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Effects of Spin Change and Unsaturation in the Axial Ligation of Carbon Monoxide and Benzyl Isocyanide to Iron(II) Macrocycles 14ane, 15ane, and TIM

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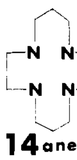
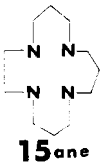
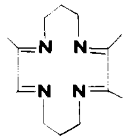
Reversible coordination of carbon monoxide to low-spin $\mathrm{Fe(14ane)(CH_3CN)_2^{2+}}$ and high-spin $\mathrm{Fe(15ane)(CH_3CN)_2^{2+}}$ is reported. A 2000-fold increase in CO lability and $P_{1/2}$ for CO binding in the 15ane system is attributed to a synergistic combination of spin change and relief of macrocycle ring strain in the dissociation of CO. Benzyl isocyanide (BzNC) complexes of Fe(14ane) and Fe(TIM) are reported. Kinetic data for the reaction $\mathrm{Fe(14ane)(CH_3CN)(BzNC)^{2+} + BzNC \rightarrow Fe(14ane)(BzNC)(BzNC)^{2+} + CH_3CN}$ are consistent with a dissociative mechanism involving a nondiscriminating reactive five-coordinate intermediate.

Introduction

The match between porphyrin hole size and the size of low- and high-spin iron is believed to play a significant role in the chemistry of hemes and heme proteins.[1-3] Busch has demonstrated how the match of metal and ring size can alter ligand field strengths, redox potentials, and spin state in iron and cobalt complexes of the series of saturated tetradentate macrocyclic amines 13–16ane.[4-7] We have previously reported data for CO and benzyl isocyanide binding to a wide variety of low-spin Fe(II)N$_4$ unsaturated macrocycles.[8-13] The Fe(14–16ane) complexes reported by Busch[7] allow a systematic assessment of the effect of ring size on axial-ligand binding properties. We report here kinetic and equilibria data for CO binding to Fe(14ane) and Fe(15ane) complexes. The Fe(15ane) system is the first example, other than hemes, of a spin change accompanying CO binding to a macrocyclic iron complex. Data are also presented for benzyl isocyanide complexes of Fe(14ane) and compared with corresponding data for the unsaturated 14-membered macrocycle Fe(TIM) (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene), reported initially by Rose.[14]


14ane


15ane


TIM

Experimental Section

14ane (cyclam) and [Fe(14ane)(CH$_3$CN)$_2$](PF$_6$)$_2$ were prepared by literature methods.[7,15] 15ane was purchased from Strem Chemicals. [FeTIM(CH$_3$CN)CO](PF$_6$)$_2$ was prepared as described by Rose.[14]

Table I. Analytical Data

		% C	% H	% N
[Fe(14ane)(CH$_3$CN)(CO)](PF$_6$)$_2$	calcd	25.38	4.42	11.38
	found	26.06	5.02	10.86
[Fe(14ane)(CH$_3$CN)(BzNC)](PF$_6$)$_2$	calcd	34.10	4.87	11.93
	found	34.26	4.22	11.76
[Fe(14ane)(BzNC)$_2$](PF$_6$)$_2$	calcd	40.01	4.91	10.77
	found	40.04	5.39	10.88
[Fe(TIM)(CH$_3$CN)(BzNC)][PF$_6$]$_2$	calcd	38.31	4.55	11.17
	found	38.10	4.35	11.16
[Fe(TIM)(BzNC)$_2$](PF$_6$)$_2$	calcd	43.49	4.62	10.14
	found	43.22	4.74	10.33

[Fe(14ane)(CH$_3$CN)(CO)](PF$_6$)$_2$. [Fe(14ane)(CH$_3$CN)$_2$](PF$_6$)$_2$ (2 g) was dissolved in 30 mL of CO-saturated acetonitrile and stirred for 2 h at room temperature in the dark until the solution was yellow-brown in color. A solution of 2 g of NH$_4$PF$_6$ in 100 mL of methanol saturated with CO was added and the solution cooled to ~−10 °C overnight, giving yellow crystals. The crystals were filtered under a CO atmosphere and washed with 25 mL of CO-saturated methanol: yield 1.2 g, ν_{CO} 1985 cm^{-1}; $\lambda_{\max}$ 422 nm (205).

