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Evidence for Steric Trans Influences and Effects in (Perfluoroisopropyl)cobaloximes. Molecular Structure of *trans*-Bis(dimethylglyoximato)(triphenylphosphine)(perfluoroisopropyl)cobalt(III)

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The preparation and isolation of $LCo(DH)_2[CF(CF_3)_2]$ complexes are described, where L is PPh_3, 4-CNpy, $PhNH_2$, $P(n\text{-}Bu)_3$, 1-methylimidazole, 4-Me_2Npy, 3-Brpy, 3-Mepy, and 2-NH_2py (DH = the monoanion of dimethylglyoxime and py = pyridine). A large number of complexes with various L ligands chosen for their different electronic and steric properties also was prepared in situ. All new compounds were characterized by ^{19}F NMR spectroscopy. The $^{19}F(CF_3)$ chemical shifts were found to be largely independent of electronic effects, if steric parameters of L were kept constant. On the other hand, ^{19}F(Co–CF) chemical shifts linearly correlated well with measures of ligand basicity such as pK_a or Hammett substituent constants for series of ligands that were sterically similar. The complex $Ph_3PCo(DH)_2[CF(CF_3)_2]$ crystallizes in the orthorhombic space group *Pbca*, with $a = 23.374$ (3) Å, $b = 17.551$ (2) Å, $c = 14.985$ (3) Å, $V = 6147.6$ (8) Å^3, and $Z = 8$, and was refined to $R = 0.056$. The structure is the first cobaloxime containing PPh_3 as a ligand where the bending of the equatorial ligands is away from the alkyl group toward PPh_3. For L = 2-NH_2py, a steric trans influence was evident, in that the ambidentate 2-NH_2py ligand showed a marked preference for coordination via the exocyclic amino group. The pseudo-first-order rate constants for ligand-exchange substitution, where L is 4-CNpy or PPh_3, were determined. In the case of PPh_3, a steric acceleration of this rate process was observed; this is the first reported example of a steric trans effect for ligand substitution in an organocobaloxime. The results are interpreted in terms of the large steric bulk of the $CF(CF_3)_2$ ligand, coupled with the weak electron-donating properties of this group.

Introduction

Bis(dimethylglyoximato)cobalt(III) compounds (trivially known as the cobaloximes) have received substantial attention as models for Co–C cleavage reactions relevant to the mechanism of action of coenzyme B_{12},[2-8] as well as agents for the delineation of the factors that influence Co–C bond energies[9-11] and stabilities.[2-4] These compounds are also noteworthy because of their ability to accommodate a wide variety of metal-bound alkyl groups containing a large number of different types of substituents.[2]

Recently, we have reported the synthesis and characterization of alkylcobaloximes containing the novel perfluoroisopropyl ligand.[12] The molecular structure of $pyCo(DH)_2[CF(CF_3)_2]$ (DH = the monoanion of dimethylglyoxime and py = pyridine) was determined;[12] comparisons to $pyCo(DH)_2i\text{-}Pr$[13] suggested that the $CF(CF_3)_2$ ligand is considerably bulkier than *i*-Pr and that significant carbanionic character could be ascribed to the carbon atom attached to cobalt in the fluorinated organometallic complex.

During the course of these studies, it became apparent that it would be of interest to structurally characterize a (perfluoroisopropyl)cobaloxime containing a sterically larger neutral ligand trans to the alkyl group. Consequently, we have prepared $Ph_3PCo(DH)_2[CF(CF_3)_2]$ (1) and determined its molecular structure. In addition, a large number of $LCo(DH)_2[CF(CF_3)_2]$ complexes, in which the electronic and steric properties of L are systematically varied, have been prepared and characterized by ^{19}F NMR spectroscopy. Correlations to measurable properties of the neutral L ligand and comparisons to structural properties of the complexes are drawn.

It was also of interest to examine specific (perfluoroisopropyl)cobaloximes for possible manifestations of a steric trans influence[3,4] or steric trans effect exerted by the large $CF(CF_3)_2$ ligand. We hypothesized that the combination of steric bulk with the poorly electron-donating character of this group might provoke easily observable measures of these occurrences. We have studied the effect of $CF(CF_3)_2$ on the equilibrium involving the coordination site of the ambidentate ligand 2-NH_2py bound to the $Co(DH)_2[CF(CF_3)_2]$ moiety. Further, the ligand-exchange rates have been determined for $LCo(DH)_2[CF(CF_3)_2]$, L = 4-CNpy or PPh_3; evidence for steric acceleration of substitution of the neutral ligand in an alkylcobaloxime

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is presented for the first time.

Experimental Section

Materials and Methods. ^{1}H and ^{19}F NMR spectra were obtained on a Varian XL-300 spectrometer at 299.943 and 282.203 MHz, respectively. Spectra obtained in $CDCl_3$ solution were referenced to internal $(CH_3)_4Si$ (^{1}H) or internal $CFCl_3$ (^{19}F). Elemental analyses were determined by Atlantic Microlab, Inc. (Norcross, GA).

$LCo(DH)_2[CF(CF_3)_2]$. Preparation and isolation of the new complexes followed the previously reported procedure involving treatment of $H_2OCo(DH)_2[CF(CF_3)_2]$ (0.10 g) with ~1.1 equiv of L in CH_2Cl_2,[12] except slight modifications for L = $(n\text{-}Bu)_3P$ or 2-NH_2py (vide infra). Yields and spectral data are as follows.

For L = Ph_3P (**1**), the yield of orange-brown powder was 0.113 g (75%). Anal. Calcd for $C_{29}H_{29}F_7N_4O_4PCo$: C, 48.35; H, 4.06; N, 7.78. Found: C, 48.23; H, 4.14; N, 7.70. ^{1}H NMR ($CDCl_3$): δ 7.26–7.46 (m, 15 H, phenyl), 1.89 (d, 12 H, DH–CH_3, ^5J(P–H) = 2.4 Hz). ^{19}F NMR ($CDCl_3$): –68.58 (m, 6 F, CF_3), –199.9 (br s, 1 F, Co–CF).

For L = 4-CNpy (**2**), the yield of orange-brown powder was 0.086 g (73%). Anal. Calcd for $C_{17}H_{18}F_7N_6O_4Co$: C, 36.31; H, 3.23; N, 14.95. Found: C, 36.49; H, 3.24; N, 14.66. ^{1}H NMR ($CDCl_3$): δ 8.76 (d, 2 H, py α-H), 7.54 (d, 2 H, py β-H), 2.24 (s, 12 H, DH–CH_3). ^{19}F NMR ($CDCl_3$): –69.12 (d, 6 F, CF_3, ^3J(F–F) = 9.5 Hz), –195.3 (br s, 1 F, Co–CF).

For L = $PhNH_2$ (**3**), the yield of orange-brown powder was 0.081 g (70%, based upon the product being a monohydrate). Anal. Calcd for $C_{17}H_{21}F_7N_5O_4Co{\cdot}H_2O$: C, 35.87; H, 4.07. Found: C, 35.85; H, 4.01. ^{1}H NMR ($CDCl_3$): δ 7.22 (d, 2 H, ortho H), 6.67 (m, 3 H, meta and para H), 3.56 (s, 2 H, NH_2), 2.12 (s, 12 H, DH–CH_3). ^{19}F NMR ($CDCl_3$): –69.44 (d, 6 F, CF_3, ^3J(F–F) = 9.8 Hz), –195.2 (br s, 1 F, Co–CF).

