Contribution from the Department of Chemistry,
The Johns Hopkins University, Baltimore, Maryland 21218

Reactions of Coordinated Trialkyl Phosphite and Related Ligands with Nucleophiles

WILLIAM C. TROGLER, LEON A. EPPS, and LUIGI G. MARZILLI*

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Reactions of trialkyl phosphites (methyl, ethyl, and isopropyl), dimethyl phenylphosphonite, and methyl diphenylphosphinite complexes of the type $RR'_2PCo(DH)_2Cl$ were studied (DH = the monoanion of dimethylglyoxime). These complexes react with nucleophiles such as halide ions, X (Cl, Br, I), and nitrogen heterocycles, L (pyridine, 1-methylimidazole), to give the alkylated nucleophile and complexes of dialkyl phosphonato or phenyl-substituted phosphonato ligands. When X is the attacking nucleophile, the product complexes are anionic $RR'P(O)Co(DH)_2X^-$ or $R_2P(O)Co(DH)_2X^-$. When the heterocycle is the attacking nucleophile, neutral complexes $RR'P(O)Co(DH)_2L$ and $R_2P(O)Co(DH)_2L$, in which the chloride has been substituted by L, result. The alkylated heterocycles were not always detected because the displaced chloride reacts with the alkylated heterocycle to produce alkyl chloride. A mechanistic investigation gave results consistent with a nucleophilic displacement at the ester carbon which proceeds by an S_N2 pathway. The complexes were characterized by spectroscopic techniques (ir and ^1H NMR). Complexes of the ligand $(C_6H_5)(CH_3O)P(O)^-$, which is asymmetric, have chemical shift nonequivalent DH methyl resonances (^1H NMR). The ^1H NMR spectral properties of these complexes are consistent with the known trans-labilizing ability of the $RR'P(O)$ and $R_2P(O)$ uninegative ligands.

Introduction

Cobaloximes[1] have become the center of increasing chemical interest. This interest was prompted initially by the discovery in Schrauzer's laboratory that these complexes are models for cobalamins. The inorganic chemistry of cobaloximes is also of interest since the properties of these complexes in some instances parallel those of the classical Werner type complexes and in other cases depart radically from such classical behavior. One such difference, which has been of interest to us, is the potentially extensive chemistry of cob(III)aloxime complexes of phosphorus donor ligands.

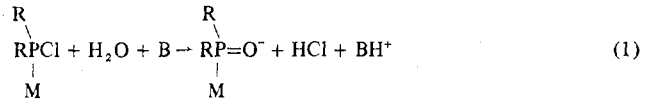
We have found that the ester carbon of phosphite ligands coordinated to the cobaloxime center (as well as other cobalt B_{12} models) has increased reactivity toward nucleophiles as compared to the free ligands. This susceptibility toward nucleophilic reagents is atypical of phosphite complexes,[2] but such reactivity has been observed in a few isolated systems.[3,4]

The products of such reactions are complexes containing the formally uninegative ligands of the type $RR'P(O)^-$, which have a terminal oxygen doubly bonded to phosphorus. In these cobaloxime complexes, these negative ligands are good trans labilizers[5] as opposed to the ligands from which they are derived and to other neutral P donor ligands. The influence of the $RR'P(O)^-$ ligands on the cobalt center is quite similar to that of alkyl ligands, and a comparative kinetic study has been reported.[5] However, the $RR'P(O)^-$ ligand is not photolabile and, therefore, complexes of these ligands are well suited to kinetic investigations.

In contrast to the countless reports of the preparation and properties of complexes of neutral trivalent P donor ligands,[6] very few accounts of the preparation of complexes of these negative ligands can be found in the literature. We report here such an investigation including a comparative rate study of the reaction of the coordinated phosphite, phosphonite, and phosphinite ligands.

Published procedures for the preparation of complexes of $RR'P(O)^-$ ligands can be classified into two general classes. The first class involves the use of a starting phosphorus compound which contains a terminal oxygen. The metathetical displacement of chloride from a metal with $Ag(RR'P(O))$ or $Na(RR'P(O))$ has been employed frequently.[7] Displacement of the coordinated $RR'P(O)^-$ ligand is difficult.

