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Complexation of $Co(DBF_2)_2$ by *N*-Methylimidazole in Acetonitrile: Formation Constants and ^1H NMR Shifts and Relaxation Times

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Introduction

In this study, the formation constants and thermodynamic parameters of the mono- and bis-adducts of $Co^{II}(DBF_2)_2$ (DBF_2 = (difluoroboryl)dimethylglyoximato) with *N*-methylimidazole (MeIm) in acetonitrile have been determined by spectrophotometry. Furthermore, the temperature and concentration dependence of the ^1H NMR shifts and relaxation rates of MeIm have been measured and analyzed to give the shift and relaxation parameters for protons in the mono- and bis-coordinated MeIm complexes.

Recent X-ray structures of cobalamin bound to proteins[1−4] have revealed that the 5,6-dimethylbenzimidazole ligand can be displaced by an imidazole ring from a histidine residue of the protein. These observations and several EPR studies[5−7] have shown that this is not an uncommon structural motif for protein-bound cobalamins. However, EPR studies have revealed that benzimidazole binding to cobalt is retained in diol dehydrase[8] and ribonucleotide reductase.[9] The biochemical aspects of this area have been reviewed recently.[10]

In biomimetic chemistry, the observed replacement of benzimidazole by an imidazole from histidine has generated a number of studies of the effect of imidazole derivatives in coenzyme-B_{12} analogues on the structure and reactivity at the cobalt center. Complexation equilibria of several alkylcobinamide ($RCbi^+$) systems have been studied by Brown and Hamza.[11] Structures and molecular mechanics calculations of Co(III)−DH models (DH = dimethylglyoximato) with imidazole as the axial base have been provided by several groups.[12−14] Sirovatka and Finke[15] found that *N*-methylimidazole accelerates the Co−C bond breaking in adenosylcobinamide ($AdoCbi^+$), but produces more heterolysis than 5,6-dimethylbenzimidazole. Marzilli and co-workers[16] have structurally and spectroscopically characterized DBF_2 derivatives with imidazole and imidazolate axial bases, along with $MeCbi^+$ [17,18] and other B_{12}-model complexes[19] to assess the bonding effects of axial bases. These studies suggest that coordinated imidazole does not cause large structural distortions of the Co(III) state and that the function of the imidazole occurs later in the catalytic cycle. This seems consistent with the results from a recent EXAFS study[20] on methylmalonyl-coenzyme A mutase. Sirovatka and Finke[21] amplified on the idea of base stabilization of the transition state and/or Co(II) product as a result of their observation that bulky bases do not bind to the Co(III) form, but do complex with $Co^{II}Cbi^+$. Their measurements on imidazole and pyridine derivatives of $Co^{II}Cbi^+$ were not quantitatively analyzed. The current study indicates why these results may have been difficult to interpret.

The present results are relevant to several earlier studies such as the effect of various axial bases (L), including imidazole, on the Co−C bond energy in $[L(DH)_2Co^{III}CHCH_3C_6H_5]$ systems;[22] the complexation of dioxygen by $Co^{II}(DBF_2)_2$ in the presence of *N*-methylimidazole;[23] and the spin-state crossover in Co(II) Schiff base complexes with 2-methylimidazole[24] that might occur in B_{12} models such as $Co^{II}(DBF_2)_2$.

Results

Formation Constants of Mono- and Bis-*N*-Methylimidazole Adducts. A solution of $Co(DBF_2)_2$ in acetonitrile has a peak at 425 nm ($\epsilon = 3.10 \times 10^3$ M^{-1} cm^{-1}) and a shoulder at 328 nm ($\epsilon = 2.45 \times 10^3$ M^{-1} cm^{-1}). Addition of MeIm increases the absorbance in the 350−400 nm region until the MeIm concentration reaches $\sim 1 \times 10^{-2}$ M. Further addition of MeIm increases the absorbance in the 450−500 nm region. These changes correspond to the formation of mono- and bis-adduct, as shown by eqs 1 and 2, respectively. Since the spectral changes occur in two well-separated MeIm concentration ranges,

$$Co(DBF_2)_2 + MeIm \overset{K_1}{\rightleftharpoons} (MeIm)Co(DBF_2)_2 \qquad (1)$$

$$(MeIm)Co(DBF_2)_2 + MeIm \overset{K_2}{\rightleftharpoons} (MeIm)_2Co(DBF_2)_2 \qquad (2)$$

