) The value for $\text{L} = \text{CO}$ was obtained from L. R. Kangas and P. M. Henry, private communication.

basic is the most firmly bound and the most difficult to replace. It is seen that both PCl_3 and CO are very easily replaced. Since these compounds are very similar in that they are weakly basic but strong π bonders⁸ these results are reasonable.

The above order of reactivity of $\text{Ni}(\text{CO})_2\text{L}$ can now be compared to that for $\text{CoNO}(\text{CO})_2\text{L}$ with similar changes in L . It should be kept in mind that the reactions of the nickel substrates are first order, whereas those of the cobalt substrates are second order. Therefore, the ordering of the rates of reaction of the cobalt compounds are necessarily for their reactions with the same nucleophile. The data in Tables I and II show that the rates of reaction of $\text{CoNO}(\text{CO})_2\text{L}$ with $\text{P}(n\text{-C}_4\text{H}_9)_3$ decrease in the order: CO (68)⁹ $\gg$ $\text{CNC}_6\text{H}_{11}$ (1.5) $>$ $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ (1.0) $\sim$ $\text{As}(\text{C}_6\text{H}_5)_3$ (1) $>$ $\text{P}(\text{OC}_6\text{H}_5)_3$ (0.34) $>$ $\text{P}(\text{OCH}_3)_3$ (0.13) $>$ $\text{P}(\text{C}_6\text{H}_5)_3$ (0.07), where the values in parentheses are the rates relative to that of the $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ derivative. The spread in rates for the nickel substrates is greater than 10^5 , whereas that of the cobalt substrates is about 10^3 .

Clearly the rates of displacement of L in $\text{CoNO}(\text{CO})_2\text{L}$ must depend on a number of factors. With regard to the nature of L , it is of interest to consider the following factors: (1) steric, (2) π bonding, and (3) σ bonding. The results obtained show that the ligands of carbon ligand atoms, $\text{L} = \text{CO}$ or $\text{CNC}_6\text{H}_{11}$, are more readily displaced than are the ligands of phosphorus or arsenic ligand atoms. This may be due to a more favorable combination of steric and π -bonding factors in the systems $\text{L} = \text{CO}$ or $\text{CNC}_6\text{H}_{11}$. Since these reactions proceed with an expansion in coordination number from four to five, it follows that there should be a steric retardation for the rates of reaction. Thus, substrates containing bulky ligands such as $\text{P}(\text{C}_6\text{H}_5)_3$ will react more slowly than those containing smaller ligands.

A second factor contributing to the greater reactivity of the systems where $\text{L} = \text{CO}$ or $\text{CNC}_6\text{H}_{11}$ is that these ligands are better π bonders than are the other groups being considered.⁸ The stability of five-coordinated transition metal complexes is known to increase with an increase in the π -bonding capacity of the ligands.¹⁰ For example, there are stable species such as $\text{Fe}(\text{CO})_5$, $\text{Ni}(\text{CN})_5^{3-}$,¹¹ and $\text{Pt}(\text{SnCl}_3)_3^{3-}$.¹² A bimolecular displacement mechanism for substitution reactions of $\text{CoNO}(\text{CO})_2\text{L}$ requires the formation of five-coordinated $\text{CoNO}(\text{CO})_2\text{LL}'$, and because π -bonding ligands stabilize this species they will tend to accelerate the reactivity of the substrate. Put another way, a lower activation energy is expected for a compound containing strong π -bonding ligands rather than weak, since strong π bonders will have a greater stabilizing influence on the

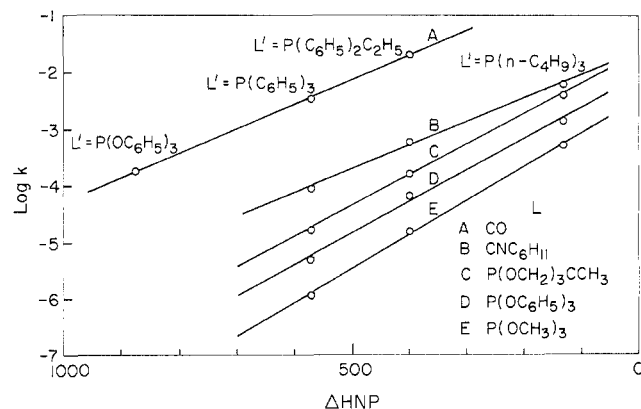


Figure 2.—Plot of $\log k$ vs. ΔHNP for the reaction $\text{CoNO}(\text{CO})_2\text{L} + \text{L}' \rightarrow \text{CoNO}(\text{CO})_2\text{L}' + \text{L}$ in toluene at 40.4° . The circles represent the different entering groups, L' , listed at the top of the columns, while the lines represent the various leaving groups, L . Values of ΔHNP are the difference in half-neutralization potentials of the reagents from that of $\text{N,N}'$ -diphenylguanidine taken as a standard, all measured toward a protonic acid in nitromethane solution.¹³ The values of ΔHNP decrease with increasing basicity (or polarizability) of L' .

trigonal-bipyramidal transition state relative to the tetrahedral ground state than will the weak ones. This is due to the geometries of the π -bonding orbitals which permit four π bonds in the transition state but only two in the ground state.

