Organocobalt B_{12} Models with Very Long Co–C(tertiary) Bonds. Synthesis and Spectroscopic, Kinetic, and Structural Properties of *trans*-Bis(dimethylglyoximato)adamantyl(L)cobalt(III) with L = Trimethyl Phosphite and Triisopropyl Phosphite

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The synthesis and kinetic and solution characterization of $(MeO)_3PCo(DH)_2R$, where DH = monoanion of dimethylglyoxime and R = alkyl group, are reported and discussed. Crystal structures of the complexes with R = 1-adamantyl, $(MeO)_3PCo(DH)_2adam$ (1) and $(i\text{-PrO})_3PCo(DH)_2adam$ (2), are reported. 1 crystallizes in space group $P2_1/c$ with $a = 15.342$ (2) Å $b = 9.826$ (3) Å, $c = 17.925$ (4) Å, $\beta = 100.40$ (3)°, and $Z = 4$. 2 crystallizes in space group *Pbca* with $a = 10.914$ (4) Å, $b = 20.201$ (4) Å, $c = 29.101$ (8) Å, and $Z = 8$. The final *R* indexes were 0.056 (1) and 0.050 (2) for 4514 (1) and 2842 (2) independent reflections. The most interesting result concerns the Co–C bond lengths which are the longest so far reported, being 2.214 (3) and 2.199 (6) Å in 1 and 2, respectively. Furthermore, the Co–P distance of 2.313 (2) Å in 1 is significantly longer than those reported for other cobaloximes containing $(MeO)_3P$. This structural feature correlates with the fastest $(MeO)_3P$ leaving rate and the most downfield ^{31}P NMR shift of any complex of the type $(MeO)_3PCo(DH)_2R$. An even longer Co–P distance of 2.367 (2) Å is found in 2, as expected on the basis of the cone angle of $(i\text{-PrO})_3P$, which is larger than that of $(MeO)_3P$. A fairly linear relationship between log *k* for the $(MeO)_3P$ dissociation and ^{31}P NMR chemical shift for the series $(MeO)_3PCo(DH)_2R$ (R = alkyl group) is found, with adam at the extreme end of good trans effect/influence ligands.

Introduction

We have recently reviewed[2] in depth the effects of changes of axial ligands on the properties of cobaloximes $LCo(DH)_2R$, where L = neutral ligand, R = alkyl group, and DH = monoanion of dimethylglyoxime. One of the most interesting features of such B_{12} models was the significant influence of the electronic and the steric properties of the axial ligands on their spectroscopic, structural, and kinetic properties. Linear relationships between solid-state and solution properties often are found[2] and allow us to rationalize the behavior of these complexes in terms of structural parameters. More recently we have reported[3] the longest accurately determined Co–C(tertiary) bond (2.154 (5) Å in $(1\text{-Nmeim})Co(DH)_2adam$ (3) (1-Nmeim = 1-methylimidazole)). This very long bond, compared to those reported in cobaloximes containing a primary (2.00 Å) or secondary (2.10 Å) C bonded to Co, mainly derives from the tertiary nature of the Cα adamantyl atom. Since we have reported that the Co–C bond in cobaloximes may be lengthened by the effect of bulkier L ligands,[2] even longer Co–C bonds should be expected with ligands L bulkier than 1-Nmeim. On the other hand, in 3 the axial Co–N bond length of 2.065 (4) Å is very similar to that reported for the methyl analogue,[4] despite the expected larger trans influence of adamantyl as compared with that of methyl. However, differences in the orientation of the 1-Nmeim ligand with respect to the $(DH)_2$ equatorial ligands and in the bending angle (α) between the two DH units were assumed to be responsible for the unexpectedly short Co–N bond in 3.

Thus, it was of interest to gain further insight into the properties of complexes with adam ligands. The adam ligand is rigid, and no solution organocobalt chemistry has been reported for these complexes.

Experimental Section

Instrumentation. Ligand exchange rates were monitored spectrophotometrically with a Durrum-Gibson D110 stopped-flow spectrophotometer or a Cary 14 spectrophotometer equipped with a thermostated cell compartment (25.0 ± 0.04 °C). ^{31}P NMR spectral measurements were made with an IBM WP200-SY (81.01 MHz) spectrometer. ^{13}C NMR spectra were obtained with a Varian CFT20 (20.0 MHz) spectrometer.

