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Registry No. **9** (R = CH_3), 101200-39-9; **9** (R = $CH(CH_3)_2$), 101200-40-2; **10**, 101200-41-3; Co(pdx-L-phe), 101200-35-5; Co(pyv-L-his), 101200-38-8; Co(sal-L-ala)·dab, 101200-42-4; $[Co(sal\text{-}L\text{-}his)H_2O]_2O_2$, 101200-43-5; $[Co(sal\text{-}L\text{-}his)py]_2O_2$, 101200-44-6; $[Co(pdx\text{-}L\text{-}his)(H_2O)_2]_2O_2$, 101226-94-2; sal, 90-02-8; L-ala, 56-41-7; L-val, 72-18-4; L-phe, 63-91-2; L-his, 71-00-1; HpdxCl, 65-22-5; pdx, 66-72-8; pyv, 127-17-3; L-hisOMe·2HCl, 7389-87-9; pdm, 85-87-0; phg, 611-73-4; O_2, 7782-44-7; 2-formylpyridine, 1121-60-4.

Supplementary Material Available: Listings of elemental analyses (Table I), complete IR data (Table III), electronic and CD spectral data in pyridine of the cobalt(II) complexes (Table V), and absorption and CD spectral data for various systems formed in situ in solution (Table VI) and electronic and CD spectra of Co(sal-L-ala) and various adducts (Figure 1), Co(sal-L-his) and Co(pdx-L-his) (Figure 2), and Co(pdx-L-val) (Figure 3) in various solvents, absorption spectra of the ternary system pyridoxamine–pyruvic acid–cobalt(II) (1:1:1) at various times (Figure 4), CD spectra of Co(pyv-L-his), Co(pyv-L-hisOMe)Cl, and the ternary system pyruvic acid–L-valine–cobalt(II) (1:1:1) (Figure 5), and absorption, CD, and frozen-solution ESR spectra recorded at various times of the oxygenation of Co(pdx-L-his) in DMF (Figure 7), Co(pdx-L-val) in pyridine (Figure 9), and Co(sal-L-val) in DMF (Figure 10) (18 pages). Ordering information is given on any current masthead page.

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Structures, ^1H NMR Spectra, and Ligand-Exchange Properties of Costa-Type Organocobalt B_{12} Models with P-Donor Ligands

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The first extensive series with L = P-donor ligands of the organocobalt B_{12} model $[LCo((DO)(DOH)pn)CH_3]X$ has been prepared and characterized by ^1H NMR spectroscopy, by L ligand dissociation rates, and by X-ray crystallography. Assignment of the CH_3 ^1H NMR signals by chemical shift alone is not possible since 1D NOE experiments demonstrate that the order of shifts is dependent on L. However, the 5-bond ^{31}P–^1H coupling constant is smaller for the oxime CH_3 than for the Schiff base CH_3. The relative dissociation rates of 10 different L ligands is ca. a factor of 2 greater than those of the analogous cobaloxime complexes. The dissociation rate increases by 10^4 across the series $P(OMe)_2Ph < P(OEt)Ph_2 < PEtPh_2 < P(OMe)_3 < P(4\text{-}Me_2NPh)_3 < PViPh_2 < P\text{-}i\text{-}PrPh_2 < PCyPh_2 < PEtCNPh_2 < PPh_3$ (Vi = vinyl). The three-dimensional structures of $[LCo((DO)(DOH)pn)CH_3]PF_6$, L = $P(OMe)_3$ (I) and L = PPh_3 (II), were determined. Crystallographic details follow. For I: $C_{15}H_{31}CoF_6N_4O_5P$, $C2/c$, a = 21.978 (4) Å, b = 8.331 (1) Å, c = 27.713 (4) Å, d(calcd) = 1.54 g cm^{-3}, Z = 8, R = 0.055 for 2893 independent reflections. For II: $C_{30}H_{37}CoF_6N_4O_2P$, $Pbca$, a = 17.115 (6) Å, b = 25.424 (3) Å, c = 14.866 (2) Å, d(calcd) = 1.48 g cm^{-3}, Z = 8, R = 0.051 for 3294 independent reflections. These are the first two P-donor ligand complexes characterized by X-ray methods in the $[LCo((DO)(DOH)pn)R]X$ class of B_{12} models. Only minor differences are found between the structures of I and II and the analogous cobaloximes (except, of course, for differences that arise from the different equatorial ligands). It can be concluded that the two different types of model do not differ greatly in the Co(III) states except for somewhat greater sensitivity to L bulk of L leaving rates of $[LCo((DO)(DOH)pn)CH_3]^+$. Combined with the well-established greater ease of reduction to Co(II) in the Costa system, these differences suggest that the Costa-type system is superior to the cobaloximes as B_{12} models.

Introduction

Organocobalt B_{12} model compounds have been the subject of much recent interest.[1-6] In particular, factors that influence Co–C bond stability in such compounds provide valuable insight into the avenues available for coenzyme B_{12}-dependent enzymes to promote Co-C bond homolysis—an important step in the catalytic process.[1,6]

The longstanding hypothesis and most widely accepted explanation for the enzymic process falls under the umbrella term "mechanochemical trigger". In general, it is felt that an enzyme-induced conformational change in the coenzyme leads to a conformation with a greatly weakened Co–C bond.[1] The subsequent more facile Co–C bond homolysis generates a deoxyadenosyl radical, which in turn promotes radical rearrangement reactions characteristic of B_{12}-dependent processes.[6]

Two different types of conformational change have been postulated as possibly being responsible for Co–C bond weakening. Both possibilities are made credible by comparison of Co–C bond dissociation energies (BDE's) to structure.

First, the longer held and more widely accepted explanation for the "trigger" mechanism involves direct steric interaction between the corrin ring and the deoxyadenosyl moiety.[1,7,8] More specifically, the amide side chains of the corrin are believed to interact with the enzyme.[7] A conformational change in the enzyme could increase steric interactions involving the adenosyl moiety—weakening and perhaps breaking the Co–C bond. In addition to evidence that conformational changes do take place in enzymic systems, studies on models provide support for this mechanism. For example, Halpern and co-workers have demonstrated weak Co–C bonds in complexes of the type $LCo(DH)_2CHMePh$, when L = bulky phosphine ligands.[9] (DH = monoanion of dimethylglyoxime and these compounds are collectively known as cobaloximes.) In turn, we have demonstrated by crystallographic and NMR methods that such bulky phosphine ligands distort the $Co(DH)_2$ moiety toward R.[10,11] Taken together, this evidence demonstrates the feasibility of promoting Co–C bond

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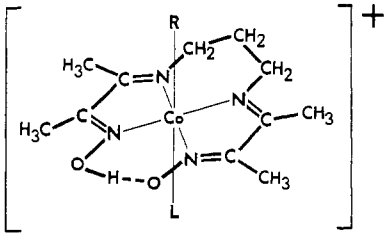
cleavage in coenzyme B_{12} by increased steric repulsion between the equatorial moiety and the adenosyl axial ligand.

