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Cobalt Complexes with Bulky Perfluorinated Alkyl Ligands. Synthesis, Characterization, and Molecular Structure of *trans*-Bis(dimethylglyoximato)(pyridine)(*F*-isopropyl)cobalt(III)

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The preparation of $pyCo(DH)_2[CF(CF_3)_2]$ (**1**) from $Na[pyCo(DH)_2]$ and $(CF_3)_2CFI$ is described, where py = pyridine and DH = the monoanion of dimethylglyoxime. The Co(I) anion reagent is prepared from $pyCo(DH)_2Cl$ and 0.25 molar equiv of $NaBH_4$. Larger proportions of reducing agent result in no isolable organocobalt(III) complex presumably due to decomposition of the alkylating agent and/or decomposition of **1** by the excess $NaBH_4$ to give $(CF_3)_2CFH$, as demonstrated by ^{19}F NMR spectroscopy. The reduction of **1** with $NaBH_4$ is proposed to proceed through the intermediacy of $(CF_3)_2CF^-$ and $Na[pyCo(DH)_2]$ from deuterium-labeling studies. Synthetic methodology is also reported for the preparation of $LCo(DH)_2[CF(CF_3)_2]$, where L = H_2O, 4-*tert*-butylpyridine (4-*t*-Bupy), and $P(OCH_3)_3$. Complex **1** crystallizes in the monoclinic space group $P2_1/m$, with $a = 9.013$ (2) Å, $b = 13.524$ (4) Å, $c = 9.412$ (2) Å, $\beta = 101.07$ (2)°, $V = 1125.8$ (5) Å^3, and $Z = 2$, and was refined to $R = 0.049$. The structure is characterized by large distortions due to the bulky alkyl group. Comparisons are made to $pyCo(DH)_2[CH(CH_3)_2]$, the structure of which had previously been determined.

The superior stability of fluoroalkyl organometallic complexes, as compared to those with simple, nonfluorinated alkyl ligands, has been recognized for some time.[1,2] This effect likely may arise from kinetic factors, such as suppression of β-hydrogen elimination decomposition pathways; however, a shortening of the M–C bond due to contributions from ionic–covalent resonance structures and rehybridization (more s character) of the carbon σ orbital may also enhance the bond stability, as well as partial double-bonding character in the metal–carbon (M–C) bond.[1-6] Although the latter suggestions can be probed via X-ray or electron diffraction analysis, relatively few *direct* structural comparisons involving organometallic molecules containing M–C (sp^3) σ-bonded alkyl ligands have appeared where *all* atoms are held constant save for H to F substitution in the alkyl ligand.[7]

The bis(dimethylglyoximato)cobalt(III) system, generically known as the cobaloximes, would seem to be nearly *ideal* for structural comparisons of this type. This class of compounds has been the object of intense study as models for vitamin B_{12} chemistry and is capable of stabilizing alkyl derivatives with a wide range of functionalities.[8] Furthermore, much is already known about their structural properties,[9,10] which should greatly facilitate the interpretation of potential variations in bonding parameters brought about by fluorine substitution at the coordinated carbon atom. As part of our investigations of highly fluorinated organocobalt(III) complexes, we have prepared and structurally characterized $pyCo(DH)_2[CF(CF_3)_2]$ (**1**). Complex **1** is the first perfluoroisopropyl derivative of a transition metal with a partially filled d subshell to be studied by X-ray diffraction methods.[11] As such, it allows for the first direct assessment of structural perturbations caused by fluorine substitution in sterically large alkyl groups in otherwise isostructural organometallic complexes.

We have also studied the decomposition of **1** by $NaBH_4$ in basic methanol solution, since this reaction impacts upon the synthesis and isolation of this complex. In addition, methods for preparing $LCo(DH)_2[CF(CF_3)_2]$ (L = H_2O, 4-*tert*-butylpyridine (4-*t*-Bupy), $P(OCH_3)_3$) are reported, along with assessments of the electronic and steric properties of the bulky perfluorinated ligand as judged from NMR spectral data.

Experimental Section

Materials and Methods. ^1H, ^{19}F, and ^{13}C NMR spectra were obtained on a Varian XL-300 spectrometer at 299.943, 282.203, and 75.429 MHz, respectively. Spectra obtained in $CDCl_3$ or Me_2SO-d_6 solution were referenced to internal $(CH_3)_4Si$ (^1H and ^{13}C) or internal $CFCl_3$ (^{19}F) unless otherwise noted. Elemental analyses were determined by Atlantic Microlabs, Inc., Atlanta, GA.