Measurement and Treatment of Rate Data. Pseudo-first-order rate data were obtained for the substitution of $(MeO)_3P$ from $(MeO)_3PCo(DH)_2R$ (0.01 M) by 1-methylimidazole (0.1–0.4 M) in CH_2Cl_2 as described previously.[5] The data were treated with the standard, integrated expression for a first-order process using linear least-squares regression analysis, yielding k_1, eq 1 ($(DH)_2R$ assumed), as the observed rate constant. These reactions are known to proceed by a nearly ideal S_N1LIM mechanism.[6]

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

$$L' + Co \xrightarrow{k_2} L'Co$$

Reagents. All reagents were from Aldrich and were used without further purification unless otherwise noted. Trimethyl phosphite and 1-methylimidazole employed in kinetic studies were purified as described previously.[5] CH_2Cl_2 was from Baker.

Preparations. All cobaloximes were prepared from a published procedure,[6] except the adamantyl derivatives. Analyses for all $(MeO)_3P$ compounds are given in the supplementary material.

$(MeO)_3PCo(DH)_2adam$. A 4.15-g (0.01 mol) sample of $C_6H_5NH_2Co(DH)_2Cl$ was suspended in MeOH (400 mL) with N_2 bubbling through. A potassium hydroxide solution (13 pellets in a minimum amount of water) was then added. When solution appeared to be complete, the solution was treated with a few drops of aqueous sodium borohydride (0.37 g, 0.01 mol, in a minimum amount of water). Then 8.56 g (0.04 mol) of 1-bromoadamantane was added, followed by the rest of the sodium borohydride so-

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Table I. Crystallographic Data for Compounds 1 and 2

	$CoPN_4O_7C_{21}H_{37}$ (1)	$CoPN_4O_7C_{27}H_{50}$ (2)
M_w	548.5	632.7
a, Å	15.342 (3)	10.914 (4)
b, Å	9.826 (3)	20.201 (4)
c, Å	17.925 (4)	29.101 (8)
β, deg	100.40 (3)	
D_{measd}, g cm^{-3}	1.36	1.31
D_{calcd}, g cm^{-3}	1.37	1.31
Z	4	8
systematic absences	$h0l$(l odd), $0k0$(k odd)	$hk0$(h odd), $h0l$ (l odd), $0kl$(k odd)
space group	$P2_1/c$	$Pbca$
μ, cm^{-1}	7.5	6.3
λ(Mo Kα), Å	0.7107	0.7107
$F(000)$	1160	2704
cryst dimens, cm	0.03 × 0.02 × 0.02	0.04 × 0.03 × 0.02
no. of reflecns measd	8386	8497
no. of indep reflecns ($I > 3\sigma(I)$)	4514	2842
no. of varied parameters	304	361
max 2θ, deg (Mo Kα)	60	60
R	0.056	0.050
Rw	0.074	0.066

lution. The reaction mixture was warmed (~40 °C) and stirred (under nitrogen) for 3–4 h; it was then poured into water (150 mL) in a separatory funnel and extracted with two 60-mL portions of carbon tetrachloride. The carbon tetrachloride extracts were washed once with 70 mL of H_2O and dried over $MgSO_4$. The filtered solution was then concentrated on a rotary evaporator and the product separated as a yellow-brown powder, which was collected and washed well with petroleum ether (yield 24%). The product, which was recrystallized from acetone–water, had an ^{1}H NMR spectrum consistent with the desired $C_6H_5NH_2Co(DH)_2$adam. A 0.59-g sample was treated with an equivalent weight of Dowex 50-X8-100 resin in 80% MeOH (100 mL). The suspension was stirred (at 25 °C) for 35 min and then filtered (paper) to remove the resin. The filtrate was collected in a 50-mL round-bottom flask and concentrated on a rotary evaporator. The dark red-brown solid which separated was collected in 65% yield and washed first with H_2O, dried, and then washed with methylene chloride. This material had an ^{1}H NMR spectrum consistent with $H_2OCo(DH)_2$adam. A solution of 0.143 g (1.15 mmol) of trimethyl phosphite was dissolved in CH_2Cl_2 (20 mL) and the solution treated with 0.3 g (0.68 mmol) of $H_2OCo(DH)_2$adam. The dark solution became clear and a light yellow-orange color. Petroleum ether was added and small yellow crystals gradually came out of the solution as the CH_2Cl_2 evaporated. The yellow crystals were washed with a small amount of petroleum ether and air-dried; yield 98%. The compound was then recrystallized from acetone–water mixture as yellow prisms, suitable for the X-ray study.

(i-PrO)$_3$PCo(DH)$_2$adam was prepared similarly, and crystals suitable for X-ray analysis were obtained from MeOH–H_2O.

