(18) R. J. Doedens, J. T. Veal, and R. G. Little, *Inorg. Chem.*, **14**, 1138 (1975).
(19) C. Barbeau and R. J. Dubey, *Can. J. Chem.*, **51**, 3684 (1973).
(20) M. R. Churchill, B. G. DeBoer, and K. L. Kalra, *Inorg. Chem.*, **12**, 1646 (1973).
(21) A. Lopex-Castro and M. R. Truter, *Acta Crystallogr.*, **17**, 465 (1964).
(22) R. Gerdil, *Helv. Chim. Acta*, **57**, 489 (1974).
(23) W. Branes and M. Sundaralingam, *Acta Crystallogr., Sect. B.* **29**, 1868 (1973).
(24) (a) J. H. Burns, W. H. Baldwin, and F. H. Fink, *Inorg. Chem.*, **13**, 1916 (1974); (b) A. D. U. Hardy and G. A. Sim, *J. Chem. Soc., Dalton, Trans.*, 1900 (1972); (c) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **10**, 572 (1971).
(25) W. Strohmeier and F. J. Muller, *Chem. Ber.*, **100**, 2812 (1967).
(26) At this time we cannot rule out the possibility that the sulfonium cation is first dissociated, then dealkylated and the sulfide molecule returned to the manganese atom.

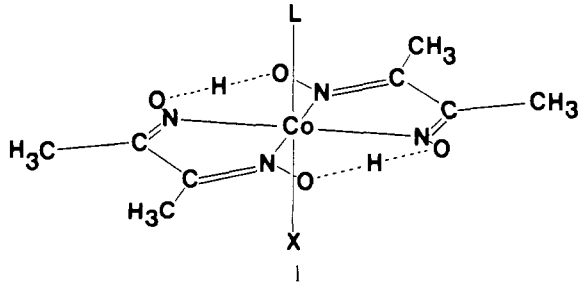
A Mechanistic Investigation of Cobaloxime Complexes Containing Good Trans Labilizing Ligands, Including Spectroscopic and Rate Comparisons

Robert Charles Stewart and Luigi G. Marzilli*

Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218. *Received March 7, 1977*

Abstract: Observed and extrapolated first-order rate constants are reported for trans ligand substitution reactions in a series of six-coordinate cobalt(III) complexes known as cobaloximes. These complexes are of the type *trans*-$LCo(DH)_2X$, where (DH) = the monoanion of bisdimethylglyoxime ($HON{=}C(CH_3)C(CH_3){=}NO^-$), and L and X are neutral and anionic ligands, respectively. The trans labilizing ability of X was sufficient to allow monitoring the substitution reactions by conventional spectrophotometric techniques at 25 °C. The nonaqueous solvent, CH_2Cl_2, was employed for these measurements. Under pseudo-first-order excess of entering ligand, L′ = 4-*tert*-butylpyridine, 1-methylimidazole, trimethyl phosphite, trimethylphosphine, dimethylphenylphosphine, tri-*n*-butylphosphine, and tri-*n*-octylphosphine, the observed rate constants for the substitution of L = 4-cyanopyridine trans to CH_3 was found to be independent of both the concentration and chemical identity of L′. The observed rate constants for the substitution of $LCo(DH)_2CH_3$ by tri-*n*-butylphosphine depended on L in the following order: 4-*tert*-butylpyridine ($1.32 \pm 0.04 \times 10^{-4}$ s^{-1}) < 4-cyanopyridine ($5.7 \pm 1.6 \times 10^{-2}$ s^{-1}) < triphenylphosphine ($8.0 \pm 0.1 \times 10^{-2}$ s^{-1}). The relative trans effect of a total of 11 different X ligands was found to increase in the following order: *p*-$SO_2C_6H_4CH_3$ < $CHBr_2$ ≤ $SC(C_6H_5)_3$ < CH_2Br < *p*-C_6H_4Br < *p*-$C_6H_6H_4OCH_3$ < C_6H_5 < *p*-$CH_2C_6H_4CN$ < CH_3 < $CH_2C_6H_5$ < C_2H_5. The relative increase in the observed rate constants for substitution of 4-cyanopyridine by tri-*n*-butylphosphine was ca. 10^4 as the trans labilizing X ligand was varied from the S-bonded *p*-$SO_2C_6H_4CH_3$ ligand to the C-bonded ethide ligand. Addition of leaving ligand, L, to reaction mixtures resulted in a mass-law rate retardation. Competition ratios were determined for 9 of the 11 X ligands and found to be ca. one for most ligands but tri-*n*-butylphosphine and tri-*n*-octylphosphine proved to be poorer competitors. Competition ratios were essentially independent of the nature of the leaving ligand L. These results provide evidence for a dissociative mechanism with the generation of a highly reactive five-coordinate intermediate which does not discriminate between sterically unhindered nucleophiles. Correlations of the observed rate constants with ^1H and ^{13}C NMR shift and coupling data reported previously are consistent with ground-state bond weakening for cobaloximes with good trans activating ligands. One of the parameters which correlated well with these rate constants was the α-^{13}C NMR chemical shift of 4-*tert*-butylpyridine (Bupy) in $(Bupy)Co(DH)_2X$.

Vitamin B_{12} coenzyme as well as methylcobalamin are octahedral Co(III) compounds containing direct Co-C bonds which occupy an axial coordinating position relative to a corrinoid ring system.[1,2] It is now very clear that the bond between the Co(III) center and the ligating atom in the trans position



I

is weakened (relative to when a normal ligand such as Cl or NH_3 replaces the alkyl ligand) leading to increased bond lengths to cobalt and higher rates of substitution of the trans ligand.[1] These phenomena are not limited to the cobalt corrinoids but have also been observed in many other cobalt(III) alkyl complexes.