$PyCo(DH)_2[CF(CF_3)_2]$ (1). NaOH (1.2 g, 52.2 mmol) in H_2O (5 mL) was added to a suspension of $pyCo(DH)_2Cl$[12] (6.0 g, 14.88 mmol) in methanol (300 mL) in a 500-mL Schlenk flask. The resulting brown-orange solution was degassed and placed under nitrogen by three freeze/pump/thaw cycles (*caution*! the large thermal expansion of the methanol necessitates careful thawing from the top of the solid in order to avoid rupturing of the flask). Under nitrogen flush, $NaBH_4$ (0.15 g, 3.72 mmol) in H_2O (5 mL) was added at −10 °C and the solution was allowed to warm to room temperature to give a dark green solution. Then $(CF_3)_2CFI$ (5.28 g, 17.85 mmol) was syringed in, resulting in an immediate color change to dark orange. The reaction mixture was stirred for 1 h and then opened to air. Acetone (10 mL) and H_2O (15 mL) were added and the organic solvents removed under reduced pressure. The precipitated light red-brown powder was collected on a frit, washed with diethyl ether (3 × 5 mL), and air-dried. The crude product was recrystallized from acetone/water. Yield: 2.3 g (29%). Anal. Calcd for $C_{16}H_{19}F_7N_5O_4Co$: C, 35.77; H, 3.56; N, 13.04. Found: C, 36.04; H, 3.52; N, 12.84. ^1H NMR ($CDCl_3$): δ 8.50 (m, 2 H, py α-H), 7.73 (m, 1 H, py γ-H), 7.29 (m, 2 H, py β-H), 2.24 (s, 12 H, DH–CH_3). ^{13}C NMR ($CDCl_3$): δ 153.28 (C=N), 149.68 (py α-C), 138.54 (py γ-C), 125.47 (py β-C), 12.63 (DH–CH_3). ^{19}F NMR ($CDCl_3$): δ −69.10 (d, ^3J(F–F) = 9.5 Hz, 6 F, CF_3), −197.1 (br s, 1 F, Co–CF).

$H_2OCo(DH)_2[CF(CF_3)_2]$. $PyCo(DH)_2[CF(CF_3)_2]$ (1.5 g, 2.74 mmol) was dissolved in methanol/water (250 mL/50 mL) and stirred with Dowex 50W-X8 (50–100 mesh, H^+ form) ion-exchange resin for 27 days. The resin was filtered, and the solvents were removed. The brown residue was washed with CH_2Cl_2 (20 mL) and air-dried. Yield: 1.3 g (98%). Anal. Calcd for $C_{11}H_{16}F_7N_4O_5Co$: C, 27.74; H, 3.39; N, 11.77. Found:

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C, 27.92; H, 3.31; N, 11.60. ^{1}H NMR (Me_2SO-d_6): δ 3.33 (s, 2 H, OH_2), 2.32 (s, 12 H, DH–CH_3). ^{13}C NMR (Me_2SO-d_6): δ 152.66 (C=N), 12.30 (DH–CH_3). ^{19}F NMR (Me_2SO-d_6): δ –67.55 (d, ^3J(F–F) = 9.2 Hz, 6 F, CF_3), –197.13 (m, ^3J(F–F) = 9.5 Hz, 1 F, Co–CF).

$LCo(DH)_2[CF(CF_3)_2]$ (L = 4-*t*-Bupy or $P(OCH_3)_3$). $H_2OCo(DH)_2[CF(CF_3)_2]$ (0.10 g, 0.21 mmol) was suspended in CH_2Cl_2 (10 mL), and a slight excess of the ligand (L) was added. The mixture was stirred until all of the solid was dissolved and filtered through a sintered frit. The product was precipitated by slow addition of petroleum ether, collected on a frit, and washed with petroleum ether.

For L = 4-*t*-Bupy, the yield of yellow-orange powder was 0.061 g (49%). Anal. Calcd for $C_{20}H_{27}F_7N_5O_4Co$: C, 40.48; H, 4.59; N, 11.80. Found: C, 40.51; H, 4.63; N, 11.83. ^{1}H NMR ($CDCl_3$): δ 8.34 (d, 2 H, py α-H), 7.23 (d, 2 H, py β-H), 2.24 (s, 12 H, DH–CH_3), 1.25 (s, 9 H, *t*-Bu–CH_3). ^{13}C NMR ($CDCl_3$): δ 163.08 (py γ-C), 153.08 (C=N), 149.01 (py α-C), 122.71 (py β-C), 34.93 (*t*-Bu–C), 30.13 (*t*-Bu–CH_3), 12.66 (DH–CH_3). ^{19}F NMR ($CDCl_3$): δ –69.11 (d, ^3J(F–F) = 9.5 Hz, 6 F, CF_3), –197.8 (br s, 1 F, Co–CF).

For L = $P(OCH_3)_3$, the yield of yellow powder was 0.088 g (72%). Anal. Calcd for $C_{14}H_{23}F_7N_4O_7PCo$: C, 28.88; H, 3.98; N, 9.62. Found: C, 29.16; H, 3.97; N, 9.48. ^{1}H NMR ($CDCl_3$): δ 3.64 (d, ^3J(P–H) = 10.5 Hz, 9 H, OCH_3), 2.27 (d, ^5J(P–H) = 2.7 Hz, 12 H, DH–CH_3). ^{13}C NMR ($CDCl_3$): δ 152.20 (C=N), 54.62 (d, ^2J(P–C) = 9.1 Hz, OCH_3), 12.34 (DH–CH_3). ^{19}F NMR ($CDCl_3$): δ –69.05 (m, CF_3), –205.43 (br s, Co–CF).

