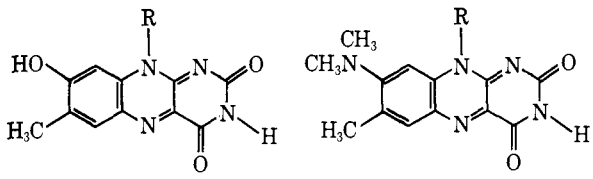


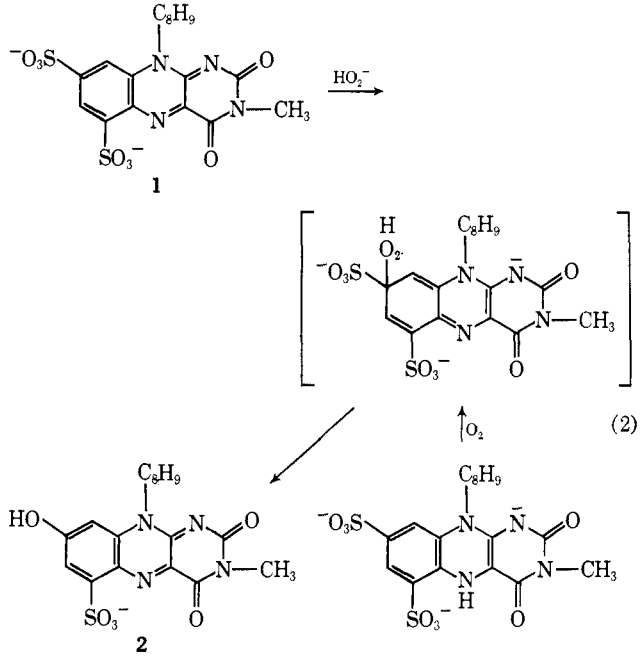
3 4

R = ribitol side chains

for **3**, λ_{max} 472 nm ($\epsilon = 4.15 \times 10^4\ M^{-1}\ cm^{-1}$)
for **4**, λ_{max} 496 nm ($\epsilon = 3.9 \times 10^3\ M^{-1}\ cm^{-1}$)
for **3**, $pK_a = 4.8$

the basic form of **2**. The analytical, nmr, spectral, and titrimetric data as well as the inability of the product to form a Cu(II) complex[8] allows an assured assignment of the structure of the product as being that of the 8-hydroxy isomer (**2**).

The kinetics[9,10] of the oxidation of 1,5-dihydroisoalloxazines (reduced flavines) have been logically interpreted to require the formation of an O_2-dihydroflavine adduct. Massey, Palmer, and Ballou[10] have suggested O_2 addition to the 1,5-dihydroisoalloxazines at the 4a and 10a positions while Hemmerich and Müller[11] have provided arguments in support of addition of O_2 at the 4a and 8 or preferably 6 positions. The 10a position has been ruled out as an obligatory position of O_2 addition in this laboratory.[12,13] If the dihydro form of **1**



1

(2)

2

exists totally or in part as the 1,5-dihydro isomer, as is the case for other dihydroisoalloxazines,[14] then O_2 addition to the 8 position would provide the same intermediate as HOO^- addition to oxidized **1**. Thus, O_2 oxidation of reduced **1** should provide **2** just as does HOO^- treatment of oxidized **1** (eq 2). Experiments carried out at pH 5.0 and 9.5 established that 20 cycles of alternate dithionite reduction and O_2 oxidation of **1** gave a *ca.* 94% yield of unaltered **1**. No absorbance at 480 nm could be detected at the end of either experiment. Therefore, the dihydro form of **1** does not undergo oxidation by addition of O_2 at either the 6 or 8 position.

It should be noted that the overall conversion of **1** to **2** represents a two-step synthesis of an 8-hydroxyisoalloxazine. Compound **2** is prepared by treatment of the corresponding isoalloxazine with sulfite in aqueous solution at ambient temperature.[4]

Acknowledgment. This work was supported by a grant from the National Science Foundation.