For L = $(n\text{-}Bu)_3P$ (**4**), the filtrate was allowed to evaporate to give a sticky residue, which was triturated with petroleum ether to give the required product; the yield of yellow-orange powder was 0.098 g (71%). Anal. Calcd for $C_{23}H_{41}F_7N_4O_4PCo$: C, 41.83; H, 6.26. Found: C, 42.00; H, 6.24. ^{1}H NMR ($CDCl_3$): δ 2.26 (d, 12 H, DH–CH_3, ^5J(P–H) = 1.8 Hz), 1.18–1.35 (m, 18 H, *n*-Bu–CH_2), 0.90 (t, 9 H, *n*-Bu–CH_3). ^{19}F NMR ($CDCl_3$): –68.83 (m, 6 F, CF_3), –206.4 (br s, 1 F, Co–CF).

For L = 1-methylimidazole (1-MeIm) (**5**), the yield of yellow powder was 0.068 g (60%). Anal. Calcd for $C_{15}H_{20}F_7N_6O_4Co$: C, 33.35; H, 3.73. Found: C, 33.69; H, 3.71. ^{1}H NMR ($CDCl_3$): δ 7.48 (br s, 1 H, Im H-2), 6.96 (m, 1 H, Im H-4 or H-5), 6.69 (m, 1 H, Im H-4 or H-5), 3.63 (s, 3 H, N–CH_3), 2.23 (s, 12 H, DH–CH_3). ^{19}F NMR ($CDCl_3$): –69.25 (d, 6 F, CF_3, ^3J(F–F) = 9.3 Hz), –200.2 (br s, 1 F, Co–CF).

For L = 4-Me_2Npy (**6**), the yield of light orange-brown powder was 0.085 g (70%). Anal. Calcd for $C_{18}H_{24}F_7N_6O_4Co$: C, 37.25; H, 4.17. Found: C, 37.28; H, 4.10. ^{1}H NMR ($CDCl_3$): δ 7.91 (d, 2 H, py α-H), 6.34 (d, 2 H, py β-H), 2.98 (s, 6 H, N–CH_3), 2.23 (s, 12 H, DH–CH_3). ^{19}F NMR ($CDCl_3$): –69.15 (d, 6 F, CF_3, ^3J(F–F) = 9.8 Hz), –199.1 (br s, 1 F, Co–CF).

For L = 3-Brpy (**7**), the yield of orange-brown powder was 0.074 g (57%). Anal. Calcd for $C_{16}H_{18}BrF_7N_5O_4Co$: C, 31.19; H, 2.94. Found: C, 31.35; H, 2.97. ^{1}H NMR ($CDCl_3$): δ 8.59 (br s, 1 H, py H-2), 8.48 (d, 1 H, py H-6), 7.86 (d, 1 H, py H-4), 7.19 (t, 1 H, py H-5), 2.25 (s, 12 H, DH–CH_3). ^{19}F NMR ($CDCl_3$): –69.09 (d, 6 F, CF_3, ^3J(F–F) = 9.9 Hz), –195.9 (br s, 1 F, Co–CF).

For L = 3-Mepy (**8**), the yield of orange-brown powder was 0.060 g (52%). Anal. Calcd for $C_{17}H_{21}F_7N_5O_4Co$: C, 37.04; H, 3.84. Found: C, 36.33; H, 3.74. ^{1}H NMR ($CDCl_3$): δ 8.31 (d, 1 H, py H-6), 8.28 (br s, 1 H, py H-2), 7.50 (d, 1 H, py H-4), 7.15 (t, 1 H, py H-5), 2.23 (s, 12 H, DH–CH_3). ^{19}F NMR ($CDCl_3$): –69.09 (d, 6 F, CF_3, ^3J(F–F) = 9.8 Hz), –197.3 (br s, 1 F, Co–CF).

For L = 2-NH_2py (**9**), the yield of maroon microcrystals after thorough washing with diethyl ether was 0.021 g (45% based upon 0.040 g of the $H_2OCo(DH)_2[CF(CF_3)_2]$ starting material). Anal. Calcd for $C_{16}H_{20}F_7N_6O_4Co$: C, 34.80; H, 3.65; N, 15.22. Found: C, 34.77; H, 3.60; N, 15.21.

Various $LCo(DH)_2[CF(CF_3)_2]$ complexes were prepared in situ in $CDCl_3$ solution in order to record their ^{19}F NMR spectra. This was accomplished by shaking a mixture of $H_2OCo(DH)_2[CF(CF_3)_2]$ (ca. 10 mg) and the ligand L (ca. 1 equiv) in $CDCl_3$ in an NMR tube. No dependence of the chemical shifts on concentration was noted. In general, the CF_3 resonance of these complexes appeared as a sharp doublet (^3J(F–F) ~8.7–9.7 Hz) for the N-donor ligands and as a multiplet for the P-donor ligands, downfield from the quadrupolar-broadened Co–CF resonance. ^{19}F chemical shift information for $LCo(DH)_2[CF(CF_3)_2]$ (L, $\delta(CF_3)$, δ(Co–CF)) follows: $P(OPh)_3$, –68.87, –203.1; $P(O\textit{i}\text{-}Pr)_3$, –68.94, –206.2; $PMePh_2$, –68.90, –202.1; 3-Clpy, –69.05, –195.8; 3-NH_2py, –69.05, –197.5; 4-NH_2py, –69.12, –198.7; allylamine ($C_3H_5NH_2$), –69.44, –198.6; *n*-$C_6H_{13}NH_2$, –69.47, –199.0; *c*-$C_6H_{11}NH_2$, –69.41, –198.6; piperidine, –69.18, –197.6; 2-aminonaphthalene (2-NH_2naph), –69.45, –195.2. The next ^{19}F NMR data are for L being a substituted aniline (position and nature of the substitution, $\delta(CF_3)$, δ(Co–CF)): 4-NO_2, –69.43, –193.6; 3-NO_2, –69.43, –194.0; 2-Br, –69.31, –194.6; 2-Cl, –69.37, –194.5; 4-Br, –69.45, –194.8; 4-Cl, –69.45, –194.8; 4-F, –69.38, –195.5; 4-Me, –69.46, –195.7; 4-MeO, –69.47, –195.9.

$[n\text{-}Bu_4N]\{(CH_3O)_2(O)PCo(DH)_2[CF(CF_3)_2]\}$ (10). $(CH_3O)_3PCo(DH)_2[CF(CF_3)_2]$ (15 mg, 0.026 mmol) was stirred with an excess of $(n\text{-}Bu_4)I$ (190 mg, 0.53 mmol) in $CHCl_3$ (1 mL) for 20 h. The solution was applied to a silica gel column (6-mm diameter by 50-mm length), and the product was eluted as a yellow band with methanol/diethyl ether (1:4). The solvent was removed from the product fraction; recrystallization from acetone/hexane afforded a bright yellow powder (8.5 mg, 41%). ^{1}H NMR (Me_2SO-d_6): δ 3.37 (d, 6 H, OCH_3, ^3J(P–H) = 10.8 Hz), 3.19 (br t, 8 H, NCH_2), 2.19 (s, 12 H, DH–CH_3), 1.65 (m, 8 H, β-CH_2 of *n*-Bu), 1.48 (m, 8 H, γ-CH_2 of *n*-Bu), 1.04 (m, 12 H, CH_3 of *n*-Bu). ^{19}F (Me_2SO-d_6): –68.69 (m, 6 F, CF_3), –212.7 (br s, 1 F, Co–CF_3).

Rate Studies. In all cases, the results presented from the rate studies are averages of three trials.