The cobaloximes I ($LCo(DH)_2X$ where DH = monoanion of dimethylglyoxime) are often studied as models for cobalamins and the alkyl complexes (X = R) have been the subject of extensive kinetic and mechanistic studies.[3-7] This activity has been motivated by the possibility that axial base release may be involved in biological mechanisms. One of the principal advantages in investigating cobaloximes is the solubility of these compounds in noncoordinating solvents. Under such conditions, it is possible to observe the substitution process uncomplicated by the intermediacy of solvato complexes.[8] Thus, although numerous studies had implied that substitution of the trans ligand in organocobaloximes and organocobalamins should be a dissociative (first order in [complex]) process, experimental studies had typically yielded second-order kinetics. Subsequently, using nonaqueous noncoordinating solvent media, Brown was able to demonstrate experimentally using equilibrium NMR relaxation techniques that the trans ligand substitution reactions were first order in complex concentration and independent of entering ligand concentration.[3] Subsequently, we confirmed this observation using similar complexes and solvents but employing spectrophotometric techniques.[7]

0002-7863/78/1500-0817$01.00/0

For a purely dissociative process, the ligand exchange mechanism is given by

$$LCo(DH)_2X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(DH)_2X + L \quad (1)$$

$$Co(DH)_2X + L' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} L'Co(DH)_2X \quad (2)$$

$$LCo(DH)_2X + L' \rightleftharpoons L'Co(DH)_2X + L \quad (3)$$

Expressions 4 and 5 can be derived by treating $Co(DH)_2X$ as a steady state intermediate and setting $k_{-2} = 0$ (an irreversible reaction).

$$\text{rate} = k_1k_2(L')(\text{complex})/(k_{-1}(L) + k_2(L')) \quad (4)$$

$$1/k_{obsd} = 1/k_1 + k_{-1}(L)/k_1k_2(L') \quad (5)$$

The important consequence of these expressions is that for $[L'] \gg [L]$, the rate of the substitution reaction will be independent of both the nature and the concentration of L', providing L' forms a more stable complex than does L. An additional consequence of these expressions is that the rate of substitution should be subject to a mass law rate retardation effect and that from eq 5 the competition ratio (k_{-1}/k_2) for the reaction of the five-coordinate intermediates with L and L' can be obtained. Such competition experiments, which provide information about the intermediate(s) along the reaction coordinate, cannot be performed using NMR relaxation techniques. In coordinating solvents, effective competition by the solvent for intermediate(s) often leads to an apparent second-order kinetic dependence for the substitution process. The special ability of water to promote substitution reactions is no doubt associated to some extent with the hydrogen bonding capability of this solvent. Therefore, in the experiments reported here, we avoided any ligands which contained NH groups.

In a preliminary report of some of the work to be described here,[7] we showed that a mass-law rate retardation could be observed for cobaloximes containing such good trans labilizing ligands as CH_3^- and $(CH_3O)_2PO^-$, and that except for tri-*n*-butylphosphine (Bu_3P), ligands such as $(CH_3O)_3P$, CNpy,[9] Bupy, MeImd, and $(C_6H_5)_3P$ were about equally effective in retarding the rate of axial ligand substitution. In terms of a dissociative mechanism, this result suggests that the competition ratio (k_{-1}/k_2) from eq 5 was ca. one and that the five-coordinate intermediate was highly reactive. We also showed that, in the absence of added leaving ligand, L, the rate of substitution by a variety of L' ligands was essentially independent of both the nature and concentration of L'.

In a later study by Jensen and Kiskis,[10] rate retardation was observed for the substitution of $(piperidine)Co(DH)_2CH_3$ by substituted pyridines in $HCCl_3$. These authors also studied the reaction between Bu_3P and $(py)Co(DH)_2CH_3$ to yield $(Bu_3P)Co(DH)_2CH_3$ in the presence of added pyridine. In terms of eq 5, they also found that (k_{-1}/k_2) was not very different from one for most entering ligands but that Bu_3P, although very nucleophilic, was a poor competitor.

In addition to the analysis of the mechanism as a purely dissociative process, Jensen and Kiskis[10] offered the following proposal for a dissociative interchange mechanism:

$$LCo(DH)_2X + L' \overset{K_1}{\rightleftharpoons} LCo(DH)_2X,L' \text{ (rapid)} \quad (6)$$

$$LCo(DH)_2X,L' \overset{k_3}{\rightleftharpoons} L'Co(DH)_2X,L \quad (7)$$

$$L'Co(DH)_2X,L \overset{\text{fast}}{\rightleftharpoons} L'Co(DH)_2X + L \quad (8)$$

The appropriate rate expressions for this mechanism would not permit rate retardation, and on this basis, Jensen and Kiskis proposed that the dissociative interchange mechanism could be differentiated from the purely dissociative process. Recently, this conclusion was criticized[11] because the equilibrium

$$LCo(DH)_2X + L \overset{K_2}{\rightleftharpoons} LCo(DH)_2X,L \quad (9)$$

cannot be ignored and for L = piperidine can be demonstrated experimentally. The rate expressions derived for the dissociative interchange mechanism which includes equilibrium 9 are given by

$$k_{obsd} = k_3K_1[L']/(1 + K_1[L'] + K_2[L]) \quad (10)$$

$$1/k_{obsd} = 1/k_3 + (1 + K_2[L])/(k_3K_1[L']) \quad (11)$$

Equations 10 and 11 have equivalent algebraic forms to eq 4 and 5 if $K_2[L] \gg 1$. Ewen and Darensbourg concluded that on the basis of rate retardation a distinction could not be made between the dissociative and dissociative interchange mechanisms. Ewen and Darensbourg were able to suggest further, on the basis of the Jensen and Kiskis[10] data only, that an interchange mechanism was equally likely and that the poor competitive ability of the Bu_3P ligand was a consequence of the low hydrogen bonding ability of Bu_3P which in turn makes K_1 relatively small for this ligand and hence leads to a larger ratio for K_2/K_1, eq 11. The similarity in the ability of the substituted pyridine ligands and piperidine to retard the substitution reactions is easily explained if $K_1 \approx K_2$. Therefore, a choice between the mechanisms is not easily made on the basis of the Jensen and Kiskis data. In this report, we will consider these arguments both on the basis of our earlier data[7] and the additional data that we report here.