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(9) Q. H. Gibson and J. W. Hastings, *Biochem. J.*, **83**, 368 (1962).
(10) V. Massey, G. Palmer, and D. Ballou in "Flavins and Flavoproteins," H. Kamin, Ed., University Park Press, Baltimore, Md., 1971, p 349.
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(14) The structure of dihydroisoalloxazines is being investigated in this laboratory.

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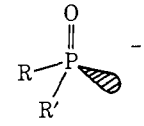
The Trans Effect of the Good σ-Donor Ligands $(CH_3O)_2PO$, $(CH_3O)(C_6H_5)PO$, and $(C_6H_5)_2PO$. Evidence for Complete Bond Breaking in the Transition State of S_N1_{lim} Reactions of Dimethylphosphonatocobaloxime and Methylcobaloxime Complexes

Sir:

The interesting class of uninegative phosphorus donor ligands of the type



have received little attention.[1-6] Since the existence of such ligands is not widely recognized, it is not surprising that no rate or mechanistic studies have been reported on metal complexes of these ligands. We felt such a study might prove valuable because dialkylphosphonates (R = alkoxy) are known to be good σ donors and to have a substantial trans influence.[6] We have therefore prepared some new cobaloxime complexes of the type $RR'P(O)Co(DH)_2L$, where L = neutral N- or P-donor ligand, DH = monoanion of dimethylglyoxime, and R and R′ = CH_3O or C_6H_5. Cobaloximes (complexes containing the $Co(DH)_2$ moiety) are particularly suitable for a comparative mechanistic study because kinetic information is avail-

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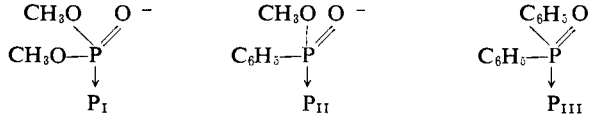
(4) R. J. Haines, I. L. Marais, and C. R. Nolte, *Chem. Commun.*, 547 (1970).
(5) R. J. Haines and C. R. Nolte, *J. Organometal. Chem.*, **24**, 725 (1970).
(6) G. G. Mather and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 560 (1973). The term trans influence is used to describe a ground state, not a kinetic, effect.

able on substitution reactions of cobaloxime complexes containing the effective trans activating alkyl and sulfito ligands.[7,8] Although the substitution reactions of cobalt(III) complexes have received great attention,[9-13] in only a few cases have unassisted dissociation reactions been well documented.[10,13] Substitution reactions of alkylcobaloximes have been extensively studied as models for B_{12} coenzyme.[11-13] However, most studies have revealed second-order kinetic behavior (except for the nmr studies of Brown's group[13]).

The specific complexes prepared contain the three ligands P_I, P_{II}, and P_{III}. The substitution reactions



studied involve replacement of neutral ligands L by other ligands L′, where L and L′ are phosphines, phosphites, or heterocyclic N donors, according to (1).

$$RR'P(O)Co(DH)_2L + L' \longrightarrow RR'P(O)Co(DH)_2L' + L \quad (1)$$

Evidence for P-bonding derives from both the large trans labilizing effect of the $RR'P(O)^-$ ligands and the characteristic $\nu(P{=}O)$ stretch.[14]

Rates of reaction 1 in the forward direction were determined for the substitution of $P_ICo(DH)_2L$ (where L = CNpy and Ph_3P) by a number of L′ in CH_2Cl_2 solvent and for the substitution of *t*-Bu(py) in $XCo(DH)_2$(*t*-Bu(py)), (X = P_I, P_{II}, P_{III}, CH_3) by Bu_3P in C_6H_6 solvent. The reactions were monitored by changes in the visible region (~5000 Å, under N_2 for X = CH_3) and found to be first order in complex concentration for up to five half-lives in some cases.[15] Some reactions were also followed using pmr spectroscopy. There was good agreement between the two techniques, but only the more precise spectrophotometric results are reported here. At sufficiently high L′ concentrations and in the absence of added L, reaction rates were essentially independent of both the concentration and the nature of L′ when (1) went to completion. The data are therefore consistent with the reaction scheme of eq 2 and 3. Formation of the five-coordinate intermediate is rate limiting and $k_{obsd} = k_1$.