The extent of nucleophilic attack by Br^- on coordinated $(CH_3O)_3P$ (eq 1), was monitored via changes in the ^{1}H NMR spectrum for the DH methyl resonances for the reactant and

$$(CH_3O)_3PCo(DH)_2[CF(CF_3)_2] + Br^- \rightarrow \{(CH_3O)_2(O)PCo(DH)_2[CF(CF_3)_2]\}^- + CH_3Br \quad (1)$$

product complexes. In a typical experiment, the starting complex (14.6 mg, 0.025 mmol) and excess $[(C_6H_5)_3(CH_3)P]Br$ (107.6 mg, 0.30 mmol) were weighed into an NMR tube. Then, CH_2Cl_2 (0.5 mL) that was prewarmed to 305 ± 0.1 K was added, the tube was shaken to dissolve the reactants, and the data were recorded on a Varian EM360A spectrometer at 2–3-min intervals. Linear regression analysis of the integrated intensities of the DH methyl resonances (obtained by the "cut and weigh" method) gave correlation coefficients >0.99 over ca. 3 half-lives.

The extent of the ligand-exchange reaction (eq 2; L = 4-CNpy, L′ = $(CH_3O)_3P$; L = PPh_3, L′ = $(n\text{-}Bu)_3P$) was monitored spectrophotometrically (Varian DMS 80 or Shimadzu UV-160) at 392 nm. In a typical experiment, the starting complex (0.0044 mmol)

$$LCo(DH)_2[CF(CF_3)_2] + L' \rightarrow L'Co(DH)_2[CF(CF_3)_2] + L \quad (2)$$

was reacted with excess L′ (0.175 mmol) in CH_2Cl_2 (3 mL). The reaction solution was kept in the dark in a constant-temperature bath at 298 ± 0.1 K, and spectra were recorded at appropriate intervals for 2–3 half-lives. The final absorbance data were taken after ca. 8 half-lives. The data were then analyzed via the standard integrated rate expression for a first-order process using a linear regression program (correlation coefficients >0.995).

Crystal Data. Crystals of $Ph_3PCo(DH)_2[CF(CF_3)_2]$ (**1**) were grown by slow evaporation of a saturated methanol/water solution at 0–4 °C in the dark. Cell parameters, determined from Weissenberg and precession photographs, were refined on an Enraf-Nonius CAD-4 single-crystal diffractometer. The results are given in Table I. The intensity data were collected by the $\omega/2\theta$ scan technique using graphite-monochromated Mo Kα radiation. Three check reflections, measured every 1 h, showed no significant intensity decay during the data collection. Reflections with $I > 3\sigma(I)$ were corrected for Lorentz–polarization effects and for anomalous dispersion for all the non-hydrogen atomic species. Significant details of the intensity collection are summarized in Table I.

Solution and Refinement of the Structure. The structure was solved by conventional Patterson and Fourier methods. The difference Fourier maps clearly showed a disorder of the perfluoroisopropyl group. This disorder was interpreted successfully by assuming two different orientations of the $CF(CF_3)_2$ group,

Table I. Crystal Collection and Refinement Data for $Ph_3PCo(DH)_2[CF(CF_3)_2]$ (1)

formula	$C_{29}H_{29}F_7N_4O_4PCo$
mol wt	720.47
a, Å	23.374 (3)
b, Å	17.551 (2)
c, Å	14.985 (3)
V, Å^3	6147.6 (8)
Z	8
D(measd), g cm^{-3}	1.55
D(calcd), g cm^{-3}	1.557
space group	*Pbca*
F(000)	2944
μ, cm^{-1}	6.8
cryst dimens, cm^3	0.05 × 0.04 × 0.06
no. of rflns measd	8103
no. of indep rflns	3087
2θ range, deg (Mo Kα)	6–56
scan range, deg (Mo Kα)	1.1 + 0.35 tan θ
aperture width, mm	1.2 + tan θ
no. of variables	505
R	0.056
R_w	0.055

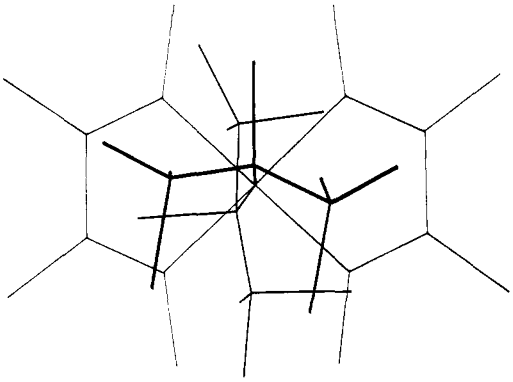

Figure 1. Scheme of the disorder, interpreted as two orientations of the perfluoroisopropyl ligand, with respect to the equatorial ligand set. The orientation with occupancy 0.6 is represented by heavy lines.

approximately related by a rotation of ~90° around an axis passing through Co and normal to the equatorial coordination plane, having occupanies 0.6 and 0.4, respectively (Figure 1). All of the peaks of the disordered group were well localized on the Fourier map, so that a full-matrix anisotropic least-squares refinement was applied to all atoms without any correlation problems. In the final refinement, the constant contribution of the hydrogen atoms at calculated positions was included, with isotropic factors 1.3 times the B equivalent of the heavy atoms to which they are bonded. The ORTEP drawing with the numbering scheme for the non-hydrogen atoms, including only the perfluoroalkyl orientation with the higher occupancy, is shown in Figure 2. The final R and R_w values are given in Table I. Final non-hydrogen positional parameters and selected bond lengths and angles are provided in Tables II and III, respectively. Hydrogen atom coordinates, anisotropic thermal parameters, and a list of calculated and observed structure factors are available (supplementary material). All calculations were done by using the SDP programs.

Results and Discussion

Synthesis of (Perfluoroisopropyl)cobaloximes. Complexes **1**–**9** were easily prepared and isolated by the reported method[12] of ligand substitution of $H_2OCo(DH)_2[CF(CF_3)_2]$ in CH_2Cl_2 solution with a variety of neutral two-electron donor ligands of different basicity and steric size. The substitutions are somewhat slower than for analogous nonfluorinated organoaquocobaloximes. The slow-exchange rate is likely due in large part to the poor electron-donating ability of the $CF(CF_3)_2$ group. The large bulk of this alkyl group (vide infra), as well as the relatively poor solubility of $H_2OCo(DH)_2[CF(CF_3)_2]$ in CH_2Cl_2, probably also contribute to this phenomenon. Approximately 20 other complexes, $LCo(DH)_2[CF(CF_3)_2]$, were prepared in situ in $CDCl_3$ solution in NMR tube scales for the purpose of measuring their ^{19}F NMR spectra by utilizing the same ligand substitution methodology. Anionic complex **10** was prepared by nucleophilic attack by I^- on the coordinated trimethylphosphite ligand of $(MeO)_3PCo(DH)_2[CF(CF_3)_2]$ in the inorganic analogue of the Arbuzov reaction.[14-16]