Crystal Data. Cell dimensions were determined from Weissenberg and precession photographs and refined on a CAD4 automated single-crystal diffractometer. The results are given in Table I. The intensity data were collected by the $\omega/2\theta$ scan technique, using monochromatized Mo Kα radiation. Three standard reflections, measured every 50 min, showed no systematic variation throughout the data collections. The intensities for which $I > 3\sigma(I)$ were corrected for Lorentz and polarization factors but not for absorption (Table I) and anomalous dispersion.

Solution and Refinement of the Structures. Structures of both 1 and 2 were solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares methods. In the final cycles, the contribution of hydrogen atoms at calculated positions (held constant at $B = 5$ Å^2) and the anisotropic temperature factors for non-hydrogen atoms were included. In 1, each oxygen atom of the $(MeO)_3P$ ligand was located at two different positions, with occupancy factors of 0.6 and 0.4, respectively. This disorder may be described as two different orientations of the $(MeO)_3P$ ligand, assuming a rotation of ~60° of the (PO_3) moiety along the Co–P bond (Figure 1). Therefore, the hydrogen atoms attached to C(19), C(20), and C(21) were not included, and the O atoms were refined isotropically. Final R values are given in Table I. The final weighting scheme was $w = 1/(\sigma^2(F) + (pF)^2 + q)$, where $p = 0.02$ and $q = 1.0$ for 1 and $p = 0.04$ and $q = 2.0$ for 2 were chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of F_o and $(\sin\theta)/\lambda$. Atomic scattering factors were those given in ref 7. All the calculations were done by using the computer programs from Enraf-Nonius SDP programs.[8] Final positional parameters for non-hydrogen atoms are given in Table II. Anisotropic thermal parameters, calculated and observed structure factors, and hydrogen atom fractional coordinates have been deposited as supplementary material.

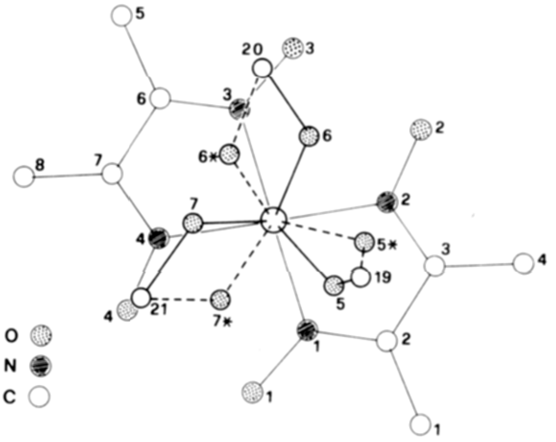

Figure 1. Atom numbering scheme for the $Co(DH)_2$ moiety for both 1 and 2. The two orientations and the atom numbering scheme of the phosphite in 1 are also shown.

Results and Discussion

Description and Discussion of the Structures. The numbering scheme of the equatorial $(DH)_2$ ligands for both 1 and 2 is shown in Figure 1, whereas ORTEP drawings of crystallographically independent molecules 1 and 2 with the numbering scheme for the atoms of the axial ligands are depicted in Figure 2.

The four N atoms of the $(DH)_2$ units are coplanar within ±0.005 Å (1) and ±0.008 Å (2). The cobalt atom displacements from their mean planes, d, are 0.015 Å (1) and 0.006 Å (2) toward adamantyl. The deviation from planarity may be represented by the dihedral angles α between the two $(DH)_2$ units, which are −7.3° (1) and −7.5° (2) (Table III). The negative sign indicates a bending toward phosphite. Bond lengths and angles of the $Co(DH)_2$ moiety are very similar in both complexes 1 and 2 and fall within the range reported for several organometallic cobaloximes.[2] The P–Co–C axial fragment is characterized by the geometrical parameters reported in Table III, where the α and d values are also reported and compared with those of other cobaloximes containing $(MeO)_3P$. Comparison shows the following: (i) The very long Co–P bond for 1 suggests that adamantyl exerts a very strong trans influence, significantly larger than that of i-Pr. Unfortunately, the isopropyl analogue has not been structurally characterized. However, the Co–P distance of 2.270 (1) Å reported[9] for $MeC(CH_2O)_3PCo(DH)_2(i\text{-}Pr)$ could be assumed to be close to that of the $(MeO)_3P$ derivative. For this reason it has been included in Table III. Data in this