The second general procedure is the reaction of coordinated phosphorus ligands. Several widely disparate examples of such reactions have been reported. For example, reaction 1 is known



$$\begin{matrix} R & & R \\ \backslash & & \backslash \\ RPCl + H_2O + B \rightarrow & RP{=}O^- & + HCl + BH^+ \\ | & | & \\ M & M & \end{matrix} \qquad (1)$$

to occur,[8] where B is a poorly coordinating basic amine such as triethylamine. Another example involves the thermolysis of a ruthenium triaryl phosphite compound, $Ru_3(CO)_9[P(OC_6H_4R)_3]_3$, in refluxing decalin to yield a diaryl phosphonate complex of ruthenium.[9] This reaction was postulated to take place by the metal-assisted loss of the aryl group as benzene or a substituted benzene. The most common synthetic pathway in this second general class (eq 2, where N is a

$$MPRR'(OR'') + N \rightarrow R''N^+ + MPRR'(O)^- \qquad (2)$$

nucleophile and $R''N^+$ is the alkylated N) is believed to involve nucleophilic attack at the ester carbon of ligands with the POC function. This pathway was first suggested by Haines.[3] The reaction is an inorganic analog of the Michaelis–Arbusov rearrangement[3] and the nucleophiles originally studied were either compounds of Mo(I)[3] or halide ions.[3,4]

Results and Discussion

Synthetic Reactions. Addition of ligands with the $POCH_3$ moiety to solutions of $LCo(DH)_2Cl$ complexes in CH_2Cl_2 resulted in the formation of $LCo(DH)_2P(O)RR'$ and CH_3Cl (L = heterocyclic N ligand). This reaction was the most useful synthetic pathway for the synthesis of phosphonato and related complexes. Most typically, L was a pyridine-type ligand. The sequence of reactions which led to the formation of products is complex. We will describe the key reaction first.

The reaction which forms the phosphonato ligand, when trimethyl phosphite is the added ligand, is given in eq 3. This

$$(CH_3O)_3PCo(DH)_2Cl + Cl^- \rightarrow (CH_3O)_2P(O)Co(DH)_2Cl^- + CH_3Cl \qquad (3)$$

reaction was followed by ^1H NMR spectroscopy.

Initially, the ^1H NMR spectrum of the reaction solution (in the upfield region) consists of two doublets in the ratio 3:4. The smaller downfield doublet (at τ 6.39, J_{PH} = 11 Hz) is assigned to the methoxy groups of the coordinated $(CH_3O)_3P$ and the larger doublet (at τ 7.72, J_{PH} = 1.5 Hz) is assigned to the four equivalent methyl groups of the $Co(DH)_2$ moiety. On addition of Cl^- (as the triphenyltetrazoleum (TTP) salt), the original set of resonances diminishes (and eventually disappears) and is replaced by doublets at τ 6.83 (J_{PH} = 11 Hz, assigned to the methoxy groups of coordinated $(CH_3O)_2PO$) and at τ 8.12 (J_{PH} = 0.8 Hz, assigned to the methyl groups of the $Co(DH)_2$ in $(CH_3O)_2P(O)Co(DH)_2Cl^-$). In addition, a new singlet appears at τ 7.02 which is half the size of the new downfield doublet and one-fourth the size of the new upfield doublet, and it is assigned to the methyl resonance of CH_3Cl.

The reaction described above is the dominant reaction when $(CH_3O)_3P$ is added to a solution of (Bupy)$Co(DH)_2Cl$, Bupy

= 4-*tert*-butylpyridine. The initial reaction is the ligand exchange[10] of Bupy for $(CH_3O)_3P$ to form $(CH_3O)_3P$-$Co(DH)_2Cl$. The liberated Bupy then attacks the ester carbon of the coordinated phosphite. The dimethyl phosphonato complex thus formed readily undergoes ligand substitution of the trans Cl to yield $(Bupy)Co(DH)_2P(O)(OCH_3)_2$. As compared to heterocyclic amines, the Cl^- generated is a much more reactive nucleophile toward the ester carbons and reacts with the phosphite complex to give CH_3Cl and the chlorophosphonato complex. Substitution of the chloride in this complex by the superior Bupy ligand regenerates uncoordinated Cl^-—hence the cycle.