That the phosphites are more readily displaced than is $\text{P}(\text{C}_6\text{H}_5)_3$ from the moiety $\text{CoNO}(\text{CO})_2$ may also be explained on the basis that the phosphites are better π -bonding ligands than are phosphines.⁸ The phosphite, $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, that is easiest to displace is the one that offers the least steric retardation to the rate of reaction. The order of reactivity $\text{P}(\text{OC}_6\text{H}_5)_3 > \text{P}(\text{OCH}_3)_3$ suggests that the greater steric hindrance of the former is more than compensated for by its better π -bonding and poorer σ -bonding (weaker base)¹³ tendency than for $\text{P}(\text{OCH}_3)_3$.

The steric factors and π -bonding properties of $\text{P}(\text{C}_6\text{H}_5)_3$ and $\text{As}(\text{C}_6\text{H}_5)_3$ are about the same, yet the arsine is more readily replaced from $\text{CoNO}(\text{CO})_2\text{L}$ than is the phosphine. This is in accord with the greater basicity or σ -bonding properties of the phosphine relative to the arsine.¹⁴ Since the Co-L bond strengths for these ligands in this system are largely due to σ bonding, it follows that the energy required to break the Co-P bond will exceed that for Co-As . Such a result is also in agreement with the ligand atom stability order $\text{N} \ll \text{P} > \text{As} > \text{Sb}$ for metal complexes of class b metals.¹⁵

Since the rates of ligand exchange for $\text{CoNO}(\text{CO})_2\text{L}$ are second order, it is also of interest to compare the nucleophilic strengths of various reagents toward a given substrate, as well as their relative strengths toward different substrates. Tables I and II give data of this type and Figure 2 shows a plot of the log of the rate constants vs. the basicity¹⁸ (or polarizability) of

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the reagent. For each of the five substrates the results show that the rates of reaction increase with an increase in the polarizability of the nucleophile. This is in accord with the affinity of a soft base for a soft acid¹⁶ (or class b metal). That the plots of the linear free energy relationships shown in Figure 2 are all approximately parallel indicates that although the various compounds differ in reactivity, they have about the same discriminating ability for the various nucleophiles.

The rate data on the second step of CO substitution presented in Table IV are arranged in order of decreasing reactivity. It is seen that the good π -bonding ligands, e.g., $\text{CNC}_6\text{H}_{11}$ and $\text{P}(\text{OCH}_3)_3$, react more rapidly than the poorer π bonders, e.g., the phosphines. This is reasonable since the good π bonders are

in better competition for the electron density on the metal atom with the two remaining CO's than are the poor π bonders. Thus, the phosphite complexes have weaker M-CO bonds than do the phosphine complexes, and this conclusion is borne out by the infrared spectra of the complexes. Furthermore, in analogy to the ligand-exchange reactions the phosphite derivatives should be more susceptible to CO substitution than the phosphine derivatives, since the phosphites can better stabilize the five-coordinated transition state through stronger π bonding. However, the size of the ligand also seems to be important, since the derivative of $\text{P}(\text{OC}_6\text{H}_5)_3$ which is a good π -bonding ligand but very bulky is very slow to react.

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Complex Compounds of Quadrivalent Molybdenum¹

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A series of complex compounds of molybdenum(IV) of the type $\text{MoBr}_4 \cdot 2\text{L}$ and $\text{MoBr}_4 \cdot \text{B}$ have been prepared, where L is a monodentate ligand and B is 2,2'-dipyridyl. Some of the corresponding molybdenum tetrachloride complexes were also prepared and characterized. Under comparable reaction conditions, reduction of MoBr_4 but not MoCl_4 was observed with pyridine at room temperature and with 2,2'-dipyridyl at elevated temperature. The benzonitrile complexes of MoCl_4 and MoBr_4 appear to be isomorphous as do the complexes obtained with 2,2'-dipyridyl. The visible and ultraviolet spectra of the complexes were examined, in the interest of both characterizing and understanding the nature of chemical bonding between metal and ligand.

Introduction

In recent years many compounds containing molybdenum halides and pseudohalides have been described. Except for the octacoordinate cyanides, $\text{M}_4\text{Mo}(\text{CN})_8$,³ complexes of molybdenum(IV) were relatively unknown until only recently. Other eight-coordinate species which have been described are the triphenylarsine oxide,⁴ the oxalate,⁵ and the carbonate⁵ complexes. Several investigators have recently reported hexahalo molybdate(IV) salts, M_2MoX_6 , as formed under a variety of conditions.⁶⁻¹⁰ The range of M included Na, K, Rb, and Cs, as well as pyridinium

and tertiary ammonium cations, and X may be Cl, Br, or in some cases F.

Starting with molybdenum(V), Fowles and co-workers¹¹ prepared an extensive number of hexacoordinate molybdenum(IV) complexes. The first of these, $\text{MoCl}_4(\text{RCN})_2$, where R is methyl, ethyl, and *n*-propyl, were prepared by the reaction of MoCl_5 with the alkyl cyanide. In later work other complexes such as the tetrahydrofuran, pentamethylene oxide, α -picoline, pyridine, triphenylphosphine oxide, and 2,6-dimethylpyrazine diadducts and the 2,2'-dipyridyl and 1,10-phenanthroline monoadducts were produced by replacement of *n*-propyl cyanide in the complex, $\text{MoCl}_4(\text{C}_3\text{H}_7\text{CN})_2$.¹² Interpretation of the infrared spectra of the monodentate ligand complexes indicated the organic ligands to be in the *cis* configuration. These complexes of MoCl_4 were characterized by spectral and magnetic measurements.

Owing to the instability of the tetrahalides of molybdenum, few complexes with organic ligands have

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