Second, we have recently postulated that steric factors could play an important role by modifying the electron donor ability of the axial ligand (5,6-dimethylbenzimidazole) trans to the alkyl group.[12-14] In particular, Halpern's work on $LCo(DH)_2CHMePh$ complexes, where L = relatively small N heterocyclic ligands, clearly demonstrates that good electron donors stabilize the Co–C bond by stabilizing the Co(III) oxidation state relative to Co(II) + R·.[15] A mechanicochemical method for achieving this same result would be to lengthen the Co–N axial bond to the 5,6-dimethylbenzimidazole. Indeed systems known to have weak Co–C bonds also have long Co–N bonds.

Although there remains considerable uncertainty about which factors are most important in Co–C bond homolysis, both of the above effects could play a role together. They are not mutually exclusive. Furthermore, a third type of conformational/structural change, Co–C–C bond angle distortion, could also play a role.[16,17]

Recent attention has focused on the Costa model system, [LCo((DO)(DOH)pn)R]X complexes.[6,18-23] These complexes



$[LCo((DO)(DOH)pn)R]^+$

and a closely related system [LCo((EMO)(EMOH)pn)R]X, where the oxime methyl groups in (DO)(DOH)pn are replaced by ethyl groups, appear to promote better the types of reactions involved in B_{12}-dependent enzymic processes.[6] In certain cases, such Costa compounds are excellent electrochemical mimics of cobalamins.[23] In particular the III → II and II → I reduction potentials for aqua cobalamins are −0.04 and −0.74 V.[23] For [(benzim)Co((EMO)(EMOH)pn)$(CH_3CN)]^{2+}$ (benzim = benzimidazole), the corresponding values are ca. −0.04 and −0.71 V.[23] This good agreement does not extend to relevant organocobalt species, however.[23] The cobaloxime model systems are very poor electrochemical mimics of cobalamins.[23]

Since our past studies[5] have provided insight into the importance of various structural changes as these can be related to important recent estimates of Co–C BDE's, we have recently begun to extend our studies to the Costa model system.[18] In this study, we describe the first structural investigation of a Costa model with L = P-donor ligands and describe some of the solution properties of this type of compound.

Table I. Crystallographic Data for Compounds I and II[a]

	I	II
formula	$CoPO_5N_4C_{15}H_{31}PF_6$	$CoPO_2N_4C_{30}H_{37}PF_6$
mol wt	582.4	720.6
a, Å	21.978 (4)	17.115 (6)
b, Å	8.331 (1)	25.424 (3)
c, Å	27.713 (3)	14.866 (2)
β, deg	97.19 (2)	
d(measd), g cm^{-3}	1.54	1.50
d(calcd), g cm^{-3}	1.54	1.48
Z	8	8
space group	*C2/c*	*Pbca*
μ, cm^{-1}	8.8	6.9
cryst dimens, cm^3	0.04 × 0.03 × 0.01	0.04 × 0.05 × 0.02
no. of reflcns measd	11 152[b]	7735
no. of indep reflcns	2893	3294
max 2*θ*, deg (Mo K*α*)	54	54
R	0.055	0.051
R_w	0.065	0.060

[a] Esd's are given in parentheses. [b] Data collected by using space group $P\bar{1}$.

Table II. Positional Parameters and Their Estimated Standard Deviations for Compound I

atom	*x*	*y*	*z*
Co	0.38899 (3)	0.02170 (9)	0.33366 (3)
P1	0.38488 (7)	−0.0803 (2)	0.40895 (5)
O1	0.3040 (2)	−0.2105 (2)	0.2908 (2)
O2	0.4122 (2)	−0.2899 (5)	0.2988 (2)
O3	0.3547 (2)	−0.2504 (5)	0.4136 (2)
O4	0.3514 (2)	0.0373 (5)	0.4409 (1)
O5	0.4514 (2)	−0.1107 (6)	0.4353 (2)
N1	0.3113 (2)	−0.0633 (6)	0.3096 (2)
N2	0.4367 (2)	−0.1550 (6)	0.3190 (2)
N3	0.4681 (2)	0.1087 (6)	0.3537 (2)
N4	0.3396 (2)	0.2021 (5)	0.3453 (2)
C1	0.2009 (3)	−0.022 (1)	0.2919 (3)
C2	0.2640 (3)	0.0288 (8)	0.3109 (2)
C3	0.2811 (3)	0.1846 (7)	0.3321 (2)
C4	0.2337 (3)	0.3066 (9)	0.3381 (3)
C5	0.3651 (3)	0.3520 (8)	0.3682 (3)
C6	0.4261 (5)	0.342 (1)	0.3984 (5)
C6*	0.4294 (7)	0.378 (2)	0.3583 (7)
C7	0.4761 (3)	0.2710 (9)	0.3742 (3)
C8	0.5796 (3)	0.051 (1)	0.3650 (3)
C9	0.5138 (3)	0.0142 (8)	0.3491 (2)
C10	0.4960 (3)	−0.1414 (7)	0.3281 (2)
C11	0.5390 (3)	−0.2704 (9)	0.3178 (2)
C12	0.3951 (3)	0.1026 (8)	0.2657 (2)
C13	0.2903 (3)	−0.2735 (8)	0.4106 (3)
C14	0.3435 (3)	0.0126 (9)	0.4908 (2)
C15	0.4702 (4)	−0.222 (1)	0.4731 (3)
P2	0.14013 (8)	0.0261 (2)	0.44533 (7)
F1	0.0737 (3)	−0.0253 (9)	0.4479 (3)
F2	0.1189 (3)	0.1997 (5)	0.4290 (2)
F3	0.2038 (3)	0.073 (1)	0.4373 (3)
F4	0.1624 (3)	−0.1440 (6)	0.4606 (2)
F5	0.1304 (3)	−0.0279 (7)	0.3905 (2)
F6	0.1436 (4)	0.0784 (7)	0.4980 (2)

Experimental Section

Reagents. The ligands $PCyPh_2$, $PViPh_2$, $P(4\text{-}Me_2NPh)_3$, P-*i*-$PrPh_2$, $PEtPh_2$, and $POEtPh_2$ were purchased from Strem (Vi = vinyl, Cy = cyclohexyl). All other ligands and reagents were from Aldrich. Elemental analyses (C, H, N) performed by Atlantic Microlabs, Atlanta, GA, were satisfactory for all complexes used in the kinetic studies. The analyses for the 10 $[LCo((DO)(DOH)pn)CH_3]ClO_4$ compounds listed in Table IV plus that for L = PBu_3 are given in the supplementary material. The analyses for other new compounds are given in the footnotes for Table IV.