This sequence of events was established by careful examination of the ^1H NMR spectra at various times during the reaction and by the demonstration that all reactions postulated were feasible and occurred rapidly enough to be involved. The most important ^1H NMR spectral evidence was the formation of the characteristic phosphonato complex resonances before the appearance of the CH_3Cl resonance in the initial stages of the reaction. Additionally, careful treatment of the reaction mixture at a preparative scale allowed the isolation of the salt, $BupyCH_3[(CH_3O)_2P(O)Co(DH)_2Cl]$. This salt can also be observed during the course of the ^1H NMR experiments. The $BupyCH_3^+$ cation is unstable toward Cl^- and eventually forms CH_3Cl and Bupy. The nucleophiles Br^- and I^- initially form CH_3Br and CH_3I when treated with $(CH_3O)_3PCo(DH)_2Cl$ but these alkyl halides also react to give CH_3Cl eventually and the appropriate (dimethyl phosphonato)halocobaloxime anion.

Structural and Spectral Considerations. It was noted above that changes in integrated intensities of the ^1H NMR signals which accompany the reactions are consistent with the postulated formulas. Other ^1H NMR spectral considerations lead us to believe that the negative phosphorus ligands are bonded to the cobalt via P. The oxime methyl resonances of the neutral products, such as $BupyCo(DH)_2P(O)(OCH_3)_2$, were 0.17–0.26 ppm *upfield* to that of the corresponding chloro complexes. We have shown that the chemical shift of this resonance is indicative of the nature of the donor atoms in the axial positions.[11] All complexes with oxygen donor ligands have oxime methyl resonances which are *downfield* to the corresponding chloro complex. Based on our analysis of the factors which influence such shifts, it is highly unlikely that the RR'P(O) ligands are O bonded. Furthermore, the magnitude of the coupling constant between P and the oxime methyl resonance is approximately 0.8 Hz. This value is similar to that found for other phosphorus donor ligands.[11]

The ^1H NMR spectral properties of complexes of the $(C_6H_5)(CH_3O)P(O)$ ligand are interesting. This ligand is both asymmetric and highly anisotropic. Molecular models reveal that there will be two sets of chemical shift nonequivalent oxime methyl groups. Each set consists of mutually trans methyl groups, one from each DH ligand. Such nonequivalence[12] has been observed previously for cobaloximes but was incorrectly interpreted.[13] All the complexes examined which contain the $(C_6H_5)(CH_3O)P(O)$ ligand exhibit the expected two oxime methyl resonances. For the $BupyCo(DH)_2P(O)(OCH_3)(C_6H_5)$ complex, Figure 1, these resonances are doublets, J_{PH} = 0.8 Hz, separated by 0.12 ppm. Spectra recorded at both 100 and 60 MHz confirmed this interpretation. The difference of 0.12 ppm is the second largest such nonequivalence ever observed for cobaloximes. However, little support for P bonding can be derived from this observation since the O-bonded ligand would also be asymmetric. The magnitude of the effect is nevertheless more in keeping with P than with O bonding.

The ir changes which accompany product formation are consistent with the generation of a PO moiety. Thus, the products usually exhibit a strong band in the 1142–1193-cm^{-1} region (KBr). This band is absent in the starting cobaloximes. Other investigators[3,4,7] have assigned bands in the 1100–1200-cm^{-1} region to the PO stretch. This band is absent in complexes with O bonding.[14] When strong intramolecular hydrogen bonding is possible or when the ligand bridges two metals (through P and O), the band shifts to below 1100 cm^{-1}.[15] These characteristic ir spectra and the spectral and kinetic arguments already advanced leave little doubt but that P bonding predominates.

