Synthesis, Characterization, and Reactivity of (Fluoroalkyl)- and (Fluorocycloalkyl)cobaloximes: Molecular Structure of a (2-Fluorocyclohexyl)cobaloxime Complex and Hindered Rotation of 2-Fluorocycloalkyl Ligands

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Reaction of $Ph_3P-[Co]^-$ ([Co] = $Co(dmgH)_2$; $dmgH_2$ = dimethylglyoxime), prepared by reduction of $Ph_3P-[Co]-Cl$ with $NaBH_4$ in methanolic NaOH, with $BrCH_2CH_2CH_2F$ resulted in formation of $Ph_3P-[Co]-CH_2CH_2CH_2F$ (**3**). In neutral methanolic solutions py*−[Co]−H/py*−[Co]$^-$ (py* = py, 4-(*t*-Bu)py, 3-Fpy; 4-(*t*-Bu)py = 4-*tert*-butylpyridine, 3-Fpy = 3-fluoropyridine) were found to react with $BrCH_2CHF_2$, yielding the 2,2-difluoroethyl complexes py*−[Co]−CH_2CHF_2 (py* = py (**4a**), 4-(*t*-Bu)py (**4b**), 3-Fpy (**4c**)). Reactions of XCH_2CH_2F (X = Br, TfO; TfO = triflate) with reduced cobaloximes in alkaline and neutral methanolic solutions resulted in formation of the 2-methoxyethyl complexes py*−[Co]−CH_2CH_2OMe (py* = py (**5a**), 4-(*t*-Bu)py (**5b**), 3-Fpy (**5c**)) with ethylene as side product. py*−[Co]−H/py*−[Co]$^-$ (py* = py, 3-Fpy) was found to react with $TfOCH_2CMe_2F$, yielding py*−[Co]−$CH{=}CMe_2$ (py* = py (**6a**), 3-Fpy (**6b**)) and $H_2C{=}CMe_2$. All these reactions indicate the formation of the (unseen) intermediate py*−[Co]−CH_2CR_2F (R = H, Me), which decomposes via nucleophilic substitution (F → OMe), heterolytic fragmentation, yielding olefins, and HF elimination, yielding vinyl complexes, respectively. Analogous reactions of reduced cobaloximes with *trans*-1-bromo-2-fluorocyclohexane and *trans*-1-bromo-2-fluorocyclopentane resulted in the formation of (2-fluorocyclohexyl)- and (2-fluorocyclopentyl)-cobaloximes, py*−[Co]−$C_6H_{10}F$ (py* = py (**7a**), 4-(*t*-Bu)py (**7b**)) and py*−[Co]−C_5H_8F (py* = py (**10a**), 4-(*t*-Bu)py (**10b**)). All these complexes were fully characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopic investigations. Molecular structures of the cobaloximes **3**, **4a**, **7b**, and **7b**·CH_2Cl_2 were obtained by single-crystal X-ray diffraction analyses, exhibiting complexes with an equatorial pseudomacrocyclic $(dmgH)_2$ ligand as well as axial base (PPh_3, py*) and organo ligand in mutually trans positions. The cycloalkyl complexes are the *ae* isomers, having the sterically demanding $Co(dmgH)_2$ moieties as equatorial substituents. The axially oriented fluoro substituents give rise to hindered rotation of 2-fluorocycloalkyl ligands, as indicated by two distinct sets of signals for dmgH ligands in the ^1H and ^{13}C NMR spectra. Further proof for this came from DFT calculations of py−[Co]−$C_6H_{10}F$ (**11**) and, for comparison, of the cyclohexyl complex py−[Co]−C_6H_{11} (**12**). The conformational energy diagrams of **11** and **12** are discussed.

1. Introduction

The strongest carbon-element single bond is the C−F bond. This, along with the small size and high electronegativity of fluorine atoms, is the reason for numerous unusual and sometimes unique stabilities and reactivities of organometallics containing fluorinated ligands. Thus, C−F bond activation is a challenge in organometallic and coordination chemistry.[1] The chemistry of organometallics with perfluorinated hydrocarbon ligands has been well explored ever since the synthesis of $[Mn(CF_3)(CO)_5]$ in 1959, the first transition-metal complex of this type.[2] On the other hand, complexes containing alkyl or cycloalkyl ligands having carbon atoms with fluorine *and* hydrogen atoms (−CH_2F, −CHF_2, −C(R)HF; R = alkyl) have been much less investigated. Thus, up to now transition-metal com-

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plexes of the type $L_xM-CH_2CH_2F$ have not been described. Only in the reaction of $[Rh(Cp)(\eta^2\text{-}H_2C{=}CH_2)(\eta^2\text{-}H_2C{=}CHF)]$ with HCl at −80 °C, have ^{1}H NMR spectroscopic investigations given some indication that $[Rh(CH_2CH_2F)Cl(Cp)(\eta^2\text{-}H_2C{=}CH_2)]$ could be formed.[3]

Organocobalt and, in a broader sense, also organorhodium complexes with the pseudomacrocyclic bis(dimethylglyoximato) ligand L−[M]−R (L = axial base, R = organo ligand, [M] = $M(dmgH)_2$, M = Co, Rh, $dmgH_2$ = dimethylglyoxime) are not only useful and widely used vitamin B_{12} coenzyme models[4] but proved to be also a suitable class of organometallics that are readily accessible with a large variety of organo ligands R, among them heteroatom-functionalized ones. In the case of alkyl and cycloalkyl cobaloximes and rhodoximes with fluorine substitution[5] at the β-carbon atom, the 2,2,2-trifluoroethyl complexes $L-[M]-CH_2CF_3$ (M = Co, Rh)[6] and 2,2-difluoroethyl complexes $L-[Co]-CF_2CHF_2$[7] (prepared via insertion of perfluoroethylene into the Co−H bond) have been prepared. Our own investigations[8] to obtain a monofluoroethyl rhodoxime complex in the reaction of $Ph_3P-[Rh]^-$ with $BrCH_2CH_2F$ resulted in a C−F activation reaction to generate the binuclear ethylene-bridged rhodoxime complex $Ph_3P-[Rh]-CH_2CH_2-[Rh]-PPh_3$[9] in high yields. This unexpected reaction prompted us to extend our investigations on cobaloximes and on analogous reactions using 2,2-difluoroethyl ($BrCH_2CHF_2$) as well as monofluoro-substituted compounds with better leaving groups and/or higher carbon substitution ($TfOCH_2CH_2F$; $TfOCH_2CMe_2F$; 1-bromo-2-fluorocyclohexane and -pentane). Thus, we succeeded in synthesizing and fully characterizing $Ph_3P-[Co]-CH_2CHF_2$, py*−[Co]−$C_6H_{10}F$, and py*−[Co]−C_5H_8F (py* = py, 4-(*t*-Bu)py; $C_6H_{10}F$ = 2-fluorocyclohexyl; C_5H_8F = 2-fluorocyclopentyl). For the first time, 2,2-difluoroethyl and 2-fluorocyclohexyl transition-metal complexes could also be characterized structurally. NMR spectroscopic investigations gave evidence for hindered rotation of 2-fluorocycloalkyl ligands around the Co−C bond. To get further proof that the C−F activation described above is restricted to fluorine substitution at the β-position, we synthesized and characterized the 3-fluoropropyl complex $Ph_3P-[Co]-CH_2CH_2CH_2F$ as well. Part of this work has been previously reported.[10]

Scheme 1

$$Ph_3P-[Co]^- \xrightarrow[-\,Br^-]{+\,BrCH_2-CH_2-CH_2F} Ph_3P-[Co]-CH_2-CH_2-CH_2F$$

(**3**)

2. Results and Discussion

2.1. (3-Fluoropropyl)cobaloximes. (a) Synthesis and Characterization. Reaction of $Ph_3P-[Co]^-$, prepared by reduction of $Ph_3P-[Co]-Cl$ with $NaBH_4$ in methanolic NaOH, with $BrCH_2CH_2CH_2F$ resulted in formation of $Ph_3P-[Co]-CH_2CH_2CH_2F$ (**3**) (Scheme 1). Complex **3** was isolated as orange microcrystals in 65% yield. The identity of **3** was confirmed by microanalysis, NMR (^{1}H, ^{13}C, ^{19}F, ^{31}P) spectroscopy, and X-ray diffraction analysis. The protons of the trimethylene group represents an AA′MM′XX′spin system that is coupled with the ^{31}P nucleus ($I = {}^1/_2$, 100% natural abundance) and the ^{19}F nucleus ($I = {}^1/_2$, 100% natural abundance). The protons of the 3-CH_2F group appear as a doublet of triplets ("dt"). A first-order treatment (i.e., to treat the protons as an $A_2M_2X_2$ spin system) results in coupling constants $^3J_{H,H} = 6.5$ Hz and $^2J_{F,H} = 47.7$ Hz. The coupling $^2J_{F,H}$ is virtually the same as that in 1-fluoropropane (48.5 Hz).[11] As for other organocobaloximes, the large electric quadrupole moment of ^{59}Co (0.42×10^{-28} m^2)[12] combined with $I = {}^7/_2$ gave rise to line broadening so that the signal of the ^{13}C nucleus directly bound to cobalt could not be detected. δ_C(*C*H_2F) and $^1J_{F,C}$ in complex **3** are close to the corresponding values in 1-fluoropropane[13] (83.3 vs 85.2 ppm, 167.3 vs 163.3 Hz).

(b) Molecular Structure. The molecular structure of complex **3**, obtained by single-crystal X-ray diffraction analysis, is shown in Figure 1. Selected bond lengths and angles are given in Table 1. Co is coordinated in a distorted-octahedral geometry by four nitrogen atoms of the pseudomacrocyclic $(dmgH)_2$ ligand in the equatorial plane and by one carbon and one phosphorus atom of the 3-fluoropropyl and triphenylphosphine ligands, respectively, in mutually trans positions (C9−Co−P = 173.9(1)°). Distortion of the $Co(dmgH)_2$ moiety is relatively small, as the distance *d* of the cobalt atom from the mean N_4 plane and the dihedral angle α between the two dmgH planes exhibit ($d = +0.066(1)$ Å, α = 1.7(2)°; positive values indicate displacement toward L and bending toward R).[14] The 3-fluoropropyl ligand exhibits a fully staggered conformation (Co−C9−C10−C11 = 175.4(3)°). The C−F bond in **3** has the same length as that in the corresponding rhodoxime $Ph_3P-[Rh]-CH_2CH_2CH_2F$ (1.357(5) vs 1.361(8) Å[8]), the only further structurally characterized 3-fluoropropyl complex. These two C−F bonds are relatively short, as comparison with

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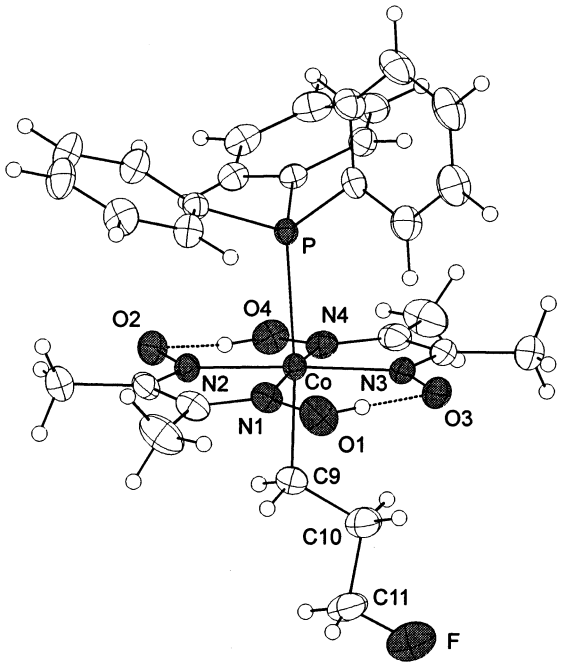


Figure 1. Molecular structure of $Ph_3P-[Co]-CH_2CH_2-CH_2F$ (**3**) showing the numbering scheme (displacement ellipsoids at 30% probability).