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Table 1. Equilibrium Constants for Formation of Mono- and Bis-MeIm Adducts of $Co(DBF_2)_2$ in Acetonitrile[a,b]

		(°C)		
		35	19	0
$K_1 \times 10^{-3}$ (M^{-1})				
observed		2.10 ± 0.17	3.83 ± 0.42	7.79 ± 0.76
predicted[c]		2.11	3.68	7.75
K_2 (M^{-1})				
observed		3.61 ± 0.22	5.16 ± 0.65	9.16 ± 0.51
predicted[c]		3.48	5.20	8.90
$\Delta H°_1$ (kcal mol^{-1})	-6.22 ± 0.21			
$\Delta S°_1$ (cal mol^{-1} K^{-1})	-4.99 ± 0.74			
$\Delta H°_2$ (kcal mol^{-1})	-4.48 ± 0.27			
$\Delta S°_2$ (cal mol^{-1} K^{-1})	-12.1 ± 0.95			

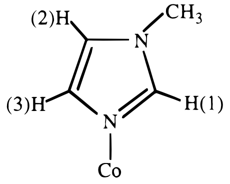
[a] K_1 and K_2 are defined in eqs 1 and 2, respectively. [b] Errors quoted are 1 standard deviation. [c] Calculated from the least-squares fits of the temperature dependence to the van't Hoff equation.

they can be used to obtain the values of K_1 and K_2 separately. The absorbance (A) at 376 nm for 3.0×10^{-5} to 6×10^{-3} M MeIm was analyzed by standard methods.[25] The A vs [MeIm] data, for concentrations in the 10−80% complexation range, were fitted by least-squares to obtain K_1 at 0, 19, and 35 °C. The absorbance changes (at 470 nm) at high MeIm concentrations (5.0×10^{-2} to ~1.5 M) were treated similarly to obtain K_2. The average values of the K_1 and K_2 from the five to seven concentrations used are summarized in Table 1.

Both K_1 and K_2 increase as the temperature decreases, and the temperature dependence was used to determine the $\Delta H°_i$ and $\Delta S°_i$ by fitting the five to seven values of K_i at each temperature to the van't Hoff equation. The K_i predicted from these fits and the $\Delta H°_i$ and $\Delta S°_i$ also are given in Table 1. The van't Hoff plot is given in the Supporting Information.

EPR of $Co(DBF_2)_2(MeIm)_2$. The EPR spectrum of an acetonitrile glass containing 4.4×10^{-4} M $Co(DBF_2)_2$ and 0.34 M MeIm at 93 K was recorded in order to test the assumption in the equilibrium study that the bis-complex, $Co(DBF_2)_2(MeIm)_2$, indeed is formed. The spectrum is typical of low-spin d^7 systems[26] and similar to those of other $Co(DBF_2)_2(L)_2$ complexes ($L = CH_3CN$[27] and py[23]). The EPR parallel components display eight lines that result from the hyperfine coupling of the unpaired electron in the d_{z^2} orbital to the nuclear spin of cobalt ($I = {}^7/_2$). The axial N-donor ligands produce superhyperfine (shf) coupling which splits each of the eight cobalt hyperfine lines into three or five lines, depending on whether one or two N-donor, axial ligands are present. The observed shf splitting confirmed the coordination of two MeIm ligands as expected for 0.34 M MeIm. The EPR spectral parameters are $g_{\|} = 2.01$, $g_{\perp} = 2.27$, $A_{\|}{}^{Co} = 77.4 \times 10^{-4}$ cm^{-1}, and $A_{\|}{}^{N} = 16.4 \times 10^{-4}$ cm^{-1}. These parameters are quite similar to those of $Co(DBF_2)_2(py)_2$,[23] and the coupling constants are clearly different from those of $Co(DBF_2)_2(NCCH_3)_2$.[27]

NMR Paramagnetic Shifts and Relaxation Rates. In order to further define the system, the proton paramagnetic shifts and line widths of excess MeIm in the presence of $Co(DBF_2)_2$ (4.4−9.9 × 10^{-4} M) have been studied as a function of [MeIm] (0.10−0.34 M) and temperature (35 to −35 °C). The designation of the protons for peaks in the NMR spectrum of *N*-methylimidazole is shown below.