Table II. Non-Hydrogen Atom Positional Parameters for 1

atom	x	y	z	B, Å^{2a}
Co	0.14195 (3)	0.10622 (4)	0.25890 (5)	3.15 (1)
P	0.07993 (6)	−0.00293 (8)	0.2514 (1)	2.80 (2)
O(1)	0.0535 (2)	0.2137 (3)	0.2912 (3)	5.9 (1)
O(2)	0.1842 (2)	0.0566 (3)	0.0916 (3)	5.3 (1)
O(3)	0.2317 (2)	−0.0004 (3)	0.2257 (3)	5.5 (1)
O(4)	0.0925 (2)	0.1475 (3)	0.4262 (3)	6.3 (1)
N(1)	0.0829 (3)	0.1758 (3)	0.2315 (4)	4.5 (1)
N(2)	0.1467 (2)	0.1002 (3)	0.1328 (3)	4.2 (1)
N(3)	0.1998 (2)	0.0349 (3)	0.2877 (3)	3.8 (1)
N(4)	0.1326 (3)	0.1070 (3)	0.3845 (3)	4.6 (1)
C(1)	0.0276 (4)	0.2387 (5)	0.1124 (7)	8.9 (3)
C(2)	0.0718 (4)	0.1840 (4)	0.1463 (5)	5.3 (2)
C(3)	0.1090 (3)	0.1402 (4)	0.0889 (4)	4.6 (2)
C(4)	0.1053 (5)	0.1396 (6)	−0.0112 (5)	7.9 (3)
C(5)	0.2541 (4)	−0.0293 (5)	0.4051 (5)	6.6 (2)
C(6)	0.2077 (3)	0.0222 (4)	0.3716 (4)	4.5 (2)
C(7)	0.1678 (3)	0.0640 (4)	0.4281 (4)	4.7 (2)
C(8)	0.1682 (5)	0.0565 (6)	0.5280 (5)	8.4 (3)
C(9a)	0.1916 (4)	0.2085 (6)	0.2682 (7)	3.8 (2)
C(10a)	0.2011 (6)	0.2463 ()	0.1820 (9)	6.8 (3)
C(11a)	0.2402 (9)	0.2072 (9)	0.330 (1)	15.3 (6)
C(9b)	0.2140 (6)	0.1822 (8)	0.257 (1)	4.1 (3)
C(10b)	0.2576 (9)	0.180 (1)	0.200 (2)	8.7 (6)
C(11b)	0.2024 (8)	0.257 (1)	0.302 (2)	11.0 (1)
C(12)	0.0860 (3)	−0.0658 (4)	0.3489 (4)	3.3 (1)
C(13)	0.0467 (4)	−0.0581 (5)	0.4172 (5)	6.9 (2)
C(14)	0.0502 (4)	−0.1039 (5)	0.4930 (5)	7.4 (2)
C(15)	0.0904 (4)	−0.1555 (5)	0.5030 (5)	6.2 (2)
C(16)	0.1286 (5)	−0.1652 (5)	0.4380 (6)	7.8 (2)
C(17)	0.1276 (4)	−0.1197 (5)	0.3601 (5)	6.9 (2)
C(18)	0.0953 (3)	−0.0569 (4)	0.1495 (4)	3.4 (1)
C(19)	0.1399 (3)	−0.1075 (4)	0.1398 (4)	5.8 (2)
C(20)	0.1530 (4)	−0.1406 (5)	0.0585 (5)	6.6 (2)
C(21)	0.1198 (4)	−0.1238 (5)	−0.0147 (5)	5.7 (2)
C(22)	0.0769 (3)	−0.0726 (5)	−0.0069 (4)	5.1 (2)
C(23)	0.0632 (3)	−0.0412 (4)	0.0744 (4)	4.3 (2)
C(24)	0.0024 (2)	0.0052 (4)	0.2451 (4)	3.7 (1)
C(25)	−0.0274 (3)	0.0723 (4)	0.2612 (5)	4.6 (2)
C(26)	−0.0875 (3)	0.0711 (5)	0.2633 (5)	6.4 (2)
C(27)	−0.1168 (3)	0.0047 (4)	0.2496 (6)	7.1 (2)
C(28)	−0.0877 (3)	−0.0612 (5)	0.2337 (5)	6.4 (2)
C(29)	−0.0289 (3)	−0.0624 (4)	0.2322 (5)	5.0 (2)
F(1a)	0.1605 (3)	0.2655 (4)	0.3240 (5)	6.3 (2)
F(2a)	0.2487 (6)	0.1930 (9)	0.140 (1)	20.4 (5)
F(3a)	0.1614 (5)	0.2729 (5)	0.1467 (7)	11.4 (3)
F(4a)	0.2331 (5)	0.3180 (6)	0.2016 (7)	12.0 (3)
F(5a)	0.2845 (3)	0.1493 (5)	0.2859 (8)	10.5 (3)
F(6a)	0.2370 (4)	0.1839 (6)	0.4061 (6)	10.9 (3)
F(7a)	0.2735 (5)	0.2686 (5)	0.3313 (9)	15.3 (3)
F(1b)	0.2545 (5)	0.1610 (7)	0.3360 (8)	7.3 (3)
F(2b)	0.2284 (5)	0.2147 (6)	0.1171 (7)	6.2 (3)
F(3b)	0.3001 (4)	0.2311 (6)	0.2025 (8)	7.0 (3)
F(4b)	0.2770 (4)	0.1179 (6)	0.1617 (9)	7.1 (3)
F(5b)	0.2423 (7)	0.3076 (6)	0.307 (1)	11.6 (5)
F(6b)	0.170 (1)	0.254 (1)	0.379 (1)	19.8 (6)
F(7b)	0.1717 (7)	0.2880 (9)	0.238 (1)	12.2 (5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

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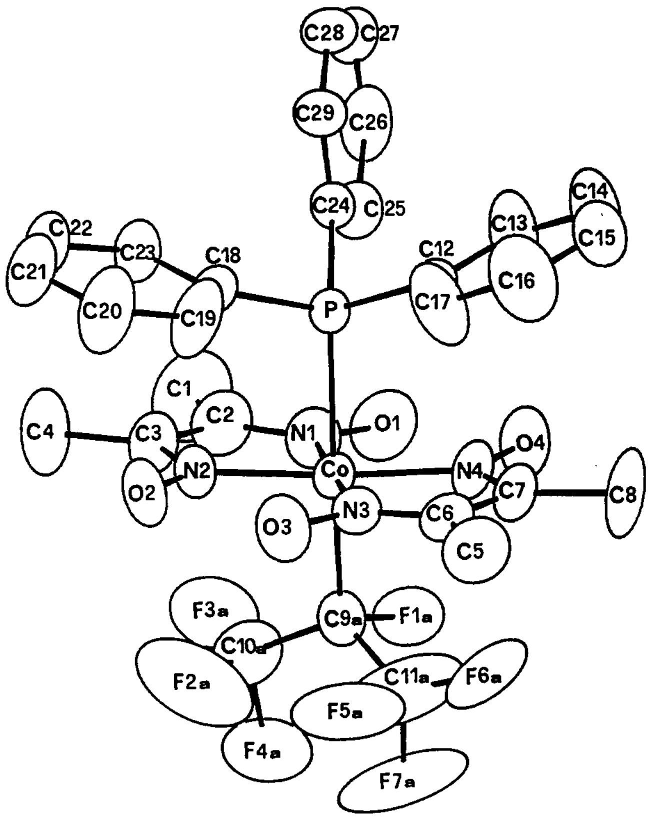

Figure 2. ORTEP drawing with the numbering scheme for the non-hydrogen atoms of 1. Only the orientation of the perfluoroisopropyl group of higher occupancy is shown.