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Table II. Atomic Parameters of Non-Hydrogen Atoms with Their ESD's in Parentheses for $(MeO)_3PCo(DH)_2$adam (1) and $(i\text{-}PrO)_3PCo(DH)_2$adam (2)[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
				1					
Co	0.74890 (3)	0.07923 (5)	0.24088 (2)	2.768 (8)	C4	1.0225 (3)	0.0315 (6)	0.2739 (4)	6.4 (1)
P	0.77407 (8)	0.2308 (1)	0.34120 (6)	4.23 (2)	C5	0.5657 (3)	0.3497 (5)	0.1225 (3)	4.46 (9)
O1	0.7502 (2)	−0.1372 (3)	0.3477 (2)	4.53 (6)	C6	0.6148 (2)	0.2417 (4)	0.1707 (2)	3.18 (7)
O2	0.8950 (2)	0.1970 (3)	0.1873 (2)	4.48 (6)	C7	0.5738 (2)	0.1453 (4)	0.2154 (2)	3.57 (8)
O3	0.7484 (2)	0.2994 (3)	0.1370 (2)	4.02 (6)	C8	0.4780 (3)	0.1410 (6)	0.2182 (3)	5.6 (1)
O4	0.6031 (2)	−0.0395 (3)	0.2942 (2)	4.48 (6)	C9	0.7267 (3)	−0.0637 (3)	0.1438 (2)	3.22 (7)
O5	0.8505 (4)	0.1839 (6)	0.4044 (3)	5.7 (1)*	C10	0.7867 (4)	−0.0295 (6)	0.0887 (3)	7.2 (1)
O5*	0.8793 (6)	0.2400 (9)	0.3790 (5)	5.7 (2)*	C11	0.6315 (4)	−0.0569 (6)	0.1018 (3)	6.8 (1)
O6	0.8100 (3)	0.3806 (6)	0.3184 (3)	4.7 (1)*	C12	0.7432 (4)	−0.2091 (5)	0.1712 (3)	6.2 (1)
O6*	0.7282 (5)	0.3730 (9)	0.3412 (5)	5.5 (2)*	C13	0.7314 (5)	−0.3107 (5)	0.1017 (3)	6.7 (1)
O7	0.6977 (4)	0.2823 (6)	0.3820 (3)	5.4 (1)*	C14	0.7931 (4)	−0.2671 (7)	0.0502 (3)	7.7 (2)
O7*	0.7337 (8)	0.169 (1)	0.4172 (7)	9.7 (3)*	C15	0.7709 (4)	−0.1299 (6)	0.0191 (3)	7.3 (1)
N1	0.7987 (2)	−0.0586 (3)	0.3078 (2)	3.47 (6)	C16	0.6791 (5)	−0.1198 (6)	−0.0186 (3)	8.1 (2)
N2	0.8683 (2)	0.1013 (3)	0.2313 (2)	3.49 (6)	C17	0.6178 (4)	−0.1593 (7)	0.0321 (3)	7.2 (1)
N3	0.6990 (2)	0.2196 (3)	0.1757 (2)	3.10 (6)	C18	0.6364 (4)	−0.2981 (6)	0.0631 (3)	7.3 (2)
N4	0.6304 (2)	0.0584 (3)	0.2514 (2)	3.32 (6)	C19	0.8964 (6)	0.2882 (9)	0.4622 (4)	15.0 (2)
C1	0.9337 (3)	−0.1639 (6)	0.3775 (3)	6.1 (1)	C20	0.7555 (4)	0.4882 (6)	0.2931 (3)	6.2 (1)
C2	0.8840 (3)	−0.0705 (5)	0.3203 (2)	3.94 (8)	C21	0.6500 (5)	0.1896 (8)	0.4276 (4)	10.6 (2)
C3	0.9260 (3)	0.0230 (5)	0.2734 (2)	4.02 (9)					
				2					
Co	0.08043 (6)	0.23938 (3)	0.12347 (3)	2.47 (1)	C8	−0.1857 (7)	0.1249 (4)	0.0582 (3)	5.3 (2)
P	0.1922 (1)	0.13951 (7)	0.13063 (6)	2.91 (3)	C9	−0.0335 (5)	0.3289 (3)	0.1189 (2)	3.0 (1)
O1	−0.0189 (4)	0.2177 (2)	0.2123 (1)	4.0 (1)	C10	−0.0212 (8)	0.3727 (4)	0.1616 (3)	6.6 (2)
O2	0.2852 (4)	0.3185 (2)	0.0980 (2)	4.1 (1)	C11	−0.1689 (6)	0.3119 (4)	0.1139 (3)	5.8 (2)
O3	0.1793 (4)	0.2604 (2)	0.0337 (1)	3.99 (9)	C12	0.0040 (8)	0.3695 (4)	0.0775 (3)	6.8 (2)
O4	−0.1290 (4)	0.1624 (2)	0.1487 (2)	3.91 (9)	C13	−0.0761 (7)	0.4351 (4)	0.0723 (3)	5.5 (2)
O5	0.1667 (4)	0.0981 (2)	0.1758 (2)	4.3 (1)	C14	−0.0549 (8)	0.4732 (4)	0.1152 (3)	6.7 (2)
O6	0.1483 (4)	0.0894 (2)	0.0921 (2)	3.8 (1)	C15	−0.1013 (8)	0.4373 (4)	0.1568 (3)	6.1 (2)
O7	0.3381 (3)	0.1362 (2)	0.1310 (2)	4.04 (9)	C16	−0.2303 (8)	0.4163 (4)	0.1509 (3)	6.8 (2)
N1	0.0721 (4)	0.2445 (2)	0.1878 (2)	3.2 (1)	C17	−0.2488 (7)	0.3772 (4)	0.1081 (3)	5.7 (2)
N2	0.2179 (4)	0.2933 (2)	0.1328 (2)	3.1 (1)	C18	−0.2032 (8)	0.4126 (4)	0.0670 (3)	6.0 (2)
N3	0.0887 (4)	0.2324 (2)	0.0586 (2)	3.08 (9)	C19	0.2389 (8)	0.0981 (4)	0.2177 (2)	5.4 (2)
N4	−0.0581 (4)	0.1852 (2)	0.1137 (2)	2.9 (1)	C20	0.157 (1)	0.0961 (5)	0.2579 (3)	8.7 (3)
C1	0.1730 (8)	0.2824 (4)	0.2587 (2)	6.0 (2)	C21	0.325 (1)	0.0438 (6)	0.2185 (3)	9.1 (3)
C2	0.1629 (6)	0.2753 (3)	0.2080 (2)	3.8 (1)	C22	0.1672 (6)	0.0180 (3)	0.0925 (3)	4.2 (2)
C3	0.2488 (6)	0.3039 (3)	0.1756 (2)	3.5 (1)	C23	0.0485 (8)	−0.0137 (4)	0.1055 (4)	8.7 (3)
C4	0.3578 (7)	0.3428 (4)	0.1890 (3)	6.1 (2)	C24	0.2098 (9)	−0.0024 (4)	0.0461 (4)	6.4 (2)
C5	0.0080 (7)	0.1804 (4)	−0.0110 (2)	5.0 (2)	C25	0.4193 (6)	0.1760 (3)	0.1026 (2)	3.9 (1)
C6	0.0067 (6)	0.1952 (3)	0.0392 (2)	3.2 (1)	C26	0.5300 (7)	0.1894 (5)	0.1309 (3)	6.9 (2)
C7	−0.0818 (6)	0.1688 (3)	0.0713 (2)	3.4 (1)	C27	0.4480 (7)	0.1405 (4)	0.0595 (3)	5.2 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2\mathrm{B}(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III.[a] Geometry of the R-Co-P Axial Fragment and α and d Values for $(MeO)_3PCo(DH)_2R$ Complexes