An experimental spectrum is shown in Figure 1, where peaks numbered 1, 2, and 3 are assigned to the corresponding protons in the above structure according to the literature.[28] The spectrum shown is truly a worst case in that these conditions give the broadest peaks.

The shifts for all three peaks are to high frequency relative to free MeIm, and their magnitudes increase as the temperature decreases. At a given set of conditions, the shifts are in the order peak 2 > peak 3 > peak 1. All three peaks become broader with decreasing temperature; peak 1 is always the narrowest, while peaks 2 and 3 are similar at high temperature, but peak 2 becomes the broadest at low temperature.

At the concentrations of 0.10, 0.18, and 0.34 M MeIm used in the NMR study, the only significant species are the mono- and bis-*N*-methylimidazole complexes. The three exchange reactions which might account for the effect of $Co(DBF_2)_2$ on the shifts and relaxation rates of the protons of uncoordinated MeIm are given in Scheme 1, where AN represents acetonitrile.

Scheme 1

$$(AN)Co(DBF_2)_2(MeIm) + MeIm \overset{k_{1ex}}{\rightleftharpoons} (AN)Co(DBF_2)_2(MeIm) + MeIm$$

$$Co(DBF_2)_2(MeIm)_2 + MeIm \overset{k_{2ex}}{\rightleftharpoons} Co(DBF_2)_2(MeIm)_2 + MeIm$$

$$(AN)Co(DBF_2)_2(MeIm) + MeIm \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Co(DBF_2)_2(MeIm)_2 + AN$$

To analyze the paramagnetic shift results, it was assumed that the system is in the fast-exchange limit. Simple extension of the Swift−Connick[29] equations allows the observed shift for a given proton of MeIm to be expressed as a function of K_2 and [MeIm] and the coordinated-proton shifts, $\nu_1{}^i$ and $\nu_2{}^i$, of the ith proton ($i = 1$, 2, and 3) in the mono- and bis-complexes, respectively. If these are assumed to follow the Curie law[30] $\nu_j{}^i = C_j{}^i/T$, where $C_j{}^i$ is a constant, then it can be shown that

$$\Delta\nu_{\text{obs}}{}^{i}\left(\frac{[\text{L}](1 + K_2[\text{L}])T}{[\text{Co(DBF}_2)_2]_\text{t}}\right) = C_1{}^i + C_2{}^i K_2[\text{L}] \tag{3}$$

If the temperature dependence of K_2 is taken from the spectro-

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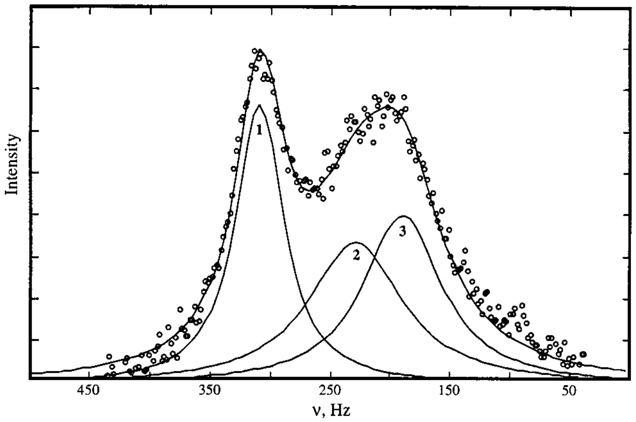

Figure 1. Experimental NMR spectrum for 0.34 M MeIm and 9.9 × 10^{-4} M $Co(DBF_2)_2$ in acetonitrile at −35 °C (showing every sixth experimental point for clarity) and the resolved curves for peaks 1, 2, and 3 that provide the calculated curve passing through the experimental points.