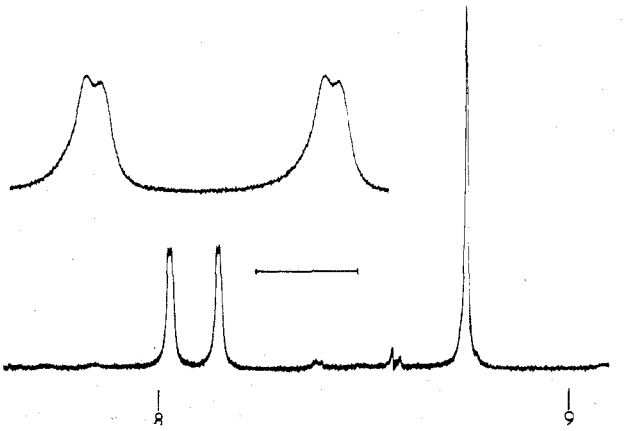


Figure 1. ^1H NMR spectrum, in the upfield region, of the complex $BupyCo(DH)_2P(O)(OCH_3)(C_6H_5)$ [CH_2Cl_2, 5% TMS, HA100 (100 MHz)]. The bar is 25 Hz long in the lower trace (downfield multiple $(DH)_2$ methyl resonance, upfield singlet butyl resonance) and is 5 Hz long for the inset, which is an expansion of the $(DH)_2$ resonance. The numbers are τ values; TMS reference.

Mechanistic Considerations. The discussion thus far has assumed that the reaction between the phosphite complexes and the nucleophile takes place without the dissociation of the phosphite ligand. There are two lines of evidence that strongly suggest that we are indeed observing the reaction of coordinated phosphite. First, over a period of several weeks, there was no evidence for the reaction of Bupy with trimethyl phosphite. The addition of small amounts of cobaloxime did not catalyze any reactions. Second, if a ligand which can displace trimethyl phosphite is added to solutions of the trimethyl phosphite complex, the rate of formation of the phosphonato complex is greatly diminished. Alternative explanations can be imagined for these results, but the results are best in keeping with the reaction of the coordinated phosphite.

It has been suggested that reactions of coordinated phosphites should be quite general.[3] However, few examples of such reactions are in the literature. Verkade has made several attempts with different systems to simulate the Michaelis–Arbuzov reaction, but without success.[2] We feel that there are several restrictions on the electronic properties of the metal center which will limit the generality of the reaction. These include the ability of the metal to withdraw electron density from the phosphite and, thus, to make the ester carbon more susceptible to nucleophilic attack. Additionally, the metal center must be able to accommodate the formation of the strong σ donors formed. Preliminary findings in these laboratories suggest that alkyl cobaloximes do not promote reaction of a trans trimethylphosphite with Br^-. The presence of two strong trans-effect ligands trans to each other is an unfavorable situation.[16] Finally, the attacking nucleophile must not be able to displace the phosphite completely. We have found that the cobalt(III)–Schiff base complex iodo-(*N*,*N*'-bis(salicylidene)dipropylenetriamine)cobalt(III),[17] reacts with trimethyl phosphite to produce CH_3I and the corresponding dimethyl phosphonato complex. This reaction was not pursued because the trimethyl phosphite could not completely displace the I ligand. However, it seems likely that

Table I. Rates of the Reaction[a] $P(OCH_3)_3Co(DH)_2Cl$[b] + $(CH_3(C_6H_5)_3P)Br \rightarrow CH_3Br$ + $Co(DH)_2P(O)(OCH_3)_2Cl^-$ + $CH_3(C_6H_5)_3P^+$

[Complex], *M*	[Salt], *M*	10^3k_{obsd}, sec^{-1}	[Complex], *M*	[Salt], *M*	10^3k_{obsd}, sec^{-1}
0.013	0.101	0.876 ± 0.12	0.089	0.69	3.56 ± 0.12
0.013	0.135	1.20 ± 0.05	0.086, 0.042[c]	0.80	4.07 ± 0.2
0.094	0.48	2.62 ± 0.23	0.105, 0.063[c]	0.90	4.23 ± 0.2
0.048	0.62	3.17 ± 0.19			

[a] At 29.5 ± 1.0°; CH_2Cl_2. [b] Reference 20. [c] Average of both readings; the differences being insignificant.

most nonalkyl B_{12} model complexes should be effective promoters of the formation of phosphonates from phosphites. These phosphonato ligands, in turn, are analogs for the alkyl ligands.[5]

Although there is every reason to suspect that the phosphonato ligands are formed by an S_N2 mechanism, we felt it best experimentally to probe this hypothesis. Visible spectral changes accompanying the formation of the RR'P(O) ligands were not large enough to monitor the reaction. Therefore, reaction rates were determined from the marked changes in the ^1H NMR spectra of reaction mixtures.