Table 1. Selected Interatomic Distances (in Å) and Angles (in deg) for $Ph_3P-[Co]-CH_2CH_2CH_2F$ (3)

Co-P	2.4121(8)	C10−C11	1.517(5)
Co−C9	2.050(3)	C11−F	1.357(5)
C9−C10	1.479(5)	Co−N_{dmgH}	1.877(3)−1.880(3)

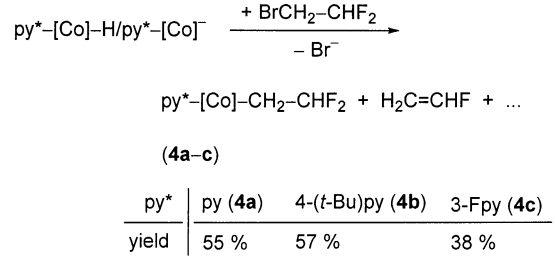
P−Co−C9	173.9(1)	Co−C9−C10	120.8(3)
N1−Co−N4	174.9(1)	C9−C10−C11	111.2(4)
N2−Co−N3	177.1(1)	C10−C11−F	110.3(4)
Co−C9−C10−C11	175.4(3)	C9−C10−C11−F	170.1(4)

C−F bonds in organic $-CH_2F$ and >CHF compounds reveals (median, 1.399 Å; lower/upper quartile, 1.389/1.408 Å; 25 observations).[15]

2.2. (2,2-Difluoroethyl)cobaloximes. (a) Synthesis and Characterization. Reduced cobaloximes L−[Co]$^-$ with phosphines (L = PBu_3, PPh_3) as axial bases were found to react with $BrCH_2CHF_2$, yielding only vinyl fluoride. The formation of 2,2-difluoroethyl complexes could not be established. In contrast to this, the reaction of py−[Co]$^-$, prepared by reduction of py−[Co]−Cl with $NaBH_4$ in methanolic NaOH, resulted in the formation of the expected 2,2-difluoroethyl complex py−[Co]−CH_2CHF_2 (**4**) in 26% yield. Vinyl fluoride was found to be a side product. Higher yields were obtained in neutral solutions. Thus, reactions of py*−[Co]−Cl (py* = py, 4-(*t*-Bu)py, 3-Fpy) with $NaBH_4$ in methanol at −30 °C gave a mixture of py*−[Co]$^-$ and py*−[Co]−H ($pK_a \approx 10$)[4a] that reacts with $BrCH_2CHF_2$, giving the 2,2-difluoroethyl complexes py*−[Co]−CH_2CHF_2 (**4a**−**c**) in 38−57% yields (Scheme 2). Vinyl fluoride was also found to be a side product.

The identities of (2,2-difluoroethyl)cobaloximes **4a**−**c** were confirmed by microanalyses and ^{1}H, ^{13}C, and ^{19}F NMR spectroscopic investigations as well as for **4a** also by X-ray crystallography. Although the protons of the CH_2CHF_2 ligand are part of an AA′MXX′ spin system

Scheme 2



(A, M = ^{1}H, X = ^{19}F), the proton resonances have a first-order appearance (see Figure 2, for example). The 1-CH_2 groups appear as pseudotriplets of doublets and the 2-CHF_2 groups as pseudotriplets of triplets. Fluorine−hydrogen couplings were obtained in first-order treatments of the spectra. They are very similar to those in 1,1-difluoroethane:[16] $^2J_{F,H}$ = 58.7−58.9 Hz vs 56.7 Hz and $^3J_{F,H}$ = 21.7−22.1 Hz vs 19.9 Hz. Splitting of the signals of the 2-C atoms into triplets ($^1J_{F,C}$ = 240.5−240.9 Hz; for comparison CH_3CHF_2 with $^1J_{F,C}$ = 233.5 Hz) is indicative of CHF_2 groups. In comparison with 1,1-difluoroethane, the ^{19}F resonances in complexes **4a**−**c** are low-field shifted by about 7−8 ppm (−101.4 to −101.8 ppm vs −109.3 ppm[16]).

(b) Molecular Structure. Crystals of py−[Co]−CH_2-CHF_2 (**4a**) suitable for X-ray diffraction measurements were obtained from thf/diethyl ether. Crystals contain discrete molecules of **4a** without unusual intermolecular interactions. The molecular structure is shown in Figure 3. The difluoroethyl ligand is disordered over three positions with occupancies of 40 (A), 35 (B), and 25% (C) (see the Experimental Section). As shown in Figure 3, this is due to a "rotation" of the CHF_2 group around the Co−C9 and C9−C10 bonds. Disorder of this type may be caused by the well-known ability of fluorine to substitute hydrogen in organics without causing gross geometrical distortions (cf. typical bond lengths 1.3 Å for C−F with 1.0 Å for C−H and van der Waals radii of 1.20−1.45 Å for H and 1.50−1.60 Å for F).[17] Pyridine and difluoroethyl ligands are in mutually trans position (N5−Co−C9A = 170.8(4)°). The Co−C bonds in cobaloximes py*−[Co]−R with fluorinated ethyl ligands (Table 2) are all of the same length (1.997(6)−2.03(2) Å) within the 3σ criterion. In organocobaloximes py−[Co]−R the length of the Co−N_{py} bond can be considered to be a measure for the (structural) trans influence of organo ligand R. Values of complexes with fluorinated ethyl ligands are shown in Table 2.[18] Although complexes having differently substituted pyridine bases and differently distorted coordination polyhedra (measured by *d* and α; see Table 2) are compared, it can be seen that all fluorine-substituted ethyl ligands exhibit a smaller (structurally) trans influence than the ethyl ligand, whereas differences within the fluorine-substi-

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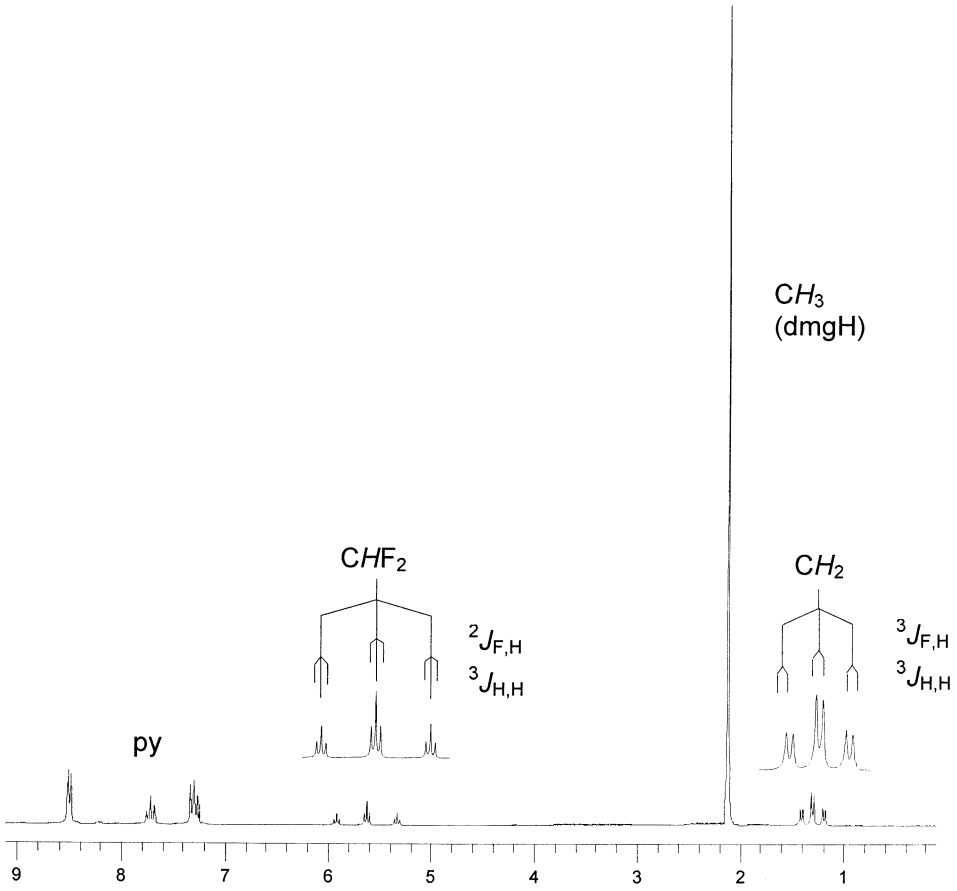

Figure 2. 200 MHz ^{1}H NMR spectrum of py−[Co]−CH_2CHF_2 (**4a**).

Table 2. Structural Parameters for Organocobaloximes py*−[Co]−R with Fluorinated Ethyl Ligands R (Values for R = Et for Comparison)

	py*	Co−N_{py} (Å)	Co−C (Å)	d^a (Å)	α^a (deg)	ref
CH_2CH_3	4-[HN=C(OMe)]py	2.081(3)	2.035(5)	0.05	9.1	18
CH_2CF_3	4-(NC)py	2.041(2)	2.010(3)	0.01	1.0	6b
CF_2CHF_2	py	2.036(4)	1.997(6)	−0.03	−9.5	7a
CH_2CHF_2	py	2.030(4)	2.03(2)	0.004(1)	1.9(4)	*b*
CF_2CF_3	py	2.024(6)	2.013(3)	−0.04	−8.8	5

[a] Displacement *d* of the Co atom out of the mean N_4-plane and interplanar angle α between the two dmgH ligands. Positive values indicate displacement toward py* and corresponding bending away from py*. [b] This work.

tuted ligands are only small. So far, complex **4a** is the only structurally characterized transition-metal complex having a 2,2-difluoroethyl ligand.

2.3. (2-Fluoroalkyl)- and (2-cycloalkyl)cobaloximes. (a) Synthesis and Reactivity. Reactions of py*−[Co]$^-$, prepared by reduction of py*−[Co]−Cl with $NaBH_4$ in methanolic NaOH, with $BrCH_2CH_2F$ resulted in formation of the (2-methoxyethyl)cobaloximes **5a**−**c** in (isolated) yields between 20 and 37% (Scheme 3). Ethylene was identified as a side product. Formation of these two products can be explained when the (unseen) 2-fluoroethyl complexes py*−[Co]−CH_2CH_2F are assumed as intermediates: nucleophilic substitution of fluorine by a methoxy group gave rise to formation of complexes **5** and heterolytic fragmentation[19] to formation of ethylene (Scheme 3). Even in neutral solutions at −30 °C, py*−[Co]−H/py*−[Co]$^-$ reacted with $BrCH_2$-CH_2F, giving ethylene and the 2-methoxyethyl complexes **5a**−**c**, but in lower yields (9−24%). Analogous results were obtained in the reaction between py−[Co]$^-$ and $TfOCH_2CH_2F$. Furthermore, a stabilization of the expected intermediate 2-fluoroethyl complex could not be achieved when the two *β*-hydrogen atoms were replaced by more bulky methyl groups: as shown in Scheme 3, reactions of $TfOCH_2CMe_2F$ with py*−[Co]−H/py*−[Co]$^-$ (py* = py, 3-Fpy) resulted in formation of complexes **6a**,**b** in low yields (15 and 5%, respectively). Isobutylene was found as a side product. From proposed (unseen) intermediates (py*−[Co]−CH_2CMe_2F), 2-methylprop-1-enyl complexes **6a**,**b** could be formed by HF elimination and isobutylene by heterolytic fragmentation.