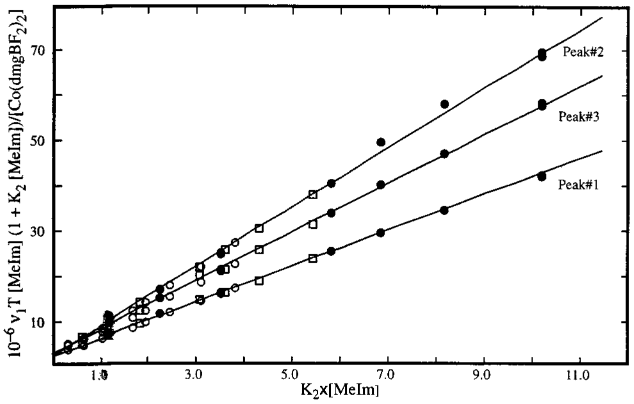

Figure 2. Dependence of the paramagnetic shift (*ν*, Hz) on the temperature and concentration of MeIm as predicted by eq 3, for MeIm concentrations of 0.10 M (○), 0.18 M (□), and 0.34 M (●).

photometric study, then this equation predicts that a plot of the left-hand side versus K_2[MeIm] should be linear.

The transverse relaxation rates ($R_{2P}{}^i$) can be treated analogously, where $R_{2P}{}^i$ is the difference between the relaxation rate of the *i*th proton in the presence and absence of $Co(DBF_2)_2$. If one assumes the fast-exchange limit and a common temperature dependence for the relaxation rate in each coordinated site[31] given by $R_2{}^i = (B_j{}^i/T)\exp(E_a/RT)$, then one obtains

$$(R_{2p})^i\left(\frac{[L](1+K_2[L])T}{[Co(DBF_2)_2]_t\exp(E_a/RT)}\right) = B_1{}^i + B_2{}^iK_2[L] \quad (4)$$

An activation energy for the relaxation process of $E_a = 2.12$ kcal mol^{-1} has been assumed from our previous NMR study of $Co(DBF_2)_2$ in acetonitrile.[31] Again, a plot of the left-hand side versus K_2[MeIm] should be linear. The complete set of data of concentrations, temperatures, and observed and calculated shifts and relaxation rates is given in the Supporting Information.

The plots predicted by eqs 3 and 4 and the lines determined by least-squares analysis are shown in Figures 2 and 3, and the fitting parameters are summarized in Table 2. The linearity of the plots is consistent with the initial assumption that the system is in the fast-exchange region.

With regard to the specific parameters in Table 2, it may be noted that C_2 is close to 2 times larger than C_1 for protons 1 and 3 as might be expected if the shift per MeIm ligand were the same in the mono- and bis-complexes. However, C_2 for proton 2 is ~50% larger than expected on this basis. The C_j parameters can be used to calculate the proton−electron scalar coupling constants (A/h)[31] for the different protons, and these also are given in Table 2. The magnitude of the values is typical for $Co(DBF_2)_2$ systems.[31]

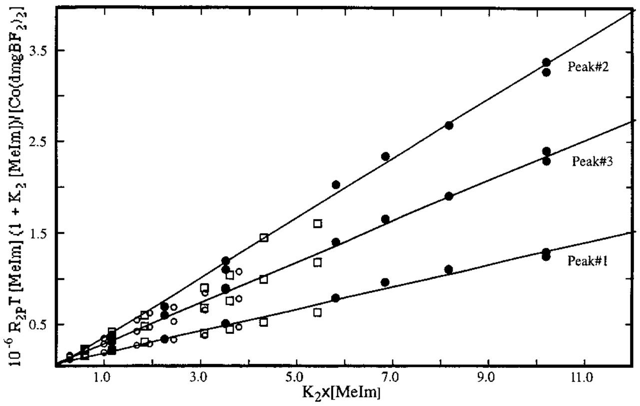

Figure 3. Dependence of the relaxation rate (R_{2P}, s^{-1}) on the temperature and concentration of MeIm as predicted by eq 4, for MeIm concentrations of 0.10 M (○), 0.18 M (□), and 0.34 M (●).