A secondary reason for carrying out this study was to examine the relationship between the extensive information on the spectroscopic trans influence (ground-state effect) of X ligands[12] with the kinetic trans effect of X. Most spectroscopic studies have involved metal centers such as Hg(II) for which extensive kinetic information is not available or Pt(II) which undergo substitution reactions by associative and, hence, complex pathways. These metals have isotopes which allow an assessment of metal ligand bonding and metal hybridization using calculations based on NMR coupling constants between the metal nucleus and ligand nuclei.

There is no convenient isotope of cobalt for measuring metal to ligand spin-spin coupling. However, we have shown that the relative spectroscopic influence of X in some cobalt(III) compounds parallels quite closely this effect in platinum(II) chemistry.[13] Additionally, cobaloximes exhibit some chemistry which is similar to that for Pt(II).[14] Brown has pointed out that good correlations can be found between activation parameters for ligand exchange and ^{59}Co NQR data on cobaloximes.[3] Thus, although ^{59}Co complexes do not exhibit useful spin-spin coupling, some insight into bonding can be derived from NQR studies, even without recourse to the demonstrated similarity between Co(III) and Pt(II) chemistry.

Results

Characterization and Stoichiometry. The ^1H spectra of all starting and product cobaloximes show a single resonance for the methyl groups of the dimethylglyoxime chelate system, indicating that the $Co(DH)_2$ moiety is planar and that X and L are situated trans to one another. All of the axial ligand exchange reactions were followed by ^1H NMR and found to proceed to completion with apparent 1:1 molar stoichiometry and complete retention of trans stereochemistry. More limited ^{13}C NMR data support the ^1H NMR data; in particular only one oxime methyl ^{13}C NMR signal was observed for both starting and product complexes. NMR spectra of product complexes were identical with those where the proposed

Table III.[a] Summary of Observed and Extrapolated First-Order Rate Constants for the Axial Ligand Substitution of L from $LCo(DH)_2CH_3$ by L′ in CH_2Cl_2 at 25.0 ± 0.1 °C

	Leaving ligand (L) = CNpy k, s^{-1}	
Entering ligand (L′)	Obsd	Extrapolated
Bupy	$6.7 \pm 0.9 \times 10^{-2}$	$6.3 \pm 1.1 \times 10^{-2}$
MeImd	$5.8 \pm 0.3 \times 10^{-2}$	$5.8 \pm 0.6 \times 10^{-2}$
$(CH_3O)_3P$	$6.4 \pm 0.4 \times 10^{-2}$	$6.0 \pm 1.3 \times 10^{-2}$
$(CH_3)_3P$	5.4×10^{-2}	$5.7 \pm 0.9 \times 10^{-2}$
$(CH_3)_2(C_6H_5)P$	$5.5 \pm 0.6 \times 10^{-2}$	$6.0 \pm 0.9 \times 10^{-2}$
Bu_3P	$5.7 \pm 1.6 \times 10^{-2}$	$4.5 \pm 1.0 \times 10^{-2}$
$(n\text{-Octyl})_3P$	$4.9 \pm 0.1 \times 10^{-2}$	$5.0 \pm 1.6 \times 10^{-2}$
	L = $(C_6H_5)_3P$	
Bupy	$8.0 \pm 0.4 \times 10^{-2}$	$7.6 \pm 1.3 \times 10^{-2}$
MeImd	$8.1 \pm 0.7 \times 10^{-2}$	$7.9 \pm 0.6 \times 10^{-2}$
$(CH_3O)_3P$	$8.5 \pm 0.3 \times 10^{-2}$	$8.2 \pm 2.2 \times 10^{-2}$
Bu_3P	$8.0 \pm 0.1 \times 10^{-2}$	$8.8 \pm 2.3 \times 10^{-2}$

[a] The observed rate constants are mean values of the rate data (Table I) taken under pseudo-first-order excess (greater than 0.2 M) of entering ligand (L′) with respect to the cobaloxime concentration (ca. 0.01 M) and without added leaving ligand (L). The extrapolated rate constants were derived from the y intercept of the least-squares regression analysis of the rate data (Table I) according to eq 5. An average k_{obsd} was used for the point corresponding to no added leaving ligand ($[L]/[L'] \simeq 0$). The uncertainties in the observed rate constants are the standard deviations about the mean. The uncertainties in the extrapolated rate constants are the standard deviations in the y intercept of the least-squares plot of eq 4 and are inherently large by this method. [b] Limited data available.

Table IV.[a] Competition Ratios between L and L′ for the Common Intermediate, $Co(DH)_2CH_3$, in CH_2Cl_2 at 25.0 ± 0.1 °C

	Leaving Ligand (L) = CNpy k_{-1}/k_2
Entering ligand (L′)	
Bupy	1.3 ± 0.3
MeImd	1.3 ± 0.2
$(CH_3O)_3P$	1.1 ± 0.3
$(CH_3)_3P$	1.7 ± 0.3
$(CH_3)_2(C_6H_5)P$	1.4 ± 0.3
Bu_3P	4.7 ± 1.0
$(n\text{-Octyl})_3P$	6.1 ± 2.0
$(C_6H_5)_3P$	1.8 ± 0.4[b]
L = $(C_6H_5)_3P$	
Bupy	0.7 ± 0.2
MeImd	0.6 ± 0.1
$(CH_3O)_3P$	0.8 ± 0.3
Bu_3P	4.0 ± 1.1

[a] Mass-law rate retardation data (Table I) were analyzed by eq 5 using a linear least-squares regression program. Uncertainties represent the standard propagation of errors combination of the standard deviations in the slope and y intercept of this analysis. An average k_{obsd} was used for the point corresponding to no added leaving ligand ($[L]/[L'] \simeq 0$). [b] From $(C_6H_5)_3P$-Bupy data.

products had been prepared by alternate methods. No evidence was found for the formation of any disubstituted products, $L'_2Co(DH)_2{}^+X^-$, for the cobaloximes used in this work, even with high L′ ligand concentrations. Such cation species can be problematical in polar solvents such as methanol.[15]

Kinetics. Treatment of the experimental absorbance vs. time rate data with the standard first-order integrated expression using a linear least-squares regression analysis resulted in good (correlation coefficients > 0.99) linear fits over 3-6 half-lives (see Tables I and II in the microfilm edition). The k_{obsd} in these tables were used to calculate the constants given in Tables III-VI. Under the conditions of pseudo-first-order excess of L′ and with no added leaving ligand (L), eq 5 reduces to $k_{obsd} = k_1$. Hence, the observed rate constants (k_{obsd}) in Tables III and V represent values for the limiting rate constants (k_1's).