Reaction of 1 with $NaBH_4$ or $NaBD_4$. The general procedure will be provided below. Four experiments were done with the following combinations of reagents: experiment 1, $NaBH_4/NaOH/CH_3OH$; experiment 2, $NaBH_4/NaOD/CD_3OD$; experiment 3, $NaBD_4/NaOH/CH_3OH$; experiment 4, $NaBD_4/NaOD/CH_3OD$. Methanol (0.5 mL containing 2.0 mg of NaOH or NaOD) was syringed under nitrogen into a serum-capped NMR tube that contained **1** (15.0 mg, 0.028 mmol), $NaBH_4$ or $NaBD_4$ (0.14 mmol), and a sealed capillary filled with D_2O for locking purposes. The starting material dissolved immediately, giving an orange solution that rapidly turned dark blue-green. The ^{19}F NMR spectra for experiments 1 and 3 were essentially identical and contained only one species, $(CF_3)_2CFH$ (ppm relative to external $CFCl_3$): –75.60 (d of d, ^3J(F–F) = 11.0 Hz, ^3J(H–F) = 5.6 Hz, 6 F, CF_3), –215.60 (d, of sept, ^2J(H–F) = 42.5 Hz, CFH) [lit.[13] (CH_3OH, internal $CFCl_3$): –76.6 (d of d, ^3J(F–F) = 11 Hz, ^3J(H–F) = 5.5 Hz), –214.7 (d of sept, ^2J(H–F) = 45 Hz)]. The ^{19}F NMR spectra for experiments 2 and 4 were essentially identical and contained virtually only one species, $(CF_3)_2CFD$, with very small amounts of $(CF_3)_2CFH$ present due to residual incomplete isotopic labeling of the starting reagents (ppm relative to external $CFCl_3$): –75.67 (d, ^3J(F–F) = 11.0 Hz, 6 F, CF_3), –216.00 (m, ^2J(D–F) = 5.8 Hz, CFD) [lit.[13] (CH_3OH, internal $CFCl_3$): –76.64 (d, ^3J(F–F) = 11 Hz), –215.14]. In the case of experiment 2, CH_3I (6.8 μg, 0.028 mmol) was added after 15 min, giving an immediate color change to orange. The ^{1}H NMR spectrum showed resonances at δ 2.16 (s, 12 H, DH–CH_3) and 0.84 (s, 3 H, Co–CH_3). Addition of a small amount of authentic $pyCo(DH)_2CH_3$ to the NMR tube resulted in attendant increases in intensity for these two resonances, thus confirming their above assignments to the organocobalt(III) complex.

Reaction of $(CF_3)_2CFI$ with $NaBH_4$. $NaBH_4$ (5.3 mg, 0.14 mmol) was dissolved in CH_3OH (0.5 mL, containing 2.0 mg of NaOH) under nitrogen in a serum-capped NMR tube equipped with a sealed capillary of D_2O. $(CF_3)_2CFI$ (7 mg, 0.028 mmol) was syringed in, and the ^{19}F NMR spectrum showed resonances at the same frequencies and with the same splitting patterns as described above for $(CF_3)_2CFH$.

X-ray Crystallographic Study. Crystals of **1** were obtained by slow evaporation of a saturated acetone/water solution at 0–5 °C and subjected to single-crystal X-ray diffraction analysis with Mo Kα radiation (λ = 0.71073 Å). The details of the crystal data, data collection methods, and refinement procedures for **1** are given in Table I and in supplementary Table S1. Atomic positional parameters are provided in Table II. Full listings of thermal parameters, bond lengths and angles, and hydrogen coordinates can be found in the supplementary material. Full details of the crystallographic methodologies may be found in ref 14.

Table I. Summary of Experimental Details for the X-ray Diffraction Study of $pyCo(DH)_2[CF(CF_3)_2]$ (**1**)

T, K	296
space group	$P2_1/m$
a, Å	9.013 (2)
b, Å	13.524 (4)
c, Å	9.412 (2)
β, deg	101.07 (2)
V, Å^3	1125.8 (5)
Z	2
D_{calcd}, g cm^{-3}	1.59
cryst color and shape	maroon block
cryst dimens, mm^3	0.30 × 0.25 × 0.35
no. reflcns collcd	2229
no. reflcns used in refinement ($\lvert F_o\rvert \geq 6\sigma\lvert F_o\rvert$)	1722
no. of params refined	157
λ(Mo Kα), Å	0.71073
abs coeff, cm^{-1}	8.11
R	0.049
R_w	0.052