Rate Measurements. Ligand substitution reactions were monitored spectrophotometrically with a Perkin-Elmer Lambda 3B instrument equipped with a 3600 Data Station for the slower reactions (k_{obsd} < 0.1

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Table III. Positional Parameters and Their Estimated Standard Deviations for Compound II

atom	x	y	z
Co	0.10799 (4)	0.13830 (3)	0.21422 (5)
P1	-0.02384 (7)	0.17056 (5)	0.22367 (9)
O1	0.1795 (2)	0.2354 (2)	0.2590 (3)
O2	0.1376 (3)	0.1817 (2)	0.3861 (3)
N1	0.1536 (3)	0.2043 (2)	0.1926 (3)
N2	0.1160 (3)	0.1390 (2)	0.3402 (3)
N3	0.0765 (3)	0.0674 (2)	0.2374 (3)
N4	0.1080 (3)	0.1365 (2)	0.0855 (3)
C1	0.2011 (4)	0.2696 (3)	0.0854 (5)
C2	0.1629 (3)	0.2189 (2)	0.1094 (4)
C3	0.1346 (4)	0.1785 (2)	0.0478 (4)
C4	0.1388 (5)	0.1878 (3)	-0.0517 (5)
C5	0.0820 (4)	0.0908 (3)	0.0335 (4)
C6	0.1004 (4)	0.0396 (3)	0.0794 (5)
C7	0.0580 (4)	0.0289 (2)	0.1663 (5)
C8	0.0582 (5)	-0.0002 (3)	0.3564 (5)
C9	0.0768 (4)	0.0535 (2)	0.3213 (4)
C10	0.0989 (4)	0.0958 (2)	0.3829 (4)
C11	0.1019 (5)	0.0914 (3)	0.4831 (4)
C12	0.2202 (3)	0.1138 (3)	0.2136 (5)
C13	-0.0811 (3)	0.1500 (2)	0.1257 (3)
C14	-0.1296 (3)	0.1059 (2)	0.1219 (4)
C15	-0.1657 (4)	0.0920 (2)	0.0415 (4)
C16	-0.1533 (4)	0.1217 (3)	-0.0351 (4)
C17	-0.1060 (4)	0.1649 (3)	-0.0319 (4)
C18	-0.0704 (4)	0.1797 (2)	0.0478 (4)
C19	-0.0485 (3)	0.2409 (2)	0.2247 (3)
C20	-0.1280 (3)	0.2539 (2)	0.2191 (4)
C21	-0.1503 (3)	0.3063 (2)	0.2204 (4)
C22	-0.0953 (4)	0.3451 (2)	0.2257 (4)
C23	-0.0172 (4)	0.3332 (2)	0.2311 (4)
C24	0.0063 (3)	0.2806 (2)	0.2315 (4)
C25	-0.0714 (3)	0.1474 (2)	0.3271 (3)
C26	-0.0905 (3)	0.0952 (2)	0.3419 (4)
C27	-0.1220 (4)	0.0789 (2)	0.4235 (4)
C28	-0.1325 (4)	0.1149 (3)	0.4919 (4)
C29	-0.1115 (5)	0.1664 (3)	0.4793 (4)
C30	-0.0806 (4)	0.1826 (2)	0.3972 (4)
P2	0.3073 (1)	-0.05468 (6)	0.2643 (1)
P1	0.3474 (5)	-0.0307 (3)	0.1843 (4)
F2	0.3135 (5)	-0.1079 (2)	0.2185 (6)
F3	0.2694 (4)	-0.0801 (3)	0.3465 (4)
F4	0.2997 (5)	-0.0016 (2)	0.3045 (6)
F5	0.3875 (4)	-0.0628 (3)	0.3104 (5)
F6	0.2254 (4)	-0.0501 (3)	0.2239 (5)

s^{-1}), or a Durrum-Gibson D-110 stopped-flow spectrophotometer for the faster reactions. Both instruments were equipped with thermostated cell compartments (25.0 ± 0.04 °C). Visible spectra of several (DO)(DOH)pn complexes in methylene chloride were recorded and then compared with the visible spectra of the same solutions after addition of a calculated excess (in most cases 100:1) of entering ligand (L'), allowing sufficient time for the reactions to reach completion (verified by a similar ^{1}H NMR experiment). Suitable wavelengths for following the exchange reactions were in the range 410–480 nm for the complexes (0.0005–0.001 M) studied. Absorbance changes over the first 3 half-lives were used in the calculations of the rate constants with the final absorbance taken at 8 half-lives. Reported rate constants are average values of at least three data sets.

Data Analysis. The rate constants are defined as

$$ML \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M + L$$

$$M + L' \xrightarrow{k_2} ML'$$

where M = Co((DO)(DOH)pn)R, and L' = *N*-methylimidazole or P(OMe)$_3$. The experimental absorbance vs. time rate data were treated with the standard integrated expression for a first-order process by using a linear-least-squares computer program.

^{1}H NMR Spectroscopy. ^{1}H NMR spectra were recorded on a Nicolet NB-360 spectrometer operating at 361.08 MHz. Spectra contained 16K data points with a spectral range of 4000 Hz. Chemical shifts are relative to Me_4Si and, unless otherwise stated, in $CDCl_3$ (see Table VII). 1D NOE experiments were performed on two samples (L = $POEtPh_2$, $PEtPh_2$; 2 mg/0.5 mL). The spectra were recorded at 22 °C in the alternate accumulation mode (4 scans) with a total of 124 transients. The difference spectra were obtained by subtracting the off-resonance spectra from the on-resonance spectra (partial saturation of the N–C–H_2–C–CH_2–N multiplet).

Preparation of [LCo((DO)(DOH)pn)CH_3]ClO_4 Complexes. To avoid cleavage of the Co–C bond, all compounds with Co–C bonds were handled with minimal exposure to light and were not subjected to temperatures above 35 °C.

Table IV. First-Order Rate Constants for L Exchange of LCo(chel)CH_3 in CH_2Cl_2 at 25 °C

L	k_1([LCo((DO)(DOH)pn)CH_3]ClO_4), s^{-1}	k_1(LCo(DH)$_2CH_3$), s^{-1}
PPh_3[a,c]	(3.2 ± 0.1) × 10^{-1}	(4.5 ± 0.1) × 10^{-2} [d]
$PEtCNPh_2$[a]	(1.06 ± 0.05) × 10^{-2}	(1.36 ± 0.17) × 10^{-3} [e]
$PCyPh_2$[b]	(8.6 ± 0.3) × 10^{-3}	(7.4 ± 0.5) × 10^{-3} [f]
P-*i*-$PrPh_2$[a]	(8.4 ● 0.1) × 10^{-3}	(6.23 ● 0.06) × 10^{-3} [e]
$PViPh_2$[a]	(4.3 ± 0.2) × 10^{-3}	(2.0 ± 0.1) × 10^{-3} [g]
P(4-$Me_2NPh)_3$[a]	(1.02 ± 0.01) × 10^{-3}	(2.27 ± 0.06) × 10^{-3} [e]
$P(OMe)_3$[b]	(7.17 ± 0.08) × 10^{-4}	(4.1 ● 0.2) × 10^{-3} [d]
$PEtPh_2$[b]	(1.90 ± 0.02) × 10^{-4}	(1.1 ± 0.1) × 10^{-4} [d]
$POEtPh_2$[b]	(8.27 ± 0.01) × 10^{-5}	(7.7 ± 0.5) × 10^{-4} [f]
$P(OMe)_2Ph$[b]	(2.64 ± 0.01) × 10^{-5}	(1.35 ± 0.04) × 10^{-4} [g]