[Fe(14ane)(CH$_3$CN)(BzNC)](PF$_6$)$_2$. [Fe(14ane)(CH$_3$CN)$_2$](PF$_6$)$_2$ (2 g) was added to a solution of 1 g of BzNC in 20 mL of CH$_3$CN under nitrogen. The solution immediately turned orange-brown. A 75 mL sample of degassed methanol containing 2 g of NH$_4$PF$_6$ was added and the solution left in the freezer overnight, giving a salmon-colored precipitate. The solid was filtered and washed with methanol and ether: yield 1.3 g; ν_{NC} 2143 cm^{-1}; $\lambda_{\max}$ 464 nm (105).

[Fe(14ane)(BzNC)$_2$](PF$_6$)$_2$. [Fe(14ane)(CH$_3$CN)$_2$](PF$_6$)$_2$ (2 g) was added to 1 g of BzNC in 20 mL of CH$_3$CN under nitrogen. The solution was refluxed for 20 min. After the mixture cooled, a solution of NH$_4$PF$_6$ in methanol was added and the solution left in the freezer overnight. The precipitate was filtered and washed with methanol and chloroform: yield 1.2 g; ν_{NC} 2155 cm^{-1}; $\lambda_{\max}$ 430 nm (253).

[Fe(TIM)(CH$_3$CN)(BzNC)](PF$_6$)$_2$. To a solution of 0.3 g [Fe(TIM)(CH$_3$CN)$_2$](PF$_6$)$_2$ in 4 mL of CH$_3$CN was added 0.08 mL of BzNC. An immediate color change from red to orange was observed. The solution was stirred for 5 min and concentrated, and 15 mL of ethanol added. As the solution cooled, brick-red crystals were obtained. These were filtered, washed with ethanol and ether, and dried in vacuo: yield 0.2 g; ν_{NC} 2189 cm^{-1}, $\lambda_{\max}$ 520 nm.

[Fe(TIM)(BzNC)$_2$](PF$_6$)$_2$. A solution containing 0.4 g of [Fe(TIM)(CH$_3$CN)$_2$](PF$_6$)$_2$ and 0.2 mL of BzNC in 5 mL of CH$_3$CN was heated at 50 °C for 1 h, giving a yellow solution ($\lambda_{\max}$ 490 nm). Ethanol was added, giving an orange precipitate. This was filtered, washed with ethanol and ether, and dried in vacuo: yield 0.4 g; $\lambda_{\max}$ 490 nm.

Equilibrium Constant Measurements. Equilibrium constants were obtained from analysis of visible spectra vs. P_{CO} (corrected for the vapor pressure of CH$_3$CN) by standard methods.[10] Data for 14ane