On preliminary examination, it was found that the changes in the oxime methyl resonances would be the most useful spectral probe. The salt $[(C_6H_5)_3CH_3P]Br$ was chosen because of its high solubility in CH_2Cl_2 and because its ^1H NMR spectrum did not overlap with the oxime resonances. Also, Br^- is more reactive than Cl^-. The reaction of this bromide salt with the phosphite–, phosphonite–, and phosphinite–chloro complexes was studied. The small amount of Cl^- released on formation of the final complex product, $RR'P(O)Co(DH)_2Br^-$ or $R_2P(O)Co(DH)_2Br^-$, did not interfere with the measurements.

The use of the ^1H NMR technique limited the range of concentrations which could be employed in the rate study. A second-order reaction profile was not obtained in agreement with typical results[18] for reactions of salts in nonaqueous solvents. Treatment of the data as arising from second-order kinetics leads to a decrease in the second-order rate constant with increasing salt concentration. The *rate* of reaction does increase with increasing salt concentration as might be expected from second-order processes.[18] Table I.

The most useful and informative rate data were obtained in the comparative rate study. From consideration of a large number of nucleophilic reactions, Streitwieser[19] has extracted the values expected for the relative S_N2 reactivity of carbon centers. These values are given in Table II along with rate data obtained here. It can be seen that the relative rates expected for an S_N2 reaction and those found here match closely. We feel that this finding provides strong evidence that the phosphonato ligands are formed by bimolecular nucleophilic attack at the ester carbon of the coordinated phosphorus ligand.[22]

Experimental Section

Materials and Instrumentation. All solvents were reagent grade. Ligands [$P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$ (Aldrich); $P(OCH_3)_2(C_6H_5)$, $P(OCH_3)(C_6H_5)_2$, $P(OCH_2)_3C(C_2H_5)$ (Strem)] were used without further purification.

^1H NMR spectra were recorded on an A-60, MH-100, or HA-100 spectrometer. The latter two instruments were operated with CH_2Cl_2 as an internal lock. Unless noted, CH_2Cl_2 was used as a solvent and TMS as a standard. Ir spectra were recorded on a Perkin-Elmer 457 grating spectrometer, using polystyrene reference peaks at 1601 and 1028 cm^{-1} and KBr pellets. Preparative reactions were carried out at ambient temperature and no precautions were taken to exclude oxygen.

Kinetic Determinations. Rates of formation of phosphonates were observed on a Varian A-60 ^1H NMR spectrometer at 29.5 ± 0.5°C. The oxime methyl resonances of the product and reactant complexes were scanned repeatedly at expanded scale and integrated intensities were determined by cutting and weighing. Kinetic plots were linear for at least 2 and in some cases 3 half-lives. For the slower reactions ^1H NMR tubes were held at 29.5 ± 0.5°C in a constant-temperature bath and spectra were recorded at appropriate intervals. Reproducibility was ±15–20%. All uncertainties reported are determined from least-squares analysis.

$(CH_3{}^+NC_5H_4(C(CH_3)_3))(Co(DH)_2P(O)(OCH_3)_2Cl^-)$. Trimethyl phosphite (0.64 g, 5.4 mmol) was added to a solution of $BupyCo(DH)_2Cl$[11] (2.4 g, 5.4 mmol) in CH_2Cl_2 (50 ml). The solution was allowed to stand for 1 day after which toluene (50 ml) was added. After allowing the solution to stand for another day, toluene (150 ml) and CH_2Cl_2 (100 ml) were added. The solution was slowly evaporated under reduced pressure (ca. 150-ml final volume) until a yellow-orange powder precipitated. The powder was collected and the filtrate saved. The powder was washed with 100 ml of toluene and dried in vacuo (110°C) (yield 6.8%). ^1H NMR: τ 7.86 (d, 12, J_{P-H} = 0.7 Hz, DH methyl), 6.64 (d, 6, J_{P-H} = 11 Hz, $POCH_3$), 5.60 (s, 3, H_3C^+Bupy), 8.61 (s, 9, Bu), 1.13 (d, 2, J = 7 Hz, α-H of $CH_3{}^+NC_5H_4(C(CH_3)_3)$), 2.05 (d, J = 7 Hz, β-H of $CH_3{}^+NC_5H_4(C(CH_3)_3)$). The ir spectrum contains a strong band at 1173 cm^{-1} attributed to the P=O stretch. Anal. Calcd for $C_{20}H_{36}CoClN_5O_7P$: C, 41.25; H, 6.23; Co, 10.11. Found: C, 41.6; H, 6.4; Co, 10.0.