The identities of (2-methoxyethyl)cobaloximes **5a**−**c** and of (2-methylprop-1-enyl)cobaloximes **6a**,**b** were confirmed unambiguously by ^{1}H and ^{13}C NMR measurements (see the Experimental Section). In complexes **5a**−**c** the protons of the Co−CH_2CH_2OMe groups give AA′XX′ (A, X = ^{1}H) spin systems. Due to nonresolved

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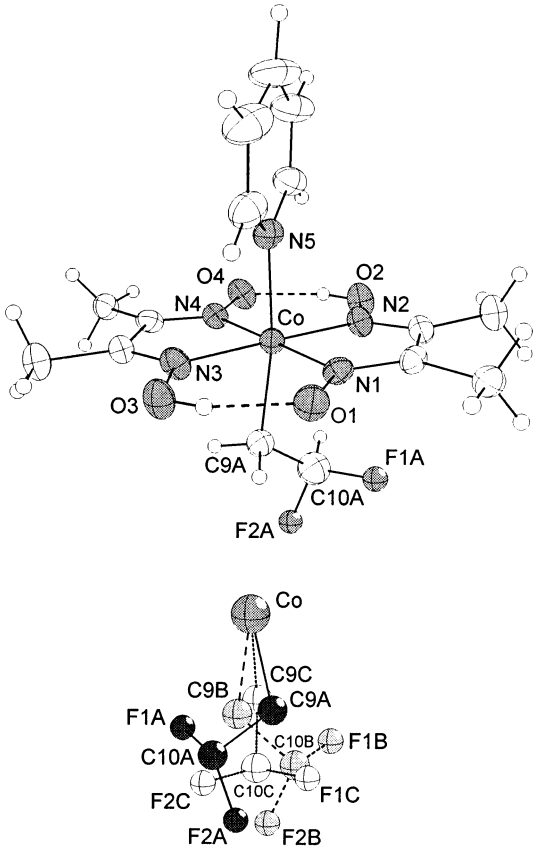


Figure 3. Molecular structure of py−[Co]−CH_2CHF_2 (**4a**, molecule A) (displacement ellipsoids at 30% probability) (top) and disorder of the 2,2-difluoroethyl ligand (bottom). Selected bond lengths (Å) and angles (deg): Co−N5 = 2.030(4), Co−C9A = 2.03(2), C9A−C10A = 1.495(8), C10A−F1A = 1.342(8), C10A−F2A = 1.345(8), Co−N_{dmgH} = 1.885(4)−1.896(4); N5−Co−C9A = 170.8(4), Co−C9A−C10A = 118(1), C9A−C10A−F1A = 108(1), C9A−C10A−F2A = 110(1), N1−Co−N4 = 179.7(2), N2−Co−N3 = 179.4(2)°. Values for molecules B and C are given in the Supporting Information.

ab subsystems,[20] the four protons appear as pairs of approximately 1:1:1 triplets with broadened middle lines ($N = J_{A,X} + J_{A,X'} = 16.0-16.6$ Hz).

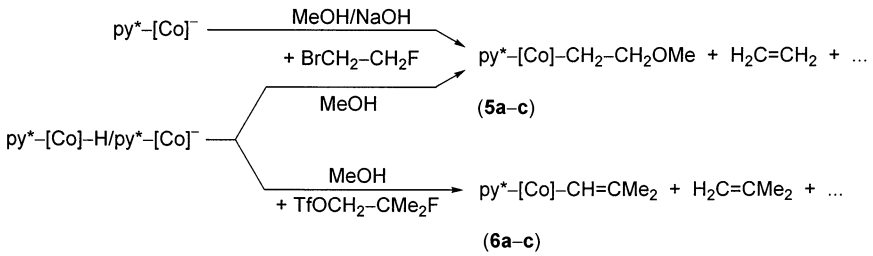
On the other hand, reactions of reduced cobaloximes with 1-bromo-2-fluorocycloalkanes proceeded with formation of the expected (2-fluorocycloalkyl)cobaloximes. Thus, reactions of py*−[Co]−H/py*−$[Co]^-$ (py* = py, 4-(*t*-Bu)py) with *trans*-1-bromo-2-fluorocyclohexane afforded the (2-fluorocyclohexyl)cobaloximes **7a**,**b** in 35 and 40% yields, respectively (Scheme 4). Cyclohexene was identified as a side product. For comparison, the analogous reaction of py−[Co]−H/py−$[Co]^-$ with bromocyclohexane was performed, giving the cyclohexylcobaloxime complex py−[Co]−C_6H_{11} (**8**) in 42% yield. Qualitatively, no difference in reactivity between bromocyclohexane and *trans*-1-bromo-2-fluorocyclohexane was observed.

The reaction of py−[Co]−H/py−$[Co]^-$ with the analogous cis derivative *cis*-1-bromo-2-fluorocyclohexane resulted also in formation of the 2-fluorocyclohexyl complex **7a**, but in much lower yield (<5%). Careful examination of the purity of the starting material made it clear that impurities of *trans*-1-bromo-2-fluorocyclohexane in the starting material (*cis*-1-bromo-2-fluorocyclohexane) as a source for complex **7a** can be excluded. In alkaline solutions, py−$[Co]^-$ was found to react with *cis*-1-bromo-2-fluorocyclohexane, forming complex **7a** in very low yield (about 3%). Longer reaction times gave rise to formation of a mixture of the desired 2-fluorocyclohexyl complex **7a** and the (cyclohex-1-enyl)cobaloxime py−[Co]−C_6H_9 (**9**; C_6H_9 = cyclohex-1-enyl) in about a 1:1 ratio (total yield ca. 3%). In close analogy to *trans*-1-bromo-2-fluorocyclohexane, *trans*-1-bromo-2-fluorocyclopentane was found to react with py*−[Co]−H/py*−$[Co]^-$ (py* = py, 4-(*t*-Bu)py) within 8 h, giving (2-fluorocyclopentyl)cobaloximes **10a**,**b** in 45 and 47% yields (Scheme 5).

The (2-fluorocyclohexyl)- (**7a**,**b**) and (2-fluorocyclopentyl)cobaloximes (**10a**,**b**) were isolated as brown (**7a**, **10a**) and orange (**7b**, **10b**) microcrystals that are stable for several days in air. They decompose at 160/150 °C (**7a**/**b**) and 155/150 °C (**10a**/**b**) without melting. Thermogravimetric investigations of **7b** and **10b** showed that decomposition takes place between 150 and 400 °C in three steps that are not well separated from each other (total mass loss about 75%). The identities of complexes **7a**,**b** and **10a**,**b** were proved by microanalysis and ^1H, ^{13}C, and ^{19}F NMR spectroscopy as well as for complex **7b** by single-crystal X-ray crystallography as well.

(b) Molecular Structure of 4-(*t*-Bu)py−[Co]−$C_6H_{10}F$ (7b). Slow evaporation of solvent at room temperature from solutions of complex **7b** in methylene chloride/*n*-hexane resulted in crystallization of brown crystals of the composition [Co($C_6H_{10}F$)(dmgH)$_2${4-(*t*-

Scheme 3

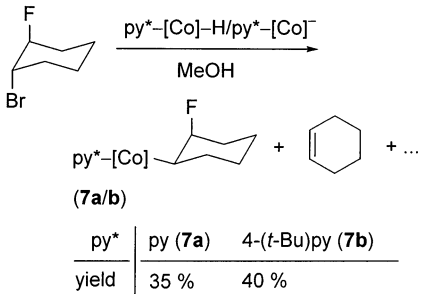


py*	py (**5a**)	4-(*t*-Bu)py (**5b**)	3-Fpy (**5c**)
yield[a]	37/24	35/21	20/9

py*	py (**6a**)	3-Fpy (**6b**)
yield	15 %	5 %

a) in % (alkaline/neutral medium)

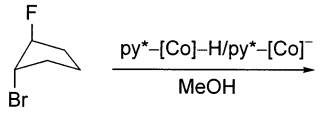
Scheme 4



(**7a**/**b**)

py*	py (**7a**)	4-(*t*-Bu)py (**7b**)
yield	35 %	40 %

Scheme 5



(**10a**/**b**)

py*	py (**10a**)	4-(*t*-Bu)py (**10b**)
yield	45 %	47 %

Bu)py}]·CH_2Cl_2 (**7b**·CH_2Cl_2). Evaporation of solvent to dryness gave rise to formation of single crystals of the composition [Co($C_6H_{10}F$)(dmgH)$_2${4-(*t*-Bu)py}] (**7b**). Both crystal structures consist of discrete molecules of [Co($C_6H_{10}F$)(dmgH)$_2${4-(*t*-Bu)py}] (and methylene chloride in **7b**·CH_2Cl_2) without unusual intermolecular interactions (shortest intermolecular contacts between nonhydrogen atoms >3.3 Å). The molecular structures along with the numbering schemes are shown in Figure 4. Selected bond lengths, bond angles, and torsion angles are given in Table 3. In both cases the space groups are nonchiral (*Pna*2$_1$, **7b**; *Cc*, **7b**·CH_2Cl_2) and the unit cells contain four formula units. The molecule of **7b** has two chiral centers with opposite configuration: $C9^R/C10^S$ and vice versa $C9^S/C10^R$. Thus, in both of these crystals each unit cell contains two pairs of enantiomers. In **7b**·CH_2Cl_2 the fluoro substituent is disordered over two positions with occupancies of 68% (−*C*10*HF*−) and 32% (−*C*14*HF*−). Both positions are equivalent, and the disorder may be due to similar van der Waals radii of H and F (1.20−1.45 vs 1.50−1.60 Å[17]). Two superimposed molecules have opposite configurations ($C9^R/C10^S$ (68%) ↔ $C9^S/C14^R$ (32%) and vice versa). Thus, the unit cell also contains the enantiomers pairwise. As shown in Table 3, both molecules exhibit a very similar structure. Due to the disorder described above, in the following all values given refer to molecules in crystals of **7b**.