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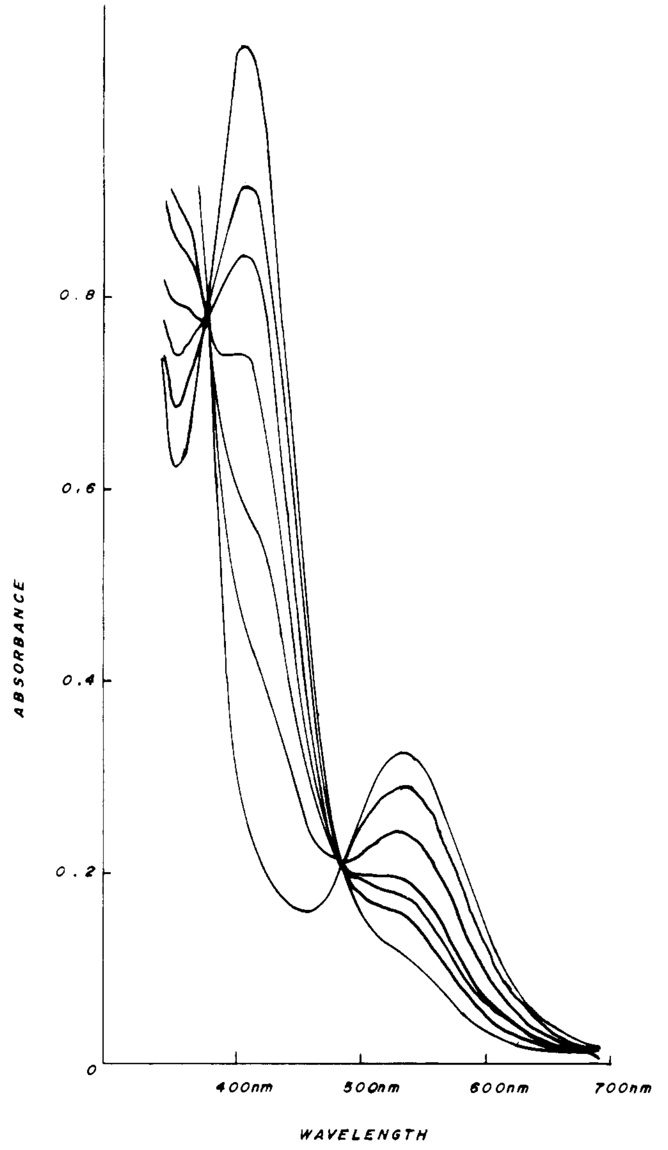

Figure 1. Spectral changes for the reaction $Fe(14ane)(CH_3CN)(CO)^{2+} + CH_3CN \rightarrow Fe(14ane)(CH_3CN)_2^{2+} + CO$ in acetonitrile 25 °C. Spectra for decreasing absorbance at 420 nm are recorded at times 0, 3.5, 7.5, 12, 20.5, 39, and 67 min.

and TIM at 25 °C and 15ane at −23 °C covered saturation ranges from $\log [y/(1-y)]$ of −0.4 to +0.4, giving slopes of plots of $\log [y/(1-y)]$ vs. P_{CO} of 0.98, 1.01, and 1.01, respectively.

Kinetic Data. Reactions at 25 °C were carried out in 1-cm optical glass cuvettes thermostated in a close-fitting brass block with use of solutions with absorbances of about 1.0 at λ_{max}. Acetonitrile-saturated nitrogen was bubbled through the solutions to prevent a buildup of CO, which otherwise leads to curved plots of $\log (A - A_\infty)$ vs. t (especially in the case of Fe(14ane); the process is carried out at complex concentrations of $\sim 10^{-2}$ M owing to the lower extinction coefficients compared to Fe(TIM)). For 15ane the iron complex was generated in situ from ferrous hexafluorophosphate (0.043 g) and 15ane 0.0084 g) in 6 mL of acetonitrile in a 2-cm path-length Pyrex Dewar cell.[16] Temperatures were maintained at −23 and −30 °C with carbon tetrachloride and bromobenzene slush baths.[17]

Table II. Visible Spectral Data[a]

complex	color	λ_{max}, nm (ϵ)
$Fe(14ane)(CH_3CN)_2^{2+}$ [a]	purple	535 (65); 370 (140)[b]
$Fe(15ane)(CH_3CN)_2^{2+}$	white	710 (3.6); 1040 (3.9)[b]
$Fe(14ane)(CH_3CN)(CO)^{2+}$	yellow	422 (205)
$Fe(14ane)(CH_3CN)(BzNC)^{2+}$	salmon	464 (160)[c]
$Fe(14ane)(BzNC)_2^{2+}$	yellow	430 (253)
$Fe(TIM)(CH_3CN)_2^{2+}$	pink	550 (8900)
$Fe(TIM)(CH_3CN)(CO)^{2+}$	yellow	430 (5000)
$Fe(TIM)(CH_3CN)(BzNC)^{2+}$	brick-red	520 (8000)
$Fe(TIM)(BzNC)_2^{2+}$	orange	490 (7800)