The paramagnetic shift mechanism remains open to question, but the same pattern of relative shifts is observed in the high-spin iron(II) complex $[Fe(MeIm)_6]^{2+}$, and this has been assigned to a direct *σ* spin delocalization mechanism.[32] There is a further source of nonequivalence in the protons designated as peaks 1 and 3 because of the extended-boat conformation adopted by the $Co(DBF_2)_2$ system in Co(II)[27] and Co(III)[16] derivatives. Then one of the protons, 1 or 3, is much closer to the BF_2 group on the same side as the MeIm ligand. There is no evidence for restricted rotation of the coordinated MeIm from the temperature dependence of the shifts in the present observations.

If the relaxation is predominantly by a scalar mechanism, then $B_j/C_j{}^2$ should be constant because the B_j depends on the square of the coupling constant (A/h) while C_j is directly dependent on A/h. The values of $B_2/C_2{}^2$ for the bis-complex are 0.74, 0.71, and 0.76 for protons 1, 2, and 3, respectively, and the constancy of the ratio is consistent with dominant scalar relaxation. If the correlation-time function has similar values for the mono- and bis-complexes, then one should expect a similar value for the ratio $B_1/C_1{}^2$. In fact, the values are 1.07, 0.24, and 0.76, and only the last value (proton 3) seems consistent. This disagreement probably results from uncertainties in B_1, as can be seen from the errors in Table 2 or small intercepts in Figure 3. The prediction that B_1 should be ~3.5 × 10^4 for protons 1 and 2 produces a very marginal effect on the calculated relaxation rates.

Our previous study[31] has given the acetonitrile solvent exchange rate constant as 1.4 × 10^5 s^{-1} at 25 °C with an activation enthalpy and entropy of 4.3 kcal mol^{-1} and −20.5 cal mol^{-1} K^{-1}, respectively. If MeIm exchange were that slow, then the system would not be in the fast-exchange limit. The kinetic limits of the system were tested using the 3-site case given by Led and Grant.[33] In their terminology the 3 sites are free MeIm (A), $Co(DBF_2)_2(MeIm)$ (B), and $Co(DBF_2)_2(MeIm)_2$ (C). The fast-exchange limit can be achieved most simply by assuming that only the k_3 step in Scheme 1 is fast, because this provides a pathway for exchange of MeIm in both the mono-

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Table 2. Least-Squares Fitting Parameters for the Shifts (C)[a] and Relaxation Rates (B)[a] for MeIm Protons in Acetonitrile Solutions of $\text{Co(DBF}_2)_2$[b]

proton	$10^{-6}C_1$ (Hz K)	$10^{-6}C_2$ (Hz K)	$10^{-5}(A/h)_1$ (Hz)	$10^{-5}(A/h)_2$ (Hz)	$10^{-4}B_1$ (s^{-1} K)	$10^{-4}B_2$ (s^{-1} K)
1	2.19 ± 0.09	3.91 ± 0.05	6.9	6.2	5.12 ± 0.60	11.2 ± 0.32
2	2.16 ± 0.18	6.46 ± 0.11	6.9	10.2	1.12 ± 0.92	30.1 ± 0.68
3	2.70 ± 0.16	5.23 ± 0.09	8.6	8.3	5.55 ± 0.86	20.9 ± 0.53

[a] Parameters determined from fits to eqs 3 and 4, with results shown in Figures 1 and 2. [b] Errors are 1 standard deviation.