The observed rate constants given in Table III were determined for the substitution of $LCo(DH)_2CH_3$ (L = CNpy, $(C_6H_5)_3P$) by a series of different entering ligands L′. At sufficiently high concentrations of L′ and in the absence of added L, the reaction rates were essentially independent of both the concentration and chemical identity of L′. Rates were consistently greater for the triphenylphosphine complex than for the cyanopyridine compound. In addition to experiments performed in the absence of added L, a series of rate measurements were made in the presence of varying concentrations of L. The observed rate constants could be treated according to eq 5. Good agreement was found between observed and extrapolated rates. The rates in the forward direction for axial ligand exchange of cobaloximes containing various X groups (Table V) show a variation in rate of approximately 10^4 when differences in leaving ligand are taken into account. Competition ratios calculated from these results are given in Tables IV and VI. Sample plots will be found in the microfilm edition.

Discussion

Three key features emerge from the kinetic data reported in Tables III-VI. First, the rate of the substitution reaction is independent of the concentration of the entering ligand. This finding is wholly consistent with a purely dissociative mechanism. It can also be accommodated by a dissociative interchange mechanism, if $K_1[L']$ is much greater than one.

Second, the rate of the substitution reaction is independent of the nature of the entering ligand. Again this result is exactly in agreement with a purely dissociative mechanism. However, an interchange mechanism requires that, although the entering ligand is in the activated complex, it has no significant influence on the rate constant, k_3, in eq 10. This restriction is, however, not severe since it is conceivable that the weak binding of the entering ligand may not influence the rate of the bond-breaking reaction.

Third, whether the data are treated according to eq 5 or eq 11, a rate retardation would be expected when excess leaving ligand is present. Such a result can algebraically be used to defend either mechanistic proposal.[11] However, the values we have obtained for the ratios k_{-1}/k_2 or K_2/K_1 are generally close to one. For a dissociative mechanism, this finding suggests that the five-coordinate intermediate formed is nonselective on the basis of the nucleophilicity of the incoming ligand.[7] This lack of selectivity is in keeping with a highly reactive intermediate. For an interchange mechanism, this result implies that the association between the complex and the entering ligands (as well as the various and different leaving ligands employed here) is independent of the ligand. Also, since these ratios appear to be independent of X and L in the complex, the association constants (K_1 and K_2) would also have to be independent of the nature of the complex. This accommodation is difficult if not impossible to rationalize. The ligands used vary considerably in size and hydrogen bonding ability as well as in basicity. That such diverse ligands would all have nearly the same affinity for the different cobaloxime complexes used here seems highly unlikely. In particular, the hydrogen bonding ability of $(CH_3)_3P$ and $(Bu)_3P$ should be quite similar but weaker than that of the N ligands. However, $(CH_3)_3P$ is equally as effective as the N donor ligands in competing for the intermediate. The ineffectiveness of the $(Bu)_3P$ ligand to compete for the reactive five-coordinate intermediate was previously attributed by us to the steric hindrance of the dangling alkyl chains.[7] The greater ineffectiveness of the $(n\text{-octyl})_3P$ ligand is consistent with this view. Also, in many of

Table V.[a] Summary of Observed and Extrapolated First-Order Rate Constants for the Axial Ligand Substitution of L from $LCo(DH)_2X$ by L′ in CH_2Cl_2 at 25.0 ± 0.1 °C

		Leaving ligand (L) = CNpy k, s^{-1}	
X	Entering ligand (L′)	Obsd	Extrapolated
$SO_2C_6H_4CH_3$	$(CH_3O)_3P$	$2.0 \pm 0.4 \times 10^{-4}$	$1.7 \pm 0.5 \times 10^{-4}$
$CHBr_2$	Bu_3P	$5.2 \pm 0.3 \times 10^{-4}$	$4.7 \pm 1.2 \times 10^{-4}$
CH_2Br	Bu_3P	$2.7 \pm 0.2 \times 10^{-3}$	
C_6H_4Br	Bu_3P	$1.0 \pm 0.2 \times 10^{-2}$	$1.0 \pm 0.1 \times 10^{-2}$
$P(O)(OCH_3)_2$	Bu_3P		$1.0 \pm 0.1 \times 10^{-2}$ [b]
$C_6H_4OCH_3$	Bu_3P	$1.6 \pm 0.3 \times 10^{-2}$	
	Bupy	$2.0 \pm 0.1 \times 10^{-2}$	
C_6H_5	Bu_3P	$2.9 \pm 0.6 \times 10^{-2}$	$2.8 \pm 1.1 \times 10^{-2}$
$CH_2C_6H_4CN$	Bu_3P	$4.5 \pm 0.3 \times 10^{-2}$	
CH_3	Bu_3P	$5.7 \pm 1.6 \times 10^{-2}$	$4.5 \pm 1.0 \times 10^{-2}$
CH_3(niox complex)	Bu_3P	$6.2 \pm 1.0 \times 10^{-2}$	$5.6 \pm 1.3 \times 10^{-2}$
		L = $(C_6H_5)_3P$	
$SC(C_6H_5)_3$ [b]	$(CH_3O)_3P$	7.3×10^{-4} [c]	$7.6 \pm 0.7 \times 10^{-4}$
$P(O)(OCH_3)_2$	Bu_3P		$2.6 \pm 0.3 \times 10^{-2}$ [b]
C_6H_5	Bu_3P	$7.4 \pm 0.4 \times 10^{-2}$	$7.3 \pm 1.7 \times 10^{-2}$
CH_3	Bu_3P	$8.0 \pm 0.1 \times 10^{-2}$	$8.8 \pm 2.3 \times 10^{-2}$
		L = Bupy	
$P(O)(OCH_3)_2$	Bu_3P		2.7×10^{-4} [d]
CH_3	Bu_3P	$1.32 \pm 0.04 \times 10^{-3}$	$1.4 \pm 0.2 \times 10^{-3}$
$P(O)(OCH_3)(C_6H_5)$	Bu_3P		3.3×10^{-3} [d]
$P(O)(C_6H_5)_2$	Bu_3P		3.6×10^{-3} [d]
$CH_2C_6H_5$	Bu_3P	$8.6 \pm 0.3 \times 10^{-3}$	$8.0 \pm 2.6 \times 10^{-3}$
C_2H_5	Bu_3P	$4.0 \pm 0.2 \times 10^{-2}$	$3.8 \pm 0.9 \times 10^{-2}$