[a] Entering ligand was $P(OMe)_3$. Vi = vinyl. [b] Entering ligand was *N*-MeIm. Cy = cyclohexyl. [c] k_1 = (3.9 ± 0.2) × 10^{-1} s^{-1} for *N*-MeIm as entering ligand. Values for k_1 were found to be (2.96 ± 0.02) × 10^{-1} s^{-1} and (2.3 ± 0.1) × 10^{-1} s^{-1} for the PF_6^- and BPh_4^- salts, respectively. The BPh_4^- salt was prepared from [H_2OCo((DO)(DOH)pn)CH_3]BPh_4 as mentioned above for [PPh_3Co((DO)(DOH)pn)CH_3]PF_6. Anal. Calcd for X = PF_6^-, $C_{30}H_{37}CoF_6N_4O_2P_2 \cdot H_2O$: C, 48.92; H, 5.34; N, 7.61. Found: C, 48.91; H, 5.06; N, 7.77. Anal. Calcd for X = BPh_4^-, $C_{54}H_{57}BCoN_4O_2P$: C, 72.48; H, 6.42; N, 6.26. Found: C, 72.29; H, 6.38; N, 6.30. [d] Reference 5. [e] Reference 35. [f] Reference 36. [g] This work. These (DH)$_2$ complexes were prepared from H_2OCo(DH)$_2CH_3$[37] by the same method reported for [$PEtPh_2Co$((DO)(DOH)pn)CH_3]ClO_4. Anal. Calcd for L = $P(OMe)_2Ph$, $C_{17}H_{28}CoN_4O_6P$: C, 43.05; H, 5.95; N, 11.81. Found: C, 42.94; H, 5.97; N, 11.75. Anal. Calcd L = $PViPh_2$, for $C_{23}H_{30}CoN_4O_4P$: C, 53.49; H, 5.86; N, 10.85. Found: C, 53.56; H, 5.90; N, 10.83. The rates for the PBu_3 complexes are very slow and were not determined.

Table V. Selected Bond Lengths (Å) with Estimated Standard Deviations for I and II

	I	II		I	II
Co–P1	2.265 (1)	2.405 (1)	Co–N3	1.902 (4)	1.913 (4)
Co–N1	1.890 (4)	1.879 (4)	Co–N4	1.905 (4)	1.914 (4)
Co–N2	1.880 (4)	1.878 (4)	Co–C12	2.021 (5)	2.018 (5)

Table VI. Selected Bond Angles (deg) for I and II

	I	II
P1–Co–N1	92.6 (1)	95.5 (1)
P1–Co–N2	89.6 (1)	90.4 (2)
P1–Co–N3	90.9 (1)	92.6 (1)
P1–Co–N4	92.9 (1)	93.8 (1)
P1–Co–C12	177.1 (2)	176.3 (2)
N1–Co–N2	97.7 (2)	97.6 (2)
N1–Co–N3	176.3 (2)	171.8 (2)
N1–Co–N4	81.2 (2)	81.4 (2)
N1–Co–C12	87.6 (2)	83.1 (2)
N2–Co–N3	81.2 (2)	81.4 (2)
N2–Co–N4	177.3 (2)	175.7 (2)
N2–Co–C12	87.5 (2)	86.4 (2)
N3–Co–N4	99.8 (2)	99.1 (2)
N3–Co–C12	88.8 (2)	88.8 (2)
N4–Co–C12	90.0 (2)	89.3 (2)
Co–P1–O3	118.6 (2)	
Co–P1–O4	111.2 (2)	
Co–P1–O5	110.3 (2)	
O3–P1–O4	106.5 (2)	
O3–P1–O5	101.2 (2)	
O4–P1–O5	108.3 (2)	
Co–P1–C13		111.0 (2)
Co–P1–C19		123.2 (2)
Co–P1–C25		110.8 (2)
C13–P1–C19		99.3 (2)
C13–P1–C25		109.7 (2)
C19–P1–C25		101.7 (2)

Table VII. ^{1}H NMR Spectral Data for $[LCo((DO)(DOH)pn)CH_3]ClO_4$ Complexes in $CDCl_3$

L	δ(C—N=C—CH_3) ($^5J_{PH}$, Hz)[a]	δ(O—N=C—CH_3) ($^5J_{PH}$, Hz)	δ(Co—CH_3) ($^3J_{PH}$, Hz)
$P(OMe)_3$	2.40 (5.8)	2.29 (3.6)	1.08 (6.1)
$P(OMe)_2Ph$	2.14 (5.4)	2.04 (3.9)	1.01 (5.5)
$POEtPh_2$	2.22 (4.7)	1.82 (2.8)	1.09 (4.1)
PBu_3	2.40 (4.5)	2.28 (2.7)	0.95 (3.3)
$PViPh_2$	2.15 (4.5)	2.07 (2.8)	1.14 (3.4)
$PEtPh_2$[b]	2.04 (4.4)	2.10 (2.8)	1.07 (3.2)
$PEtCNPh_2$[b]	2.05 (4.3)	2.15 (2.7)	1.16 (3.4)
P-*i*-$PrPh_2$[b]	2.07 (4.2)	2.17 (2.4)	1.09 (3.2)
$PCyPh_2$[b]	2.07 (4.2)	2.16 (2.4)	1.08 (3.2)
$P(4\text{-}Me_2NPh)_3$	2.19 (4.5)	1.96 (2.8)	0.98 (3.4)
PPh_3[c]	2.18 (4.3)	1.96 (2.7)	1.16 (3.3)
PPh_3[d]	2.18 (4.7)	1.95 (2.9)	1.16 (3.2)
PPh_3[e]	2.17 (4.4)	1.96 (2.7)	1.16 (3.4)
PPh_3[f]	1.80 (4.4)	1.83 (2.7)	1.02 (3.4)
PPh_3[g]	1.99	1.91	1.07

[a] ±0.5 Hz. [b] Complexes with oxime CH_3 shift at lower field than the Schiff base CH_3 shift. [c] Poorly soluble and unstable in $CDCl_3$. [d] CD_2Cl_2. [e] CD_2Cl_2, PF_6^- salt. [f] $CDCl_3$, BPh_4^- salt (see footnote *c*, Table IV). [g] CD_2Cl_2, BPh_4^- salt.

$[H_2OCo((DO)(DOH)pn)CH_3]ClO_4$ was prepared by a modification of Costa's method b.[24]

$[H_2OCo((DO)(DOH)pn)CH_3]PF_6$ was prepared by dissolution of the perchlorate salt (1.5 g, 3.5 mmol) in warm H_2O (100 mL) followed by precipitation of the product by slow addition of aqueous NH_4PF_6 (ca. 8 equiv). Yield: 1.4 g (84%).

$[LCo((DO)(DOH)pn)CH_3]ClO_4$ (L = $PEtPh_2$, $PEtCNPh_2$, $POEtPh_2$, $P(OMe)_2Ph$, $P(OMe)_3$). A mixture of $[H_2OCo((DO)(DOH)pn)CH_3]ClO_4$ (300 mg, 0.7 mmol) in CH_2Cl_2 (10 mL) was treated with L (1.2 equiv) and stirred until a clear solution resulted (ca. 10 min). The solution was filtered and treated with petroleum ether until it became cloudy. Acetone was used to dissolve any oil that formed. The flask containing the solution was scratched. A powder formed upon cooling (0 °C) or further addition of petroleum ether. The yellow precipitate was collected and washed with diethyl ether. For L = $PEtCNPh_2$, the CH_2Cl_2/petroleum ether was removed, the oily residue was redissolved in $CHCl_3$, and a precipitate was obtained on addition of diethyl ether. Yields: $PEtPh_2$, 360 mg (82%); $PEtCNPh_2$, 67 mg (15%); $POEtPh_2$, 375 mg (80%); $P(OMe)_2Ph$, 412 mg (93%); $P(OMe)_3$, 327 mg (87%).