Table 3. Formation Constants of Cobalt(II)−Glyoximate Complexes with N-Donor Heterocycles[a]

cobaloxime[b]	base[b] (pK_a)	solvent	Q[c]	log Q	$\Delta H°$ [d]	$\Delta S°$ [d]
$\text{Co(DBF}_2)_2$	2-EtIm (7.99)	DMF	K_1[e]	2.50		
$\text{Co(DBF}_2)_2$	Im (7.03)	DMF	K_1[e]	4.04		
$\text{Co(DBF}_2)_2$	*N*-MeIm (6.97)	CH_3CN	K_1[f]	3.47	−6.22	−4.99
$\text{Co(DBF}_2)_2$	*N*-MeIm (6.97)	CH_3CN	K_2[f]	0.64	−4.48	−12.1
$\text{Co(DBF}_2)_2$	α-Pic (5.97)	DMF	K_1[e]	0.16		
$\text{Co(DBF}_2)_2$	py (5.27)	DMF	K_1[e]	2.25		
Co(DH)_2	py (5.27)	CH_3OH	K_1[g]	2.24	−3.9	−2.8
Co(DH)_2	py (5.27)	CH_3OH	K_2[g]	−0.08	−3.9	−13.5
$\text{Co(DPBF}_2)_2$	2-EtIm (7.99)	DMF	K_1[e]	3.18		
$\text{Co(DPBF}_2)_2$	Im (7.03)	DMF	β_2[e]	7.19		
$\text{Co(DPBF}_2)_2$	γ-Pic (6.02)	DMF	β_2[e]	4.46		
$\text{Co(DPBF}_2)_2$	α-Pic (5.97)	DMF	β_2[e]	0.97		
$\text{Co(DPBF}_2)_2$	py (5.27)	DMF	β_2[e]	4.20		
Co(DPH)_2	py (5.27)	DMF	K_1[e]	2.94		

[a] At 25 °C. [b] DBF_2, (difluoroboryl)dimethylglyoximato; DH, dimethylglyoximato; DPBF_2 (difluoroboryl)diphenylglyoximato; DPH, diphenylglyoximato; Im, imidazole; py, pyridine; *N*-MeIm, *N*-methylimidazole; 2-EtIm, 2-ethylimidazole, α-Pic, α-picoline; γ-Pic, γ-picoline. [c] The equilibrium constant determined; Q is either the stepwise constant K_1 or K_2 or the overall constant, $\beta_2 = K_1K_2$. [d] $\Delta H°$ in kcal mol^{-1} and $\Delta S°$ in cal mol^{-1} K^{-1}. [e] Reference 25, determined by visible spectrophotometry. [f] This work. [g] Reference 33, determined by EPR spectroscopy.

and bis-complexes. If an activation enthalpy of 4.5 kcal mol^{-1} is assumed for k_3, then the activation entropy must increase to ~0 for the system to be in the fast-exchange limit at the lowest temperature of the present study. The k_3 step might be the fastest process if the coordinated MeIm labilizes the acetonitrile for replacement by MeIm, or if the mono-MeIm complex is really five-coordinate.

Discussion

The results of the present and previous studies[25,34] on the complexation of Co(II) bis-dimethylglyoxime derivatives are collected in Table 3. From the earlier work, it has been concluded that the formation constants increase with increasing basicity of the nitrogen heterocyclic base (as measured by the pK_a in water), with due allowance for steric effects in cases such as 2-EtIm and α-picoline. Unfortunately there are only two systems for which both K_1 and K_2 and the enthalpy and entropy have been determined. In both of these, K_2 is substantially smaller than K_1, and the entropy change is more negative for K_2.

The more negative entropy change for K_2 might be attributed to the $\text{Co(DBF}_2)_2\text{(L)}$ species being partially or completely five-coordinate, rather than six-coordinate $\text{Co(DBF}_2)_2\text{(L)(AN)}$. The entropic compensation due to L coordination and loss of AN would not be observed for the five-coordinate species. Such an effect was invoked by Brown and Wu[35] to explain entropy trends in the base-on/base-off equilibrium for alkylcobalt corrinoids.