Table III. Selected Bond Distances and Angles for 1

	Bond Lengths (Å)		
Co–P	2.405 (2)	Co–N(1)	1.889 (6)
Co–N(2)	1.895 (6)	Co–N(3)	1.892 (5)
Co–N(4)	1.895 (5)	Co–C(9a)	2.14 (1)
Co–C(9b)	2.15 (1)		
	Bond Angles (deg)		
N(1)–Co–N(2)	82.1 (2)	N(1)–Co–N(3)	178.6 (2)
N(1)–Co–N(4)	97.3 (2)	N(2)–Co–N(3)	98.5 (2)
N(2)–Co–N(4)	175.7 (2)	N(3)–Co–N(4)	82.0 (2)
P–Co–N(1)	93.7 (2)	P–Co–N(2)	86.8 (2)
P–Co–N(3)	85.1 (2)	P–Co–N(4)	89.0 (2)
P–Co–C(9a)	175.7 (3)	P–Co–C(9b)	165.1 (4)
N(1)–Co–C(9a)	82.5 (3)	N(1)–Co–C(9b)	99.7 (4)
N(2)–Co–C(9a)	94.6 (3)	N(2)–Co–C(9b)	88.7 (5)
N(3)–Co–C(9a)	98.8 (3)	N(3)–Co–C(9b)	81.6 (4)
N(4)–Co–C(9a)	89.6 (3)	N(4)–Co–C(9b)	95.6 (5)

Structural Chemistry. The cobalt center of 1 exhibits a distorted octahedral geometry, with the $(DH)_2$ ligands occupying the four equatorial positions (see Figure 2). The displacement of the cobalt atom out of the four nitrogen-donor plane, *d*, is −0.046 Å (toward the perfluoroalkyl group), and the interplanar angle between the two DH units, *α*, is −5.2° (toward PPh_3). We note that compound 1 is the first cobaloxime complex, incorporating the relatively large PPh_3 ligand, that has negative values for *α* and *d* (vide infra).[3,4]

Table IV. Co–L Axial Distances in $LCo(DH)_2R$ Complexes Together with the α and *d* Values[a]

	L = py			
R	$CF(CF_3)_2$[b]	CH_2CF_3[c]	Me	*i*-Pr
Co–N(py), Å	2.037 (3)	2.041 (2)	2.068 (3)	2.099 (2)
α, deg	−10.3	1.0	3.2	4.0
d, Å	−0.075	0.01	0.04	0.02
	L = PPh_3			
R	$CF(CF_3)_2$[d]	CH_2CF_3	Me	*i*-Pr
Co–P, Å	2.405 (2)	2.383 (1)	2.418 (1)	2.412 (4)
α, deg	−5.2	1.7	14.0	14.0
d, Å	−0.046	0.04	0.11	0.17

[a] Positive values of *α* and *d* indicate bending toward R and displacement toward L, respectively. All data are from ref 4 unless otherwise stated. [b] Reference 12. [c] The L ligand is 4-CNpy. [d] Present work.

The axial bond lengths, Co–P and Co–C (mean value), are 2.405 (2) and 2.15 (1) Å, respectively. Owing to the observed disorder, the geometry of the Co–$CF(CF_3)_2$ moiety is affected by large errors and cannot be discussed in detail. However, in both conformations, each $CF(CF_3)_2$ group seems to bend in such a manner so as to relieve the steric interaction with the equatorial ligand set (Figure 1). The long Co–C bond is that to be expected from comparison to the corresponding bond length of 2.084 (5) Å reported for $pyCo(DH)_2[CF(CF_3)_2]$.[12] The difference in Co–C bond lengths in the structures of these two perfluoroisopropyl complexes, if significant, is due to the larger steric trans influence of PPh_3,[3,4] as also suggested by the *α* and *d* values of Table IV. On the other hand, the Co–C bond lengths in the $CF(CF_3)_2$ derivatives are similar to those in the corresponding *i*-Pr analogues, which are 2.085 (3) and 2.22 (2) Å in the py and PPh_3 complexes, respectively. This suggests that the steric bulk of the perfluoroisopropyl group is larger than that of isopropyl; however, the size differential is manifested only in the "inversion" of the *α* and *d* values (Table IV) and not in lengthening of the Co–C bond.[4] In general, shorter Co–C bond lengths are observed in complexes having less bulky alkyl groups with electron-withdrawing substituents.[3,4] Apparently, the perfluoroisopropyl ligand is too large to accommodate significant shortening of the bond, causing the observed changes in the equatorial ligand *α* and *d* parameters.

The Co–P bond length is only slightly shorter than that of 2.418 (1) Å reported for the $Ph_3PCo(DH)_2Me$ derivative and longer than that of 2.383 (1) Å in $Ph_3PCo(DH)_2CH_2CF_3$.[4] This is in contrast to data relative to the axial Co–N(py) bonds in the analogous py series, where the Co–N(py) distances for the $CF(CF_3)_2$ and CH_2CF_3 derivatives are very similar but shorter than that of the Me analogue (Table IV). Since the σ-donating power of $CF(CF_3)_2$ is expected to be significantly lower than that of CH_2CF_3, on the basis of ^{13}C NMR spectral data,[12] these results may be interpreted by assuming that the trend of the electronic trans influence of R is modified by the bulk of the perfluoroisopropyl group, which bends the equatorial ligand set toward the trans neutral ligand (L). As a consequence, the steric interaction between L and the equatorial moiety should be relieved by a lenghtening of the Co–L distance. This effect is more pronounced in the PPh_3 series, because PPh_3 is significantly larger in bulk than py. The trend of the *α* and *d* values given in Table IV is in agreement with this hypothesis.

^{19}F NMR Spectral Data. Previous ^1H and ^{19}F NMR investigations involving ethyl-,[17,18] methyl-,[18] and fluorinated phenyl-[19] or benzylcobaloximes[20,21] and ^1H NMR

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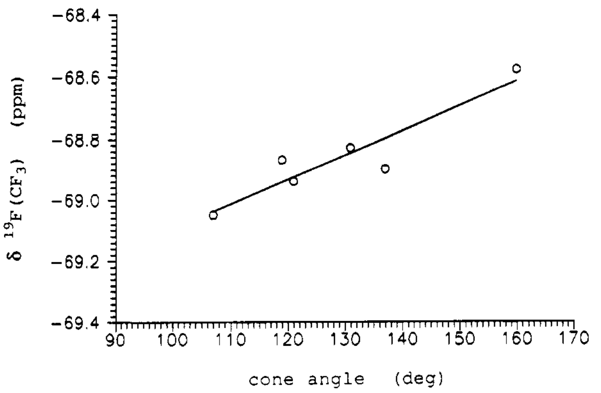

Figure 3. ^{19}F chemical shift (ppm) for the CF$_3$ group of CF(CF$_3$)$_2$ versus the "calculated" cone angle[22] (deg) for cobaloxime systems. Points from left to right are P(OMe)$_3$, P(OPh)$_3$, P(O*i*-Pr)$_3$, P(*n*-Bu)$_3$, PMePh$_2$, and PPh$_3$.

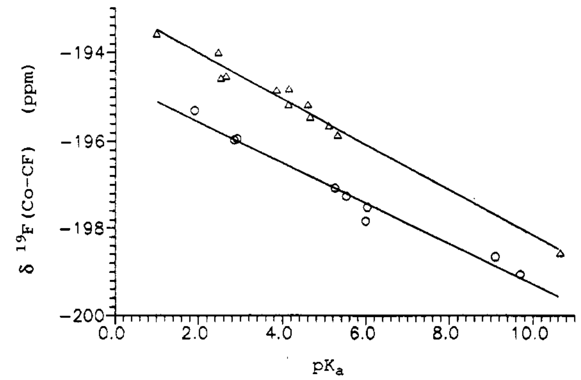

Figure 4. ^{19}F chemical shift (ppm) for the Co–CF moiety versus pK_a[37] of L. Lower line (circular points) is for L = X–py. Points from left to right are for X being 4-CN, 3-Cl, 3-Br, H, 3-Me, 3-NH$_2$ (upper), 4-t-Bu (lower), 4-NH$_2$, and 4-NMe$_2$. Upper line (triangular points) is for L = X–PhNH$_2$. Points from left to right are for X being (except as noted) 4-NO$_2$, 3-NO$_2$, 2-Br, 2-Cl, 4-Br, 4-Cl, 2-aminonaphthalene, H, 4-F, 4-Me, 4-OMe and *c*-C$_6$H$_{11}$NH$_2$.

results regarding isopropylcobaloximes[4] have proven fruitful for delineating spectroscopic and structural trends with regard to basicity (in the former cases) and size (in the latter case) of the trans L ligand. Thus during the course of this research, it became of interest to more fully examine the ^{19}F NMR data for a large series of LCo(DH)$_2$[CF(CF$_3$)$_2$] complexes for the examination of possible correlations and trends with electronic and steric parameters of L.

