the reaction center; benzoic acid (pK_a = 4.22[20]) providing a less basic ligand than acetic acid (pK_a = 4.74[20]) also has a weaker labilizing effect. However, the pK_a values represent the σ-donor abilities of the oxygen rather than the π-donor properties that have been invoked to explain the labilizing properties of ligands of this sort.[1,21] We are extending the study to a much wider range of carboxylate ligands to see whether the labilizing effect is significantly dependent upon substituents or whether it is markedly insensitive as in the case of amine donors.

The Hg^{2+}-catalyzed aquation of *trans*-$[Co(en)_2CH_3COOCl]^+$ conforms to the usual pattern of behavior now fully documented in the literature. Furthermore, if the data for this complex are plotted on the graph of log k_{aq} *vs.* log k_{Hg} constructed by Bifano and Linck,[13] the point sits very close to their line (a rate constant of 3.1×10^{-6} sec^{-1} at 25° for the spontaneous aquation would require a rate constant of 0.2 M^{-1} sec^{-1} at 25° for the Hg^{2+}-catalyzed aquation ($\mu = 1.0\ M$)). The form of the base-hydrolysis reaction is also reasonably typical of these *trans*-$[Co(en)_2ACl]^{n+}$ species. The complex is neither excessively labile like the dichloro species nor unduly inert as the hydroxochloro species but in both its rate constant and activation parameters resembles the other members of the series (A = N_3, NCS, CN, NO_2, NH_3, etc.).[22] Illuminati, *et al.*,[9,23,24] have examined the kinetics of the base hydrolysis of a variety of *cis*- and *trans*-dicarboxylatobis(ethylenediamine)cobalt(III) complexes and showed that the rate of reaction is very sensitive to the nature of the substituents in the carboxylate ligand. Obviously a major part of the effect is due to the relationship between the basicity and lability of the carboxylato leaving group but it is hoped that the data for the rates of replacement of the chloride from a series of *trans*-chlorocarboxylatobis(ethylenediamine)cobalt(III) complexes will help separate the leaving-group effect from the trans (and cis) effect. On the basis of our observations on the acetato complex and the bis-ethylenediamine complexes in general, we would be surprised if the rate of base hydrolysis was particularly sensitive to the nature of the nonparticipating ligand. This seems to be true when the *trans*-chloroacetato complex is compared with the chlorobenzoato analog. However, the rate constants for the base hydrolysis of the *trans*-diacetato- and *trans*-dibenzoatobis(ethylenediamine)cobalt(III) cations (5.1×10^{-2} M^{-1} sec^{-1} [24] and 3.20×10^{-2} M^{-1} sec^{-1} [23] at 25.0°, $\mu \approx 0.027$) do not differ greatly either, in spite of the trends noted in the rest of the series.

It has been reported that the base hydrolysis of *trans*-$[Co(en)_2(CH_3COO)_2]^+$ [9] gives 100% *trans*-$[Co(en)_2OHCH_3COO]^+$ but if the dissociative mechanism, now accepted for these base hydrolyses (dissociation of the conjugate base), was operating one would expect to find that the steric course was independent of the nature of the leaving group.[25] Thinking that the observations of retention in the base hydrolysis of *trans*-$[Co(en)_2(CH_3COO)_2]^+$ might indicate C–O bond fission, we have reexamined this reaction with our own techniques. We find that, having made correction for the second stage of base hydrolysis (which really cannot be ignored in this case) and the unreacted starting material, the spectrum of the product, after acidification, is identical with that found after base hydrolysis of *trans*$[Co(en)_2CH_3COOCl]^+$ and indicates that here, too, contrary to the previous report,[9] the initial product contains 20% of the cis isomer.