The geometry around the central Co atom is distorted octahedral with four N-atom donors of the pseudomacrocyclic (dmgH)$_2$ ligand in equatorial positions. 4-*tert*-Butylpyridine and the 2-fluorocyclohexyl ligand are axially coordinated (C9−Co−N5 = 176.9(1)°). The cyclohexyl ring exhibits a chair conformation in a very good approximation:[21] the C−C−C−C torsion angles of the six-membered cycle are between 52.8(5) and 56.0(4)° with alternate signs. The 1,2-disubstituted cyclohexane adopts the (cis) *ae* conformation. As expected, the bulky Co(dmgH)$_2$ moiety occupies an equatorial position and the much smaller fluoro substituent an axial position. The C−F bond (1.428(5) Å) is long

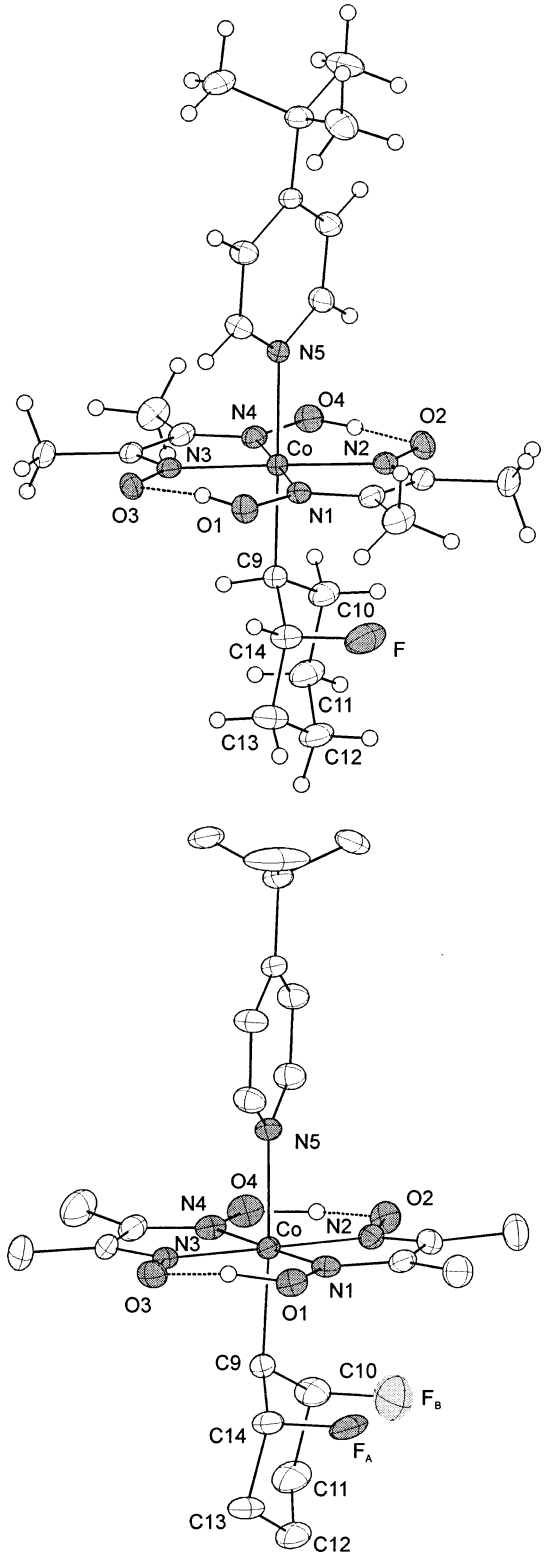


Figure 4. Molecular structure of 4-(*t*-Bu)py−[Co]−$C_6H_{10}F$ ($C_6H_{10}F$ = 2-fluorocyclohexyl) in crystals of **7b** (top) and **7b**·CH_2Cl_2 (bottom, without H atoms bound to carbon) showing the numbering scheme (F_A/F_B major/minor occupied position, 68/32%; displacement ellipsoids at 30% probability).

(20) Günther, H. *Angew. Chem.* **1972**, *84*, 907−920.
(21) Bucourt, R. *Top. Stereochem.* **1974**, *8*, 159−224.

Table 3. Selected Bond Lengths (in Å) and Angles (in deg) for 4-(*t*-Bu)py−[Co]−$C_6H_{10}F$ in Crystals of 7b and 7b·CH_2Cl_2 and Calculated Values for py−[Co]−$C_6H_{10}F$ (11a)

	7b	7b·CH_2Cl_2	11a[a]
Co−N5	2.085(3)	2.086(3)	2.142
Co−C9	2.082(3)	2.066(4)	2.046
C14−F	1.428(5)	1.434(6)[b]	1.422
C−C_{c-hex}	1.501(7)−1.532(5)	1.495(8)−1.547(6)	1.526−1.545
Co−N_{dmgH}	1.885(3)−1.890(2)	1.884(4)−1.898(3)	1.908−1.931
N5−Co−C9	176.9(1)	176.5(2)	176.47
N1−Co−N4	179.2(1)	179.1(2)	178.42
N2−Co−N3	179.1(1)	179.2(2)	178.48
C9−C14−F	109.7(3)	109.6(4)[c]	110.03
Co−C9−C14	116.1(2)	115.9(3)[d]	116.21
C−C−C−C_{c-hex}[e]	52.8(5)−56.0(4)	51.3(7)−55.7(5)	53.2−57.7

[a] Fully optimized structure at the DFT level of theory (B3LYP/BS2). [b] C14−F_A. C10−F_B = 1.49(2) Å. [c] C9−C14−F_A. C9−C10−F_B = 101.9(7)°. [d] Co−C9−C10 = 116.2(3)°. [e] Absolute values are given.

compared with C−F bonds in 1,2-disubstituted fluorocyclohexanes (median, 1.394 Å, lower/upper quartile, 1.383/1.404 Å; $n = 5$).[22] The Co−C9 bond in **7b** is as long as that in the cyclohexylcobaloxime complex Me_3bzm−[Co]−C_6H_{11} (Me_3bzm = 1,5,6-trimethylbenzimidazole):[23] 2.082(3) vs 2.073(4) Å.

(c) NMR Spectroscopic Investigations. Selected ^{1}H, ^{13}C, and ^{19}F NMR parameters of (2-fluorocycloalkyl)-cobaloximes are given in Table 4. All these data clearly indicate the constitution of the complexes. Protons of CHF groups appear at lower field (δ 4.70−4.83), and thus they are well separated from other cycloalkyl protons. The large quadrupole moment of the ^{59}Co nucleus combined with $I = {}^7/_2$ gave rise to broadening the C1 carbon resonances. Therefore, good signal-to-noise ratios were necessary to detect them. The resonances of carbon atoms C1 (δ 46.4, **7b**; δ 41.9, **10a**), C2 (δ 96.4−101.5), and fluorine atoms (δ −177.1 to −189.2) are low-field shifted compared with those in fluorocyclohexane and -pentane ($C_6H_{11}F/C_5H_9F$: δ_{CH_2CHF} 32.2/33.4; δ_{CHF} 91.0/96.5; δ_F −170.5/−174.2).[13a,24]

The most striking features in the ^{1}H and ^{13}C spectra are the two sets of all signals of the dimethylglyoximato ligands (except for the methyl carbon resonances in **10a**,**b**), showing that there is a hindered rotation of 2-fluorocycloalkyl ligands around the Co−C bonds: the 2-fluorocycloalkyl ligands in py*−[Co]−$C_6H_{10}F$ (**7a**,**b**) and py*−[Co]−C_5H_8F (**10a**,**b**) contain a chiral carbon atom. Free rotation around the Co−C bond gives rise to chemical equivalence of all four methyl groups of the equatorial $(dmgH)_2$ ligand. Thus, due to the mean C_{2v} symmetry, methyl groups in ^{1}H and ^{13}C NMR spectra should appear as singlet resonances (averaged chemical shifts result in coalescence to one resonance signal on the NMR time scale). Frozen rotation, the other borderline case, reduces the symmetry to C_1, and four distinct signals should be found. Due to the symmetry of $(dmgH)_2$ ligand, hindered rotation results in pairwise symmetrically equivalent positions that are interrelated by C_2 symmetry. One preferred orientation (having two equivalent positions) gives rise to two distinct signals with 1:1 intensities. This case was found experimentally (see Table 4). Temperature-dependent ^{1}H NMR spectroscopic measurements for **7b** support this interpretation: the shift difference $\Delta\delta$ between the two methyl proton resonances decreases from 31.9 Hz at −80 °C to 6.5 Hz at +99 °C (for details, see the Experimental Section). The solvent properties did not allow us to extend the temperature range. Thus, the two expected borderline situations (four distinct resonances vs one averaged resonance) could not be detected experimentally. Furthermore, NOE experiments (DPFGSE-NOE: double pulsed field gradient spin−echo NOE) of complex **7b** support this argument: saturating the very well shift-separated −C*H*F resonance (δ 4.70) of the 2-fluorocyclohexyl ligand of **7b** resulted in enhancement of intensity of one of the two methyl signals (intensity ratio $\delta(CH_3)_{1065\ Hz}/\delta(CH_3)_{1058\ Hz}$ in the NOE spectrum ca. 1/3). A similar phenomenon has been already observed: thus, hindered rotation of the axial 2-aminopyridine ligand in 2-(H_2N)py−[Co]−CH_2CF_3, caused by H-bonding of the NH_2 group to O−H···O bridges of the dimethylglyoximato ligands, resulted in splitting of glyoximato CH_3 group signals into two separate resonances.[25]

(d) Quantum Chemical Calculations. To get further insight into hindered rotation, quantum chemical calculations on the DFT level of theory were performed. As a model complex, we chose py−[Co]−$C_6H_{10}F$ (**11**), which is identical with complex **7a**. Calculations were performed in the gas phase, and solvation effects were not considered. The calculated structure of the most stable conformer **11a** (Figure 5) proved to be very similar to the molecular structure of 4-(*t*-Bu)py−[Co]−$C_6H_{10}F$ (**7b**) in the solid state, as comparison to Table 3 reveals. Especially, the orientation of the axial 2-fluorocyclohexyl ligand with respect to the equatorial $(dmgH)_2$ ligand measured by means of the torsion angle N1−Co−C9−C14 (16.5°) is close to that found in **7b** (2.6°) and **7b**·CH_2Cl_2 (25.6° for the major occupied position and N2−Co−C9−C14 = −26.8° for the minor occupied position). In all these structures the fluoro substituent lies approximately above a C=N carbon atom (Figure 6). As the conformational energy diagram

Table 4. Selected NMR Spectroscopic Data (δ in ppm, J in Hz) of (2-Fluorocyclohexyl)cobaloximes py*−[Co]−$C_6H_{10}F$ (7a,b) and (2-Fluorocyclopentyl)cobaloximes py*−[Co]−C_5H_8F (10a,b)

	organo ligand							$(dmgH)_2$		
	C^2HF			C^1H	C^3H_2	C^5H_2	C^4H_2/C^6H_2	CH_3		C=N
	δ_C ($^1J_{F,C}$)	δ_H ($^2J_{F,H}$)	δ_F	δ_C	δ_C ($^2J_{F,C}$)	δ_C	δ_C	δ_C	δ_H	δ_C
py−[Co]−$C_6H_{10}F$ (**7a**)	96.4 (171.1)	4.70 (47.5)	−189.2	*a*	34.6 (24.1)	20.9	29.2/29.6	11.97/12.01	2.10/2.12	150.1/150.9
4-(*t*-Bu)py−[Co]−$C_6H_{10}F$ (**7b**)	96.4 (170.7)	4.70 (47.3)	−187.7	46.4	34.6 (24.0)	20.9	29.2/29.5[b]	11.96/12.01	2.10/2.11	149.8/150.6
py−[Co]−C_5H_8F (**10a**)	101.2 (173.6)	4.82 (53.4)	−177.1	41.9	30.6 (24.4)	19.1	28.5	11.8	2.06/2.07	150.0/150.6
4-(*t*-Bu)py−[Co]−C_5H_8F (**10b**)	101.5 (173.2)	4.83 (53.3)	−177.1	*a*	30.7 (24.9)	19.2	28.5	11.9	2.08/2.09	149.8/150.5

[a] Not found, due to line broadening. [b] $^3J_{F,C}$ = 2.9 Hz.