R	Co-P/Å	Co-R/Å	P-Co-R/deg	α/deg[b]	d/Å
adam	2.313 (1)	2.214 (3)	178.9 (8)	−7.3	−0.015
i-Pr[c]	2.270 (1)	2.13 (1)	171.4 (1)	+4.2	+0.01
Me	2.256 (4)	2.014 (14)	177.5 (2)	+10	+0.10
CH_2CF_3	2.256 (2)	2.032 (7)	174.0 (2)	+3	+0.01
CH_2CN	2.244 (2)	2.036 (7)	176.3 (2)	+7	+0.05
CN	2.225 (2)	1.909 (8)	177.8 (2)	+4	+0.02
2	2.367 (2)	2.199 (6)	176.3 (2)	−7.5	−0.006

[a] Values are reported in ref 2, except those of the present work. Data for 2 are also reported. [b] Positive values of α and d indicate the bending is toward R and displacement toward phosphite; negative values indicate bending and displacement in the opposite direction. [c] The neutral ligand is the "caged" phosphite $MeC(CH_2O)_3P$.

table suggest that the Co–P lengthening should be due to a combined effect of the steric and electronic trans influence.[10] (ii) The even longer Co–P bond for 2 may be attributed to the bulk of $(i\text{-}PrO)_3$ which is larger than that of $(MeO)_3P$. We have found that the bulk of the phosphines in $PR_3Co(DH)_2X$, expressed as Tolman's cone angle,[11] increases linearly with the Co–P distance and that an increase of ~50° in the cone angle provokes a lengthening of ~0.12 Å.[12] From the observed lengthening of 0.05 Å, we calculate the difference in cone angles between phosphites in 1 and 2 is 23°. (iii) The Co–C bond length of 2.214 (3) Å in 1 is the longest so far reported.