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3)

	x	*y*	*z*	*U*(eq)[a]
Co	1818 (1)	2500	986 (1)	33 (1)
F(1)	4870 (3)	2500	2527 (3)	64 (1)
F(2)	3628 (3)	743 (2)	3093 (3)	95 (1)
F(3)	2290 (3)	1485 (3)	4465 (3)	107 (1)
F(4)	4711 (3)	1573 (2)	4955 (3)	103 (1)
O(1)	674 (3)	605 (1)	1531 (2)	47 (1)
O(2)	2790 (3)	589 (2)	162 (3)	55 (1)
N(1)	530 (3)	1587 (2)	1674 (3)	36 (1)
N(2)	3012 (3)	1587 (2)	144 (3)	40 (1)
N(3)	322 (4)	2500	–935 (3)	35 (1)
C(1)	3426 (5)	2500	2900 (5)	49 (2)
C(2)	3496 (5)	1565 (4)	3829 (4)	76 (2)
C(3	–201 (4)	1650 (2)	–1586 (3)	48 (1)
C(4)	–1261 (4)	1635 (2)	–2841 (4)	56 (1)
C(5)	–1817 (6)	2500	–3468 (5)	57 (2)
C(6)	–605 (3)	1952 (2)	2188 (3)	39 (1)
C(7)	–1736 (4)	1313 (3)	2677 (4)	59 (1)
C(8)	3972 (3)	1953 (3)	–565 (3)	48 (1)
C(9)	4933 (5)	1328 (3)	–1348 (4)	75 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

Preparation of $PyCo(DH)_2[CF(CF_3)_2]$ (1) and Related Derivatives. Reaction of $Na[pyCo(DH)_2]$, prepared from $pyCo(DH)_2Cl$ and only *0.25 molar equiv* of $NaBH_4$, with 1.2 molar equiv of $(CF_3)_2CFI$ in basic, degassed methanol under N_2, followed by usual workup, gave **1** in 25–30% yield based upon starting cobalt complex. Larger molar quantities of reducing agent, which are routinely employed in analogous procedures involving nonfluorinated alkylating agents,[8,15] resulted in *no* isolable organocobalt complex. Interestingly, the reaction of $Na[Mn(CO)_5]$ with perfluoroalkyl iodides, such as $(CF_3)_2CFI$, produces $Mn(CO)_5I$ rather than the organometallic complex.[16,17] This result can be understood in terms of a reversal in polarities in the C–I bond brought about by the electron-withdrawing fluorine atoms and possible shielding of the secondary carbon site by fluorine lone pairs.[18] The isolation of **1** in the present case, instead of $pyCo(DH)_2I$, suggests that a single electron transfer, rather than S_N2 mechanism, may be operative.[19]

The py ligand of **1** may be replaced by H_2O by ion-exchange-resin-assisted substitution. The reaction is essentially quantitative but is extremely slow (the typical reaction time is ca. 4 weeks; only 60% conversion is realized after 2 weeks). This result is in keeping with the poor electron-donating character of the $(CF_3)_2CF$ group (vide infra) and is comparable to the 11-day reaction period required for the analogous substitution of pyCo-