[a] The observed rate constants are mean values of the rate data (Table II except for X = CH_3, see Table I) taken under pseudo-first-order excess (greater than 0.2 M) of entering ligand (L′) with respect to the cobaloxime concentration (ca. 0.01 M) and without added leaving ligand (L). The description of the extrapolated rate constants and the uncertainities are given in footnote *a*, Table III. [b] Reported previously in ref 7. [c] A 2.5×10^{-3} M solution was employed. Limited data are available. [d] Estimated from data reported previously[7] where benzene was the solvent. Rates were 3.3 times slower in benzene as compared with methylene chloride, based on the data reported in this work for the methylcobaloxime complex, $BupyCo(DH)_2CH_3$.

Table VI.[a] Competition Ratios between L and L′ for the Common Intermediate, $Co(DH)_2X$, in CH_2Cl_2 at 25.0 ± 0.1 °C

	Leaving ligand (L) = CNpy	
X	Entering ligand (L′)	k_{-1}/k_2
$SO_2C_6H_4CH_3$	$(CH_3O)_3P$	1.2 ± 0.6
$CHBr_2$	Bu_3P	3.0 ± 0.8
C_6H_4Br	Bu_3P	3.0 ± 0.4
C_6H_5	Bu_3P	5.4 ± 2.1
CH_3	Bu_3P	4.7 ± 1.0
CH_3(niox complex)	Bu_3P	3.6 ± 0.9
	L = $(C_6H_5)_3P$	
$SC(C_6H_5)_3$	$(CH_3O)_3P$	0.7 ± 0.2
C_6H_5	Bu_3P	2.8 ± 0.7
CH_3	Bu_3P	4.0 ± 1.1
	L = Bupy	
CH_3	Bu_3P	4.2 ± 0.7
$CH_2C_6H_5$	Bu_3P	3.0 ± 1.0
C_2H_5	Bu_3P	4.5 ± 1.0

[a] Mass-law rate retardation data (Table II) were analyzed by eq 5 using a linear least-squares regression program. See footnote *a*, Table IV, for an explanation of the uncertainties.

our studies we used low leaving ligand concentrations and the condition that $K_2[L] \gg 1$ is not so likely to hold as in the studies by Jensen and Kiskis.[10]

The key and overwhelmingly important step in the reaction is the bond-breaking step and this step is insignificantly influenced by the entering ligand. Thus, we feel that cobalt(III) complexes are superior to platinum(II) complexes for comparing reaction rates with spectroscopic parameters.

The relative trans labilizing effects of X ligands used in this study vary by a factor of about 10^4. By utilizing information obtained in other solvents in the manner suggested by Deutsch,[15] we can make comparisons spanning a range of 10^6. We have made numerous comparisons between the rate data measured here and NMR spectroscopic information collected in other studies.[13,16,17] Neither parameter which reflects metal rehybridization, the α hydrogen resonances or the ^{31}P-^{1}H coupling (between the coordinated P and the oxime methyl groups) adequately reflects the changes in rate. The α hydrogen resonance is subject to a number of anomalous effects[13] and we believe that, contrary to previous results which suggested a good correlation,[15] this parameter is not useful. These shifts for X = CH_3 and C_2H_5 are essentially indistinguishable. However, the rates of reaction are appreciably different. The ^{31}P-^{1}H couplings, which are not subject to anomalous anisotropic effects and which more closely reflect the metal rehybridization, also suggest relatively little if any difference in the hybridization of the metal center for a number of alkyl ligands. The rates of substitution reactions do vary considerably.

The parameters which best reflect the rate data are those which exhibit a considerable difference between the shifts or couplings in the CH_3 and C_2H_5 complexes. Principal among these are the shift of the αC in the Bupy ligand in $Bupy\text{-}Co(DH)_2X$ complexes (Figure 1) and the ^{31}P-^{13}C NMR coupling between the coordinated phosphorus and the directly bonded C in $Bu_3PCo(DH)_2X$ complexes. There is presently theoretical support for the contention that the chemical shifts of aromatic carbons reflect the total σ plus π electron density at the carbon.[18] Thus, it is probable that the ^{13}C shifts are reflecting the ability of the $Co(DH)_2X$ moiety to withdraw electron density from the pyridine ring. In turn this shift may

be a measure of the ability of X to donate charge to the cobalt as the Co(III)-L bond is broken.

Brown has been able to interpret ^{59}Co NQR measurements in cobaloximes in terms of the covalency of the ligands in the axial position. Such spectroscopic data correlated very well with activation parameters for ligand exchange of methylcobaloximes. It would be quite interesting to extend such NQR studies to complexes in which the labilizing ligands were varied. In this study, those spectroscopic parameters which measured the influence of the entire $XCo(DH)_2$ moiety on L gave the better correlation. NQR appears to offer a technique for examining the bonding of L to the Co center whereas most of our NMR studies primarily provide information on the effect of X on the cobalt(III) center.