Since the Co–C bond length is also significantly longer than those reported in $LCo(DH)_2$adam, with L = 1-Nmeim (2.154 (5) Å)[3] and L = $4Me_2N$-pyridine (2.160 (4) Å),[13] this result is further evidence that the Co–C bond length may be influenced by steric effects.[10] In fact, this influence becomes evident only when the Co–C bond is already

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Table IV. Rate and ^{31}P and NMR Spectroscopic Data for $(MeO)_3PCo(DH)_2R$[a]

R	k_1, s^{-1}	^{31}P NMR[b]	^{13}C NMR[e]	$^2J_{PC}$, Hz
adam	$(5.1 \pm 0.5) \times 10^1$	136.7 [c]	52.27[c]	6.4
i-Pr	2.3 ± 0.3	131.9	52.18	6.4
i-C_4H_9	$(1.9 \pm 0.3) \times 10^{-1}$	130.6[c]	52.25	6.5
C_2H_5	$(8.6 \pm 0.7) \times 10^{-2}$	131.1	52.16	5.6
$(CH_2)_3CN$	$(9.0 \pm 0.8) \times 10^{-3}$	129.4	52.51	6.6
Me	$(4.1 \pm 0.2) \times 10^{-3}$	128.2	52.24	5.9
CH_2Br	$(2.3 \pm 0.4) \times 10^{-4}$	126.3	52.87	6.7
CH_2Cl	$(2.2 \pm 0.3) \times 10^{-4}$	126.5	52.77	6.8
$CHCl_2$	$(1.7 \pm 0.3) \times 10^{-4}$[d]	122.4	53.41	7.9
CH_2CN		122.2	53.40	7.6
CH_2CF_3		121.9	53.19	7.4
CN		102.9	54.45	8.6
$(MeO)_3P$		141.0	49.14	10.6

[a] *Rate and spectroscopic measurements made in* CH_2Cl_2 (25 °C) and $CDCl_3$ (probe temperature), respectively. Also see ref 2. [b] ppm from external H_3PO_4; from: Kargol, J. A.; Crecely, R. W.; Burmeister, J. L.; Toscano, P. J.; Marzilli, L. G. *Inorg. Chim. Acta* **1980**, **40**, 79 unless otherwise noted. [c] This work. [d] Rates for additional R groups can be found in: Ramsden, J. H. Ph.D. Thesis, The Johns Hopkins University, 1980. [e] ppm from internal Me_4Si.

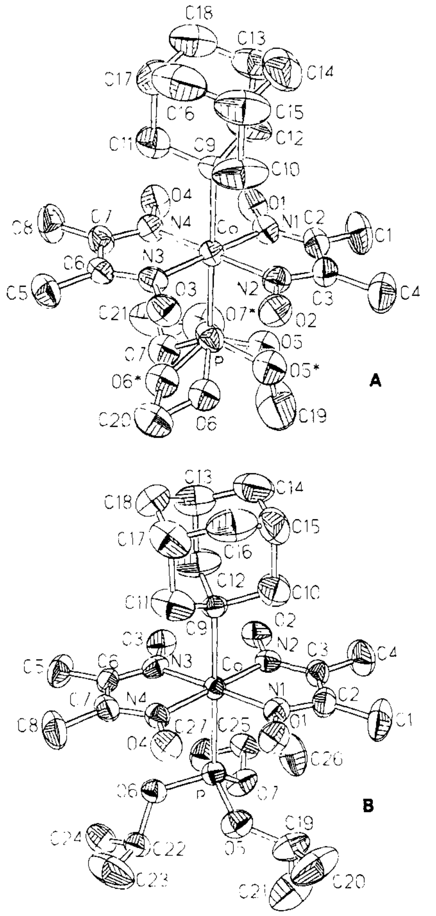

Figure 2. ORTEP drawings for 1 (A) and 2 (B) together with the *numbering scheme for the axial ligands.*

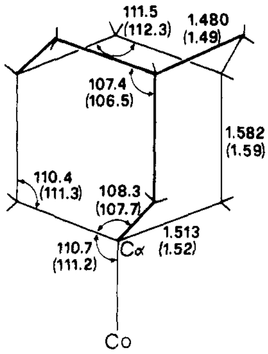

Figure 3. Mean values (assuming a threefold symmetry) of the adamantyl ligand both lengths (Å) and angles (deg). Figures in *parentheses refer to 2.*

lengthened by the interaction of the bulky alkyl group with the equatorial moiety and the ligand trans to the alkyl is bulky. For example, in $LCo(DH)_2R$ (R = Me, CH_2CMe_3) complexes the Co–Me distance is 1.990 (5) and 2.056 (6) Å for L = H_2O and PPh_3, respectively, while the Co–CH_2CMe_3 distance is 2.044 (7) and 2.118 (9) Å for the same neutral ligands.[14]