Despite the relatively large chemical shift range for ^{19}F nuclei, the CF$_3$ resonance of (perfluoroisopropyl)cobaloximes is surprisingly insensitive to electronic effects of L. For two extensive series of sterically similar ligands, such as the 3- and 4-substituted pyridines or anilines, the CF$_3$ resonance appears at δ −69.10 ± 0.05 and −69.45 ± 0.02 (for 2-substituted anilines, this resonance occurs at δ −69.34 ± 0.03), respectively. On the other hand, for a series of three-coordinate phosphorus ligands, where the donor atom is held constant but steric bulk is varied, δ[^{19}F(CF$_3$)] tends to move further downfield as the bulk of L increases (see Figure 3). It is interesting that this downfield trend is opposite to the general effect observed for the case of δ[^{1}H(CH$_3$)] of the *i*-Pr ligand in the ^{1}H NMR spectrum of isopropylcobaloximes.[4] At this time, we have no explanation for this reversal, though we note that the ^{1}H chemical shifts of the isopropyl complexes are also significantly affected by electronic as well as steric factors.[4]

Two points may be made from these observations with reference to relevant X-ray structural determinations.[3,4] First, within a series of neutral ligands such as the substituted anilines, the relative invariance of the ^{19}F(CF$_3$) chemical shift with electronic substitution on the phenyl ring correlates well with the corresponding relative structural invariance observed in salient cases. For example, in the following pairs of compounds 4-*X*-PhNH$_2$Co(DH)$_2$R (R = Cl, X = H[23] or Cl;[24] R = Me, X = H[25] or OMe;[26] R = *i*-Pr, X = H[25] or OMe[26]), bonding parameters in the molecular structures are essentially identical. Second, although comparisons between series are potentially (and probably) complicated by small electronic nuances, the above ^{19}F(CF$_3$) data would suggest that aniline is somewhat sterically smaller than py since δ[^{19}F(CF$_3$)] for aniline is upfield of that for py. Thus, the fact, that Co–N(PhNH$_2$) bonds are ~0.06–0.12 Å longer than Co–N(py) bonds for LCo(DH)$_2$R complexes (R held constant) can be ascribed as arising mostly from the larger radius of sp^3-hydridized nitrogen as compared to sp^2-hybridized nitrogen.[27] 1-Methylimidazole (1-MeIm) also appears to be sterically "smaller" than py but "larger" than PhNH$_2$ on the basis of this NMR criterion (vide infra).

The ^{19}F chemical shift of the Co–CF moiety appears to be affected by both electronic and steric factors of the neutral L ligand. However, with steric factors held constant, better electron donation by L appears to cause this resonance to shift upfield, presumably due to increased electron density on the perfluoroalkyl ligand. It is interesting to note that δ[^{19}F(Co–CF)] values for the cobaloxime complexes in this study are significantly further upfield from those found for perfluoroisopropyl ligands bound to organometallic complexes with strongly π-accepting ligands,[28-32] such as CO, and approach those observed for d^{10} metal complexes,[33-35] where the CF(CF$_3$)$_2$ group is strongly carbanionic in character.[33] Although detailed correlations are impossible due to steric effects, P-donor ligands appear to be generally better electron donors than N-donor ligands on the basis of the upfield trend for δ[^{19}F(Co–CF)] for these ligands. This is in agreement with relevant bond length data in the literature[4] that indicate that P donors have a stronger trans influence compared to N donors. The anionic complex, {(CH$_3$)$_2$(O)PCo(DH)$_2$[CF(CF$_3$)$_2$]}$^-$, has the furthest upfield ^{19}F chemical shift for the Co–CF moiety, as might be expected on electronic grounds. We note that changes in magnetic anisotropy of the cobalt ion as a function of ligand substitution may also contribute to the observed shifts of the Co–CF resonance.[36]

Within sterically similar series of L (such as 3- and 4-

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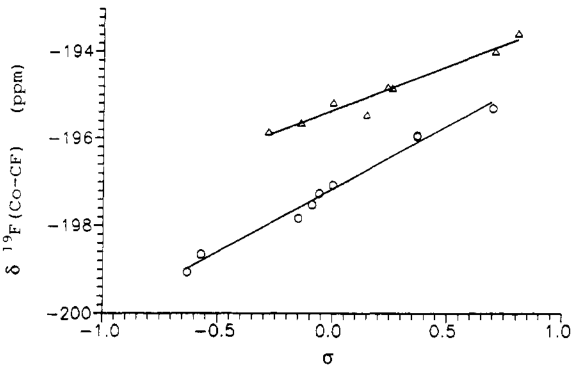

Figure 5. ^{19}F chemical shift (ppm) for the Co–CF moiety versus Hammett substituent constant (σ)[38,39] of X. Lower line (circular points) is for L = X-py. Points from left to right are for X being 4-NMe$_2$, 4-NH$_2$, 4-*t*-Bu, 3-NH$_2$, 3-Me, H, 3-Cl and 3-Br (superimposed), and 4-CN. Upper line (triangular points) is for L = X–PhNH$_2$. Points from left to right are for X being 4-OMe, 4-Me, H, 4-F, 4-Cl, 4-Br, 3-NO$_2$, and 4-NO$_2$.

X–py or 2-, 3-, and 4-X–PhNH$_2$), excellent correlations of $\delta[^{19}F(Co–CF)]$ with pK_a[37] of L are observed (see Figure 4). The relevant statistics, including r (correlation coefficient) for the regression lines are

$$\delta(\mathrm{Co–CF}) = [-0.464\ (23)][\mathrm{p}K_a(\mathrm{X–py})] - 194.6\ (1)$$

$$r = -0.988$$

$$\delta(\mathrm{Co–CF}) = [-0.519\ (22)][\mathrm{p}K_a(\mathrm{X–PhNH_2})] - 193.0\ (1)$$

$$r = -0.991$$

The expected upfield shift with increased electron-donating ability of L is observed. The displacement of the "aniline" line from the "pyridine" line suggests that the sp^2-nitrogen atom of the pyridine ligands interacts more strongly with the cobalt center than the sp^3-nitrogen atom of the aniline ligands. Interestingly, 1-MeIm, which also has an sp^2-hybridized nitrogen donor atom, has a ^{19}F(Co–CF) chemical shift that is much further upfield than would be predicted on the basis of its pK_a (6.95)[37] and the "pyridine" regression line in Figure 4. This may be due to slightly smaller steric constraints which allow the five-membered ring imidazole ligand to interact more strongly with cobalt than the six-membered ring pyridine.[36] Available crystal structure data lend some credence to this notion; Co–N(Im) bonds are in general slightly but significantly shorter than Co–N(py) bonds.[4] In a similar vein, we find that *c*-$C_6H_{11}NH_2$, which should be sterically similar to substituted aniline bases, "fits" well with the "aniline" regression line (Figure 4). On the other hand, the ^{19}F(Co–CF) chemical shifts (see Experimental Section) for *n*-$C_6H_{13}NH_2$ (pK_a 10.6)[37] and CH$_2$=CHCH$_2$NH$_2$ (pK_a 9.5)[37] fall significantly away from this line in the direction suggesting stronger interaction with cobalt than the monosubstituted anilines, while the secondary-amine donor, piperidine (pK_a 11.1),[37] and 2,6-Me$_2$PhNH$_2$ (pK_a 4.0)[37] are well off the line in the other direction, suggesting weaker binding to cobalt. These observations are in accord with the expected smaller steric bulk for the aliphatic primary-amine donors and larger bulk for the secondary-amine and 2,6-disubstituted aniline donors as compared to that of aniline.