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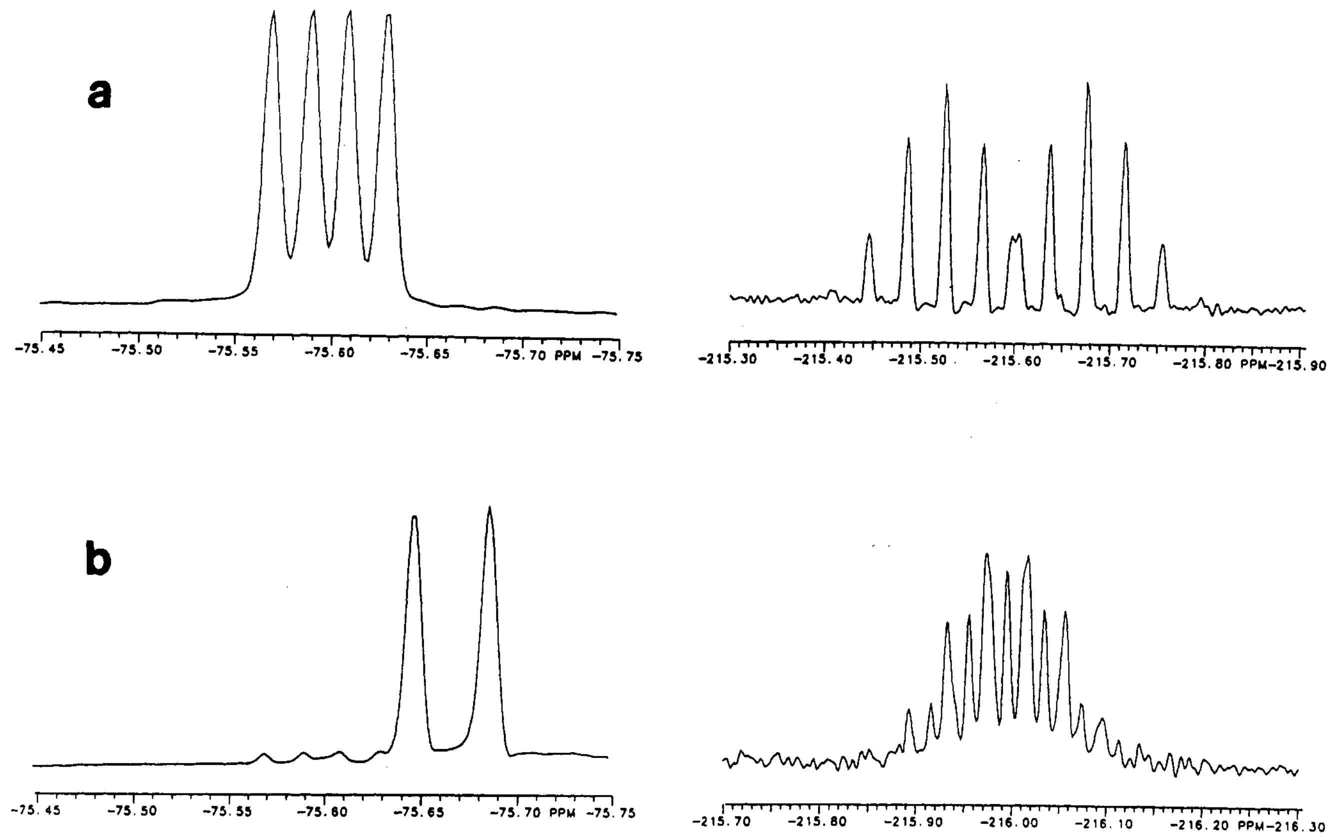

Figure 1. ^{19}F NMR spectra for the reduction of **1** by (a) $NaBH_4$ in $CH_3OH/NaOH$ to give $(CF_3)_2CFH$ and (b) $NaBH_4$ in $CD_3OD/NaOD$ to give $(CF_3)_2CFD$ with a trace of $(CF_3)_2CFH$. In each case, the CF_3 resonance is displayed to the left and the CF resonance to the right. The reduction of **1** with $NaBD_4$ in $CH_3OH/NaOH$ and $NaBD_4$ in $CH_3OD/NaOD$ gave spectra analogous to (a) and (b), respectively.

$(DH)_2CF_3$.[20] The aquo ligand of $H_2OCo(DH)_2[CF(CF_3)_2]$ is facilely replaced by other neutral two-electron donors, such as 4-*t*-Bupy and $P(OCH_3)_3$ (see Experimental Section).

Decomposition of 1 by $NaBH_4$. The amount of reducing agent employed is critical to the successful preparation and isolation of **1** and was studied in some detail. Both $(CF_3)_2CFI$ and **1** are decomposed rapidly under the reaction conditions by excess $NaBH_4$ to give $(CF_3)_2CFH$, as judged by ^{19}F NMR spectroscopy (see Experimental Section). Thus, the observation regarding usage of only 1 reducing equiv per starting Co complex (vide supra) in order to obtain **1** is likely due to consumption of alkylating agent and/or organocobalt product[21] by excess reducing equivalents.

The reduction of **1** by excess $NaBH_4$ in basic methanol solution to give $Na[pyCo(DH)_2]$ and $(CF_3)_2CFH$ is much more rapid than for analogous nonfluorinated alkyl cobaloximes (e.g., for R = $CH(CH_3)_2$), presumably due to a lower reduction potential for **1** as a result of fluorine substitution. In support of this argument, electrochemical studies of $H_2OCo(chel)R$ (where chel is a tetradentate N_2O_2 Schiff base ligand) have demonstrated a significantly greater ease of electroreduction and lower reduction potentials for these complexes when R is perfluorinated.[22,23]

Product studies were performed to identify the reaction products and their mode of formation. The presence of the Co(I) anionic complex could be inferred by the prompt color change from dark blue-green to orange upon addition of methyl iodide to yield $pyCo(DH)_2CH_3$ (identified by ^1H NMR spectroscopy; see Experimental Section). When the reduction was accomplished with $NaBD_4$ in $CH_3OH/NaOH$, only $(CF_3)_2CFH$ was formed. On the other hand, reductions with $NaBH_4$ in $CD_3OD/NaOD$ or $NaBD_4$ in $CH_3OD/NaOD$ gave essentially only $(CF_3)_2CFD$ (see Figure 1). The latter experiment implies that a $(CF_3)_2CF^-$ carbanion is formed during the decomposition, since the alkyl radical would be expected to abstract a hydrogen atom from CH_3OD on thermodynamic grounds.