We have shown[15] that the interaction of axial ligands with the $Co(DH)_2$ moiety may provoke geometrical distortions in the axial ligand itself in addition to lengthening of the axial bond. Inspection of the geometry of the adam group shows that distortions, very similar in both 1 and 2, occur. However, the threefold symmetry along the Co–Cα direction is almost preserved. The mean values of bond lengths and angles are reported in Figure 3. The distortions may be described as a slight squeeze of the Cα tetrahedron with increase of the Co–Cα–C angles (111°) and, correspondingly, decrease of C–Cα–C angles (108°) with respect to tetrahedral values. Analogously, the cyclohexyl ring opposite to Cα is squeezed with opening of the internal C–C–C angles to 112° and shortening of the C–C bonds to 1.48 Å. Consequently, a decrease of the external angles (107°) and a lengthening of the C–C bonds (1.58 Å) nearly parallel to the Co–Cα direction is observed. Typical values of bond lengths and angles reported for substituted adamantane are those found for 1,3,5,7-tetranitroadamantane,[16] which range from 1.528 to 1.539 (3) Å and from 110.3 to 111.5 (3)°, respectively. The neutral ligands have the expected geometry, within the experimental errors.[2]

Solution Properties. A very long Co–P bond is observed for $(MeO)_3PCo(DH)_2adam$. The consideration of the structural features of this and similar complexes discussed above prompted us to compare also their solution properties (Table IV and Figure 4).

The most noteworthy feature of this comparison is that $(MeO)_3PCo(DH)_2adam$ has a dissociation rate and a ^{31}P NMR shift for the $(MeO)_3P$ ligand which is at the extreme end of the complexes with good trans effect/influence ligands. Characteristically, when R is a good trans influence ligand, the chemical shifts of the coordinated L ligand

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(14) Bresciani-Pahor, N.; Calligaris, M.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1982**, 2549.

(15) Bresciani-Pahor, N.; Randaccio, L.; Toscano, P. J.; Marzilli, L. G. *J. Chem. Soc., Dalton Trans.* **1982**, *567.*

(16) George, C.; Gilardi, R. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 674 and references therein.

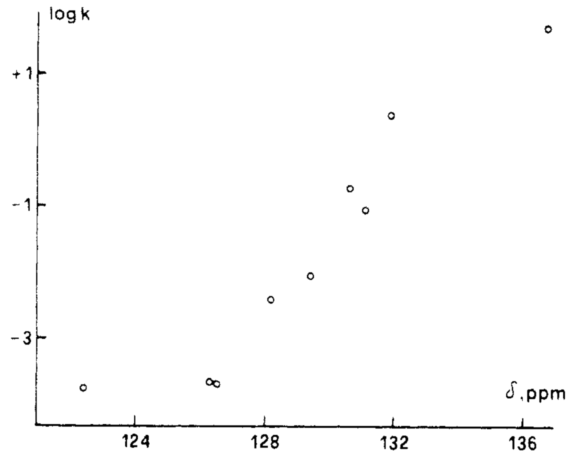

Figure 4. Plot of the log *k* for the $(MeO)_3P$ dissociation vs. ^{31}P NMR chemical shifts for the $(MeO)_3PCo(DH)_2R$ series with R (from left) = $CHCl_2$, CH_2Cl, CH_2Br, Me, $(CH_2)_3CN$, C_2H_5, *i*-C_4H_9, *i*-Pr, and adamantyl.

are closer to those of the uncoordinated L than when L is coordinated to a cobaloxime with a poor trans influence ligand. Typically, ^{31}P NMR data for coordinated P-donor ligands are complicated by steric as well as electronic effects.[17,18] However, ^{31}P NMR shifts of coordinated $(MeO)_3P$ do appear to reflect primarily the electronic properties of R. These shifts move downfield as R becomes a better electron donor. The observed shift for the adamantyl complex of 136.7 ppm can be compared to the free ligand value of 141.0 ppm. Thus, the value for the adamantyl derivative is midway between the free ligand shift and the shift for the complex with the very good electron-donating *i*-Pr group. Correspondingly, the Co–P bond length is 2.313 (1) Å, and it may be assumed to be 2.27 Å in the *i*-Pr analogue (Table III).