$$RR'P(O)Co(DH)_2L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RR'P(O)Co(DH)_2 + L \quad (2)$$

$$RR'P(O)Co(DH)_2 + L' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} RR'P(O)Co(DH)_2L' \quad (3)$$

In order to compare the kinetic parameters of the cobaloxime complexes over a temperature range, benzene was employed as a solvent. The reaction of the *t*-Bu(py) complexes (0.01 *M*) of P_I, P_{II}, P_{III}, and CH_3 with Bu_3P (0.2 *M*) gave the following results for k_{obsd} (25°, sec^{-1}), $\Delta H^{\pm}$ (kcal/mol), and $\Delta S^{\pm}$ (eu), respectively: P_I, 8.3×10^{-5}, 26.7 ± 0.3, 12.0 ± 1.0; P_{II}, 1.0×10^{-3}, 26.4 ± 0.4, 16.0 ± 1.3; P_{III}, 1.1×10^{-3}, 24.9 ± 0.6, 11.0 ± 2.0; and CH_3, 3.9×10^{-4}, 23.7 ± 0.6, 5.0 ± 2.0. Activation parameters for methylcobaloximes (in nonaqueous solutions) have been reported.[13,16] It is clear that the $RR'P(O)^-$ ligands are very good trans labilizers. Combining our data with other comparisons in the literature,[7,8,10,17] we find the kinetic trans effect order to be $P_{III} \sim P_{II} > CH_3 > P_I \sim SO_3 \gg NO_2$. The higher trans effect of P_{III} and P_{II} *vs.* P_I is most likely due to the greater electron donating inductive effect of the phenyl group than the methoxy group.[18,19]

Extensive theoretical and experimental effort has been devoted toward explaining the kinetic trans effect.[20] A clear understanding of the effect depends on an accurate knowledge of the nature of the activated complex. Competition studies allow insight into the degree of bond breaking in the transition state of dissociative reactions in suitable cases. This is because competition ratios close to unity imply a very reactive intermediate.[9,10] It follows from Hammond's postulate[21] that, in such a case, almost complete bond rupture has occurred in the transition state of the dissociative reaction. The merits of using noncoordinating solvents in competition studies have been summarized by Covey and Brown.[22]

Competition ratios were determined by utilizing the mass law retardation effect. Typical rate data are given in Table I and competition ratios are given in Table II. These data are the first such results for nonaqueous solutions of complexes containing ground state trans labilizing ligands.

The implication of the competition ratios is clearly that the intermediates discriminate very little. Bond breaking in the dissociative process may be essentially complete in the transition state. Competition ratios close to unity have been observed for a series of ligands competing for $Mo(CO)_5$.[22] However, the relative in-

(7) A. L. Crumbliss and W. K. Wilmarth, *J. Amer. Chem. Soc.*, **92**, 2593 (1970).

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(9) A. M. Sargeson, "Coordination Chemistry-XIV," A. B. P. Lever, Ed., Butterworths, London, 1973, p 527. Induced dissociation reactions and solvent effects on competition ratios are discussed here, as well.

(10) J. E. Byrd and W. K. Wilmarth, *Inorg. Chim. Acta*, 7 (1971). Classic studies include: A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573, 583 (1962); R. Grassi, A. Haim, and W. K. Wilmarth, *ibid.*, 6, 237 (1967). See also: J. Halpern, R. A. Palmer, and L. Blakely, *J. Amer. Chem. Soc.*, **88**, 2877 (1966).

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(13) L. M. Ludwick and T. L. Brown, *J. Amer. 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).

(14) Abbreviations not defined in the text are as follows: Ph_3P = triphenylphosphine, Bu_3P = tri-*n*-butylphosphine, Me_2PhP = dimethylphenylphosphine, CNpy = 4-cyanopyridine, *t*-Bu(py) = 4-*tert*-butylpyridine, MeImd = 1-methylimidazole. All complexes had elemental analyses and ir and pmr spectra consistent with formulas and structures reported here.

(15) All uncertainties are one standard deviation determined from least-squares analysis. Error limits for rate constants are not given since these are extrapolated values.