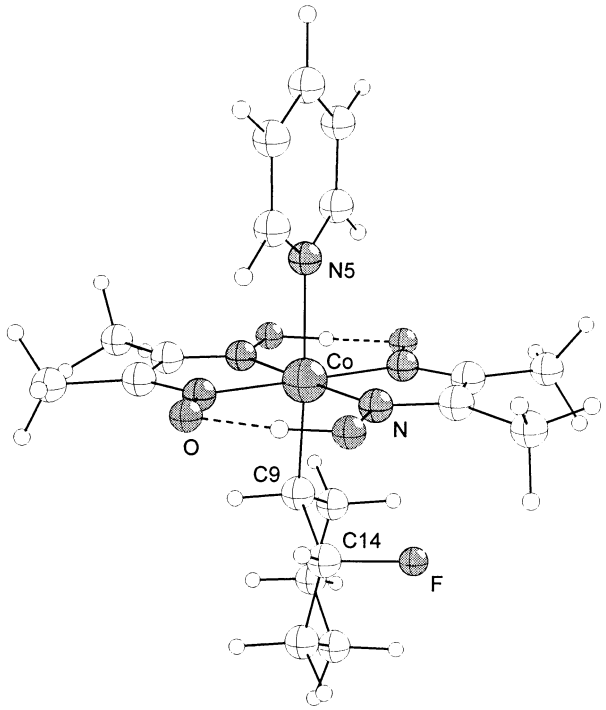


Figure 5. Calculated structure of py−[Co]−$C_6H_{10}F$ (**11**; $C_6H_{10}F$ = 2-fluorocyclohexyl).

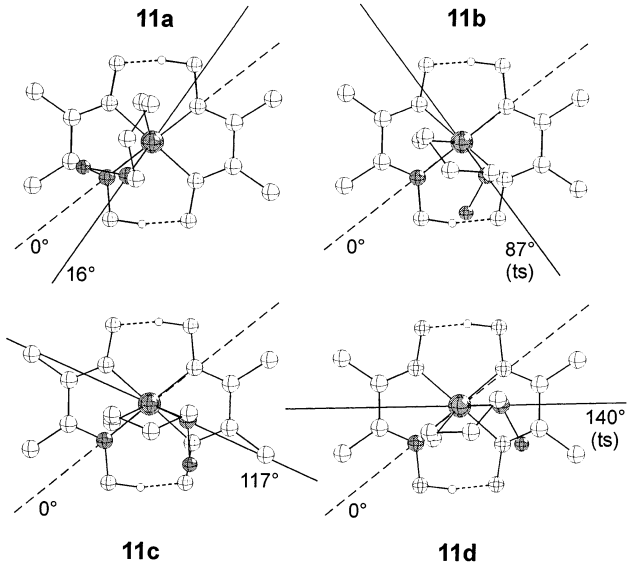


Figure 6. Calculated structures of rotational conformers of py−[Co]−$C_6H_{10}F$ (**11a**,**c**, equilibrium structures, N−Co−C−C = 16/117°; **11b**,**d**, transition states, N−Co−C−C = 87/140°) (view from above, pyridine ligand was omitted). Reference atoms for measuring the torsion angle N−Co−C−C (see Figure 7) and the fluoro substituent are shown in gray.

(Figure 7) exhibits, rotation of 2-fluorocyclohexyl ligands around the Co−C bond by 180° (giving a complete picture due to the C_2 symmetry of the $(dmgH)_2$ ligand) results in two minima and two maxima of potential energy. In the other minimum (N1−Co−C9−C14 = 117°) the fluoro substituent also lies above one C=N carbon atom (Figure 6). In the (global) transition state with the highest potential energy (N1−Co−C9−C14 = 87°) and in the local transition state (N1−Co−C9−C14 = 140°), the fluoro substituent lies above the O−H···O

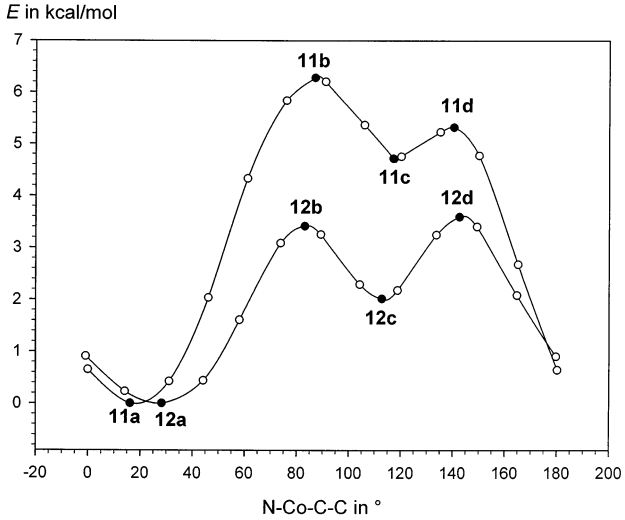


Figure 7. Conformational energy diagram for py−[Co]−$C_6H_{10}F$ (**11**) and py−[Co]−C_6H_{11} (**12**). Equilibrium structures and transition states are marked by closed circles. Structures **11a**−**d** and structure **12a** are shown in Figures 6 and 8, where the reference atoms for the torsion angle N−Co−C−C are given.

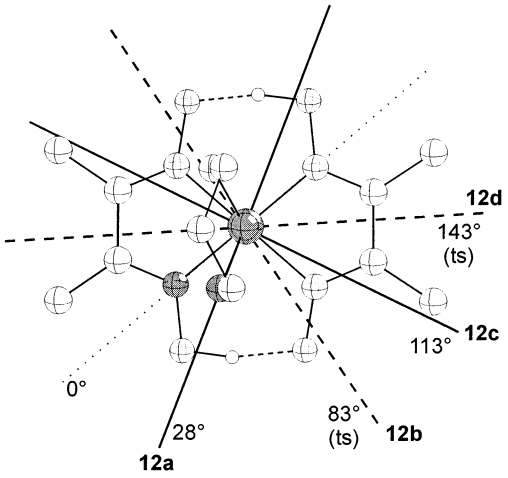


Figure 8. Calculated structure of the rotational conformer of py−[Co]−C_6H_{11} (**12a**, equilibrium structure, N−Co−C−C = 28°) (view from above, the pyridine ligand was omitted). Reference atoms for measuring the torsion angle N−Co−C−C (see Figure 7) are shown in gray. The magnitude of torsion angles in the other equilibrium structure **12c** is drawn as a solid line and in the transition states **12b** and **12d** as dashed lines.

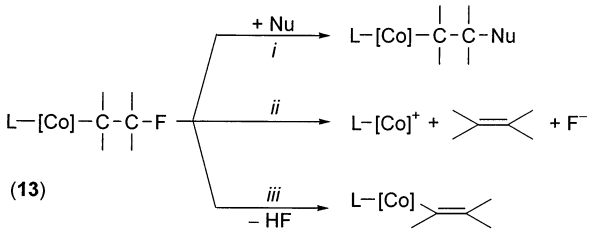
bridge and a methyl group, respectively (Figure 6). This can be rationalized in terms of electrostatic and steric repulsion between the fluoro substituent and the O−H···O and methyl groups, respectively. A conformational energy diagram for the analogous cyclohexylcobaloxime complex py−[Co]−C_6H_{11} (**12**) is shown in Figure 7. The energy barrier in complex **12** (**12a** → **12d**, ΔE = 3.59 kcal/mol) is roughly half of that of the fluoro-substituted complex **11** (**11a** → **11b**, ΔE = 6.28 kcal/mol; see Table 5). The absolute magnitude must not be overestimated: energy calculations of the optimized structures with a better basis set (see the Experimental Section) gave smaller barriers (Table 5), but the ratio ($\Delta E_{12}/\Delta E_{11}$) remains the same. Furthermore, consideration of solvent effects may result in a shift of these values.

Table 5. Energies of Equilibrium Structures and Transition States (ΔE in kcal/mol) for py−[Co]−$C_6H_{10}F$ (11) and py−[Co]−C_6H_{11} (12)[a]

	N−Co−C−C	ΔE^b	ΔE^c
py−[Co]−$C_6H_{10}F$ (**11**)			
eq str (global min) (**11a**)	16.1	0.00	0.00
ts (global max) (**11b**)	87.0	6.28	4.32
eq str (local min) (**11c**)	117.2	4.72	2.77
ts (local max) (**11d**)	140.4	5.32	4.03
py−[Co]−C_6H_{11} (**12**)			
eq str (global min) (**12a**)	109.8	0.00	0.00
ts (local max) (**12b**)	83.1	3.42	2.74
eq str (local min) (**12c**)	112.8	2.02	1.33
ts (global max) (**12d**)	142.6	3.59	2.98

[a] Conformations are characterized by the torsion angle N−Co−C−C (in deg), See Figures 6 and 7. [b] Basis set BS1. [c] Basis set BS2 (see the Experimental Section).

Scheme 6



3.4. Conclusions. The steric course of reactions of reduced cobaloximes with cyclohexyl derivatives has been shown to proceed with inversion of configuration at carbon, establishing the backside approach of the cobaloxime unit toward the C−X bond.[26] Furthermore, due to the large steric requirement of the cobaloxime group, Co(dmgH)$_2$ is forced to take an equatorial conformation. Formation of *cis*-(2-fluorocycloalkyl)cobaloximes (*ae* isomers) **7a**,**b** and **10a**,**b** starting from *trans*-1-bromo-2-fluorocycloalkanes is in accord with this. The corresponding reaction with *cis*-1-bromo-2-fluorocyclohexane did not proceed with formation of *trans*-(2-fluorocyclohexyl)cobaloxime (*ee* isomer) but with formation of the cis isomers **7a** in very small yield. In contrast, analogous reactions of *cis*- and *trans*-1-bromo-2-fluorocyclohexane with *trans*-[IrCl(CO)(PMe$_3$)$_2$] proceeded with loss of stereochemistry at carbon, forming a mixture of two isomers of [Ir($C_6H_{10}F$)Cl(Br)(CO)(PMe$_3$)$_2$].[27]

The remarkable activation of β-C−F bonds described in this work can be explained by alkylcobaloximes of type **13** (Scheme 6) as (unseen) intermediates. When these intermediates are presumed, the formation of products observed here can be understood by cleavage of the C−F bond in three different ways, namely (i) by nucleophilic substitution of F$^-$ (Nu/NuH = MeO$^-$/MeOH), (ii) by heterolytic fragmentation to form olefins, and (iii) by HF elimination to yield vinyl complexes. The last two reactions should be governed by stereoelectronic effects. Thus, concerted heterolytic fragmentation reactions and E2 elimination reactions normally require an antiperiplanar conformation.[28] Stable alkyl/cycloalkyl complexes that are only monofluorinated at the 2-position could only be obtained in cobaloximes with cycloalkyl ligands where conformational mobility is severely limited due to the space-demanding Co(dmgH)$_2$ moiety, which can only be bound in an equatorial position. The stability of these complexes with fluorine in an axial position can most probably be explained by the fact that heterolytic fragmentation is hampered by stereoelectronic effects. Once formed, (2-fluorocycloalkyl)cobaloximes proved to be very stable. HF elimination yielding allyl type complexes, (cyclohex-2-enyl)-/(cyclopent-2-enyl)cobaloximes, was not observed.