$[PPh_3Co((DO)(DOH)pn)CH_3]ClO_4$. A mixture of $[H_2OCo((DO)(DOH)pn)CH_3]ClO_4$ (1.0 g, 2.3 mmol) in CH_2Cl_2 (30 mL) was treated with PPh_3 (15.2 g, 58 mmol). A solution containing a brownish green suspension formed. The mixture was stirred for 1 day. An orange powder was collected and washed with diethyl ether. Yield: 540 mg (33%).

$[LCo((DO)(DOH)pn)CH_3]ClO_4$ (L = P-*i*-$PrPh_2$, $PCyPh_2$, $P(4\text{-}Me_2NPh)_3$, $PViPh_2$, PBu_3). A solution of $[(ANIL)Co((DO)(DOH)pn)CH_3]ClO_4$[25] (ANIL = aniline) (400 mg, 0.8 mmol) in CH_2Cl_2 (10 mL) was stirred with $MgSO_4$ (500 mg). The solution was filtered and treated with L (1.6 mmol). After 15 min., the yellow solution was poured into stirred petroleum ether (30 mL) and an oil formed. The supernatant was decanted. The oil was dissolved in acetone (10–30 mL) and treated with L (ca. 0.7 mmol). After a few minutes, diethyl ether was added to the yellow solution until a precipitate formed. The yellow powder was collected and washed with diethyl ether. Yields: L = P-*i*-$PrPh_2$, 200 mg (39%); L = $PCyPh_2$, 350 mg (65%); L = $P(4\text{-}Me_2NPh)_3$, 600 mg (93%); L = $PViPh_2$, 430 mg (87%); L = PBu_3, 230 mg (45%).

$[P(OMe)_3Co((DO)(DOH)pn)CH_3]PF_6$. A yellow powder of this compound obtained as described above for the perchlorate salt was dissolved in acetone–methanol (2:1). Diethyl ether was added until the solution became cloudy. After 10 min at 23 °C, X-ray quality crystals were obtained.

$[PPh_3Co((DO)(DOH)pn)CH_3]PF_6$. A suspension of $[H_2OCo((DO)(DOH)pn)CH_3]PF_6$ in CH_2Cl_2 was treated with 1.2 equiv of PPh_3 and stirred (3 h). A solution containing a fine suspension was produced. Petroleum ether was added to the mixture until precipitation was complete. The orange powder was dissolved in CH_2Cl_2–acetone (10:1). After 30 min at 23 °C, X-ray quality crystals were obtained.

X-ray Methods. Crystal Data. Crystals of $[LCo((DO)(DOH)pn)CH_3]PF_6$, L = $P(OMe)_3$ (I) and L = PPh_3 (II), were obtained as detailed above. Cell dimensions, determined from Weissenberg and precession photographs, were refined on a CAD4 Enraf-Nonius single-crystal diffractometer by the $\omega/2\theta$ scan technique, using monochromatic Mo Kα radiation. Crystal data are given in Table I. Intensities of three check reflections were measured about every 100 reflections during data collection. No decay of intensity occurred throughout the data recording. Intensities having $I > 3\sigma(I)$ were corrected for Lorentz and polarization factors. An anomalous dispersion correction was applied. No correction for absorption was included because of the small size of the crystals used and the small values of the absorption coefficients (Table I).

Solution and Refinement of Structures. The structures of I and II were solved by conventional Patterson and Fourier methods and refined by full-matrix anisotropic least-squares methods to final *R* values of 0.055 and 0.051, respectively. The contribution of hydrogen atoms, located at calculated positions, was held constant (B = 5 Å^2) in both structures. Hydrogen atoms attached to C(6) and C(6*) (vide infra) were not included in the final calculations. The weighting scheme was $w = 1/(\sigma^2(F) + (pF)^2 + q)$ where $p = 0.02$ and $q = 2.0$ for both structures. Atomic scattering factors were those given in ref 26. All calculations were carried out by using the SDP-CAD4 programs on a PDP11-44 computer. Final positional parameters are given in Tables II and III. Anisotropic thermal parameters, hydrogen atom coordinates, and final calculated and observed structure factors are given in the supplementary material.

Results

Synthetic Methods. In contrast to the numerous cobaloxime complexes of the types $LCo(DH)_2R$, $LCo(DH)_2X$, $[L_2Co(DH)_2]^+$, $[LCo(DH)_2L']^+$, $LCo^{II}(DH)_2$, and $L_2Co^{II}(DH)_2$, where L = P-donor, L′ = neutral ligand, R = alkyl and X = acido ligand, that are known,[5] only four compounds, all of the type $[LCo((DO)(DOH)pn)CH_3]X$, have been reported (L = $P(OMe)_3$, PEt_3, PBu_3, PPh_3).[27,28] The preparation of $PPh_3Co^I((DO)(DOH)pn)$ has also been reported.[24]

Thus, in this paper we report the first detailed syntheses of a variety of $[LCo((DO)(DOH)pn)CH_3]X$ complexes, where L = phosphorus ligand. $[LCo((DO)(DOH)pn)CH_3]ClO_4$ complexes with phosphines more bulky than $PEtPh_2$ could not be prepared by replacement of L = H_2O. An attempt to prepare the L = $PCyPh_2$ complex by the method reported for L = $PEtPh_2$ resulted in a mixture of aqua (75%) and $PCyPh_2$(25%) adducts (by ^{1}H NMR).

Attempts to prepare $[LCo((DO)(DOH)pn)CH_3]ClO_4$ (L = $P(CH_2Ph)_3$, $P(EtCN)_3$) complexes were totally unsuccessful. Solutions of P-donor ligand and $[(ANIL)Co((DO)(DOH)pn)CH_3]ClO_4$ (1:1) revealed (by ^{1}H NMR) that ANIL remained at least 90% coordinated.

Rate Measurements. The L ligand-exchange rate constants (k_1) were determined for 10 $[LCo((DO)(DOH)pn)CH_3]ClO_4$ salts in the noncoordinating solvent CH_2Cl_2 and are listed in Table IV with the analogous $LCo(DH)_2CH_3$ compounds. Identical ligand-exchange rates were found with L′ = *N*-MeIm (1-methylimidazole) or $P(OMe)_3$ for $[PPh_3Co((DO)(DOH)pn)CH_3]ClO_4$. From 20- to 100-fold excess L′, the rates measured were independent of [L′]. Therefore, as found previously for $[pyCo((DO)(DOH)pn)R]ClO_4$ complexes,[18] the rate expression is first order in complex concentration as expected for a S_N1 LIM reaction. A plot of log k_1 (s^{-1}) for dissociation of L from $LCo(DH)_2CH_3$ vs. log k_1 (s^{-1}) for dissociation of L from $[LCo((DO)(DOH)pn)CH_3]ClO_4$ is shown in Figure 1. Phosphorus ligands found to exchange faster in the (DO)(DOH)pn system than in the $(DH)_2$ system lie above the line in Figure 1. This line is the "45° line".