(16) Activation parameters were determined by nmr techniques[13] in the aromatic solvents C_6H_5Br and $C_6H_5NO_2$. The methyl complexes generally have lower values for both $\Delta H^{\pm}$ and $\Delta S^{\pm}$ than the P_I, P_{II}, and P_{III} complexes, but the differences are not significant.

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(18) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2953 (1970).

(19) M. I. Karachnik, *Proc. Acad. Sci. USSR, Chem. Sect.*, **110**, 577 (1956).

(20) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 355 and 369.

(21) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

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Table I. Representative Rate Data[a]

[CNpy]/[Me_2PhP]	10^3k_{obsd} (sec^{-1})	[Ph_3P]/[*t*-Bu(py)]	10^2k_{obsd} (sec^{-1})
	$P_ICo(DH)_2$		
0.025	8.5 ± 0.1	0.013	2.7 ± 0.1
0.771	4.2 ± 0.1	0.981	1.6 ± 0.1
1.994	2.5 ± 0.1	2.174	0.93 ± 0.05
	$CH_3Co(DH)_2$		
0.013	59.0 ± 1.0	0.013	8.4 ± 0.1
1.017	25.5 ± 0.5	0.966	5.0 ± 0.1
1.675	17.1 ± 0.5	1.663	3.9 ± 0.1

[a] Errors are rounded up, so as to allow for possible errors in weighings, value measurements, etc. These values represent only part of the data used to compute the competition ratios in Table II. CNpy and Ph_3P are the leaving ligands. T = 25°.

Table II. Competition Data[a]

Entering ligand	$P_ICo(DH)_2$ k_{-1}/k_2	$P_ICo(DH)_2$ 10^3k_1 (sec^{-1})	$CH_3Co(DH)_2$ k_{-1}/k_2	$CH_3Co(DH)_2$ 10^2k_1 (sec^{-1})
	Leaving Ligand CNpy			
$(CH_3O)_3P$	0.97 ± 0.1	8.3 ± 1.0	1.2 ± 0.2	6.2 ± 1.3
MeImd	1.1 ± 0.2	9.0 ± 1.0	1.3 ± 0.2	5.8 ± 1.0
t-Bu(py)	1.3 ± 0.1	9.1 ± 1.0	1.3 ± 0.2	6.1 ± 1.0
Me_2PhP	1.3 ± 0.1	8.8 ± 1.0	1.6 ± 0.2	6.4 ± 1.0
Ph_3P	1.4 ± 0.2[b]		1.8 ± 0.4[b]	
Bu_3P	5.9 ± 0.6	10.0 ± 1		
	Leaving Ligand Ph_3P			
t-Bu(py)	0.9 ± 0.1	29 ± 5	0.7 ± 0.13	7.8 ± 1.5
Bu_3P	3.5 ± 0.4	26 ± 3	3.6 ± 0.7	8.1 ± 1.5

[a] Data were analyzed using the equation $1/k_{obsd} = (1/k_1) + (k_{-1}/k_2k_1)([L]/[L'])$. The values of the limiting rate constant k_1 and the competition ratio k_{-1}/k_2 were determined from least-squares regression analyses. Errors were rounded up. The values of k_1 were not significantly different before the error limits were increased. T = 25°. [b] From the Ph_3P-*t*-Bu(py) data.

effectiveness of the highly nucleophilic Bu_3P[23] suggests that steric factors influence the competition ratios in cobaloximes. Competition ratios influenced by both steric factors and ligand nucleophilicites have been observed for carbonyl complexes.[24] Once coordinated, Bu_3P is less bulky than Ph_3P[25] but it is likely that the dangling alkyl groups interfere with the competition of Bu_3P for the five-coordinate intermediate.