3. Experimental Section

3.1. General Comments. All reactions with Co^I were carried out under argon using Schlenk techniques. Solvents were dried and distilled under argon according to standard methods. The cobaloximes L−[Co]−Cl (L = PPh$_3$, py, 3-Fpy, 4-(*t*-Bu)py) and TfOCH$_2$CH$_2$F and TfOCH$_2$CMe$_2$F were obtained by published methods or in analogy to them.[29−32] Reactions of cyclohexene and cyclopentene with Et$_3$N·3HF/*N*-bromosuccinimide afforded *trans*-1-bromo-2-fluorocyclohexane and -pentane.[33] Ring opening of epoxycyclohexane with HF/py (*Warning!* Extreme care should be exercised while handling HF/py reagent. HF is extremely corrosive to human tissue.[34]) resulted in formation of *trans*-2-fluorocyclohexanol,[35] which reacted with PBr$_3$ to yield *cis*-1-bromo-2-fluorocyclohexane.[36] The other chemicals were commercial materials used without further purification. Microanalyses were performed by the University of Halle microanalytical laboratory using a CHNS-932 (LECO) and Vario EL (elementar Analysensysteme) elemental analyzer, respectively. The ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were obtained with Varian Unity 500, VXR 400, and Gemini 200 spectrometers (^{1}H at 500/400/200 MHz). Solvent signals (^{1}H, ^{13}C) were used as internal standards. δ(^{19}F) and δ(^{31}P) are relative to PhCF$_3$ (0.05% in C_6D_6, δ −63.9) and H_3PO_4 (85%, δ 0), respectively. In higher order multiplets *N* gives the distance between the most intense lines. Thermoanalytic investigations were performed on a STA 409C (Netzsch) instrument under an argon atmosphere. A CP9000 (Chrompack) chromatograph was used for gas chromatographic analyses.

3.2. L−[Co]$^-$/L−[Co]−H (L = PPh$_3$, py, 4-(*t*-Bu)py, 3-Fpy). To a solution of L−[Co]−Cl (1.3 mmol) in methanolic

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NaOH (0.15 M, 100 mL) was added a solution of $NaBH_4$ (75 mg, 2.0 mmol) in methanolic NaOH (0.15 M, 25 mL) dropwise, and the mixture was stirred for about 1−2 h at room temperature to give deep blue (L = PPh_3) and green (L = py, 4-(*t*-Bu)py, 3-Fpy) solutions of L−[Co]$^-$. To L−[Co]−Cl (L = py, 4-(*t*-Bu)py, 3-Fpy) (1.3 mmol) in methanol (50 mL) was added $NaBH_4$ (75 mg, 2.0 mmol) in small portions at −30 °C, and the mixture was stirred for a further 30 min at this temperature to give a green suspension of L−[Co]$^-$/L−[Co]−H.

3.3. Ph_3P−[Co]−$CH_2CH_2CH_2F$ (3). To Ph_3P−[Co]$^-$ (prepared from 1.3 mmol of Ph_3P−[Co]−Cl) in methanolic NaOH (125 mL, 0.15 M) was added $BrCH_2CH_2CH_2F$ (367 mg, 2.6 mmol) in MeOH (20 mL) dropwise. After the mixture had turned yellow (about 15 min), stirring was continued for 30 min and water (100 mL) was added. Then the reaction mixture was neutralized (pH 7−8) with solid CO_2. After 30 min the orange precipitate was filtered off, washed with water (3 × 5 mL) and diethyl ether (3 × 5 mL), and dried in vacuo. Yield: 438 mg (65%). Anal. Calcd for $C_{29}H_{35}CoFN_4O_4P$ (612.53): C, 55.17; H, 5.97. Found: C. 55.17; H, 5.97. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (m, 2H, 1-CH_2), 1.69 (m, 2H, 2-CH_2), 1.80 (d, $^5J_{P,H}$ = 3.30 Hz, 12H, CH_3 of dmgH), 4.32 ("dt", $^3J_{H,H}$ = 6.49 Hz, $^2J_{F,H}$ = 47.65 Hz, 3-CH_2), 7.24−7.53 (m, 15H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6 (s, *C*H_3 of dmgH), 30.2 (d, $^2J_{F,C}$ = 15.8 Hz, 2-*C*H_2), 83.3 (dd, $^1J_{F,C}$ = 167.3 Hz, $^4J_{P,C}$ = 10.1 Hz, 3-CH_2), 128.3 (d, $^3J_{P,C}$ = 8.7 Hz, *m-C*), 130.0 (d, $^4J_{P,C}$ = 2.1 Hz, *p-C*), 130.4 (d, $^1J_{P,C}$ = 28.2 Hz, *i*-C), 133.8 (d, $^2J_{P,C}$ = 9.5 Hz, *o-C*), 148.7 (s, *C*═N). ^{19}F NMR (188 MHz, $CDCl_3$): δ −215.9 (m). ^{31}P NMR (81 MHz, $CDCl_3$): δ 21.0 (br).

3.4. py*−[Co]−CH_2CHF_2 (py* = py (4a), 4-(*t*-Bu)py (4b), 3-Fpy (4c)). To py*−[Co]−H/py*−[Co]$^-$ (prepared from 1.3 mmol of py*−[Co]−Cl; py* = py, 4-(*t*-Bu)py, 3-Fpy) in methanol (50 mL) was added a solution of $BrCH_2CHF_2$ (377 mg, 2.6 mmol) in MeOH (20 mL) dropwise at −30 °C. Then the solution was warmed to room temperature. After the mixture had turned orange (about 2 h), stirring was continued for 30 min and water (100 mL) was added. After 30 min the orange precipitate was filtered off, washed with water (3 × 5 mL) and diethyl ether (3 × 5 mL), and dried in vacuo.

4a (py* = py): yield 310 mg (55%). Anal. Calcd for $C_{15}H_{22}CoF_2N_5O_4$ (433.30): C, 41.58; H, 5.12. Found: C, 41.22; H, 5.35. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.29 ("td", $^3J_{H,F}$ = 21.83 Hz, $^3J_{H,H}$ = 5.01 Hz, 2H, CH_2), 2.13 (s, 12H, CH_3 of dmgH), 5.62 ("tt", $^2J_{H,F}$ = 58.89 Hz, $^3J_{H,H}$ = 4.98 Hz, 1H, C*H*F_2), 7.27 (m, 2H, 3/5-C*H* of py), 7.53 (m, 1H, 4-C*H* of py), 8.49 ("d", *N* = 4.88 Hz, 2H, 2/6-C*H* of py). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.1 (s, *C*H_3 of dmgH), 120.9 (t, $^1J_{F,C}$ = 240.5 Hz, *C*HF_2), 125.4 (s, 3/5-*C*H of py), 137.9 (s, 4-*C*H of py), 149.8 (s, 2/6-*C*H of py), 150.6 (s, *C*═N). ^{19}F NMR (188 MHz, $CDCl_3$): δ −101.6 ("td", $^2J_{F,H}$ = 62.1 Hz, $^3J_{F,H}$ = 21.9 Hz).

4b (py* = 4-(*t*-Bu)py): yield 363 mg (57%). Anal. Calcd for $C_{19}H_{30}CoF_2N_5O_4$ (489.41): C, 46.63; H, 6.19. Found: C, 46.39; H, 6.30. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (s, 9H, CH_3 of *t*-Bu), 1.28 ("td", $^3J_{H,F}$ = 22.05 Hz, $^3J_{H,H}$ = 4.98 Hz, 2H, CH_2), 2.13 (s, 12H, CH_3 of dmgH), 5.63 ("tt", $^2J_{H,F}$ = 58.87 Hz, $^3J_{H,H}$ = 5.19 Hz, 1H, C*H*F_2), 7.24 (m, *N* = 6.49 Hz, 2H, 3/5-C*H* of 4-(*t*-Bu)py), 8.34 ("d", *N* = 6.48 Hz, 2H, 2/6-C*H* of 4-(*t*-Bu)py). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0 (s, *C*H_3 of dmgH), 30.1 (s, *C*H_3 of *t*-Bu), 34.8 (s, *C* of *t*-Bu), 121.1 (t, $^1J_{F,C}$ = 240.9 Hz, *C*HF_2), 122.6 (s, 3/5-*C*H of 4-(*t*-Bu)py), 149.4/150.6 (s/s, 2/6-*C*H of 4-(*t*-Bu)py/*C*═N), 162.5 (s, 4-*C* of 4-(*t*-Bu)py). ^{19}F NMR (188 MHz, $CDCl_3$): δ −101.4 ("td", $^2J_{F,H}$ = 58.5 Hz, $^3J_{F,H}$ = 22.0 Hz).

4c (py* = 3-Fpy): yield 223 mg (38%). Anal. Calcd for $C_{15}H_{21}CoF_3N_5O_4$ (451.29): C, 39.92; H, 4.69. Found: C, 40.40; H, 4.70. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.33 ("dt", $^3J_{H,F}$ = 21.68 Hz, $^3J_{H,H}$ = 4.88 Hz, 2H, CH_2), 2.14 (s, 12H, CH_3 of dmgH), 5.62 ("tt", $^2J_{H,F}$ = 58.70 Hz, $^3J_{H,H}$ = 5.01 Hz, 1H, C*H*F_2), 7.46 (m, 1H, 4-C*H* of 3-Fpy), 7.52 (m, 1H, 5-C*H* of 3-Fpy), 8.37 ("d", *N* = 5.28 Hz, 1H, 6-C*H* of 3-Fpy), 8.44 (m, 1H, 2-C*H* of 3-Fpy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.3 (s, *C*H_3 of dmgH), 120.7 (t, $^1J_{F,C}$ = 240.7 Hz, *C*HF_2), 125.3 (d, $^2J_{F,C}$ = 18.2 Hz, 4-*C*H of 3-Fpy), 125.9 (d, $^3J_{F,C}$ = 5.3 Hz, 5-*C*H of 3-Fpy), 139.0 (d, $^2J_{F,C}$ = 29.8 Hz, 2-*C*H of 3-Fpy), 146.2 (s, $^4J_{C,F}$ = 3.9 Hz, 6-*C*H of 3-Fpy), 150.9 (s, *C*═N), 160.0 (d, $^1J_{F,C}$ = 255.5 Hz, 3-*C*H of 3-Fpy). ^{19}F NMR (188 MHz, $CDCl_3$): δ −101.8 ("td", $^2J_{F,H}$ = 58.5 Hz, $^3J_{F,H}$ = 22.0 Hz, C*H*F_2), −122.2 (s, C*F* of 3-Fpy).