$BupyCo(DH)_2P(O)(OCH_3)_2$. The filtrate from above was allowed to evaporate to 10 ml, and the translucent red crystals (a yellow powder when dried) were collected and washed with water and ether and dried (110°C) in vacuo; yield 65%. ^1H NMR: τ 7.88 (d, 12, J_{P-H} = 0.8 Hz, DH methyls), 6.57 (d, 6, J_{P-H} = 11 Hz, $POCH_3$), 1.68 (m, 2, α-H of Bupy), 2.71 (m, 2, β-H of Bupy). The ir spectrum contained a strong band at 1193 cm^{-1} attributed to the P=O stretch. Anal. Calcd for $C_{19}H_{33}CoN_5O_7P$: C, 42.79; H, 6.24; Co, 11.06. Found: C, 42.8; H, 6.0; Co, 11.1. This compound could also be prepared by adding Bupy to $P(OCH_3)_3Co(DH)_2Cl$.

$BupyCo(DH)_2P(O)(OCH_3)(C_6H_5)$. 4-*tert*-Butylpyridine (1.7 ml, 11.8 mmol) was added to a solution of $P(OCH_3)_2(C_6H_5)Co(DH)_2Cl$[20] (2.5 g, 5.1 mmol) in CH_2Cl_2 (30 ml). After allowing 1 day for reaction, toluene (30 ml) and CH_2Cl_2 (25 ml) were added. The solution was rapidly evaporated to ca. 35-ml volume with a Roto-vac and the hot solution was quickly filtered. The filtrate was allowed to cool and evaporate (final volume 20 ml). The orange powder which precipitated was collected and washed with toluene and ether and dried (110°C) in vacuo; yield 72%. ^1H NMR: τ 8.12 (m, 12, DH methyl; nature of the multiplet described in the text), 8.78 (s, 9, *t*-Bu), 6.56 (d, 3, J_{P-H} = 11 Hz, $POCH_3$), 1.70 (m, 2 α-H of Bupy); the β-H and C_6H_5 resonances overlapped. The ir spectrum contained two peaks, one intense one at 1167 cm^{-1} and a shoulder at 1167 cm^{-1} attributed to the P=O stretch. Anal. Calcd for $C_{24}H_{35}CoN_5O_6P$: C, 49.75; H, 6.09; Co, 10.17. Found: C, 49.4; H, 5.7; Co, 10.0.

$BupyCo(DH)_2P(O)(C_6H_5)_2$. $P(C_6H_5)_3Co(DH)_2Cl$[21] (16.0 g, 27 mmol) was dissolved in N_2-purged CH_2Cl_2 (80 ml) and $P(OCH_3)(C_6H_5)_2$ (9.3 g, 43 mmol) was added. The resulting solution was stoppered. After 4 days Bupy (11.3 ml, 80 mmol) was added. After 3 more days, the solution was evaporated to 40-ml volume and ether (250 ml) *slowly* added to induce precipitation. The orange powder was twice recrystallized from a small amount of CH_2Cl_2 by *slowly* adding ether; final yield 68%. ^1H NMR: τ 8.31 (d, 12, J_{P-H} = 0.8

Table II. Comparative Rates for the Reaction[a] $P(OR)R'R''Co(DH)_2Cl + (CH_3(C_6H_5)_3P)Br \rightarrow RBr + P(O)R'R''Co(DH)_2Cl^- + CH_3(C_6H_5)_3P^+$