Deutsch[15] has studied the sulfinato ligand, $SO_2C_6H_4CH_3^-$, in an effort to determine whether this ligand or the SO_3^{2-} ligand can induce trans labilization by a mechanism involving an interaction of the type

Our spectral comparisons indicate that the ligand substitution rate for the cobaloxime containing this sulfur donor ligand is not appreciably different from that expected from extrapolation of the spectral data for such purely σ donor ligands as CH_3 and $CHBr_2$. Additionally, the competition ratios we have measured are insensitive to the following properties of the trans labilizing X group: (a) the nature of the donor atom (S or C); (b) the hybridization of the donor atom (sp^3 or sp^2); and (c) the effectiveness of the X group in labilizing the trans ligand. Therefore, there is no need to invoke any change in mechanism to account for the trans labilizing ability of sulfinato ligands. In conclusion, all of our data can readily be accommodated by a purely dissociative process which leads to a reactive, nonselective, five-coordinate intermediate for all complexes studied.

Experimental Section

Reagents. 4-Cyanopyridine was recrystallized from a mixture of CH_2Cl_2 and Et_2O. Triphenylphosphine was recrystallized from a mixture of 95% EtOH and Et_2O. All other materials were reagent grade and were used without further purification. Methylene chloride, used as the solvent in these kinetic determinations, was spectroquality grade. Prepurified nitrogen was used to deoxygenate the solutions. Caution! The alkylating agents used here may be carcinogenic. Bromoform is toxic and readily absorbed through the skin. Benzyl halides are potent lachrymators.

Preparation of Complexes. The preparation of complexes used in this study and a few compounds used to obtain spectroscopic parameters are described here. The preparation and characterization of other complexes (L = Bupy; X = NO_2, CH_3, $P(O)(OCH_3)_2$, $P(O)(OCH_3)(C_6H_5)$, $P(O)(C_6H_5)_2$ and L = CNpy, $(C_6H_5)_3P$; X = $P(O)(OCH_3)_2$) used here may be found elsewhere.[16,19,20]

$CNpyCo(DH)_2C_6H_4Y$ (Y = H, Br, OCH_3). These complexes were prepared by the procedure described by Schrauzer[21] but using $CNpyCo(DH)_2Cl$. Anal. Calcd for $C_{20}H_{23}O_4N_6Co$ (X = H): C, 51.1; H, 4.9; Co, 12.5. Found: C, 50.9; H, 5.2; Co, 12.3. Calcd for $C_{20}H_{22}O_4N_6BrCo$ (X = Br): C, 43.7; H, 4.0; Co, 10.7. Found: C, 44.0; H, 4.4; Co, 10.6. Calcd for $C_{21}H_{25}O_5N_6Co$ (X = OCH_3): C, 50.4; H, 5.0; Co, 11.8. Found: C, 50.1; H, 5.0; Co, 11.8. The triphenylphosphine derivative (X = H) was prepared by dissolving the corresponding CNpy compound in CH_2Cl_2 together with an excess of $(C_6H_5)_3P$ and stirring. The extent of reaction was followed by monitoring the decrease of the ^1H NMR singlet of the CH_3 groups of the $(DH)_2$ ligand of the starting material and the corresponding increase of the doublet of the product complex. Once the reaction was complete the solvent was evaporated and the product was washed with diethyl ether to remove the excess triphenylphosphine and the displaced CNpy. The product was recrystallized from a CH_2Cl_2-Et_2O mixture. Anal. Calcd for (X = H) $C_{32}H_{34}O_4N_4PCo$: C, 61.2; H, 5.5. Found: C, 60.1; H, 5.5.

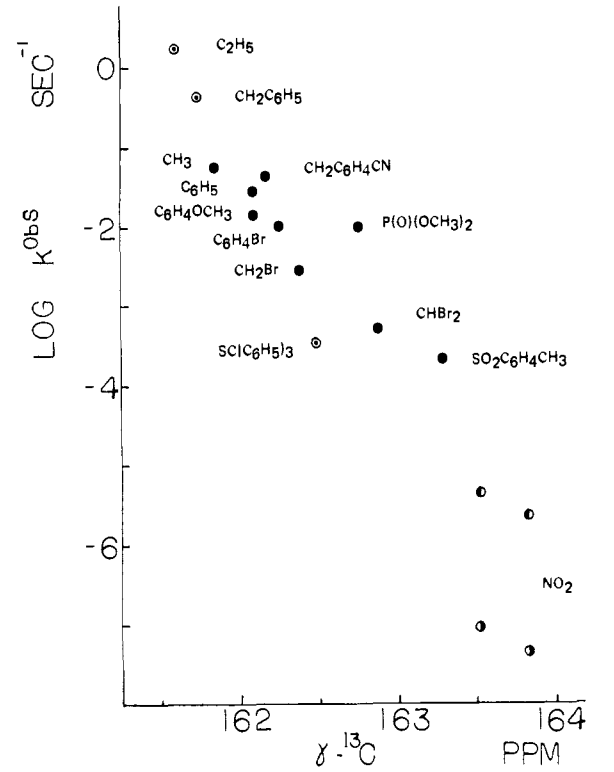


Figure 1. Comparison of the logarithm of the observed rate constants, Table V, for $(CNpy)Co(DH)_2X$ + (excess)L′ → $L'Co(DH)_2X$, with the γ-^{13}C NMR shifts of the Bupy ligand in $(Bupy)Co(DH)_2X$.[17] Points labeled (⊙) indicate that relative rates were employed. Points labeled (◑ and ◐) indicate that rates (from ref 10) are relative to X = CH_3 and $SO_2C_6H_4CH_3$ (this work), respectively.