[a] Acetonitrile solution. [b] Reference 7. [c] Acetone solution

Results

The synthesis, characterization, and visible spectra of $Fe(14ane)(CH_3CN)_2^{2+}$ and $Fe(15ane)(CH_3CN)_2^{2+}$ have been previously reported by Busch.[7] The purple Fe(14ane) complex is low spin, giving two visible bands, 540 nm (65) and 367 nm (140). The colorless Fe(15ane) complex is high spin, with bands in the near-IR region at 1038 (3.6) and 711 nm (3.9). Addition of CO to acetonitrile solutions of $Fe(14ane)(CH_3CN)_2^{2+}$ results in a color change to yellow and spectral changes that are fully reversible and readily assigned to the equilibrium

$$Fe(14ane)(CH_3CN)_2^{2+} + CO \rightleftharpoons Fe(14ane)(CH_3CN)(CO)^{2+} + CH_3CN$$

Typical spectral changes for the reverse reaction are shown in Figure 1.

The corresponding reaction of colorless solutions of $Fe(15ane)(CH_3CN)_2^{2+}$ with 1 atm of CO in acetonitrile gives a pale yellow color at room temperature and only slight spectral changes, indicating the corresponding equilibrium lies to the left in this case. Addition of CO to Fe(15ane) in acetonitrile at lower temperatures (−23 to −30 °C) results in the development of an intense band at 432 nm analogous to the 14ane complex and the disappearance of the near-IR bands.

The spectral changes in the Fe(15ane) case are also reversible on removing the CO at low temperatures or on warming to room temperature. While an increase in absorbance in the 350–450-nm region is also observed upon air oxidation of these complexes, these spectral changes are distinct from those for CO binding and are irreversible.

Kinetic studies of the replacement of CO from $Fe(14ane)(CH_3CN)(CO)^{2+}$ and $Fe(15ane)(CH_3CN)(CO)^{2+}$ were made by following spectral changes with time in acetonitrile. Pseudo-first-order rate constants derived from log plots linear over 3 half-lives were assigned to the rate of dissociation of CO with assumption of the classic limiting dissociative mechanism observed for all of the $Fe(N_4)XY$ systems investigated to date.[8-13] In the 15ane case, rates were determined at −23 and −30 °C. Eyring analysis of these two data points gives $\Delta H^\ddagger = 19.2$ kcal/mol and $\Delta S^\ddagger = 7$ cal/(K mol). A more extensive temperature study was not possible owing to the limitations of the freezing point of the solvent.

The equilibrium constant in terms of $P_{1/2}$ for CO binding was determined from spectral data for equilibrium solutions in acetonitrile as a function of CO pressure. Equilibration times were typically 2 h, and solutions were kept in the dark since photochromic effects analogous to those described for other $Fe(N_4)(L)(CO)$ systems are also observed in these complexes.[12] Absorbance data were analyzed as a function of CO pressure, P_{CO}, by using the equation

$$\log P_{1/2} = \log \left[\frac{A - A_\infty}{A_0 - A} \right] + \log P_{CO}$$

and limiting spectra for the pure acetonitrile (A_0) and carbonyl complexes (A_∞).

Unlike all other complexes of the form FeN_4XY investigated to date, the Fe(14ane) system shows no evidence for coordination of ligands such as imidazoles, pyridine, etc. Addition of excess imidazole or pyridine to acetonitrile solutions of $[Fe(14ane)(CH_3CN)_2]^{2+}$ results in loss of the visible bands.