The clarity of the competition data and our conclusions prompted a similar study for methylcobaloximes (Tables I and II). Our interpretation of the data for $P_ICo(DH)_2$ requires that the competition ratios for $CH_3Co(DH)_2$ be similar. The greater reactivity in aqueous solutions of thiols than thiolate anions toward $CH_3Co(DH)_2$ was explained[11] by suggesting that thiols π bond to $CH_3Co(DH)_2$ during formation of the product, $CH_3Co(DH)_2$(thiol). Our data suggest that a preferable explanation is that the thiolate anions are strongly solvated and therefore less reactive.[9,26]

More work on these systems is needed before a detailed knowledge of the degree of residual bonding in the transition state can be assessed. Insight into this problem might be gained by studying both stronger and weaker[26] ligands. We are currently pursuing several lines of research in these areas and have evidence that dimers similar to those observed for $CH_3Co(DH)_2$[27] can be formed. The RR'P(O) ligands act as *pseudoalkyls* with respect to their influence on the metal center.[28]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

(23) Reference 20, p 396. The ligands in Table II cover a wide range of nucleophilicities and form cobaloximes differing in stability by at least a factor of 10^3.

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(25) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

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(28) In addition to the similarities between the $P_ICo(DH)_2$ and $CH_3Co(DH)_2$ complexes reported here, we have noted that in the pmr spectra of complexes of these moieties the resonances have nearly identical chemical shifts: W. C. Trogler, R. C. Stewart, L. A. Epps, and L. G. Marzilli, *Inorg. Chem.*, in press. These shifts were quite different from other complexes of the type $XCo(DH)_2L$. The affinities of different ligands for $P_ICo(DH)_2$ and $CH_3Co(DH)_2$ are quite similar and very different from that for $ClCo(DH)_2$. For example, CNpy is *ca.* five times better than Ph_3P for $P_ICo(DH)_2$, whereas Ph_3P is *ca.* 100 times better than CNpy for $ClCo(DH)_2$. Incidentally, pmr determination of the stability constant for the reaction $P_ICo(DH)_2(CNpy) + Ph_2P \rightleftharpoons P_ICo(DH)_2(Ph_3P) + CNpy$ yields a values of 0.20, whereas data in Table II give $K = k_1k_2/k_{-1}k_{-2} = 0.23$. For $CH_3Co(DH)_2$, these values are 0.43 and 0.39, respectively. A further similarity found was that exchange reactions of neither P_I nor CH_3 complexes are catalyzed by cobalt(II). Most other cobaloximes of the type $XCo(DH)_2L$ undergo exchange of the neutral ligand (in CH_2Cl_2) exclusively by a cobalt(II)-catalyzed pathway: L. G. Marzilli, J. G. Salerno, and L. A. Epps, *Inorg. Chem.*, **11**, 2050 (1972).

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Anisotropic Reaction with Ammonia Gas of a Crystal of a Carboxylic Acid with Linear Hydrogen-Bonded Chains. An Example of Unitropic Attack

Sir:

Previous studies on the reaction of gaseous amines with single crystals of aromatic carboxylic acids have concentrated on cases where the acids form hydrogen-bonded dimers.[1-3] This is by far the most common packing arrangement for those carboxylic acids that are devoid of other substituents capable of taking part in hydrogen bonding.[4] In a number of crystals of benzoic acid and derivatives, fast and approximately equal rates of reaction were noted in the direction perpendicular to the plane of the carboxylic acid group (and hence of its dimer) and in the direction along the O···O vector of a particular carboxylic acid residue, while the reaction was slow along the vector defined by the C–C bond from the carboxylic acid carbon atom, *i.e.*, the direction protected by the phenyl ring.[1,3] We propose giving the name *ditropic* (in two ways) to this type of crystal reactivity. With the aim of finding a different type of reactivity pattern, we have examined the reaction of ammonia with crystals of an optically active carboxylic

(1) R. S. Miller, D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.*, **93**, 2784 (1971).

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(3) R. S. Miller, D. Y. Curtin, and I. C. Paul, manuscript in preparation.

(4) The known exceptions to this generalization are mostly compounds whose volatility, low melting point, or other properties make them undesirable or difficult candidates for such studies. Examples are formic acid, acetic acid, β-oxalic acid [see R. W. G. Wyckoff, "Crystal Structures," Vol. 5, 2nd ed, Interscience, New York, N. Y., 1966], and β-tetrolic acid [V. Benghiat and L. Leiserowitz, *J. Chem. Soc., Perkin Trans. 2*, 1763 (1972)].