Further evidence that this ^{19}F NMR parameter is responding to mainly electronic effects when steric factors are kept constant can be found in the excellent correlations of $\delta[^{19}F(Co–CF)]$ with Hammett σ parameters (see Figure 5).[38,39] The regression lines and correlation coefficients in these cases are

$$\delta(\mathrm{Co–CF}) = [2.88\ (11)][\sigma(\mathrm{X–py})] - 197.16\ (5)$$

$$r = 0.992$$

$$\delta(\mathrm{Co–CF}) = [2.03\ (17)][\sigma(\mathrm{X–PhNH_2})] - 195.36\ (7)$$

$$r = 0.970$$

The somewhat larger slope for the "pyridine" regression line vs the "aniline" line (2.88 vs 2.03) might reflect the stronger interaction of the pyridine ligands with the cobalt center as compared to the aniline ligands (vide supra). However, this result may also be due to the fact that, in the pyridine case, the nitrogen-donor atom is a part of the substituted aromatic ring, while for the anilines, the nitrogen donor is simply attached to the aromatic ring and is somewhat less directly affected by substitution on the ring.

Attempts to prepare LCo(DH)$_2$[CF(CF$_3$)$_2$], where L is a 2-substituted pyridine ligand, were unsuccessful except for L = 2-NH$_2$py (complex **9**). This ligand is potentially ambidentate, having endocyclic pyridyl nitrogen (endo) and exocyclic amino nitrogen (exo) donor sites.[40,41] The ^1H NMR spectrum of **9** in CDCl$_3$ was complex throughout most of the accessible temperature range, presumably due to several dynamic processes that have been observed earlier in analogous cobaloximes, including endo–exo linkage isomer equilibrium and rotational barriers.[42] At room temperature, however, the ^{19}F NMR spectrum is comparatively simple, consisting of a relatively sharp doublet at δ -69.01 and a broadened doublet at δ -69.37 in the ratio 15:85 and each with ^3J(F–F) = 9.8 Hz. If 2-NH$_2$py is added to the solution of **9**, the smaller downfield peak diminishes in intensity relative to the now sharper upfield resonance.

We believe that the above observations are consistent with the interpretation that the downfield ^{19}F NMR resonance is associated with the endo linkage isomer, while the upfield one can be assigned to the exo linkage isomer. First, it has been demonstrated previously that added 2-NH$_2$py shifts the endo–exo equilibrium to the exo side by interfering with the intramolecular hydrogen bonding between the exo amino group and the oxime oxygens that helps to stabilize the endo isomer.[40] Furthermore, the chemical shift of the downfield (endo) resonance is about where it would be expected for a ligand that is presumably somewhat bulkier, due to substitution at the 2-position, than the unhindered pyridine ligands (vide supra for the pertinent discussion). Likewise, the upfield (exo) resonance is within the expected range for an aniline-type ligand substituted at the 2-position (see Experimental Section). The equilibrium constant for the endo–exo equilibrium at room temperature is 5.7, which is considerably higher than those values observed for other LCo(DH)$_2$R (the largest K was 0.86 for R = 1-adamantyl).[40] The strong preference for the rather poorly basic exo donor site in the present case likely occurs because the CF(CF$_3$)$_2$ group combines very large steric bulk with very poor electron-donating ability. Thus, although the pyridyl

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[42] In the present case, rotational dynamics involving the perfluoroisopropyl ligand[30,31] are possible, in addition to those involving the 2-NH$_2$py base.[40]

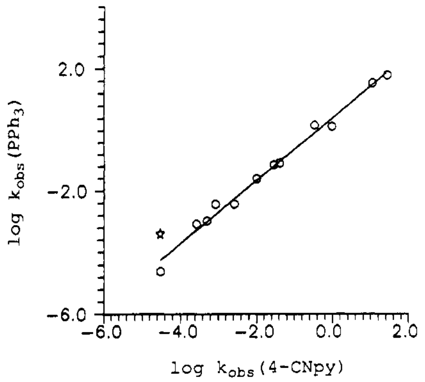

Figure 6. log k_{obs} for ligand exchange for $Ph_3PCo(DH)_2R$ versus log k_{obs} for ligand exchange for $4\text{-}CNpyCo(DH)_2R$. Circular points[4,43] from left to right are for R being CH_2CN, CH_2CF_3, $CHBr_2$, $CHCl_2$, CH_2Br, $P(O)(OMe)_2$, Ph, Me, $CH_2C(Me)(CO_2Et)_2$, Et, CH_2CMe_3, and *i*-Pr. The starred point is for R = $CF(CF_3)_2$.

nitrogen donor is far more basic than the amino nitrogen donor, unfavorable steric factors that are amplified by the tendency toward shorter Co–L bonds due to the poor trans influence of $CF(CF_3)_2$ apparently weaken the endo interaction to a sufficient extent that exo coordination predominates at equilibrium.

Rate Studies. The logarithm of the pseudo-first-order rate constants for nucleophilic attack of Br^- on complexes of type $(MeO)_3PCo(DH)_2R$ (eq 1) has been shown to linearly correlate very well with $\delta[^{13}C(OMe)]$ of the coordinated trimethyl phosphite ligand.[14] This latter parameter is a sensitive indicator of the electron-donating ability of R in these systems. The rate constant for the compound with R = $CF(CF_3)_2$ is 3.33 (8) × 10^{-4} s^{-1}, which is consistent with the previously measured ^{13}C chemical shift for this complex.[12,14]

The study of ligand-exchange reactions for (perfluoroisopropyl)cobaloximes proved more interesting. The pseudo-first-order rate constant k_{obs} for the dissociative ligand-exchange process in eq 2 was determined for $LCo(DH)_2[CF(CF_3)_2]$, L = 4-CNpy and PPh_3, in the noncoordinating solvent CH_2Cl_2. The respective values for k_{obs} are 3.07 (4) × 10^{-5} and 4.05 (4) × 10^{-4} s^{-1}. As expected,[4] these rate constants are relatively small due to the poor electron donation of the $CF(CF_3)_2$ group.

In prior studies,[4,36] it has been observed generally that there is no change in the relative leaving ability of a given ligand L in reaction 2 compared to other ligands as the trans ligand R is varied. Put more simply, plots of $k_{obs}(L)$ vs $k_{obs}(L')$ for any two leaving ligands, L and L′, tend to be linear for many different R ligands. This relationship is most conveniently displayed in log–log graphs, such as Figure 6. Here, we have plotted log k_{obs} for dissociation of PPh_3 from $Ph_3PCo(DH)_2R$ vs log k_{obs} for dissociation of 4-CNpy from $4\text{-}CNpyCo(DH)_2R$; these values (circular points) are taken from the literature[4,43] and give the following linear relationship:

$$\log k_{obs}(PPh_3) = [1.03\ (3)][\log k_{obs}(4\text{-}CNpy)] + 0.41\ (8)$$

$$r = 0.995$$

All circular points are less than 2.0 standard deviations from the least-squares line (standard deviation of y is 0.19). From the intercept in the regression analysis, one derives that in general calculated $k_{obs}(PPh_3)$ values are about 2.6 ± 0.4 times larger than k_{obs}(4-CNpy). We note that no measured $k_{obs}(PPh_3)$ value is bigger than 4.5 times that of the corresponding k_{obs}(4-CNpy).