$CNpyCo(DH)_2R$ (R = CH_3, CH_2Br, $CHBr_2$, p-$CH_2C_6H_4CN$). These complexes were prepared by the procedure described by Hill[22] using $CNpyCo(DH)_2Cl$ and the appropriate alkylating agent (CH_3I, CH_2Br_2, $CHBr_3$, or p-$ICH_2C_6H_4CN$). However, the $NaBH_4$ was introduced after adding excess alkylating agent instead of adding the alkylating agent after the reduction. Also, acetone (ca. 5 mL) was added to destroy any remaining excess $NaBH_4$. Anal. Calcd for $C_{15}H_{21}O_4N_6Co$: C, 44.0; H, 5.2; Co, 14.4. Found: C, 43.9; H, 5.0; Co, 14.6. Calcd for $C_{15}H_{20}O_4N_6BrCo$: C, 37.0; H, 4.1; Co, 12.1. Found: C, 37.3; H, 4.2; Co, 12.4. Calcd for $C_{15}H_{19}O_4N_6Br_2Co$: C, 31.8; H, 3.4; Co, 10.4. Found: C, 32.3; H, 3.6; Co, 10.4. Calcd for $C_{22}H_{24}O_4N_7Co\cdot H_2O$: C, 50.1; H, 5.0; Co, 11.2. Found: C, 49.7; H, 5.2; Co, 11.8. $(C_6H_5)_3PCo(DH)_2CH_3$ was prepared by the same procedure but using $(C_6H_5)_3PCo(DH)_2Cl$. The methyl (X = CH_3) derivative may also be prepared by reaction of a 1:1 molar amount of triphenylphosphine and the "alkyl dimer", $(Co(DH)_2CH_3)_2$, in a noncoordinating solvent such as acetone or CH_2Cl_2. Anal. Calcd for $C_{27}H_{32}O_4N_4PCo$: C, 57.3; H, 5.7; Co, 10.4. Found: C, 57.0; H, 5.4; Co, 10.3.

$BupyCo(DH)_2R$ (R = C_2H_5, $CH_2C_6H_5$). These complexes were also prepared by Hill's procedure[22] but using $BupyCo(DH)_2Cl$ and the appropriate alkylating agent (C_2H_5I or $BrCH_2C_6H_5$). Anal. Calcd for $C_{19}H_{32}O_4N_5Co$: C, 50.3; H, 7.1; Co, 13.0. Found: C, 50.0; H, 6.8; Co, 13.0. Calcd for $C_{24}H_{34}O_4N_5Co$: C, 55.9; H, 6.7; Co, 11.4. Found: C, 56.0; H, 6.5; Co, 11.1.

$(C_6H_5)_3PCo(DH)_2SC(C_6H_5)_3$. $(C_6H_5)_3PCo(DH)_2Cl$ (0.01 mol) was suspended in 90% aqueous methanol (100 mL) and the pH adjusted to ca. 8 with NaOH. $HSC(C_6H_5)_3$ (0.01 mol) and NaOH (0.01 mol) were dissolved with stirring in H_2O (25 mL). These solutions were then mixed with stirring. The resulting solution was heated at just below the boiling point for ca. 5 min and then rotoevaporated to ca. 50% of the original volume. Addition of H_2O (100 mL) precipitated a brown product. Anal. Calcd for $C_{45}H_{44}O_4N_4PSCo\cdot 2H_2O$: C, 62.6; H, 5.6. Found: C, 63.1; H, 5.4. The complex, $CNpyCo(DH)_2S$-t-C_4H_9, was also prepared by this procedure but using $CNpyCo(DH)_2Cl$ and HS-t-C_4H_9. Anal. Calcd for $C_{18}H_{27}O_4N_6SCo\cdot H_2O$: C, 43.2; H, 5.8; Co, 11.8. Found: C, 43.2; H, 5.9; Co, 11.9.

BupyCo(DH)I. This complex was prepared by the direct air oxida-

tion procedure described by Schrauzer.[21] Anal. Calcd for $C_{14}H_{18}O_4N_6ICo$: C, 37.0; H, 4.9. Found: C, 37.5; H, 4.9.

$BupyCo(DH)_2CH_2Si(CH_3)_3$. This complex was prepared in low yield (10%) by Hill's method[22] but using $BupyCo(DH)_2I$. Schrauzer's method,[23] for preparation of the corresponding pyridine complex, was unsuccessful for preparation of the Bupy complex when attempted by us. The yellow compound isolated in our laboratories was characterized by ^1H and ^{13}C NMR showing the correct numbers of resonances in the correct ratios but no kinetic studies were done using this material since insufficient quantities could be isolated.

$CNpyCo(DH)_2SO_2C_6H_4CH_3$. This complex was prepared by the procedures given by Palmer and Deutsch[15] but using CNpy. Anal. Calcd for $C_{21}H_{25}O_6N_6SCo$: C, 46.0; H, 4.6; Co, 10.7. Found: C, 46.3; H, 4.6; Co, 10.5.

$CNpyCo(niox)_2CH_3$. (niox) represents the monoanion of 1,2-cyclohexanedione dioxime, $^-ONCC_4H_8CNOH$. This complex and those needed for its preparation were prepared according to the procedures given for the corresponding (DH) compounds but substituting (niox) for (DH). Anal. Calcd for $C_{19}H_{25}O_4N_6Co$: C, 49.6; H, 5.5; Co, 12.8. Found: C, 49.3; H, 5.4; Co, 12.8.

Apparatus. The ligand exchange kinetics were monitored spectrophotometrically using a Cary 14 equipped with a thermostated cell compartment and cell holder which maintained the reaction solution at 25.0 ± 0.1 °C. ^1H NMR measurements were made on a Varian HA-100 spectrometer. ^{13}C NMR spectra were recorded on a Varian CFT-20. Details and spectral assignments are reported elsewhere.[13,16,17]

Kinetic Procedure. Visible spectra of methylene chloride solutions of each starting cobaloxime were recorded and then compared with the visible spectra of the solutions after adding a calculated excess (ca. 40:1) of entering ligand L′ and allowing sufficient time (as estimated by a similar NMR experiment) for the reaction to near completion. The wavelength which gave the greatest difference in absorbance was used to monitor the kinetics. Suitable wavelengths were in the range of 450–520 nm for the complexes studied.