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Table III. Kinetic Dependence of k_{obsd} on CH_3CN and BzNC for the Reaction $Fe(14ane)(CH_3CN)(BzNC)^{2+} + BzNC \rightarrow Fe(14ane)(BzNC)_2{}^{2+}$ in Acetone at 25 °C

$[CH_3CN]$, M	[BzNC], M	10^2k_{obsd}, s^{-1}
0	0.20	2.5
0.024	0.14	2.1
0.024	0.066	1.6
0.12	0.056	0.64
0.12	0.065	0.70
0.12	0.14	1.06
0.12	0.21	1.30
0.12	0.25	1.42

This may be due to imidazole replacement of the 14ane ligand or formation of a high-spin pentacoordinate complex. These reactions were not further investigated.

Reactions of $[Fe(14ane)(CH_3CN)_2]^{2+}$ with benzyl isocyanide, however, show characteristics similar to those previously reported in $Fe(DMGH)_2$,[11] $[FeTAAB]^{2+}$,[12] and $[FeTIM]^{2+}$ [18] systems. The reaction proceeds in two distinct steps with characteristic spectral shifts (see Table II).

$$[Fe(14ane)(CH_3CN)_2]^{2+} + BzNC \xrightarrow{\text{fast}} [Fe(14ane)(CH_3CN)(BzNC)]^{2+} + CH_3CN$$

$$[Fe(14ane)(CH_3CN)(BzNC)]^{2+} + BzNC \xrightarrow{\text{slow}} [Fe(14ane)(BzNC)_2]^{2+} + CH_3CN$$

The rate of the first step is too fast to measure by conventional spectrophotometric methods. The rate of the second step was determined as a function of $[CH_3CN]/[BzNC]$ in acetone solution. Pseudo-first-order rate constants in Table III were analyzed with assumption of the classic D mechanism previously found for all other FeN_4XY systems studied to date, giving $k_{-CH_3CN}{}^{BzNC} = 2.3 \times 10^{-2}\ s^{-1}$ and $k_{+CH_3CN}/k_{+BzNC} = 1.2$. These data are remarkably similar to corresponding values for $Fe(TAAB)(CH_3CN)(BzNC)^{2+}$ in acetone ($k_{-CH_3CN}{}^{BzNC} = 1.3 \times 10^{-2}\ s^{-1}$, $k_{+CH_3CN}/k_{+BzNC} = 1.1$), in spite of gross differences in the structure of the macrocyclic ligand.

While several possible isomers of 14ane and 15ane exist and some of these have been differentiated in cobalt complexes,[6] we have no evidence for the existence of more than one isomer in these iron complexes. Only a single kinetic process is detected in the CO dissociation reactions of these complexes, and several different samples of $Fe(14ane)(CH_3CN)(CO)^{2+}$ prepared in situ or by dissolution of the solid gave identical kinetic data. The lability and air sensitivity of the iron complexes make attempts to separate and detect possible isomers difficult.

Discussion

Data for the 14ane, 15ane, and TIM systems are collected in Table IV along with those for an analogous unsaturated 16-membered macrocycle TAAB reported previously.[12]

Corresponding data for a variety of other systems including porphyrins, phthalocyanines, bis(dioximes), etc., are reported elsewhere.[8-13] We limit our discussion here to the +2-charged systems. Comparing the 14-membered 14ane and TIM systems, one sees that the effect of unsaturation is not very large on the equilibrium for CO bonding, the rate of CO dissociation, or the rate of CH_3CN dissociation trans to BzNC. The 14ane complexes show lower CO and NC stretching frequencies compared to their TIM analogues, consistent with greater back-bonding in the 14ane complexes. The higher stretching frequencies in the TIM system may result from competition with π bonding to the macrocycle.