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Cobalt(II)-Catalyzed Ligand Exchange Reactions of *trans*-Chloro(triphenylphosphine)bis(dimethylglyoximato)cobalt(III)

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The reaction of cobaloximes, $LCo(DH)_2X$ (where L = a neutral monodentate ligand, DH = monoanion of dimethylglyoxime, and X = an acido ligand), with neutral monodentate nitrogen or phosphorus donor ligands (L′) has been found to yield $L'Co(DH)_2X$ rather than $[L'Co(DH)_2L]X$. When L = $(C_6H_5)_3P$ and L′ = pyridine or substituted pyridines, the equilibrium constant for the exchange reaction $(C_6H_5)_3PCo(DH)_2Cl + X\text{–py} \rightleftharpoons (X\text{–py})Co(DH)_2Cl + (C_6H_5)_3P$ could be determined. The values of K were found to be markedly dependent on the nature of the substituted pyridine. Qualitative evidence suggested the exchange was catalyzed by Co(II) species. The exchange reaction when L = $(C_6H_5)_3P$ and L′ = pyridine was too rapid to measure by conventional techniques in 10^{-5} M $(C_6H_5)_3PCo(DH)_2$ solution. However, the analogous reaction with X = NO_2 was slower and the rate expression was found to be $-d[Co(III)]/dt = 1.5 \times 10^4[Co(III)][Co(II)]$. A mechanism was proposed to account for the exchange reaction which involves an inner-sphere electron transfer *via* the acido bridge as the rate-limiting step.

Introduction

Cobaloximes, $LCo^{III}(DH)_2X$ (where DH = monoanion of dimethylglyoxime, L = a number of neutral ligands, and X = a number of uninegative ligands), have been studied extensively, particularly by Schrauzer,[1] as vitamin B_{12} models and are usually formulated as having the geometry I (X = Cl). Costa has

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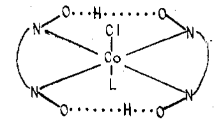
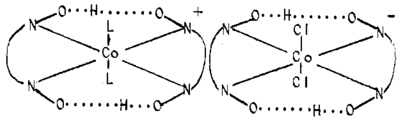
[1] G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968).



I



II

found that some methods of preparation may lead to considerable percentages of the coordination isomer of I depicted by structure II, when L = phosphine ligand and X = Cl.[2,3] One mechanism proposed[2] to account for the formation of the cation $L_2Co(DH)_2^+$ involves a nucleophilic attack on I, according to eq 1,

$$LCo(DH)_2Cl + L \longrightarrow [L_2Co(DH)_2]Cl \qquad (1)$$

and displacement of the relatively labile Cl by nucleophiles is the normal mode of reaction of these and other cobalt(III) chloride complexes.

We now report that reactions between type I complexes and various nucleophiles (L′) in *nonprotic* solvents lead to the facile displacement of the normally nonlabile ligand L (eq 2). Reaction 2 occurs for a

$$LCo(DH)_2Cl + L' \rightleftharpoons L'Co(DH)_2Cl + L \qquad (2)$$

number of ligands when L = triphenylphosphine and L′ = pyridine, substituted pyridines, 1-methylimidazole, morpholine, etc. We have also observed reactions for phosphorus donor ligands such as tri-*n*-butylphosphine.

Experimental Section

Instrumentation.—Visible spectra were obtained on a Cary 14 spectrophotometer thermostated at 25.0 ± 0.1°. The pmr spectra were obtained on a Varian A-60 instrument and chemical shifts referenced to internal tetramethylsilane. Infrared spectra were determined using a Perkin-Elmer 337 spectrometer. Cobalt was analyzed by dissolving the complexes in *N,N′*-dimethylformamide and determining the cobalt concentration using the Perkin-Elmer 303 atomic absorption spectrometer (2407 Å, analytical wavelength). Analyses for carbon and hydrogen were performed on a Coleman Model 33 analyzer.

Kinetic Studies.—Solutions used for kinetic studies were thoroughly degassed with prepurified nitrogen. An aliquot of a stock solution of cobalt(II) complex was added using a syringe to a cobalt(III) solution before the latter was diluted to a known volume. Aliquots (2.5 ml) of such solutions were transferred to spectrophotometer cells which were then sealed with serum stoppers. Reaction was initiated by injecting pyridine through the stopper. *Caution!* Prolonged contact between the stopper and the solution leads to oxidation of cobalt(II).