The ^{13}C and J_{PC} NMR data, presented in Table IV, show an interesting independence on the nature of R, when R is Me or a better electron donor. We have no good explanation for this phenomenon. It is not observed, for example, in the ^{13}C spectra of pyridine cobaloximes.[2] We have speculated that the J_{PC} value may change sign going from free to coordinated ligand since usually spectroscopic parameters approach free ligand values for the complexes with good electron-donating R groups.[18] However, for $(MeO)_3P$, the free ligand value is 10.6 Hz, and, for example, in contrast to the alkyl compounds in Table IV, $(CH_3O)_3PCo(DH)_2NO_3$ has a J_{PC} value of 9.2 Hz.

The ^{13}C NMR data anomaly can be explained if some conformational changes could lead to downfield shifts counteracting the upfield shifts resulting from increased electron donation by R. This interpretation seems to be supported by data of Table III. In fact, the lengthening of the Co–P distance occurs along with a change of the α bending from positive to negative values, particularly along the series Me < *i*-Pr < adam.

The structural and spectroscopic data reflect the ground-state properties of the complex. Since the ligand dissociation rate reflects not only the ground-state structure and stability but also the nature of the transition-state species, correlations between rates and structure are usually less successful than those comparing ground-state properties. However, a remarkably good correlation is found between log k_1 for $(MeO)_3$ dissociation and the number of substituents on Me bound to Co (Figure 5). Since the Co–C bond length also reflects the number of substituents, we can conclude that the log k_1 also reflects Co–C bond length.

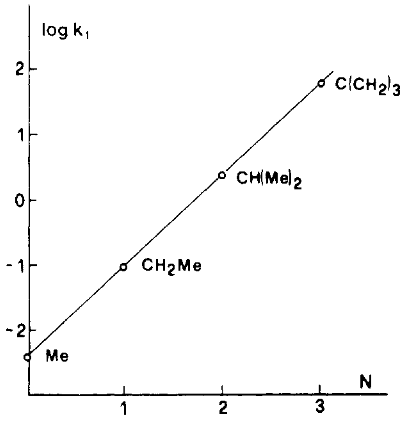

Figure 5. Plot of the log k_1 for $(MeO)_3P$ dissociation vs. *N* (*N* = number of X groups (X = CH_3 or CH_2) on the Co-bound carbon) for $(MeO)_3PCo(DH)_2CH_{3-N}X_N$.

It is difficult to understand the significance of this observation. If the Co–C bond length reflects primarily steric interactions[3,8] between R and the $Co(DH)_2$ moiety, which it clearly does, and if the Co–C bond length is relatively unchanged as the electronic properties of R change, which also appears to be true, then the linear relationship just described could be due to a fortuitous relationship between incremental electronic and steric effects across the series. Both electron donation and steric acceleration of rate should increase going from Me to adam. Thus, the 10^4-fold increase in rate is not surprising. Ligand exchange data are not available for the CH_2CF_3 or CH_2CN complexes. However, these rates should be much slower than those of the Me complex, even though the Co–C bond lengths are slightly longer than for the Me complex. Finally, this study has not given us a clear explanation for the unexpectedly short Co–N bond length in **3**. We are currently trying to obtain a crystalline $LCo(DH)_2$adam complex with an N donor L ligand for which structural comparisons can be made with the related $LCo(DH)_2Me$ compound.

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Registry No. 1, 98540-69-3; 2, 98540-70-6; $C_6H_5NH_2Co(DH)_2$adam, 98540-67-1; $H_2OCo(DH)_2$adam, 98540-68-2; $C_6H_5NH_2Co(DH)_2Cl$, 23575-27-1; $(MeO)_3PCo(DH)_2$(*i*-Pr), 68307-63-1; $(MeO)_3PCo(DH)_2$(*i*-C_4H_9), 72167-26-1; $(MeO)_3PCo(DH)_2C_2H_5$, 68307-64-2; $(MeO)_3PCo(DH)_2(CH_2)_3CN$, 68307-61-9; $(MeO)_3PCo(DH)_2Me$, 25586-92-9; $(MeO)_3PCo(DH)_2CH_2Br$, 42934-27-0; $(MeO)_3PCo(DH)_2CH_2Cl$, 42934-25-8; $(MeO)_3PCo(DH)_2CHCl_2$, 42934-26-9; 1-bromoadamantane, 768-90-1.

Supplementary Material Available: Tables of analytical data, H atom parameters, bond lengths and bond angles, thermal parameters, and observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

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[17] Kargol, J. A.; Crecely, R. W.; Burmeister, J. L.; Toscano, P. J.; Marzilli, L. G. *Inorg. Chim. Acta.* **1980**, *40*, 79.

[18] Randaccio, L.; Bresciani-Pahor, N.; Orbell, J. D.; Calligaris, M.; Summers, M. F.; Snyder, B.; Toscano, P. J.; Marzilli, L. G. *Organometallics*, in press.