The 15ane system is of particular interest since it represents the first nonheme iron complex to undergo a spin change on CO binding. Comparison with the analogous low-spin 14ane complex allows an assessment of the effect of spin change and macrocycle ring size on axial ligation, features given special significance in heme proteins.

The data show a 2000-fold greater CO dissociation rate in the 15ane complex compared to the 14ane system. The ideal strain-free metal–nitrogen distances of these rings are estimated to be 2.13 and 2.28 Å, respectively.[4] These estimates indicate both rings are too large to accommodate a low-spin iron (Fe–N $\simeq$ 1.95 Å) (Fe–N distances of ~2.16 Å are observed in a high-spin NO adduct of iron tetramethylcyclam[19]). As a result of the larger size of the 15ane macrocycle, the low-spin carbonyl complex is closer to the spin-crossover region than the 14ane complex. A spin change could occur earlier along the reaction coordinate for CO dissociation and thus may be an important factor in the greater lability of CO in the 15ane complex. The results can also be explained in terms of ring-strain energies advanced by Hung and Busch[6] to account for a 1000-fold increase in rates of aquation of *trans*-$Co(14,15ane)Cl_2{}^+$ complexes. They find a correlation between aquation rates and calculated ring-strain energies and attribute the increased rate of the 15ane system to relief of strain in the pentacoordinate transition state. The relief of ring strain and spin change in the iron complexes are expected to be synergistic since the increase in Fe–N distances on going high spin would also reduce the strain in the macrocycle.

We note that the much smaller hole size of the porphyrin ring (~2.0 Å) and greater rigidity[1] compared to those of these macrocycles make any detailed comparisons difficult. The 14ane and 15ane systems do demonstrate how a change in ring size can alter axial ligation.

In hemoglobin, myoglobin, and pentacoordinate model hemes, CO binding occurs via addition to a vacant coordination site.

$$FeN_4L + CO \underset{k_{-CO}}{\overset{k_{+CO}}{\rightleftharpoons}} FeN_4(L)(CO)$$

The equilibrium constant is then simply related to the "on" and "off" rate constants.

$$K_{CO} = k_{+CO}/k_{-CO}$$

In six-coordinate systems, CO binding occurs via a dissociative mechanism where the overall equilibrium constant is related to on and off rate constants for both L and CO.

$$FeN_4L_2 \underset{k_{+L}}{\overset{k_{-L}}{\rightleftharpoons}} FeN_4L \underset{k_{-CO}}{\overset{k_{+CO}}{\rightleftharpoons}} FeN_4(L)(CO)$$

$$K_{CO} = k_{-L}k_{+CO}/k_{+L}k_{-CO}$$

All nonheme systems investigated to date are of this type as are hemes studied in the presence of bases such as imidazole and pyridine.[20,21] The 14ane and TIM complexes are clearly six-coordinate low-spin complexes.

While analytical results of Busch[7] for the solid $[Fe(15ane)(CH_3CN)_2](PF_6)_2$ suggest a six-coordinate formulation for this high-spin complex, it is reasonable to consider the possibility that the complex may be five-coordinate in acetonitrile solution, especially in light of the fact that all high-spin hemes were known to be five-coordinate until the recent report of the six-coordinate high-spin $FeTPP(H_2O)_2{}^+$ ion.[22] Assuming a five-coordinate $[Fe15ane(CH_3CN)]^{2+}$, we calculate at −23 °C $K = 7.2 \times 10^{-3}\ torr^{-1} = 525\ M^{-1}$ (assuming a