Structural Studies. ORTEP drawings of cations I and II with the atom-numbering schemes are depicted in Figures 2 and 3. In both compounds, cobalt exhibits a distorted octahedral stereochemistry and the (DO)(DOH)pn ligand occupies the four equatorial positions. Selected bond lengths and angles are reported in Tables V and VI. The four equatorial N atoms are coplanar within ±0.009 (I) and ±0.033 Å (II), and cobalt is displaced (*d*)

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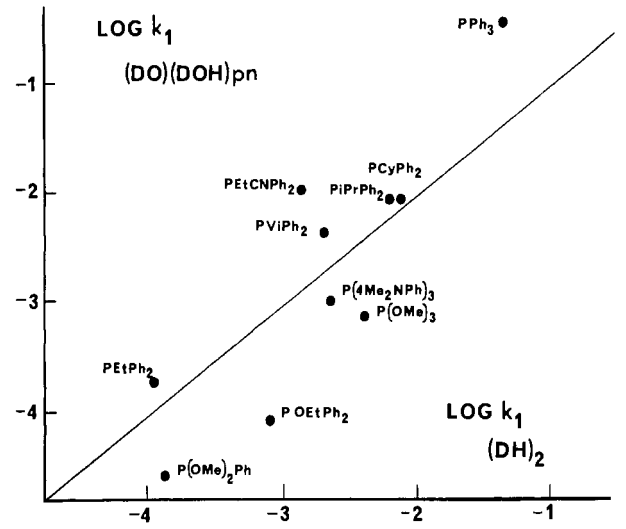

Figure 1. Plot of log k_1 (s^{-1}) for $LCo(DH)_2CH_3$ vs. log k_1 (s^{-1}) for $[LCo((DO)(DOH)pn)CH_3]ClO_4$.

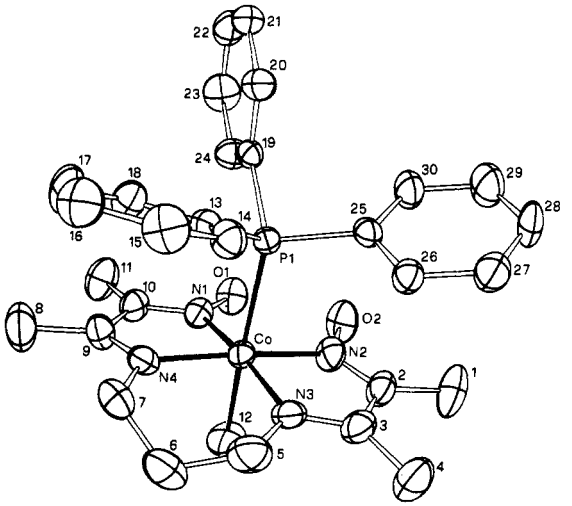

Figure 2. Structure and labeling scheme for the non-hydrogen atoms of I (thermal ellipsoids; 50% probability).

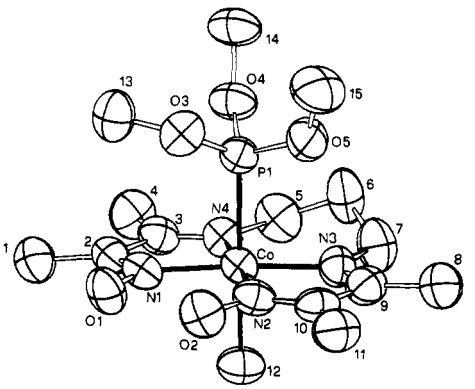

Figure 3. Structure and labeling scheme for the non-hydrogen atoms of II (thermal ellipsoids; 50% probability).

by 0.05 (I) and 0.1 Å (II) from these mean planes toward the axial phosphorus ligand. The two chemically equivalent halves of the equatorial macrocycle, with the exclusion of C(6), are approximately planar. These planes have dihedral angles (α) of 3.3 (I), and 8.2° (II) and bend toward the axial methyl group. The C(6) atom of the propylene bridge was found to be disordered in I with occupancy factors of 0.6, C(6), and 0.4, C(6*), for the two orientations. The six-membered chelate ring in II has the expected conformation with the C(6) atom out of the chelate plane, away from the bulkier axial ligand (PPh_3). The torsional angles

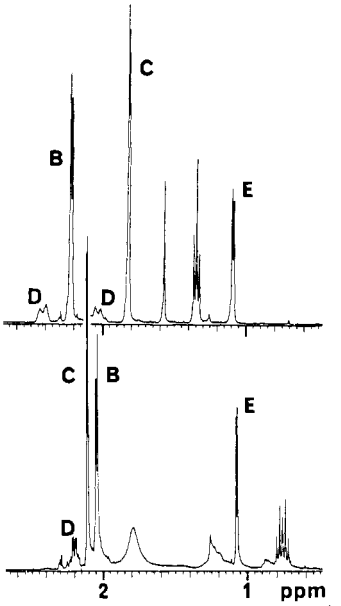

Figure 4. Partial ^1H NMR spectra of $[POEtPh_2Co((DO)(DOH)pn)CH_3]ClO_4$ (top) and $[PEtPh_2Co((DO)(DOH)pn)CH_3]ClO_4$ (bottom) in $CDCl_3$. The two multiplets arising from the $N-CH_2-C-CH_2-N$ protons have been designated A and are not shown. The labeled signals are assigned as follows: (B) $C{=}N{=}C{-}CH_3$; (C) $O{-}N{=}C{-}CH_3$; (E) $Co{-}CH_3$. The two small multiplets centered at 2.41 and 2.03 ppm (top) and the multiplet at 2.20 ppm (bottom) arise from the $N-C-CH_2-C-N$ protons and are designated D. The remaining signals are as follows: (top) H_2O, 1.58 ppm; $P-O-C-CH_3$, 1.34 ppm and (bottom) H_2O, 1.78 ppm; $P-C-CH_3$, 0.76 ppm. Several solvent impurity signals are also evident, particularly at ca. 1.25 ppm.

around C(5)–C(6) and C(6)–C(7) bonds are −66.2 and 62.9° in II.

The O···O distances of the oxime bridge are 2.451 (5) (I) and 2.438 (5) Å (II). These values are within the experimental error of values reported for other Costa models[18,29-31] but are significantly shorter than the mean value of 2.487 (2) Å in cobaloximes.[5]

Discussion

Ingraham has partially assigned the ^1H NMR spectrum of $[H_2OCo((DO)(DOH)pn)CH_3]ClO_4$ in Me_2SO-d_6.[32] The sharper upfield equatorial methyl peak (δ = 2.27) was assigned to $C{-}N{=}C{-}CH_3$ without any justification. In disagreement with this, Pellizer has suggested that the sharper equatorial methyl peaks correspond to $O{-}N{=}C{-}CH_3$.[33] This assignment was based on the observations that the chemical shift of the sharper signal was more affected by replacement of the O–H···O by $O-BF_2-O$ and by deprotonation of the oxime.[33]

Although this argument is reasonable, we found that the broader and sharper resonances interchanged their relative shifts as a function of L (Table VII and Figure 4). Therefore, we assigned the signals by 1D NOE methods for complexes with L = $PEtPh_2$ and $POEtPh_2$, complexes representative of the two classes. In each case, irradiation of a propylene CH signal induced an NOE at the broader signal.