3.5. Reactions of py*−[Co]$^-$ with $BrCH_2CH_2F$, Yielding py*−[Co]−CH_2CH_2OMe (py* = py (5a), 4-(*t*-Bu)py (5b), 3-Fpy (5c)). To py*−[Co]$^-$ (prepared from 1.3 mmol of py*−[Co]−Cl; py* = py, 4-(*t*-Bu)py, 3-Fpy) in methanol (125 mL) or in methanolic NaOH (0.15 M, 125 mL) was added a solution of $BrCH_2CH_2F$ (330 mg, 2.6 mmol) in MeOH (20 mL) dropwise at −30 °C. Then the solution was warmed to room temperature. After the mixture had turned orange (about 30 min), stirring was continued for 30 min and water (100 mL) was added. Then the reaction mixture was neutralized (pH 7−8) with solid CO_2. The solution was extracted with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4, and solvent was completely evaporated in vacuo. The residue was taken up in CH_2Cl_2 (5 mL), and diethyl ether (7 mL) was added, yielding an orange microcrystalline precipitate, which was filtered off, washed with diethyl ether (3 × 5 mL), and dried in vacuo.

5a (py* = py): yield (neutral/alkaline medium) 133/206 mg (24/37%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.53 (m, *N* = 16.21 Hz, 2H, 1-CH_2), 2.08 (s, 12H, CH_3 of dmgH), 3.01 (m, *N* = 16.40 Hz, 2H, 2-CH_2), 3.17 (s, 3H, OCH_3), 7.27 (m, 2H, 3/5-C*H* of py), 7.69 (m, 1H, 4-C*H* of py), 8.52 ("d", br., *N* = 5.08 Hz, 2H, 2/6-C*H* of py). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.9 (s, CH_3 of dmgH), 57.7 (s, O*C*H_3), 74.2 (s, 2-*C*H_2), 125.2 (s, 3/5-*C*H of py), 137.5 (s, 4-*C*H of py), 149.6 (s, *C*═N), 149.8 (s, 2/6-*C*H of py).

5b (py* = 4-(*t*-Bu)py): yield (neutral/alkaline medium) 131/220 mg (21/35%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.23 (s, 9H, CH_3 of *t*-Bu), 1.52 (m, *N* = 16.60 Hz, 2H, 1-CH_2), 2.10 (s, 12H, CH_3 of dmgH), 3.03 (m, *N* = 16.41 Hz, 2H, 2-CH_2), 3.19 (s, 3H, OCH_3), 7.23 ("d", *N* = 4.88 Hz, 2H, 3/5-C*H* of 4-(*t*-Bu)py), 8.37 (m, *N* = 6.80 Hz, 2H, 2/6-C*H* of 4-(*t*-Bu)py). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.9 (s, *C*H_3 of dmgH), 30.3 (s, *C*H_3 of *t*-Bu), 34.7 (s, *C* of *t*-Bu), 57.6 (s, O*C*H_3), 74.2 (s, 2-*C*H_2), 122.3 (s, 3/5-*C*H of 4-(*t*-Bu)py), 149.3 (s, 2/6-*C*H of 4-(*t*-Bu)py), 149.5 (s, *C*═N), 161.7 (s, 4-*C* of 4-(*t*-Bu)py).

5c (py* = 3-Fpy): yield (neutral/alkaline medium) 52/116 mg (9/20%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.56 (m, *N* = 16.02 Hz, 2H, 1-CH_2), 2.08 (s, 12H, CH_3 of dmgH), 2.99 (m, *N* = 16.22 Hz, 2H, 2-CH_2), 3.18 (s, 3H, OCH_3), 7.30 (m, 1H, 4-C*H* of 3-Fpy), 7.43 (m, 1H, 5-C*H* of 3-Fpy), 8.40 ("d", *N* = 5.08 Hz, 1H. 6-C*H* of 3-Fpy), 8.47 (m, 1H, 2-C*H* of 3-Fpy). ^{13}C NMR-(100 MHz, $CDCl_3$): δ 11.8 (s, *C*H_3 of dmgH), 57.7 (s, O*C*H_3), 74.2 (s, 2-*C*H_2), 124.9 (d, $^2J_{F,C}$ = 18.1 Hz, 4-*C*H of 3-Fpy), 125.9 (d, $^3J_{F,C}$ = 5.0 Hz, 5-*C*H of 3-Fpy), 139.0 (d, $^2J_{F,C}$ = 29.2 Hz, 2-*C*H of 3-Fpy), 146.2 (s, $^4J_{C,F}$ = 4.0 Hz, 6-*C*H of 3-Fpy), 150.1 (s, *C*═N), 160.1 (d, $^1J_{F,C}$ = 256.5 Hz, 3-*C*H of 3-Fpy). ^{19}F NMR-(188 MHz, $CDCl_3$): δ −122.8 (m).

3.6. Reactions of py*−[Co]−H/py*−[Co]$^-$ with $TfOCH_2CMe_2F$, Yielding py*−[Co]−CH═CMe_2 (py* = py (6a), 3-Fpy (6b)). To py*−[Co]−H/py*−[Co]$^-$ (prepared from 1.3 mmol of py*−[Co]−Cl; py* = py, 3-Fpy) in methanol (50 mL) was added a solution of $TfOCH_2CMe_2F$ (583 mg, 2.6 mmol) in MeOH (20 mL) dropwise at −30 °C. Then the solution was warmed to room temperature. After the mixture had turned orange (about 16 h), stirring was continued for 30 min and water (100 mL) was added. After 30 min the orange precipitate was filtered off, washed with water (3 × 5 mL) and diethyl ether (3 × 5 mL), and dried in vacuo.

6a (py* = py): yield 83 mg (15%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.66 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 2.07 (s, 12H, CH_3 of dmgH), 5.29 (s, 1H, ═C*H*), 7.29 (m, 2H, 3/5-C*H* of py), 7.65 (m, 1H, 4-C*H* of py), 8.63 ("d", br, *N* = 4.84 Hz, 2H, 2/6-C*H* of py). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.9 (s, *C*H_3 of dmgH), 19.2 (s, *C*H_3), 28.8 (s, *C*H_3), 125.2 (s, 3/5-*C*H of py),

136.3 (s, =*C*Me$_2$), 137.5 (s, 4-*C*H of py), 149.8 (s, *C*=N), 150.0 (s, 2/6-*C*H of py).

6b (py* = 3-Fpy): yield 29 mg (5%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.65 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 2.09 (s, 12H, CH_3 of dmgH), 5.25 (s, 1H, =C*H*), 7.24−7.45 (m, 2H, 4/5-C*H* of 3-Fpy), 8.50 ("d", N = 4.69 Hz, 1H, 6-C*H* of 3-Fpy), 8.58 (m, 1H, 2-C*H* of 3-Fpy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.9 (s, *C*H$_3$ of dmgH), 20.1 (s, *C*H$_3$), 29.6 (s, *C*H$_3$), 125.9 (d, $^2J_{F,C}$ = 17.8 Hz, 4-*C*H of 3-Fpy), 126.8 (d, $^3J_{F,C}$ = 5.8 Hz, 5-*C*H of 3-Fpy), 137.5 (s, =*C*Me$_2$), 140.0 (d, $^2J_{F,C}$ = 29.4 Hz, 2-*C*H of 3-Fpy), 147.3 (s, 6-*C*H of 3-Fpy), 151.1 (s, *C*=N), 161.1 (d, $^1J_{F,C}$ = 255.7 Hz, 3-*C*H of 3-Fpy). ^{19}F NMR (188 MHz, $CDCl_3$): δ −122.9 (s).

3.7. (2-Fluorocyclohexyl)- and (2-Fluorocyclopentyl)-cobaloximes py*−[Co]−R (7a,b and 10a,b). To py*−[Co]−H/py*−[Co]$^-$ (1.3 mmol) in MeOH (50 mL) was added a solution of *trans*-1-bromo-2-fluorocyclohexane, *cis*-1-bromo-2-fluorocyclohexane, and *trans*-1-bromo-2-fluorocyclopentane (2.6 mmol), respectively, in MeOH (20 mL) dropwise at −30 °C. Stirring was continued for 1 h at this temperature and for 16 (**7**) and 6 h (**10**), respectively, at room temperature. Then water (100 mL) was added. The product that precipitated was filtered off, washed with water (3 × 10 mL) and diethyl ether (3 × 10 mL), and dried in vacuo.

7a (py* = py, R = *cis*-2-fluorocyclohexyl): yield 214 mg (35%). Anal. Calcd for $C_{19}H_{29}CoFN_5O_4$ (469.40): C, 48.62; H, 6.23. Found: C, 48.32; H, 6.01. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.28−1.78 (m, 9H, C*H*/CH_2 of c-hex), 2.10/2.12 (s/s, 12H, CH_3 of dmgH), 4.70 ("d", $^2J_{F,H}$ = 47.49 Hz, 1H, C*H*F), 7.24 (m, 2H, 3/5-C*H* of py), 7.65 (m, 1H, 4-C*H* of py), 8.54 ("d", N = 5.08 Hz, 2H, 2/6-C*H* of py). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.97/12.01 (s/s, *C*H$_3$ of dmgH), 20.9 (s, 5-*C*H$_2$ of c-hex), 29.2/29.6 (s/s, 4-*C*H$_2$/6-*C*H$_2$ of c-hex), 34.6 (d, $^2J_{F,C}$ = 24.1 Hz, 3-*C*H$_2$ of c-hex), 96.4 (d, $^1J_{F,C}$ = 171.1 Hz, *C*HF), 125.2 (s, 3/5-*C*H of py), 137.4 (s, 4-*C*H of py), 150.0 (s, 2/6-*C*H of py), 150.1/150.9 (s/s, *C*=N). ^{19}F NMR (188 MHz, $CDCl_3$): δ −189.2 (m).

7b (py* = 4-(*t*-Bu)py, R = *cis*-2-fluorocyclohexyl): yield 273 mg (40%). Anal. Calcd. for $C_{23}H_{37}CoFN_5O_4$ (525.51): C, 52.57; H, 7.10. Found: C, 52.64; H, 6.85. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (s, 9H, C(CH_3)$_3$), 1.31−1.68 (m, 9H, C*H*/CH_2 of c-hex), 2.10/2.11 (s/s, 12H, CH_3 of dmgH), 4.70 ("d", $^2J_{F,H}$ = 47.26 Hz, 1H, C*H*F), 7.19 ("d", N = 4.03, 2H, 3/5-C*H* of 4-(*t*-Bu)py), 8.37 ("d", N = 4.03 Hz, 2H, 2/6-C*H* of 4-(*t*-Bu)py). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.96/12.01 (s/s, *C*H$_3$ of dmgH), 20.9 (s, 5-*C*H$_2$ of c-hex), 29.2/29.5 (s/d, $^3J_{F,C}$ = −/2.9 Hz, 4-*C*H$_2$/6-*C*H$_2$ of c-hex), 30.1 (s, C(*C*H$_3$)$_3$), 34.6 (d, $^2J_{F,C}$ = 24.0 Hz, 3-*C*H$_2$ of c-hex), 34.7 (s, *C*(CH$_3$)$_3$), 46.4 (br, 1-*C*H of c-hex), 96.4 (d, $^1J_{F,C}$ = 170.7 Hz, *C*HF), 122.3 (s, 3/5-*C*H of 4-(*t*-Bu)py), 149.4 (s, 2/6-*C*H of 4-(*t*-Bu)py), 149.8/150.6 (s/s, *C*=N), 161.7 (s, 4-*C* of 4-(*t*-Bu)py). ^{19}F NMR (188 MHz, $CDCl_3$): δ −187.7 (m). Temperature dependence: ^{1}H NMR (500 MHz, $C_6D_5CD_3$; CH_3 of dmgH): −80 °C, δ 1.899/1.837 ($\Delta\delta$ = 31.9 Hz); −50 °C, δ 1.781/1.729 ($\Delta\delta$ = 25.7 Hz); −10 °C, δ 1.819/1.782 ($\Delta\delta$ = 18.8 Hz); +27 °C, δ 1.852/1.825 ($\Delta\delta$ = 13.7 Hz); +50 °C, δ 1.869/1.847 ($\Delta\delta$ = 11.1 Hz); +85 °C, δ 1.889/1.874 ($\Delta\delta$ = 7.6 Hz); +99 °C, δ 1.896/1.883 ($\Delta\delta$ = 6.5 Hz).