Materials.—All materials were of reagent grade or higher purity. They were used without further purification except for triphenylphosphine, which was recrystallized from methylene chloride by adding ethanol, and 4-picoline, which was distilled just prior to use.

Preparations.—All neutral complexes prepared by the accepted routes[2,4] were further purified by recrystallization from methylene chloride–ethanol. Complexes of the type $(C_6H_5)_3PCo(DH)_2X$ were prepared by Schrauzer's method.[4] *Anal.* Calcd for $CoC_{26}H_{29}N_4O_4ClP$ (X = Cl): Co, 10.04; C, 53.2; H, 5.0. Found: Co, 9.94; C, 53.1; H, 5.1. Calcd for $CoC_{26}H_{29}N_4O_4BrP$ (X = Br): Co, 9.35; C, 49.2; H, 4.6. Found: Co, 9.15; C, 49.4; H, 4.8. Calcd for $CoC_{26}H_{29}N_5O_6P$ (X = NO_2): Co, 9.86; C, 52.2; H, 4.9. Found: Co, 9.74; C, 51.9; H, 5.3.

Other complexes of the type $LCo(DH)_2Cl$ were prepared by a modification of Costa's method.[2] *Anal.* Calcd for $CoC_{13}H_{19}N_5O_4Cl$ (L = pyridine): Co, 14.60; C, 38.9; H, 4.7. Found: Co, 14.65; C, 38.8; H, 5.0. Calcd for $CoC_{17}H_{27}N_5O_4Cl$ (L = 4-*tert*-butylpyridine): Co, 12.81; C, 44.4; H, 5.9. Found: Co, 12.90; C, 44.4; H, 6.3. Calcd for $CoC_{12}H_{20}N_6O_4Cl$ (L = 1-methylimidazole): Co, 14.49; C, 35.5; H, 4.9. Found: Co, 14.67; C, 35.9; H, 5.4. Calcd for $CoC_{20}H_{41}N_4O_4PCl$ (L = tri-*n*-butylphosphine): Co, 11.18; C, 45.5; H, 7.8. Found: Co, 11.27; C, 45.6; H, 7.8. The complex $[(Bu_3P)_2Co(DH)_2][Co(DH)_2Cl_2]$ was prepared and recrystallized following Costa's procedures.[2] *Anal.* Calcd for $Co_2C_{40}H_{82}N_8O_8P_2Cl_2$: Co, 11.18; C, 45.5; H, 7.8. Found: Co, 11.30; C, 45.5; H, 7.7. The pmr spectrum of this compound in methylene chloride contains two methyl resonances of equal intensity, a singlet at δ 2.45 and a triplet centered at δ 2.37.

Product Isolations.—Pyridine (0.38 g) was added to a concentrated solution of $(C_6H_5)_3PCo(DH)_2Cl$ (0.5 g) in chloroform (3.5 ml) and the solution warmed *slightly* for 10 min to ensure complete reaction. After this mixture was cooled in an ice bath for 15 min, the large light brown crystals formed were collected and washed with anhydrous ether (yield 0.18 g, 54%). The 1-methylimidazole complex was prepared similarly (yield 0.22 g, 68%). The 4-*tert*-butylpyridine and tri-*n*-butylphosphine complexes were also prepared similarly, but since these complexes were very soluble, anhydrous ether (20 ml) was added before cooling. Yields by this last procedure were greater than 95%. However, after recrystallization the final yield was *ca.* 40% for the phosphine complex and 80% for the 4-*tert*-butylpyridine complex.