The $^5J_{PH}$ values are relatively insensitive to the nature of L when L is a phosphine (Table VII). However, $^5J_{PH}$ increases significantly as the alkyl or aryl groups are replaced by alkoxy groups. In every case, the $^5J_{PH}$ for the oxime CH_3 is smaller than for the

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Table VIII. Relevant Geometrical Data for $LCo(chel)CH_3$ Complexes[a]

L	chel	Co–C, Å	Co–L, Å	α, deg	d, Å	k_1, s^{-1}
$P(OMe)_3$	(DO)(DOH)pn	2.021 (5)	2.265 (1)	+3.3	+0.05	7.17×10^{-4}
	$(DH)_2$[b]	2.01 (1)	2.256 (4)	+10.0	+0.10	4.1×10^{-3}
	$(GH)_2$[c]	2.041 (4)	2.268 (1)	+4.0	+0.08	5.3×10^{-5}
PPh_3	(DO)(DOH)pn	2.018 (5)	2.405 (1)	+8.2	+0.10	4.37×10^{-1}
	$(DH)_2$[d]	2.026 (6)	2.418 (1)	+14.0	+0.11	4.5×10^{-2}
	$(GH)_2$[c]	2.033 (3)	2.428 (1)	+6.0	+0.11	4.6×10^{-3}

[a] Positive values of α and *d* indicate that the bending of the equatorial ligand is toward the alkyl group and that the displacement of Co is out of the N4 equatorial donor set toward L. [b] Reference 38. [c] Reference 39. GH = glyoxime monoanion. [d] Reference 40.

Schiff base CH_3. Similarly, $^3J_{PH}$ values are insensitive to changes in the phosphine ligands but increase significantly as the alkyl or aryl substituents are replaced by alkoxy groups. By comparison, the values of $^5J_{PH}$ for cobaloximes are similar to those found here for the oxime CH_3 signal.[5]

It is interesting that the BPh_4^- salt of $[PPh_3Co((DO)(DOH)pn)CH_3]^+$ has significantly different shifts from the other salts (Table VII). In particular, the signal assigned to the Schiff base methyl group is shifted upfield ca. 0.4 ppm whereas the oxime methyl signal is shifted less than 0.2 ppm. In low dielectric solvents, the $[LCo((DO)(DOH)pn)CH_3]X$ salts are undoubtedly ion-paired. The propylene bridge should be the more positively charged part of the cation since the oxime bridge carries one negative charge. The ion pairs, although in rapid exchange, should have a geometry in which the anion is close to the propylene part of the cation. Thus, the influence of the anisotropic BPh_4^- anion on the Schiff base methyl signal can be easily understood. In support of this hypothesis, the center of the multiplet for the terminal propylene bridge protons is shifted from ca. 3.5 ppm for the ClO_4^- and PF_6^- salts to ca. 2.7 ppm for the BPh_4^- salt. In CD_2Cl_2, this signal for the BPh_4^- salt is at 3.15 ppm, indicating less ion pairing in this more polar solvent. The oxime O–H···O signal is relatively insensitive to the anion (CD_2Cl_2: BPh_4^-, 18.95 ppm; ClO_4^-, 18.99 ppm), as expected from the preferred average geometry of the ion pairs.

Except for cobaloximes, P-donor B_{12} model complexes have received little structural study.[6,27,28] However, the Co–L bond is usually a highly sensitive function of the equatorial ligand when L = N- or O-donor.[12-14] For L = $P(OMe)_3$, there is no significant difference in the Co–P bond length. For L = PPh_3, the Co–P bond in II is actually slightly shorter than that in cobaloximes. One criterion for a good coenzyme B_{12} model is that the Co–L bond be relatively long.[12-14] Thus, on this basis, the Costa model does not appear to be a good "structural" model for B_{12}, in which Co–N axial bond lengths are unusually long. The lack of significant variation in Co–C bond lengths between comparable cobaloximes and Costa models (Table VIII) is expected since this bond length appears to be insensitive to the equatorial ligand,[13,30] but for bulky R, it is highly sensitive to R ligand bulk.[5,34]

A second structural criterion for a good model could be the degree of flexibility of the equatorial moiety. An indirect criterion for assessing flexibility is the deviation from planarity of the Co(chel) (chel = chelate) moiety and the range of values typically encountered. Although such deviations are subject to lattice effects, a sufficiently large number of structural studies might give some insight into the ease of distortion of the Co(chel) moiety. We have used two measures of this distortion.[5] First, the displacement of Co out of the 4N plane typically requires a bulky R or L ligand.[5] For the Costa and cobaloxime models, this displacement, *d*, is very similar when L = PPh_3 but is somewhat smaller for I, where L = $P(OMe)_3$ (Table VIII). Second, the bending between the two equivalent halves of the equatorial ligand, as measured by the dihedral angle, α, between the planes, is not unusually large unless one of the ligands is bulky.[5] Again, the α values for the Costa model are somewhat smaller than for the cobaloximes. In summary, the Costa models, when L = P-donor, are not significantly different from cobaloximes as structural models for cobalamins.

Cobaloximes are not good models for cobalamins in that the dissociation rate of the neutral axial ligand is relatively low compared to that of cobalamins.[13] If we initially restrict the comparison to L = $P(OMe)_3$ and PPh_3, we find dissociation rates for the Costa model system (Table VIII) to be greater for L = PPh_3 but lesser for L = $P(OMe)_3$.

If comparisons are extended to all $[LCo((DO)(DOH)pn)CH_3]ClO_4$ and $LCo(DH)_2CH_3$ (Figure 1 and Table IV) it is clear that the relative reactivity is dependent on L. There are six complexes in which $[LCo((DO)(DOH)pn)CH_3]ClO_4$ are more reactive and four complexes in which $LCo(DH)_2CH_3$ are more reactive. In general, the less reactive $[LCo((DO)(DOH)pn)CH_3]ClO_4$ have L with P–O bonds. This finding could reflect the apparently somewhat greater sensitivity of $[LCo((DO)(DOH)pn)CH_3]ClO_4$ to L bulk in comparison to $LCo(DH)_2CH_3$. In addition, for L of similar bulk (PPh_3, $P(4\text{-}Me_2NPh)_3$), increasing ligand basicity leads to a greater decrease in rate for $[LCo((DO)(DOH)pn)CH_3]ClO_4$ than for $LCo(DH)_2CH_3$. For compounds of the type $PRPh_2$, the effects of basicity and bulk are evident. For $PEtCNPh_2$ and $PEtPh_2$, ligands of similar bulk, the rate ratio (DO)(DOH)pn/$(DH)_2$ is 7.8 for the less basic $PEtCNPh_2$ compounds and 1.7 for the more basic $PEtPh_2$ compounds. Similar comparison of P-*i*-$PrPh_2$ with $PEtPh_2$ give a ratio of 1.3 and 1.7, respectively. Compared to $PEtPh_2$, the bulkier P-*i*-$PrPh_2$ ligand should be a better leaving ligand for the (DO)(DOH)pn system based on bulk but a worse leaving ligand based on basicity. The net result is that these ligands and $PCyPh_2$ have rate ratios for (DO)(DOH)pn/$(DH)_2$ of ca. 1.5. For all L in Table IV, the average value of this ratio is 2.2.

From a broader perspective, these differences are small and it must be concluded that there is really no significant difference between the $Co(DH)_2$ and Co((DO)(DOH)pn) systems as far as structure and reactivity of the L ligand are concerned. Somewhat larger, but nevertheless still small differences were found for L = py ligands in a previous study.[18]

In a previous study,[18] we found little difference between the two systems with L = py-type ligands and R = alkyl groups, which were varied in bulk and electron-donor ability. However, py type ligands are relatively nonbulky. Therefore, on the basis of the results presented here and preliminary studies, the steric effects are expected to be more significant for the Costa system when *both* L and R are bulky.