P(OR)R'R''[b]	10^3k_{obsd}, sec^{-1}	Rel rate	P(OR)R'R''[b]	10^3k_{obsd}, sec^{-1}	Rel rate
$P(OCH_3)_3$	3.9 ± 0.2	1.00 (1.00)[c]	$P(OC_2H_5)_3$	0.037 ± 0.002	0.0095 (0.033)[c]
$P(OCH_3)_2(C_6H_5)$	1.22 ± 0.06	0.31	$P(O\text{-}i\text{-}C_3H_7)_3$	0.00404 ± 0.0002	0.0010 (0.0008)[c]
$P(OCH_3)(C_6H_5)_2$	0.0664 ± 0.001	0.017	$P(OCH_2)_3CCH_2CH_3$	No reaction	

[a] At 29.5 ± 1.0°; CH_2Cl_2; [Co] = 0.08 *M*; [salt] = 0.8 *M*. [b] The syntheses of the complexes have been reported elsewhere.[20] [c] Relative rates expected for S_N2 reaction; from ref 19.

Hz, DH methyl), 8.78 (s, 9, Bu), 1.69 (m, 2, α-H of Bupy); the β-H and C_6H_5 resonances overlap. The ir spectrum contained two medium-intensity peaks at 1160 and 1142 cm^{-1} attributed to the P=O stretch. Anal. Calcd for $C_{29}H_{37}CoN_5O_5P$: C, 55.69; H, 5.96; Co, 9.42. Found: C, 55.4; H, 5.7; Co, 8.73.

$H_2OCo(DH)_2P(O)(OCH_3)_2 \cdot 1.5H_2O$. This compound is a convenient intermediate for synthesizing $LCo(DH)_2P(O)(OCH_3)_2$ compounds. A solution of $P(OCH_3)_3Co(DH)_2Cl$ (4.0 g, 8.9 mmol) in methanol (200 ml) was boiled (2 hr) before water (100 ml) was added. Heating was continued (1 hr). The solution was allowed to evaporate slowly (ca. 3 days) until translucent maroon crystals (85% yield) formed. These were collected, washed with water, ether, and CH_2Cl_2, and dried in vacuo. The ir spectrum contains a strong band at 1175 cm^{-1} attributable to the P=O stretch. The compound is insoluble in CH_2Cl_2. ^1H NMR (D_2O, DSS standard): τ 7.67 (s, 2, DH methyl), 6.49 (d, 1, J_{P-H} = 11 Hz, $POCH_3$). Anal. Calcd for $C_{10}H_{25}CoN_4O_{9.5}P$: C, 27.10; H, 5.69; Co, 13.30. Found: C, 27.1; H, 5.48; Co, 13.3.

$P(C_6H_5)_3Co(DH)_2P(O)(OCH_3)_2$. To a solution of $H_2OCo(DH)_2P(O)(OCH_3)_2$ (2.0 g, 4.8 mmol), in 40 ml of methanol, triphenylphosphine (1.6 g, 6.0 mmol) was added. After warming and stirring (15 min), the solution was evaporated to dryness. The residue was dissolved in CH_2Cl_2 (30 ml) and the solution was filtered. Isooctane (140 ml) was added, whereupon the solution became cloudy. Enough acetone was added to produce a clear solution. This solution was kept under a hood in an open beaker to air-evaporate. At a volume of 20–50 ml, red crystals formed. These were collected, washed with ether, and dried in vacuo. The product may be recrystallized from CH_2Cl_2–isooctane–acetone; yield 69%. ^1H NMR: τ 8.16 (t, 12, J = 2.3 Hz, DH methyls), 6.59 (m, 6, $POCH_3$), 2.66 (m, 15, C_6H_5). The ir spectrum had a medium-intensity band at 1185 cm^{-1} and a weak band at 1160 cm^{-1} attributed to the P=O stretch. Anal. Calcd for $C_{28}H_{35}CoN_4O_7P_2$: C, 50.92; H, 5.80; Co, 8.92. Found: C, 50.6; H, 5.7; Co, 8.64.