Results

Stoichiometry.—The product of the reaction of $(C_6H_5)_3PCo(DH)_2Cl$ with the ligands (L′) pyridine, *tert*-butylpyridine, 1-methylimidazole, and tri-*n*-butylphosphine was established to be $L'Co(DH)_2Cl$ by spectral comparisons (ir, visible, pmr) of isolated products with the known complexes prepared by accepted procedures. Also, the changes in the pmr spectra of solutions of $(C_6H_5)_3PCo(DH)_2Cl$ were in agreement with the formation of $L'Co(DH)_2Cl$ and $(C_6H_5)_3P$. In particular, the methyl resonance (doublet, δ 2.00) in the pmr spectrum of $(C_6H_5)_3PCo(DH)_2Cl$ (CH_2Cl_2) was replaced by resonances at δ 2.35, 2.35, 2.33 (singlets), and 2.31 (doublet) on addition of pyridine, *tert*-butylpyridine, 1-methylimidazole, and tri-*n*-butylphosphine, respectively.

Visible spectra were utilized to establish the quantitative nature of the reactions, and results using 4-*tert*-butylpyridine and tri-*n*-butylphosphine are given in Tables I and II, where it is shown that these reactions were quantitatively complete and stereospecific within

TABLE I

ABSORPTIONS OF SOLUTIONS[a] CONTAINING (A) $(C_6H_5)_3PCo(DH)_2Cl$, (B) $(C_6H_5)_3PCo(DH)_2Cl$ AND *tert*-BUTYLPYRIDINE (0.3 *M*), AND (C) (*t*-Bupy)$Co(DH)_2Cl$

λ, mμ	A	B[b]	C
600	0.155	0.074	0.074
580	0.179	0.093	0.093
560	0.215	0.123	0.120
540	0.353	0.166	0.161
520	0.670	0.246	0.238
500	1.107	0.335	0.335
480	1.454	0.412	0.415
460	1.622	0.554	0.554
440	>2.0	0.943	0.944

[a] 0.005 *M* solutions of complex in CH_2Cl_2. [b] The absorption spectra of all pyridine complexes were virtually identical.

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[2] G. Costa, G. Tauzher, and A. Puxeddu, *Inorg. Chim. Acta*, **3**, 45 (1969). The preparative procedure of aerial oxidation (L. A. Tschguaeff, *Ber.*, **40**, 3498 (1907)) reported by these authors differs somewhat from that described in ref 4.

[3] G. Costa, G. Tauzher, and A. Puxeddu, *Inorg. Chim. Acta*, **3**, 41 (1969).

[4] G. N. Schrauzer, *Inorg. Syn.*, **11**, 61 (1968).

TABLE II

ABSORPTION SPECTRUM OF $Bu_3PCo(DH)_2Cl$ (0.005 *M*) (IN METHYLENE CHLORIDE) MADE BY DIFFERENT METHODS

λ, mμ	A[a]	B[a]	C[b]	ε
600	0.064	0.063	0.062	13
580	0.096	0.095	0.095	19
560	0.134	0.135	0.137	27
540	0.188	0.187	0.188	38
520	0.248	0.247	0.247	49
500	0.395	0.394	0.390	79
480	0.821	0.821	0.817	164
470	1.140	1.139	1.145	228
460	1.522	1.498	1.495	300
440[c]	1.901	1.850	1.850	370

[a] A and B are final spectra of reactions of tri-*n*-butylphosphine with (*t*-Bupy)$Co(DH)_2Cl$ and $(C_6H_5)_3PCo(DH)_2Cl$, respectively. [b] C is spectrum of known material. [c] Small plateau occurs at this point in all three spectra.

the limits of experimental error. Quantitatively the same absorption spectrum was obtained on addition of tri-*n*-butylphosphine to (*t*-Bupy)$Co(DH)_2Cl$ or $(C_6H_5)_3PCo(DH)_2Cl$, consistent with the displacement of the neutral monodentate ligand (Table II).

Other evidence supported this stoichiometry. The equilibrium studies involving the displacement of triphenylphosphine by substituted pyridines described below, especially the one involving 4-*tert*-butylpyridine, would not have led to constant equilibrium constants if the stoichiometry was other than one entering ligand to one cobalt. Equilibrium experiments suggested that a spectral titration was feasible for some ligands, and the following ratios of entering ligand to $(C_6H_5)_3PCo(DH)_2Cl$ complex were found: 1-methylimidazole, 1.02; tri-*n*-butylphosphine, 1.03.