It is much easier to reduce Costa-type compounds than cobaloximes.[23] Since Co–C bond homolysis in B_{12}-dependent enzymic reactions involves both steric factors and the formation of Co(II) species,[1-7] the Costa-type compounds are clearly superior to the cobaloximes as B_{12} models.

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Registry No. I, 101224-80-0; II, 101224-81-1; $[PEtPh_2Co((DO)(DOH)pn)CH_3]ClO_4$, 101224-59-3; $[P(EtCN)Ph_2Co((DO)(DOH)pn)CH_3]ClO_4$, 101224-61-7; $[P(OEt)Ph_2Co((DO)(DOH)pn)CH_3]ClO_4$, 101224-63-9; $[P(OMe)_2PhCo((DO)(DOH)pn)CH_3]ClO_4$, 101224-65-1; $[P(OMe)_3Co((DO)(DOH)pn)CH_3]ClO_4$, 101224-66-2; $[PPh_3Co((DO)(DOH)pn)CH_3]ClO_4$, 101224-68-4; $[P(Cy)Ph_2Co((DO)(DOH)pn)CH_3]ClO_4$, 101224-70-8; $[P(i\text{-}Pr)Ph_2Co((DO)(DOH)pn)CH_3]ClO_4$, 101224-72-0; $[P(4\text{-}Me_2NPh)_3Co((DO)(DOH)pn)CH_3]ClO_4$, 101224-74-2; $[P(Vi)Ph_2Co((DO)(DOH)pn)CH_3]ClO_4$, 101224-76-4; $[PBu_3Co((DO)(DOH)pn)CH_3]ClO_4$, 57385-47-4; $[H_2OCo((DO)(DOH)pn)CH_3]ClO_4$, 23940-46-7; $[(ANIL)Co((DO)(DOH)pn)CH_3]ClO_4$, 101224-78-6; $[H_2OCo((DO)(DOH)pn)CH_3]PF_6$, 101224-79-7.

Supplementary Material Available: Tables of elemental analyses, anisotropic thermal parameters, hydrogen atom coordinates, and complete bond lengths and bond angles (11 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (26 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Complexes of Thallium(I) and -(III) Containing 1,4,7-Triazacyclononane (L) Ligands. Kinetics and Mechanism of the Reduction of $[L_2Tl^{III}]^{3+}$. Crystal Structure of (*N*,*N*′,*N*″-Trimethyl-1,4,7-triazacyclononane)thallium(I) Hexafluorophosphate

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The macrocycles 1,4,7-triazacyclononane (L), $C_6H_{15}N_3$, and *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane (L′), $C_9H_{21}N_3$, reacted with $TlCl_3 \cdot 4H_2O$ (1:1) in chloroform, affording $LTlCl_3$ and $L'TlCl_3$, respectively. $LTlI_3$, $L'TlI_3$, and $LTlBr_3$ were prepared as orange-red solid materials. From a suspension of thallium(III) nitrate and 1,4,7-triazacyclononane (1:4) in chloroform colorless $[TlL_2](NO_3)_3$ was obtained. Thallium(I) nitrate reacted with *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane in water to give upon addition of $NaPF_6$ or $NaClO_4 \cdot H_2O$ the colorless salts $L'Tl(PF_6)$ and $L'Tl(ClO_4)$, respectively. The crystal structure of $L'Tl(PF_6)$ has been determined by X-ray crystallography. Crystals of $L'Tl(PF_6)$ belong to the orthorhombic space group *Pbca* with a = 11.77 (1) Å, b = 11.89 (1) Å, c = 23.19 (2) Å, V = 3245.3 Å^3, and Z = 8. Least-squares refinement of the structure based on 1409 observations led to final discrepancy indices of R = 0.039. The structure consists of discrete $L'Tl^+$ cations and PF_6^- anions. The lone pair of valence electrons of thallium(I) are considered to be stereochemically active in the solid. The kinetics of the reduction of $[TlL_2]^{3+}$ with the strong one-electron reductant $[Co^{II}L_2]^{2+}$ in aqueous solution (pH 7; I = 0.5 M ($LiNO_3$)) have been measured. The stoichiometry of the reaction has been determined: 2Co(II) + Tl(III) → 2Co(III) + Tl(I). A simple second-order rate law has been established for the formation of $[Co^{III}L_2]^{3+}$ and TlL^+ ($k = 3.4 \times 10^{-2}$ M^{-1} s^{-1}, 25 °C, I = 0.5 M). Outer-sphere one-electron transfer from Co(II) to Tl(III) with concomitant formation of a very reactive intermediate Tl(II) species is proposed to be the rate-determining step.

Introduction

In two papers we have shown that the small tridentate macrocycles 1,4,7-triazacyclononane (L) and *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane (L′) form stable complexes with the heavier main-group metals lead(II)[2] and indium(III)[3] even in aqueous solution. The tridentate N-donor ligands coordinate facially in an octahedral ligand environment to these metal centers.

We here wish to report a series of such complexes containing the large thallium(I) and thallium(III) metal centers, respectively. Thallium porphyrin complexes have been investigated fairly extensively,[4-7] but structural information on thallium compounds with saturated macrocyclic N-donor ligands is very scarce. Moras and Weiss[8] have reported the X-ray structure of the thallium(I) cryptate (222), $[(C_{18}H_{36}N_2O_6)Tl]HCOO \cdot H_2O$, Farago[9] has reported thallium(I) complexes with macrocyclic crown polyethers, and Popov et al. have measured some stability constants of macrocyclic thallium(I) complexes,[10] but no structural determinations had been carried out. We have determined the crystal structure of $L'Tl(PF_6)$, which contains $L'Tl^+$ cations and noncoordinated PF_6^- anions. This complex appears to be the first example of a thallium(I) complex with a saturated N-donor ligand, which has been characterized by X-ray crystallography.

In addition, the preparation of $[Tl^{III}L_2](ClO_4)_3$ consisting of $[Tl^{III}L_2]^{3+}$ cations, which are stable in aqueous solution, has prompted us to study the kinetics of its noncomplementary redox reaction with the strong outer-sphere one-electron-transfer reagent $[Co^{II}L_2]^{2+}$ according to eq 1. The exact nature of reduced Tl(I) species has not been identified unambiguously.

$$2[Co^{II}L_2]^{2+} + [Tl^{III}L_2]^{3+} \rightarrow 2[Co^{III}L_2]^{3+} + LTl^+ + L \qquad (1)$$

Attempts to identify a thallium(II) intermediate species, which is proposed from the kinetic study, using normal and ultrafast cyclic voltammetry have failed.[28]

Experimental Section

The ligands 1,4,7-triazacyclononane (L)[11a] and *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane (L′)[11b] have been prepared as described in the literature.

Preparation of Complexes. $L'Tl(PF_6)$. A solution of thallium(I) nitrate (0.27 g; 1 mmol) and *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane (0.18 g; 1 mmol) in water (50 mL) was heated to 90 °C for 30 min, after which time 0.4 g of potassium hexafluorophosphate was added. When the mixture was cooled to room temperature, a colorless solid precipitated, which was filtered off. X-ray-quality crystals were grown from a more dilute solution (300 mL of water) within 14 days at room temperature in an open vessel (yield 86%).

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