The starting cobaloxime in each case was weighed directly into the cuvette used in the kinetic determination. If a mass-law rate retardation experiment was to be done, the calculated excess of leaving ligand was also weighed into the cuvette. In cases where the leaving ligand was a liquid (Melmd, $(CH_3O)_3P$, Bupy) the ligand was added after addition of 2.5 mL of degassed solvent. The cuvette was placed in the thermostated (25.0 ± 0.1 °C) spectrometer and allowed to thermally equilibrate (ca. 15 min). During this time the sample was moved out of the light path to minimize a photodecomposition reaction know to occur for certain R groups (CH_3, CH_2Br, $CHBr_2$, C_2H_5).[2] Next, a calculated excess of the neat entering ligand was injected using a microsyringe. The reaction solution was then quickly shaken and placed back into the spectrophotometer. Absorbance changes with time were monitored. Where photodecomposition reactions were likely absorbance readings were taken only intermittently by moving the sample in and out of the light path. Absorbance data were collected over at least 3 half-lives with final absorbance data taken after ca. 20 half-lives.

Data Analysis. The experimental absorbance vs. time rate data were treated with the standard integrated expression for a first-order process using a linear least-squares computer program.

The pseudo-first-order rate constants obtained from the slope of the least-squares fit of the raw data were then plotted as $1/k_{obsd}$ vs. (L)/(L′) by a linear least-squares regression analysis. For systems undergoing reaction by an S_N1 limiting mechanism and exhibiting mass-law rate retardation, this analysis yields $1/k_1$ as the y intercept and k_{-1}/k_1k_2 as the slope. The meaning of these values will be shown in the Results section. All uncertainties represent standard deviations in the y intercept of the least-squares analysis, unless otherwise noted.

Supplementary Material Available: Plots of (a) the absorption spectra in methylene chloride of $LCo(DH)_2CH_3$ (L = CNpy and Bu_3P) and of the reaction mixture: $(CNpy)Co(DH)_2CH_3$ + (excess)$Bu_3P \rightarrow (Bu_3P)Co(DH)_2CH_3$; (b) $1/k_{obsd}$ vs. [L]/[L′]; and (c) log k_{obsd} vs. various NMR spectroscopic data and Tables I and II, listing the experimental rate data (21 pages). Ordering information is given on any current masthead page.

References and Notes

(1) J. M. Pratt, "Inorganic Chemistry of Vitamin B_{12}", Academic Press, New York, N.Y., 1972.
(2) G. N. Schrauzer, *Acc. Chem. Res.*, **1**, 97 (1968).
(3) L. M. Ludwick and T. L. Brown, *J. Am. Chem. Soc.*, **91**, 5188 (1969); T. L. Brown, L. M. Ludwick, and R. S. Stewart, *ibid.*, **94**, 384 (1972); R. J. Guschl and T. L. Brown, *Inorg. Chem.*, **12**, 2815 (1973); R. J. Guschl, R. S. Stewart, and T. L. Brown, *ibid.*, **13**, 417 (1974); T. L. Brown, *Acc. Chem. Res.*, 7, 408 (1974); R. A. LaRossa and T. L. Brown, *J. Am. Chem. Soc.*, **96**, 2072 (1974).
(4) K. L. Brown, D. Chernoff, D. J. Keljo, and R. G. Kallen, *J. Am. Chem. Soc.*, **94**, 6697 (1972); K. L. Brown and R. G. Kallen, *ibid.*, **94**, 1894 (1972).
(5) G. Tauzher, R. Dreos, G. Costa, and M. Green, *J. Chem. Soc., Chem. Commun.*, 413 (1973); J. H. Espenson and R. Russell, *Inorg. Chem.*, **13**, 7 (1974). (This article summarizes the uncertainties associated with substitution reactions in aqueous solutions.)
(6) A. L. Crumbliss and W. K. Wilmarth, *J. Am. Chem. Soc.*, **92**, 2593 (1970); P. H. Tewari, R. H. Grover, H. K. Wilcox, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 611 (1967); H. G. Tsiang and W. K. Wilmarth, *ibid.*, 7, 2535 (1968).
(7) W. C. Trogler, R. C. Stewart, and L. G. Marzilli, *J. Am. Chem. Soc.*, **96**, 3697 (1974). The absence of significant amounts of Bu_3PO was confirmed by ^{13}C NMR.
(8) W. D. Covey and T. L. Brown, *Inorg. Chem.*, **12**, 2820 (1973).
(9) The following abbreviations are used in this report: (Bu_3P) = tri-*n*-butylphosphine, (Bupy) = 4-*tert*-butylpyridine, CNpy = 4-cyanopyridine, Melmd = 1-methylimidazole, (niox) = 1,2-cyclohexanedione dioxime.
(10) F. R. Jensen and R. C. Kiskis, *J. Am. Chem. Soc.*, **97**, 5820 (1975).
(11) J. A. Ewen and D. J. Darensbourg, *J. Am. Chem. Soc.*, **98**, 4317 (1976).
(12) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).
(13) L. G. Marzilli, P. Politzer, W. C. Trogler, and R. C. Stewart, *Inorg. Chem.*, **14**, 2389 (1975).
(14) G. W. Parshall, *J. Am. Chem. Soc.*, **86**, 5367 (1964); **88**, 704 (1966); H. A. O. Hill, K. G. Morallee, G. Pellizer, G. Mestroni, and G. Costa, *J. Organomet. Chem.*, **11**, 167 (1968).
(15) J. M. Palmer and E. Deutsch, *Inorg. Chem.*, **14**, 17 (1975).
(16) W. C. Trogler, R. C. Stewart, L. A. Epps, and L. G. Marzilli, *Inorg. Chem.*, **13**, 1564 (1974).
(17) R. C. Stewart and L. G. Marzilli, *Inorg. Chem.*, **16**, 424 (1977).
(18) J. B. Stothers, "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1972, Chapter 7.
(19) W. C. Trogler, L. A. Epps, and L. G. Marzilli, *Inorg. Chem.*, **14**, 2748 (1975).
(20) L. G. Marzilli, J. G. Salerno, and L. A. Epps, *Inorg. Chem.*, **11**, 2050 (1972).
(21) G. N. Schrauzer, *Inorg. Synth.*, **11**, 68 (1968).
(22) H. A. O. Hill and K. G. Morallee, *J. Chem. Soc. A*, 554 (1969).
(23) G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, **88**, 3738 (1966).