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Table IV. Data for CO and BzNC Complexes[a]

complex	ν_{CO}, cm^{-1}	$k_{-CO}{}^{CH_3CN}$, s^{-1} [b]	log ($P_{1/2}$ (torr))	K_{CO}[b,e]	ν_{NC}, cm^{-1}	$k_{-CH_3CN}{}^{BzNC}$, s^{-1} [c]
$Fe(14ane)(CH_3CN)(X)^{2+}$	1985	7.7×10^{-4}	2.33	6.5×10^3	2145	2.3×10^{-2}
$Fe(15ane)(CH_3CN)(X)^{2+}$		9.3×10^{-4} (−30 °C)				
		2.9×10^{-3} (−23 °C)	2.14 (−23 °C)	1×10^4 (−23 °C)		
		1.7[d] (25 °C)				
$Fe(TIM)(CH_3CN)(X)^{2+}$	2029	4.3×10^{-4}	1.94	1.6×10^4	2189	5×10^{-3}
$Fe(TAAB)(CH_3CN)(X)^{2+}$	2038			86[c]	2194	1.3×10^{-2}

[a] At 25 °C unless stated otherwise. [b] Acetonitrile solution. [c] Acetone solution. [d] Calculated from low-temperature data; $\Delta H^\ddagger = 19.2$ kcal/mol and $\Delta S^\ddagger = +7$ cal/(deg mol). [e] Standard state 1 M for CO and CH_3CN; $K_{CO} = ([FeN_4(CH_3CN)(CO)][CH_3CN])/([FeN_4(CH_3CN)_2][CO])$. A solubility of CO in acetonitrile of 1.05×10^{-2} M is assumed, independent of temperature. This value is within ±10% of reported data for the solubility of CO in acetone and propionitrile at 25 °C: J. C. Gjaldbaek and E. K. Andersen, *Acta Chem. Scand.*, 8 1398 (1954).

solubility of CO in acetonitrile of 1.05×10^{-2} M). From K and k_{-CO} the CO on rate constant at −23 °C may be calculated; $k_{+CO} = 1.5\ M^{-1}\ s^{-1}$. Rate constants for CO addition to five-coordinate hemes are of the order of 10^6–$10^7\ M^{-1}\ s^{-1}$.[23] We can think of no reasonable explanation for such a low value in the 15ane system, and therefore, we reject the five-coordinate formulation on kinetic grounds.

In the low-spin 14ane and TIM cases the equilibria clearly involve a displacement of CH_3CN. The equilibrium constant K may then be calculated from $P_{1/2}$ by using the solubility of CO in acetonitrile (conversion from a standard state of 1 torr to that of 1 M for CO) and the molarity of CH_3CN (conversion from standard state of unit activity to 1 M for CH_3CN). Using an assumed solubility of CO of 1.05×10^{-2} M, we obtain $K_{CO}{}^{14ane} = 6.6 \times 10^3$ and $K_{CO}{}^{TIM} = 1.6 \times 10^4$. Using the value of $k_{-CH_3CN}{}^{CH_3CN} = 122\ s^{-1}$ for TIM calculated from data reported by Kildahl[25] gives a $k_{+CH_3CN}/k_{+CO} = 17$.

We do not have data for CH_3CN in the 14ane and 15ane systems. In the 14ane case, since the equilibrium constant and dissociation rate are similar to those in the TIM system, we expect k_{+CH_3CN}/k_{+CO} and k_{-CH_3CN} to be similar to TIM. We note that, trans to BzNC, the CH_3CN dissociation rates are very similar in the 14ane and TIM systems. Analysis of the 15ane data at −23 °C with assumption of a six-coordinate $Fe(15ane)(CH_3CN)_2{}^{2+}$ complex gives $K = 1.0 \times 10^4$. We then calculate $k_{-CH_3CN}k_{+CO}/k_{+CH_3CN} = 29$. If k_{+CO}/k_{+CH_3CN} is similar to that in TIM, one obtains $k_{-CH_3CN} \simeq 500\ s^{-1}$ at −23 °C. This may be compared with a k_{-CH_3CN} of $0.5\ s^{-1}$ for TIM extrapolated from data of Kildahl[25] to −23 °C. With assumption of reasonable values of ΔH^*, the k_{-CH_3CN} at 25 °C would be $\sim 10^4\ s^{-1}$ for $Fe(15ane)(CH_3CN)_2{}^{2+}$, a value not unreasonable for a high-spin iron(II) complex. Reported rates of acetonitrile exchange on hexasolvated Ni^{2+} and Co^{2+} ions are 2×10^3 and $3 \times 10^5\ s^{-1}$.[26] Water exchange on high-spin Fe^{2+} is typically 2 orders of magnitude faster than that on Ni^{2+} and slightly faster than that on Co^{2+}.[27] However, the values for Co^{2+} and Ni^{2+} are considerably less in a hindered $M(Me_6tren)(CH_3CN)^{2+}$ complex, where $k \lesssim 10^2\ s^{-1}$.[28] This is attributed to steric hindrance of solvent assistance in the dissociative interchange mechanism. A similar explanation could rationalize the value of k_{-CH_3CN} for Fe(15ane) derived from assumptions given above.