Table III. Cobalt Coordination Environment for **1**

Bond Lengths (Å)			
Co-N(1)	1.892 (2)	Co-N(2)	1.908 (2)
Co-N(3)	2.037 (3)	Co-C(1)	2.084 (5)
Bond Angles (deg)			
N(1)-Co-N(2)	98.8 (1)	N(1)-Co-N(3)	87.6 (1)
N(1)-Co-C(1)	94.3 (1)	N(2)-Co-N(3)	87.8 (1)
N(2)-Co-C(1)	90.3 (1)	N(3)-Co-C(1)	177.5 (2)

Two scenarios are possible to explain the above results: the first would entail a one-electron reduction of the starting perfluoroalkyl complex to give the Co(II) anionic complex $\{pyCo(DH)_2[CF(CF_3)_2]\}^-$, which undergoes Co-C bond heterolysis to give $(CF_3)_2CF^-$ and $[pyCo(DH)_2]$. The latter is then quickly reduced by $NaBH_4$ to give $[pyCo(DH)_2]^-$. Alternatively, two rapid one-electron reductions might occur to give dianionic $\{pyCo(DH)_2[CF(CF_3)_2]\}^{2-}$, which could decompose to give the perfluorinated carbanion and the Co(I) anionic complex. Electrochemical reductions of $H_2OCo(chel)R$ indicate that both processes are possible, although the latter occurs only during very rapid scans.[22,23] We note that previous studies involving the reductive decomposition of (nonfluorinated alkyl)cobaloximes by $NaBH_4$ obtained similar results in deuteration experiments, even though Co-C bond homolysis to give alkyl radicals was demonstrated by other methods.[21d] In the present case, however, we feel that the $(CF_3)_2CF^-$ carbanion forms, rather than $(CF_3)_2CF^•$, by analogy to the electrochemical studies that demonstrated perfluorocarbanion formation in the electrochemical reductions of

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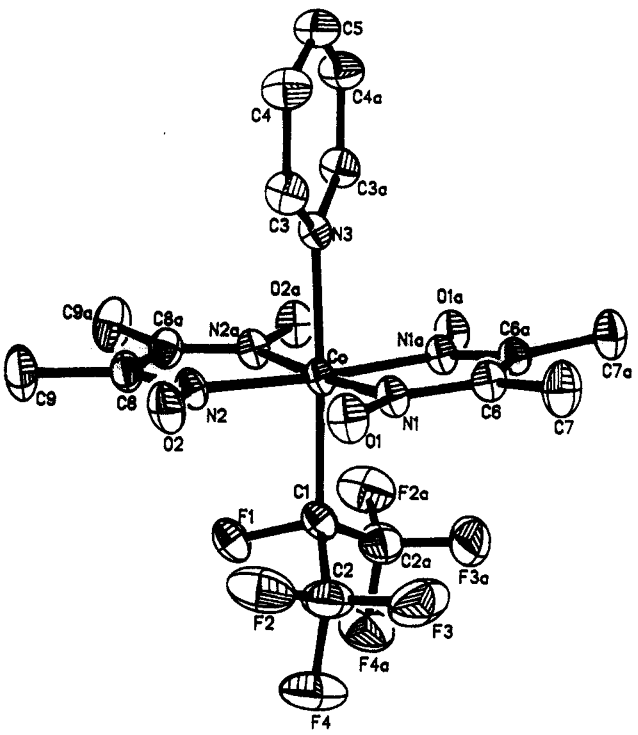

Figure 2. ORTEP drawing the numbering scheme for **1**. Atoms related by the crystallographic mirror plane are indicated by the letter "a" affixed to the label for one of the atoms in the pair.

Table IV. Comparisons of Selected Structural Parameters for PyCo(DH)$_2$[CX(CX$_3$)$_2$] (X = F, H)

X	F[a]	H[b]
Co-N(py), Å	2.037 (3)	2.099 (2)
Co-C, Å	2.084 (5)	2.085 (3)
N(py)-Co-C, deg	177.5 (2)	174.1 (2)
Co-C(1)-C(2), deg	116.0 (2)	114.0 (2), 114.3 (2)
Co-C(1)-X, deg	107.9 (3)	
C(2)-C(1)-C(2a), deg	111.3 (3)	112.3 (3)
d, Å[c]	−0.075	+0.04
α, deg[d]	−10.3	+4.0

[a] This work. [b] Reference 24. [c] Displacement of the Co atom out of the N$_4$ donor plane; positive values indicate toward the neutral py ligand, while negative values indicate toward the alkyl ligand. [d] Interplanar angle between DH ligands; positive values indicate bending away from the neutral py ligand, while negative values indicate bending away from the alkyl ligand.