$CNpyCo(DH)_2P(O)(OCH_3)_2$. To a suspension of $H_2OCo(DH)_2P(O)(OCH_3)_2$ (10.0 g, 21.7 mmol) in methanol (100 ml) 4-cyanopyridine (CNpy; 3.1 g, 30 mmol) was added. After 1–2 hr of stirring, a yellow precipitate was collected, washed with ether, and dried in vacuo; yield 46%. ^1H NMR: τ 7.89 (d, 12, J_{P-H} = 0.6 Hz, DH methyl), 6.55 (d, 6, J_{P-H} = 11 Hz, $POCH_3$), 1.50 (m, 2, α-H of CNpy), 2.61 (m, 2, β-H of CNpy). The ir spectrum had two medium-intensity peaks at 1190 and 1165 cm^{-1} attributable to the P=O stretch. Anal. Calcd for $C_{16}H_{24}CoN_6O_7P$: C, 38.26; H, 4.82; Co, 11.73. Found: C, 38.3; H, 4.5; Co, 11.6.

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Registry No. $BupyCo(DH)_2Cl$, 38985-28-3; $P(OCH_3)_3$, 121-45-9; $P(OCH_3)_2(C_6H_5)Co(DH)_2Cl$, 56403-84-0; $P(C_6H_5)_3Co(DH)_2Cl$, 23295-34-3; $P(OCH_3)_3Co(DH)_2Cl$, 52654-86-1; $P(C_6H_5)_3$, 603-35-0; $(CH_3{}^+NC_5H_4(C(CH_3)_3))(Co(DH)_2P(O)(OCH_3)_2Cl^-)$, 56403-86-2; $BupyCo(DH)_2P(O)(OCH_3)_2$, 52896-11-4; $BupyCo(DH)_2P(O)(OCH_3)(C_6H_5)$, 52896-12-5; $BupyCo(DH)_2P(O)(C_6H_5)_2$, 52880-68-9; $H_2OCo(DH)_2P(O)(OCH_3)_2$, 56403-87-3; $P(C_6H_5)_3Co(DH)_2P(O)(OCH_3)_2$, 52880-70-3; $CNpyCo(DH)_2P(O)(OCH_3)_2$, 52880-69-0; $P(OCH_3)(C_6H_5)_2Co(DH)_2Cl$, 56403-88-4; $P(OC_2H_5)_3Co(DH)_2Cl$, 56403-89-5; $P(O\text{-}i\text{-}C_3H_7)_3Co(DH)_2Cl$, 56403-90-8; $(CH_3(C_6H_5)_3P)Br$, 1779-49-3.

References and Notes

(1) Trivial name for complexes containing the $Co(DH)_2$ "planar" moiety, where DH = monoanion of dimethylglyoxime: G. N. Schrauzer, *Acc. Chem. Res.*, **1**, 97 (1968).
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(22) There is an extensive literature on platinum complexes containing the two *cis*-$R_2P(O)$ which in turn simultaneously hydrogen bond to a proton in effect producing a phosphorus donor bidentate ligand, $R_2PO\text{–}H\text{–}OPR_2^-$. Recent work on the synthesis of such species from the Pt complexes of $R'OPR_2$ type ligands suggests that uncoordinated rather than coordinated ligands are hydrolyzed: W. B. Beaulieu, T. B. Rauchfuss, and D. M. Roundhill, *Inorg. Chem.*, **14**, 1732 (1975). These hydrolyzed ligands then coordinate to the metal. Although we took no precautions to exclude moisture, we did perform several experiments which indicate that water did not attack the coordinated R_2POR' ligand (see Results and Discussion). We refer to some examples of $R_2POHOPR_2^-$ ligands in ref 7 and 15. Other references are included in the Roundhill article.
(23) Note Added in Proof. Several other examples of $R_2P(O)$ and $X_2P(O)$ complexes have come to our attention since the acceptance of this paper. These include: J. Grosse and R. Schmutzler, *Z. Naturforsch., Teil B*, **28**, 515 (1973); *J. Chem. Soc., Dalton Trans.*, in press: references in the dissertation of J. Grosse, Carolo-Wilhelmina Technical University at Braunschweig, 1974. We thank Professor Schmutzler for making us aware of this work.