Equilibrium Studies.—The pmr studies indicated that equilibria existed between the pyridine complexes and the triphenylphosphine complex. From Tables I and II, it is clear that a large difference in intensity exists between the spectrum of the triphenylphosphine complex and the spectra of complexes containing other ligands, especially at *ca.* 500 mμ. These differences were utilized to determine the value of the equilibrium constants for reaction 2 when L = $P(C_6H_5)_3$, X = Cl, Br, and L′ = a number of substituted pyridine ligands (Tables III and IV). The equilibrium constant was too large ($>10^2$) to allow an accurate determination when L′ = 1-methylimidazole. The equilibrium constant for the reaction when L = 1-methylimidazole and L′ = tri-*n*-butylphosphine was also too large to measure accurately.

TABLE III

VALUES AT VARIOUS REACTANT CONCENTRATIONS OF THE CONSTANTS FOR THE EQUILIBRIUM

$$(C_3H_5)_3PCo^{III}(DH)_2Cl + L' \rightleftharpoons L'Co^{III}(DH)_2Cl + (C_6H_5)_3P$$

(A) [Co] = 0.01 *M*; [$(C_6H_5)_3P$] = 0.2 *M*			
10^3[py], *M*	*K*	10^3[py], *M*	*K*
8.9	5.7	46.6	6.3
17.9	6.7	56.3	6.3
27.5	5.8	66.0	6.2
37.0	6.1		
(B) [Co] = 0.005 *M*; [$(C_6H_5)_3P$] = 0.1 *M*			
10^3[4-*t*-Bupy], *M*	$10^{-1}K$	10^3[4-*t*-Bupy], *M*	$10^{-1}K$
4.7	4.3	12.0	4.0
7.0	4.6	14.6	4.2
9.5	4.4		
(C) [Co] = 0.005 *M*; [$(C_6H_5)_3P$] = 0.2 *M*			
3.3	4.5	10.2	4.0
5.4	4.3	12.5	4.1
7.7	4.1	17.7	3.9

TABLE IV

CONSTANTS FOR THE EQUILIBRIUM[a]

$$(C_6H_5)_3PCo^{III}(DH)_2X + L' \rightleftharpoons L'Co^{III}(DH)_2X + (C_6H_5)_3P$$

[$(C_6H_5)_3P$], *M*	L′	*K*
0.05	3-Butylpyridine	$(2.3 \pm 0.2) \times 10^{-1}$
0.10	3-Butylpyridine	$(2.2 \pm 0.1) \times 10^{-1}$
0.05	Pyridine	(5.9 ± 0.5)
0.10	Pyridine	(6.3 ± 0.7)
0.20	Pyridine	(6.8 ± 0.5)
0.20[b]	Pyridine	(6.2 ± 0.5)
0.10	4-Picoline	$(3.6 \pm 0.2) \times 10$
0.20	4-Picoline	$(3.3 \pm 0.2) \times 10$
0.10	4-Ethylpyridine	$(3.7 \pm 0.4) \times 10$
0.20	4-Ethylpyridine	$(3.9 \pm 0.2) \times 10$
0.10	4-Butylpyridine	$(4.3 \pm 0.3) \times 10$
0.20	4-Butylpyridine	$(4.2 \pm 0.4) \times 10$
0.20	1-Methylimidazole	Large[c]
0.20	Tri-*n*-butylphosphine	Very large[d]
0.10[e]	Pyridine	(6.1 ± 0.4)
0.20[f]	Pyridine	(6.0 ± 0.6)
0.30[e]	Pyridine	(6.1 ± 0.6)

[a] 25°, CH_2Cl_2 solution, [Co] = 5×10^{-3} *M*, and X = Cl, except as noted. [b] [Co] = 10^{-2} *M*. [c] $>10^2$. [d] Tri-*n*-butylphosphine will completely replace 1-methylimidazole from its complex even with a large excess of 1-methylimidazole present (>0.3 *M*). [e] [Co] = 4×10^{-3} *M*, X = Br. [f] [Co] = 2.5×10^{-3} *M*, X = Br.