H$_2$OCo(chel)R, where R is a perfluoroalkyl ligand and chel is a tetradentate N$_2$O$_2$ Schiff base ligand.[22,23]

X-ray Structural Study of 1. The crystals of **1** consist of discrete pyCo(DH)$_2$[CF(CF$_3$)$_2$] units lying on a crystallographic mirror plane that bisects the DH and axial ligands (Figure 2). Selected bond lengths and angles involving the cobalt coordination sphere and structural comparisons to pyCo(DH)$_2$[CH(CH$_3$)$_2$] (**2**)[24] of interest are collected in Tables III and IV, respectively. The data suggest that the CF(CF$_3$)$_2$ group is a significantly sterically larger but much poorer electron-donating ligand (Co–N(py) bond length decreases by about 0.06 Å) than CH(CH$_3$)$_2$. The d value of −0.075 Å (Co moves toward the alkyl ligand) in **1** is the largest value ever observed for this parameter in a pyridine-substituted cobaloxime;[9,10,25] the negative α value (bending *away* from the alkyl ligand) is only surpassed in the pyridyl complex containing the bulky CH$_2$C(CH$_3$)(COOEt)$_2$ ligand.[26] Apparently, the 10–15% increase in van der Waals radius[27] of F vs H causes a profound difference in overall size of the alkyl ligands.

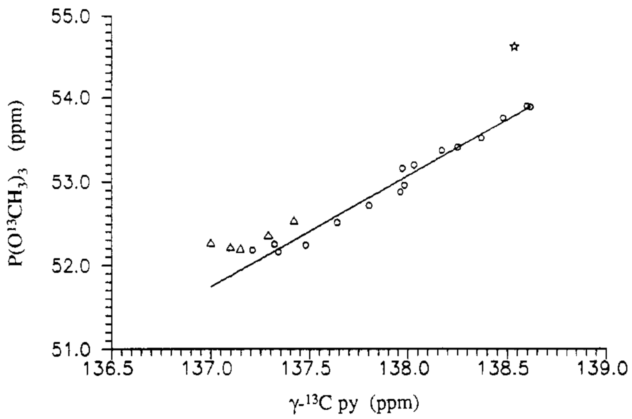

Figure 3. Linear regression correlation for the ^{13}C chemical shift of the γ-C of coordinated py vs the ^{13}C chemical shift of the ester carbon of coordinated P(OCH$_3$)$_3$ in LCo(DH)$_2$R. Data are taken from refs 9, 28, and 29a and this work. The circular data points are included in the least-squares analysis, while the triangular points are not. Circular data points (left to right): CH(CH$_3$)$_2$, CH$_2$CH(CH$_3$)$_2$, CH$_2$CH$_3$, CH$_3$, (CH$_2$)$_3$CN, (CH$_2$)$_2$CN, CH$_2$Br, CH$_2$I (lower), CH$_2$CO$_2$CH$_3$ (upper), CH$_2$CF$_3$, CH(CN)CH$_3$, CH$_2$CN, CF$_2$CFClH, CH$_2$NO$_2$, CH(CN)Cl, CH(CN)CH$_2$CN. Triangular data points (left to right): 1-adamantyl, CH(CH$_2$CH$_3$)$_2$, c-C$_6$H$_{11}$, CH$_2$C(CH$_3$)$_3$, CH$_2$Si(CH$_3$)$_3$. The star is for CF(CF$_3$)$_2$.

Further evidence for the above assertions may be derived by a comparison of the ^{13}C NMR chemical shifts of the γ-C of coordinated pyridine and the ester carbon of coordinated P(OCH$_3$)$_3$ in the corresponding LCo(DH)$_2$R compounds. It has previously been noted that both of these NMR parameters are sensitive indicators of the electron-donating ability of the trans alkyl ligand.[9] If R is relatively small in size, then a reasonably good linear correlation (correlation coefficient = 0.98) is found between these two chemical shifts (see Figure 3). However, if R is large, then significant deviations from the regression line are observed. It is believed that these deviations arise from increased lengthening of the Co–C bond in the P(OCH$_3$)$_3$ complex vis-à-vis the py complex in response to increased unfavorable steric interactions with the equatorial ligands in the phosphite complex.[9,24] Thus, the alkyl ligand appears to be a poorer electron-donating ligand in the P(OCH$_3$)$_3$ complex than in the py case. For R = CF(CF$_3$)$_2$, we have the first example of this effect being observed for a poorly electron-donating alkyl ligand. As can be seen in Figure 3, the CF(CF$_3$)$_2$ data point has the largest departure from the regression line for ligands of small to moderately large steric bulk.