The present results are relevant to the earlier work of Busch and co-workers[23] on the complexation of $\text{Co(DBF}_2)_2$ by dioxygen in the presence of excess MeIm (0.14 M) in acetonitrile. Busch et al. observed that complexation of O_2 is primarily with the $\text{Co(DBF}_2)_2\text{(L)}$ species, and becomes more favorable at lower temperature. To compare the complexation of $\text{Co(DBF}_2)_2\text{(MeIm)}$ by MeIm and O_2, the equilibrium constants of Busch et al. in Torr^{-1} can be converted to M^{-1}, using the solubility of O_2 in acetonitrile,[36] with the assumption that the solubility is independent of temperature. Then the concentration of $\text{Co(DBF}_2)_2\text{(MeIm)}$ can be calculated from the K_1 and K_2 determined here, and the equilibrium constant for reaction 5 can be calculated. The results give $\Delta H° = -17.4$ kcal mol^{-1} and $\Delta S°$

$$(\text{MeIm})\text{Co}(\text{DBF}_2)_2 + \text{O}_2 \overset{K_{\text{O}_2}}{\rightleftharpoons} (\text{MeIm})\text{Co}(\text{DBF}_2)_2(\text{O}_2) \qquad (5)$$

$= -47.4$ cal mol^{-1} K^{-1}, with $K_{\text{O}_2} = 2.5 \times 10^2$ M^{-1} at 25 °C. A comparison to the values for K_2 in Table 1 shows that complexation of $\text{Co(DBF}_2)_2\text{(MeIm)}$ by O_2 is far more favorable than by the second MeIm. It may be noted that the parameters for K_{O_2} are not atypical for such reactions with other Co(II) systems.[37]

The values of K_1 (Table 3) are fairly large (~10^2 to 10^4 M^{-1}) for sterically unimpaired N-donor ligands, and the magnitudes do not show much solvent dependence. However, it is noteworthy that they predict ~50% or less complexation for equal concentrations of L and $\text{Co(DBF}_2)_2$ or Co(DH)_2 at ~10^{-3} M concentrations. In the earlier studies of the bond dissociation enthalpy of $[\text{L(DH)}_2\text{Co}^{\text{III}}\text{CHCH}_3\text{C}_6\text{H}_5]$, Halpern and co-workers[22] used $\Delta H°$ for reaction 6 in acetone, as determined from the temperature dependence of the equilibrium constant. The

$$\text{L(DH)}_2\text{Co}^{\text{III}}\text{CH(CH}_3)\text{C}_6\text{H}_5 \rightleftharpoons \text{L(DH)}_2\text{Co}^{\text{III}} + \text{C}_6\text{H}_5\text{CHCH}_2 + {}^1\!/_2\text{H}_2 \qquad (6)$$

measurements were done[22a] with total cobalt in the 3×10^{-5} to 1.5×10^{-4} M range and apparently without excess added L. The available K_1 values suggest that a significant amount of the equilibrium product would be $(\text{DH})_2\text{Co}^{\text{III}}$ and free L. Then the reverse reaction would produce $[(\text{solvent})(\text{DH})_2\text{Co}^{\text{III}}\text{CHCH}_3\text{C}_6\text{H}_5]$. This suggests that the published bond dissociation enthalpies do not fully reflect the influence of L on the process. In a later study,[22b] loss of L from the Co^{III} reactant was taken into account, and added L was noted to have "some effect on the final spectra" of the Co^{II} product, but the effect of the loss of L on the energetics was not taken into account. There is probably less of a problem in the first study of this type[38] which was done in toluene and where the observations were independent of the addition of free pyridine up to 2×10^{-3} M. Loss of L might be a problem in a recent study[39] of the chemical and

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electrochemical reduction of [$CH_3Co(DBF_2)_2L$] in DMSO and THF, although species concentrations are not given. The one electron reduction product [$CH_3Co^{II}(DBF_2)_2L$]$^-$ might lose the L ligand, possibly in kinetic competition with homolysis of the $Co^{II}-C$ bond.