Rates of Reaction.—Immediate reaction was observed in the pmr studies which employed *ca.* 0.1 *M* complex. Surprisingly, the same reactions were very slow in the dilute solutions used for the visible spectral studies. For example, a 0.005 *M* CH_2Cl_2 solution of $(C_6H_5)_3PCo(DH)_2Cl$ reacted with pyridine (0.4 *M*) with a half-life of *ca.* 5–10 min. Furthermore, the time required for half-reaction was not the same for different samples of the complex, and upon repeated recrystallization of a sample the time required for half-reaction changed erratically. When the cobalt concentration was doubled, the time required for half-reaction was halved. Addition of a moderately strong oxidizing agent such as bromotrichloromethane inhibited these reactions.

Effect of Cobalt(II) Complexes.—Ligand exchange was effected immediately by addition of $(C_6H_5)_3PCo(DH)_2$. The ligand exchange reaction of $(C_6H_5)_3PCo(DH)_2Cl$ with pyridine was too rapid to measure by conventional techniques in solutions as dilute as 10^{-5} *M* in $(C_6H_5)_3PCo(DH)_2$. However, the analogous exchange reaction of $(C_6H_5)_3PCo(DH)_2NO_2$ could be measured by conventional means (Table V). The

TABLE V

RATES OF REACTION OF $(C_6H_5)_3PCo(DH)_2NO_2$ WITH PYRIDINE CATALYZED BY $(C_6H_5)_3PCo(DH)_2$[a]

10^5[Co(II)], *M*	10[py], *M*	k_{obsd}, sec^{-1}	$10^{-4}k_{sec}$, $M^{-1}\ sec^{-1}$
0.32	0.36	0.045	1.4
0.32	0.72	0.05	1.6
0.94	0.36	0.15	1.6
0.94	3.60	0.14	1.5
0.94	1.40	0.14	1.5
2.35	1.40	0.38	1.6
2.35	0.36	0.38	1.6
2.46[b]	0.72	0.38	1.5
2.46[b]	3.60	0.35	1.4

[a] CH_2Cl_2 solution, 25°, [Co(III)] = 4×10^{-3} *M* except as noted. [b] [Co(III)] = 5×10^{-3} *M*.

reaction was pseudo first order in [Co(III)] over several half-lives and the data fit the rate expression

$$-\mathrm{d}[\mathrm{Co(III)}]/\mathrm{d}t = 1.5 \times 10^4[\mathrm{Co(III)}][\mathrm{Co(II)}]$$

Discussion

The unexpected behavior of complexes of the type $LCo(DH)_2X$ with added ligands L′ can be explained if these complexes prepared by the usual procedure contain cobalt(II) catalysts.[5] For example, addition of oxidizing agents did not affect the spectrum of the complexes but did inhibit the exchange reaction. This result can be understood as arising from the oxidation of the cobalt(II) species to inactive cobalt(III) complexes. The half-life of the exchange reaction increased linearly with increasing complex concentration in the absence of added cobalt(II) catalysts. This behavior is predicted by the rate expression $R = k[\mathrm{Co(III)}][\mathrm{Co(II)}]$ found in studies utilizing known concentrations of cobalt(II).

Two possibilities can be suggested as the source of the cobalt(II) catalysts. All the reagents needed to prepare cobalt(II) complexes of the type $LCo(DH)_2$[4] are present in preparations of $LCo(DH)_2X$. The cobalt(II) complexes are probably similar in size and shape to the cobalt(III) complexes and could possibly occupy lattice sites in the crystals of the cobalt(III) complexes. Alternatively, these cobalt(III) complexes may be sufficiently thermally or photolytically unstable to generate sufficient cobalt(II) species to account for our results. This latter explanation is supported by our observation that $(C_6H_5)_3PCo(DH)_2Cl$ undergoes rapid ligand exchange with 4-*tert*-butylpyridine even after recrystallization from solutions containing $BrCCl_3$.