This kinetic approach, while admittedly involving several assumptions, provides a fairly consistent view of axial ligation to Fe(II) macrocycles. We would argue that on rates are not greatly affected by the spin state of the intermediate and that these are likely to be very fast, analogous to those reported for hemes. Off rates are especially sensitive to the spin state of the iron and also depend greatly on the nature of the macrocycle and trans ligand.

The suggestion that on rates are not especially sensitive to the spin state of the iron is contrary to a proposal first reported by Stynes and James[8] to explain unique features of iron porphyrins. It was argued that a high-spin intermediate would be more discriminating than a low-spin intermediate. Unfortunately, this proposal was largely based on data for hemes[9] now known to be in error.[23,29] Known on rates to hemes and relative on rates for other macrocyclic iron systems do not show great variations with the possible exception of the ligand CO. Carbon monoxide on rates are much slower than those of more conventional donors in hemes ($k_{+CO} = 1.1 \times 10^7\ M^{-1}\ s^{-1}$,[23] $k_{+BuNC} = 2.2 \times 10^8\ M^{-1}\ s^{-1}$,[30] $k_{+CH_3IM} = 1.6 \times 10^8\ M^{-1}\ s^{-1}$, $k_{+py} = 4.5 \times 10^8\ M^{-1}\ s^{-1}$, $k_{+pip} = 3.4 \times 10^8\ M^{-1}\ s^{-1}$ [29]), and this feature seems to be reflected in discrimination ratios in other models. $k_{+L}/k_{+CO} = 4$ for L = CH_3Im in FePc, and $k_{+L}/k_{+CO} = 17$ for L = CH_3CN in FeTIM. On the other hand, discrimination ratios when isocyanides[10,12] or phosphines[31] are considered instead of CO are often very close to unity. This lack of a large variation in on rates to five-coordinate intermediates is also observed in studies of ligand substitution in Fe(III)(14ane) complexes[32] and in $Mo(CO)_5$[33] systems. In contrast, nucleophilic discrimination factors in square-planar platinum complexes, which undergo substitution reactions by an A mechanism, span a range of 10^9.[34]

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Registry No. $[Fe(14ane)(CH_3CN)(CO)](PF_6)_2$, 80327-29-3; $[Fe(14ane)(CH_3CN)(BzNC)](PF_6)_2$, 80327-27-1; $[Fe(14ane)(BzNC)_2](PF_6)_2$, 80327-25-9; $[Fe(TIM)(CH_3CN)(BzNC)](PF_6)_2$, 80327-23-7; $[Fe(TIM)(BzNC)_2](PF_6)_2$, 80327-45-3; $[Fe(14ane)(CH_3CN)_2](PF_6)_2$, 57550-29-5; $[Fe(TIM)(CH_3CN)_2](PF_6)_2$, 43223-41-2; $Fe(15ane)(CH_3CN)_2{}^{2+}$, 57550-33-1; $Fe(TIM)(CH_3CN)(CO)^{2+}$, 49861-54-3; BzNC, 10340-91-7.

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