It is interesting to note that the complexation of AdoCbi$^+$ by MeIm[15] gives $K_1 = 0.5$ M^{-1}, with $\Delta H° = -7.8$ kcal mol^{-1} and $\Delta S° = -28$ cal mol^{-1} K^{-1} in ethylene glycol. The K_1 is much smaller than that for $Co(DBF_2)_2$ in acetonitrile, largely due to a 23 cal mol^{-1} K^{-1} less favorable $\Delta S°$. This may imply that the axial base can provide some stabilization for the Co(II) state in the homolysis product as suggested vide supra and discussed in detail by Sirovatka and Finke.[21] The possibility that Co^{II}-Cbi$^+$ complexes similarly to $Co(DBF_2)_2$ is consistent with the qualitative observations of Sirovatka and Finke[21] that there is significant bis-complex formation for ligand titrations in the 0.05−2.0 M range and suggests that the titrations should be in the millimolar range to obtain K_1.

The NMR measurements for protons of MeIm coordinated to $Co(DBF_2)_2$ and may be useful in future applications using NMR to probe analogous Co(II) systems. The dominant relaxation mechanism appears to be the scalar interaction. The temperature dependence of the NMR parameters is quite normal and does not suggest any spin crossover from low-spin to high-spin Co(II), although spin crossover has been observed in other B_{12} models.

Experimental Section

Materials and Sample Preparation. $Co(DBF_2)_2{\cdot}2H_2O$ was prepared by the method of Espenson et al.[27] The *N*-methylimidazole (MeIm) was reagent grade from Aldrich. Acetonitrile was Anachemia reagent containing 0.3% water and was dried over 4-Å molecular sieves (BDH) for at least 24 h before use.

The NMR samples were prepared in vacuo in a flask with a side arm and closed by a stopcock. The MeIm was transferred to the side arm with a microsyringe, and a weighed amount of $Co(DBF_2)_2{\cdot}2H_2O$ was placed in the flask. The apparatus was evacuated and pumped to remove the water of crystallization on the solid, while the MeIm was frozen in a dry-ice/methanol bath. Then about 12−15 mL of acetonitrile, previously deoxygenated by two freeze−pump−thaw cycles, was vacuum-distilled into the flask containing the cobalt complex, the solvent was thawed, and the Melm was added by rotating the side arm. The resulting yellow-brown solution was weighed to determine the exact amount of solvent. Part of the solution was transferred, under vacuum, to a 5-mm NMR tube which contained a small amount of C_6D_6 (General Intermediates) for field locking during the NMR measurements, and the tube was flame sealed under vacuum. The molar concentrations were calculated from the weight of cobalt complex and the known densities of the solvent and MeIm.

The formation constants were determined at 35, 19, and 0 °C by spectrophotometry. To 250 mL of a deoxygenated acetonitrile solution of $Co(DBF_2)_2$ (1.0×10^{-4} M) were added various amounts of MeIm with a microsyringe. After each addition, the solution was stirred and then 5.00 mL was transferred with a syringe under argon to an argon-filled 2-cm path length cylindrical cell that was sealed with a serum cap. For concentrations >0.1 M, neat MeIm was added by syringe to the solution in the cell.

Instrumentation. Proton NMR spectra were recorded on a Bruker AM 400 MHz spectrometer. The temperature was controlled by a B-VP 1000 unit with an accuracy of ±0.5° measured by a copper−constantan thermocouple.

The EPR spectrum was recorded at 93 K for a frozen sample containing 4.4×10^{-4} M $Co(DBF_2)_2$ and 0.34 M MeIm. The instrument was a Bruker ER 200 D-SRC electron spin resonance spectrometer operating at 9.38 GHz, and the temperature was controlled by a Bruker variable temperature unit ER 4111VT.

The electronic spectra from 300 to 600 nm were recorded on a Hewlett Packard 8451 diode array spectrophotometer equipped with a standard temperature-controlled (±0.2 °C) water flow system.

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Supporting Information Available: Equation development for the analysis of absorbance changes and temperature/concentration dependence of NMR parameters; tables of concentrations, temperatures, and observed and calculated paramagnetic shifts and relaxation rates for the $Co(DBF_2)_2$ + *N*-methylimidazole system in acetonitrile; and the van't Hoff plot for the equilibrium constants. This material is available free of charge via the Internet at http://pubs.acs.org.

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