10a (py* = py, R = *cis*-2-fluorocyclopentyl): yield 266 mg (45%). Anal. Calcd for $C_{18}H_{27}CoFN_5O_4$ (455.38): C, 47.48; H, 5.98. Found: C, 47.57; H, 5.74. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18−1.66 (m, 7H, C*H*/CH_2 of c-pent), 2.06/2.07 (s/s, 12H, CH_3 of dmgH), 4.82 (d, $^2J_{F,H}$ = 53.41 Hz, 1H, C*H*F), 7.44 (m, 2H, 3/5-C*H* of py), 7.67 (m, 1H, 4-C*H* of py), 8.55 ("d", N = 4.88 Hz, 2H, 2/6-C*H* of py). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.8 (s, *C*H$_3$ of dmgH), 19.1 (s, 5-*C* of c-pent), 28.5 (s, 4-*C* of c-pent), 30.6 (d, $^2J_{F,C}$ = 24.4 Hz, 3-*C* of c-pent), 41.9 (br, 1-*C*H of c-pent), 101.2 (d, $^1J_{F,C}$ = 173.6 Hz, *C*HF), 125.1 (s, 3/5-*C*H of py), 137.5 (s, 4-*C*H of py), 149.9 (s, 2/6-*C*H of py), 150.0/150.6 (s/s, *C*=N). ^{19}F NMR (188 MHz, $CDCl_3$): δ −177.1 (m).

10b (py* = 4-(*t*-Bu)py, R = *cis*-2-fluorocyclopentyl): yield 313 mg (47%). Anal. Calcd for $C_{22}H_{35}CoFN_5O_4$ (511.48): C, 51.75; H, 6.90. Found: C, 51.66; H, 6.81. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (s, 9H, CH_3 of *t*-Bu), 1.38−1.62 (m, 7H, C*H*/CH_2 of c-pent), 2.08/2.09 (s/s, 12H, CH_3 of dmgH), 4.83 (d, $^2J_{F,H}$ = 53.32 Hz, 1H, C*H*F), 7.21 ("d", N = 6.66 Hz, 2H, 3/5-C*H* of 4-(*t*-Bu)py), 8.40 ("d", N = 6.41 Hz, 2H, 2/6-C*H* of 4-(*t*-Bu)py). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.9 (s, *C*H$_3$ of dmgH), 19.2 (s, 5-*C* of c-pent), 28.5 (s, 4-*C* of c-pent), 30.1 (s, *C*H$_3$ of *t*-Bu), 30.7 (d, $^2J_{F,C}$ = 24.9 Hz, 3-*C* of c-pent), 34.7 (s, *C* of *t*-Bu), 101.5 (d, $^1J_{F,C}$ = 173.2 Hz, *C*HF), 122.4 (s, 3/5-*C*H of 4-(*t*-Bu)py), 149.3 (s, 2/6-*C*H of 4-(*t*-Bu)py), 149.8/150.5 (s/s, *C*=N), 161.9 (s, 4-*C* of 4-(*t*-Bu)py). ^{19}F NMR (188 MHz, $CDCl_3$): δ −177.1 (m).

3.8. py−[Co]−C$_6$H$_{11}$ (8) and py*−[Co]−C$_6$H$_9$ (9). Complex **8** was prepared from py−[Co]$^-$ (prepared from 1.3 mmol of py−[Co]−Cl) and cyclohexyl bromide (424 mg, 2.6 mmol) as described for complexes **7**. Yield: 256 mg (42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.78−2.26 (m, 11H, C*H*/CH_2 of c-hex), 2.09 (s, 12H, CH_3 of dmgH), 7.19 (m, 2H, 3/5-C*H* of py), 7.65 (m, 1H, 4-C*H* of py), 8.55 ("d", N = 4.77 Hz, 2H, 2/6-C*H* of py). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.9 (s, *C*H$_3$ of dmgH), 27.3 (s, 4-C of c-hex), 29.7 (s, 3/5-*C* of c-hex), 36.9 (s, 2/6-*C* of c-hex), 50.4 (br, 1-*C*H of c-hex), 125.1 (s, 3/5-*C*H of py), 137.3 (s, 4-*C*H of py), 149.6/150.1 (s/s, 2/6-*C*H of py/*C*=N).

Complex **9** (py*−[Co]−C$_6$H$_9$, C$_6$H$_9$ = cyclohex-1-enyl) in a mixture with **7a** (total yield: ca. 3%) was prepared from py−[Co]$^-$ and *cis*-1-bromo-2-fluorocyclohexane analogously to the procedure described for complexes **7**. Signals of **7a** were as reported. Data for **9** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29−1.97 (m, 8H, C*H*/CH_2), 2.07 (s, 12H, CH_3 of dmgH), 5.02 (s, br, 1H, =C*H*), 7.25 (m, 2H, 3/5-C*H* of py), 7.67 (m, 1H, 4-C*H* of py), 8.62 ("d", N = 5.29 Hz, 2H, 2/6-C*H* of py). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0 (s, *C*H$_3$ of dmgH), 23.4/26.4/28.5/33.4 (s/s/s/s, 3−6-*C*H$_2$), 124.8 (s, =*C*H), 150.02 (s, 2/6-*C* of py), 150.04 (s, *C*=N) (3,5-/4-*C* of py at 125.2/137.4 ppm are overlapped with corresponding signals of **7a**). NMR data are in accordance with those given in the literature.[37]

3.9. Crystallographic Studies. Intensity data for **3** were collected on a STOE-STADI4 four-circle diffractometer and for **4a**, **7b**, and **7b**·CH_2Cl_2 on a STOE IPDS diffractometer with Mo Kα radiation (0.710 73 Å, graphite monochromator). A summary of crystallographic data, data collection parameters, and refinement parameters is given in Table 6. Absorption corrections were not applied. The structures were solved by direct methods with SHELXS-86[38] and refined using full-matrix least-squares routines against F^2 with SHELXL-93.[38] Non-hydrogen atoms were refined with anisotropic and hydrogen atoms with isotropic displacement parameters. The hydrogen atom positions were calculated and allowed to ride on their corresponding atoms. The hydrogen atoms in the O−H···O bridges in **3** and **7b** were found in the difference Fourier map. In **4a** the CH_2CHF_2 group is disordered over three positions with 40, 35, and 25% site occupancies. For the refinement the bond lengths C9−C10, C10−F1, and C10−F2 were fixed at 1.330(8) and 1.510(8) Å. In **7b**·CH_2Cl_2 the fluorine atom is disordered over two positions with a major (F1, 68%) and a minor (F1a, 38%) site occupancy.

3.10. Computational Details. All reported DFT calculations were performed by employing the Gaussian98 program[39] using the hybrid functional B3LYP.[40] An effective core potential (ECP) was used to represent the innermost electrons of the cobalt atom.[41,42] Two different basis sets were used throughout the investigations. Geometries of complexes, intermediates, and transition states were optimized using the LANL2DZ basis set[41,43] (denoted as BS1) without imposing any symmetry restrictions. The localized stationary points were identified exactly as equilibrium structures and transition states, respectively, at this level of approximation by the curvature ot the potential-energy surface at these points,

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Table 6. Crystal Data and Structure Refinement for 3, 4a, 7b, and 7b·CH_2Cl_2

	3	**4a**	**7b**	**7b·CH_2Cl_2**
empirical formula	$C_{29}H_{35}CoFN_4O_4P$	$C_{15}H_{22}CoF_2N_5O_4$	$C_{23}H_{37}CoFN_5O_4$	$C_{24}H_{39}Cl_2CoFN_5O_4$
fw	612.51	433.31	525.51	610.43
T, K	293(2)	293(2)	203(2)	293(2)
cryst syst	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$Pna2_1$	Cc
a, Å	10.757(2)	9.676(2)	16.124(2)	8.881(2)
b, Å	14.748(1)	12.381(2)	13.225(2)	16.570(3)
c, Å	18.520(3)	15.625(3)	12.280(2)	19.647(4)
β, deg				92.71(3)
V, Å^3	2938.2(8)	1871.9(6)	2618.6(7)	2888(1)
Z	4	4	4	4
ρ_{calc}, g/cm^3	1.385	1.538	1.333	1.404
μ(Mo Kα), mm^{-1}	0.685	0.967	0.699	0.824
F(000)	1280	896	1112	1280
scan range, deg	1.77−26.02	2.10−26.15	1.99−25.99	2.08−25.90
no. of rflns collected	9216	14 126	15 166	11 064
no. of indep rflns	5103	3566	4970	5043
no. of obsd rflns	4690	2942	4116	4121
no. of params refined	370	257	315	351
goodness of fit on F^2	1.065	1.043	1.011	1.073
final R ($I > 2\sigma(I)$)	R1 = 0.0354	R1 = 0.0635	R1 = 0.0359	R1 = 0.0433
	wR2 = 0.0934	wR2 = 0.1568	wR2 = 0.0810	wR2 = 0.0942
R (all data)	R1 = 0.0413	R1 = 0.0743	R1 = 0.0478	R1 = 0.0589
	wR2 = 0.1030	wR2 = 0.1630	wR2 = 0.0867	wR2 = 0.1022
largest diff peak/hole, e Å^{-3}	0.386/−0.240	1.098/−0.387	0.331/−0.234	0.524/−0.526

corresponding to the eigenvalues of the analytical Hessian. Zero-point vibrational energies were found to affect the calculated activation potential energies $\Delta E^{\ddagger}$ to only a minor extent. Therefore, uncorrected activation potential energies are reported.

To obtain more reliable energetics, single-point energy calculations at the B3LYP level, using the Stuttgart/Dresden effective core potential (SDD[42]) and the associated basis set for Co and 6-31G(d) basis sets for main group elements (denoted as BS2), have been performed at the B3LYP/BS1 optimized geometries. Furthermore, the structure of complex **11a** was fully optimized using basis set BS2 without imposing any symmetry restrictions. The two fully optimized structures of **11a** (B3LYP/BS1 vs B3LYP/BS2) proved to be very similar, exhibiting the reliability of structures that were obtained using the B3LYP/BS1 level of theory. Cartesian coordinates of atom positions of all localized stationary points are provided as Supporting Information.

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Supporting Information Available: Complete tables of atomic coordinates, H atom parameters, bond distances, bond angles, and anisotropic displacement parameters for **3**, **4a**, **7b**, and **7b**·CH_2Cl_2 and complete tables of Cartesian coordinates of atom positions calculated for equilibrium structures and transition states (see Table 5) of **11** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC-219022 (**3**), CCDC-219023 (**4a**), CCDC-219024 (**7b**), and CCDC-219025 (**7b**·CH_2Cl_2). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Read, Cambridge CB2 1EZ, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk).

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