The geometry of the alkyl ligand is also of interest. The Co–C bond lengths are nearly identical in **1** and **2**. In general, a shortening of the M–C bond by ca. 0.05–0.12 Å has previously been observed upon substitution of F for H in complexes with less bulky perfluorinated alkyl ligands.[3-6,29,30] Presumably, the large size of the CF(CF$_3$)$_2$ ligand (vide supra) precludes the usual reduction in bond length. However, the C(1)–F(1) distance of 1.412 (5) Å is significantly longer than typical C–F distances of 1.33–1.34 Å.[31] This result could possibly be considered as arising from contributions from a "no-bond" resonance structure involving back-bonding from filled cobalt orbitals into the C(1)–F(1) antibonding orbital.[32] The highly shielded ^{19}F chemical shift of

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−197.1 ppm for F(1) lends some support to this notion. Alternatively, this C–F bond lengthening and high-field ^{19}F chemical shift may be due to a rehybridization by C(1) such that more p character is found in the orbital used to form the bond to F(1), or they may reflect a significant ionic contribution in the Co–C bonding.[1] There is a pronounced flattening of the tetrahedron involving Co, C(1), C(2), and C(2a) (Co–C(1)–C(2) = 116.0 (2)°; summation of the angles involving these atoms is 343.3°; F(1)–C(1)–C(2) = 101.7 (3)°) suggesting that more s character might be utilized in the C–C bonds. However, the C(1)–C(2) bond distance is 1.532 (5) Å, which would seem to argue against rehybridization. Thus, the best explanation at this time would appear to be that there is significant carbanionic character involving the carbon atom bonded to the cobalt atom.

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Supplementary Material Available: Tables of crystallographic, intensity, and structure solution and refinement data, bond lengths and angles, thermal parameters, and hydrogen atom coordinates (3 pages); a listing of structure factors for pyCo(DH)$_2$[CF(CF$_3$)$_2$] (7 pages). Ordering information is given on any current masthead page.

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Reduction Pathways in Lateral and Diagonal (η^5-C_5Me_5)Re(CO)$_2$Br$_2$. Synthesis, Structure, and Reactivity of [(η^5-C_5Me_5)Re(CO)$_2$Br$^-$]

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The rhenium anion [(η^5-C_5Me_5)Re(CO)$_2$Br$^-$] (**2**$^-$) has been prepared in high yield from the reaction of lateral or diagonal (η^5-C_5Me_5)Re(CO)$_2$Br$_2$ (**1**) with alkyl/aryllithium and Grignard reagents, trialkylborohydrides, and one-electron reducing agents. The molecular structure of **2**$^-$ (as the [PPP$^+$] salt) was established by X-ray crystallography. [(η^5-C_5Me_5)Re(CO)$_2$Br][PPP] crystallizes in the orthorhombic space group *Pbca* with a = 20.646 (5) Å, b = 17.690 (5) Å, c = 17.555 (3) Å, V = 6412 Å^3, and Z = 8. Solution FT-IR studies of **2**$^-$ (in THF) reveal the presence of only solvent-separated ion pairs when the gegencation is [Li$^+$], [K$^+$], or [PPP$^+$] from −70 °C to room temperature. [**2**][Na] at room temperature displays a 39:61 mixture of carbonyl oxygen–sodium and solvent-separated ion pairs, respectively. Variable-temperature FT-IR examination of [**2**][Na] reveals a reversible temperature-dependent equilibrium involving both anionic species. The equilibrium constant for these ion pairs has been determined by IR band-shape analysis over the temperature range −70 °C to room temperature, and values of ΔH and ΔS are reported. The reactivity and stability of **2**$^-$ are described.

Introduction

Synthetic routes to the (cyclopentadienyl)dicarbonylrhenium dihalide compounds CpRe(CO)$_2$X$_2$ (where X = Br, I) have been known for several years.[1–4] Of these dihalides, the dibromide has received much attention in terms of chemical investigation[5] and as a precursor in the synthesis of other four-legged piano-stool complexes based on the CpRe fragment.[6–13] However, synthetic pathways to the corresponding (pentamethylcyclopentadienyl)dicarbonylrhenium dihalides, Cp*Re(CO)$_2$X$_2$ (where Cp* = C_5Me_5), have only recently been described in detail. While the diiodide Cp*Re(CO)$_2$I$_2$, initially obtained from the reaction of Cp*$_2$Re$_2$(CO)$_5$ with I$_2$, was the first compound of this genre prepared,[14] it was not until the work of Sutton et al. that reliable and stereoselective syntheses of these dihalide compounds were reported.[15–18] As such, the reactivity of these dihalides remains to be explored and established. Four-legged piano-stool complexes of the form CpMX$_2$Y$_2$ may exist as two nonequivalent stereoisomers that are commonly referred to as *cis* and *trans* isomers. We have adopted King's nomenclature[2] to describe the isomeric dibromides discussed in this paper. Here the descriptors lateral and diagonal correspond to the cis and trans stereoisomers, respectively.

The reaction of CpRe(CO)$_2$Br$_2$ with Grignard reagents has been reported.[6] However, no mention was made of the relationship between the product dependence and initial dibromide stereochemistry. Furthermore, while the reported physical data dealing with such compounds as CpRe(CO)$_2$Br(Me), CpRe(CO)$_2$I(Me), and CpRe(CO)$_2$(Me)$_2$ are not in question, we do not believe that these represent products of direct alkyl/bromide exchange.

In related reactivity studies using the isomeric dibromides, CpRe(CO)$_2$Br$_2$, we have observed that a direct metathetical re-

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