The starred point in Figure 6 is derived from the values in the current study for the $CF(CF_3)_2$ group (vide supra) and has not been included in the regression analysis. This data point is 4.5 standard deviations from the best-fit line; from another point of view, $k_{obs}(PPh_3)$ for $CF(CF_3)_2$ is 13.2 times larger than k_{obs}(4-CNpy), a factor that is 3 times greater than for any individual point in Figure 6, as pointed out above. In addition, $k_{obs}(PPh_3)$ for $CF(CF_3)_2$ is ca. 17 times greater than $k_{obs}(PPh_3)$ for the electronically similar, but sterically much smaller, CH_2CN group,[4] notwithstanding the fact that the Co–P bond lengths for these two compounds are similar. Though comparatively modest in size, we feel that these observations indicate a significant deviation from the general trend for relative leaving ability for PPh_3 vis-â-vis 4-CNpy (vide supra) and result from a bona fide steric trans effect caused by the large bulk of the $CF(CF_3)_2$ group.

As such, the present instance would be the first example in which the relative leaving ability of L (i.e., PPh_3) was found to be a function of R (i.e., $CF(CF_3)_2$). This is contrary to what has been noted in earlier studies involving large R groups, where no dependence on R was found (leading to the linear relationships typified by Figure 6).[4] The plausible argument put forth to explain this phenomenon can be stated as follows.[4] A large L ligand could exert a steric trans influence on R, thereby lengthening the Co–C bond and reducing the electron-donating ability of R. However, as the trans influence of R decreases, the Co–L bond length should decrease, which would be unfavorable in the case of a large L ligand. This ground-state steric repulsion between L and the equatorial dioximato plane could be released in the dissociative transition state, enhancing the apparent trans effect of the poorly electron-donating R group. These two effects would contrapose each other and effectively cancel each other out.

We feel that the occurrence of ligand-exchange rate dependence on R in this study most likely originates from the extremely large bulk of the $CF(CF_3)_2$ group, as delineated in the crystallographic and NMR data, coupled with the proportionately large trans PPh_3 ligand (as compared to 4-CNpy). To the extent that trans influence parameters are transferrable to rate processes, the available data tend to support this hypothesis. For example, the Co–N(py) bond length decreases by ca. 0.06 Å for $pyCo(DH)_2R$ in going from R = *i*-Pr to R = $CF(CF_3)_2$. On the other hand for $Ph_3PCo(DH)_2R$, the Co–P bond lengths are essentially the same. In both series, the equatorial ligands are significantly bent toward the L ligand in the solid state for the $CF(CF_3)_2$ derivative, but not the *i*-Pr (Table IV). For $pyCo(DH)_2[CF(CF_3)_2]$, these unfavorable steric interactions are easily accommodated by the flat py ligand, which is situated in the plane (cleft) that bisects the O···O vectors. It would be expected that for the trigonally symmetric PPh_3 ligand, this would not be the case. The effect of L on the Co–C bond length, and by inference the electron-donating ability of R, is harder to assess, since the relevant structures of the PPh_3 derivatives are less than optimal. However, a larger increase in the Co–C bond length in going from L = py to L = PPh_3 is observed for R = *i*-Pr (ca. 0.14 Å) compared to R = $CF(CF_3)_2$ (ca. 0.07 Å). If significant, this suggests that any decrease in R donor ability due to bond lengthening is less in the $CF(CF_3)_2$ case than for *i*-Pr. In any event, the net result is that a modest steric trans effect is observed for $CF(CF_3)_2$, but not for *i*-Pr.

Conclusions

The molecular structure determination of complex 1, $Ph_3PCo(DH)_2[CF(CF_3)_2]$, confirms that the $CF(CF_3)_2$

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[43] Chen, Q.; Marzilli, L. G.; Bresciani-Pahor, N.; Randaccio, L.; Zangrando, E. *Inorg. Chim. Acta* **1988**, *144*, 241.

group has a large steric trans influence that is significantly greater than that of *i*-Pr. Though the Co–C bond in 1 is quite long for a poor electron-donating alkyl group, the most striking manifestation of the steric bulk of $CF(CF_3)_2$ is the bending of the dimethylglyoximato ligands toward the relatively large PPh_3 ligand (negative α angle) and movement of the Co atom toward C(9) (negative *d* value). This is the first example of such a reversal in these structural parameters for a cobaloxime containing PPh_3, which itself has a significant steric trans influence.[4].

A series of $LCo(DH)_2[CF(CF_3)_2]$ complexes was prepared, and the ^{19}F NMR spectra were compared. The ^{19}F chemical shift of the CF_3 group was largely dependent upon the steric size of the trans L ligand and for the most part, independent of electronic effects of L. Thus, for individual series of L ligands such as remotely substituted pyridine or aniline compounds, $\delta[^{19}F(CF_3)]$ remained essentially constant. This observation is consistent with relevant crystal structure results that indicate that there is very little dependence of structural parameters on electronic changes in L brought about by remote substitution.

On the other hand, the position of the ^{19}F resonance for the Co–CF moiety was highly dependent upon the electronic nature of L. In cases where steric constraints were kept constant, such as the substituted pyridine or aniline ligands, good to excellent correlations of $\delta[^{19}F(Co–CF)]$ with pK_a values of L and Hammett substituent constants were found. In all cases $\delta[^{19}F(Co–CF)]$ is significantly further upfield from values reported for other transition-metal perfluoroisopropyl complexes;[28-32] the chemical shifts in the present study approach those in main-group organometallic compounds.[33-35] This suggests that the alkyl group is more electron rich and/or that the M–C bonding in the cobaloxime complexes may be more ionic than in the complexes containing π-acceptor ligands. Differences in metal magnetic anisotropy[36] cannot be ruled out as being a pertinent factor.

The apparently very large bulk of the $CF(CF_3)_2$ group manifests itself in some notable thermodynamic and kinetic results. While most 2-substituted pyridine ligands evince little tendency to bind to the $Co(DH)_2[CF(CF_3)_2]$ fragment, $2\text{-}NH_2py$ does bind. The ambidentate nature of this ligand allows it to bind through either the "endo" pyridyl nitrogen or the "exo" amino nitrogen atoms. The steric trans influence of the $CF(CF_3)_2$ group is sufficient that the endo–exo equilibrium is shifted considerably to the exo side.

Most interestingly, we have observed for the first time a demonstrably measurable steric trans effect for ligand-exchange substitution for organocobaloxime complexes. For $LCo(DH)_2[CF(CF_3)_2]$, the complex with L = PPh_3 is substituted more rapidly than would be expected on the basis of the substitution rate for the complex with L = 4-CNpy. This result, as well as others mentioned above, can be ascribed for the most part to the large size of the perfluoroisopropyl ligand. However, the poor electron-donating ability of $CF(CF_3)_2$ undoubtedly plays a significant role as well. Thus, similar consequences might obtain for other alkyl ligands that are sufficiently sterically bulky and similarly electronically deficient.

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Supplementary Material Available: For 1, complete tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates (7 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.