Three observations suggest that the cobalt(II) catalysis probably involves an inner-sphere electron-transfer step. First, the slower reaction when $X = NO_2$ than when X = Cl can be explained since the nitro ligand is recognized as a poor bridging ligand[7] (it is also a poor leaving group). Second, these exchange reactions require the presence of a bridging ligand and complexes of the type $L_2Co(DH)_2^+$ do not undergo ligand exchange. Third, we have found that when X = thiocyanate, S to N bonded equilibration of linkage isomers is catalyzed by these cobalt(II) complexes.[6] One further point is that inner-sphere electron transfer *via* the acido bridge would lead to the retention of the acido group and loss of the neutral ligand as was observed. Since it is known that ligand exchange occurs rapidly for these cobalt(II) complexes,[8] the following mechanism is suggested to account for the results

$$\text{Fast} \quad (C_6H_5)_3PCo^{II}(DH)_2 + L' \longrightarrow L'Co^{II}(DH)_2 + P(C_6H_5)_3$$

$$\text{Slow} \quad L'Co^{II}(DH)_2 + (C_6H_5)PCo^{III}(DH)_2X \longrightarrow (C_6H_5)PCo^{II}(DH)_2 + L'Co(DH)_2X$$

$$\overline{(C_6H_5)_3PCo^{II}(DH)_2X + L' \longrightarrow L'Co(DH)_2X + P(C_6H_5)_3}$$

Catalysis of the ligand exchange reaction by the addition of reducing agents is a well-accepted phenomenon. Relatively few of these exchange reactions involve the same metal and the retention of the ligands occupying most of the coordination sphere. One of the closest analogies is the Pt(II)-catalyzed reactions of several Pt(IV) complexes in which exchange occurs at only two of the six coordination positions.[9] A unique aspect of our observations is that the reduced complexes were already present in the complexes prepared in this study.

Rapidly established substitution equilibria (especially those involving neutral ligands) are rare in cobalt(III) chemistry unless strongly trans activating ligands such as sulfite are present.[10] Therefore, the equilibrium constants for this exchange reaction were determined (Table IV). Comparison of these data is difficult because of the lack of similar studies on other cobalt(III) systems. Equilibrium studies of the stability of LCo^{II}(saloph) complexes (saloph = *N*,*N*′-bis(salicylidene)-*o*-phenylenediamino)[11] can be used to estimate the equilibrium constant for reaction 3.

$$(C_6H_5)_3PCo^{II}(\mathrm{saloph}) + L \rightleftharpoons LCo^{II}(\mathrm{saloph}) + (C_6H_5)_3P \quad (3)$$

The values calculated for various displacing ligands (L) are 3.5 (3-bromopyridine), 17 (pyridine), 100 (1-methylimidazole), and 100 (tri-*n*-butylphosphine). Two interesting features emerge from comparison of the data for the two systems. First, the stabilities of the cobalt(III) complexes are much more sensitive to the nature of the entering ligand than are the stabilities of the cobalt(II) complexes. In particular, the basicity of the pyridine ligand is a more important factor in influencing the stability of the cobalt(III) complexes. Second, the ability of the phosphine ligands to coordinate relative to the N-donor ligands is greater for the cobalt(III) system than for the cobalt(II) system. Both of these results are consistent with a "soft" cobalt(III) center. Such centers generally exhibit "hard" characteristics, and the coordinated dimethylglyoxime ligands are exerting a "softening" influence. This conclusion explains several observations[6,12] that considerable stability is associated with S-bonded thiocyanate ligands in this type of complex, whereas N-bonding is generally observed in cobalt(III) complexes. Similar conclusions have been drawn from kinetic studies of other bis(dimethylglyoximato)cobalt(III) complexes.[13]

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(5) Although every effort was made to follow published procedures, $LCo(DH)_2X$ complexes prepared by others may not contain the catalysts. However, cobalt(II) catalysis can account for qualitative rate observations (on linkage isomerism) obtained by other groups.[6] Our data allow us to place an upper limit of *ca.* 0.1% catalyst. This low level would make detection difficult and probably accounts for our having no difficulty obtaining pmr spectra.

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