formation should be greatly favored by hydrophobicity.[16,19,23,24] (2) Below CAgC, R should be a constant (R_m), because only intramolecular excimers are formed. (3) **2** cannot form an intramolecular excimer.

Information shown in Figure 2 bears out all of the above expectations. Take the Me_2SO–H_2O system for illustration, the increasing R_m values for ϕ = 0.65, 0.60, 0.55, and 0.50 are 0.11, 0.18, 0.31, and 0.50, respectively. In fact, the log R_m vs. ϕ plot actually yields a straight line (log R_m = -4.18ϕ + 1.79, r = 0.9989). Notably, here greater hydrophobic forces are manifested in three different ways by the following: (1) larger R_m's for the intramolecular coiling process, (2) steeper slopes (θ) of the lines at concentrations >CAgC for the intermolecular aggregation process, and (3) smaller CAgC values reflecting higher aggregating abilities of the media. These conclusions are strengthened by the dioxane–H_2O curves in the same figure. Incidentally, the R vs. [S] plot may turn out to be a new and general spectroscopic method for obtaining CAgC values. Expectation (3) has been established by experiments which show that there is no 400-nm emission for **2** in ϕ = 0.50 Me_2SO–H_2O below its CAgC (5×10^{-6} M).

A final proof is provided by the addition of amylose which can separately wrap up **1** in its straightened up conformations,[1a,25,26] i.e., with **1** both at 3.0×10^{-7} M and 3.9×10^{-7} M in Me_2SO–H_2O (below CAgC, ϕ = 0.50), addition of amylose (7.14×10^{-5} M) reduced the R_m from 0.50 to 0.02.

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Geminate Recombination of Iron(II) Porphyrin with Methyl, *tert*-Butyl, and Tosylmethyl Isocyanide and 1-Methylimidazole

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Mechanisms of reactions of ligands such as dioxygen, carbon monoxide, and isocyanides with transition-metal complexes in general and metalloporphyrin complexes in particular have recently drawn much attention.[1-3] Nitric oxide and dioxygen have shown recombination in heme proteins and protoheme with rate constants greater than 10^{10} s^{-1}.[4-6] However, no such fast recombination has been reported for the reaction of diagmagnetic ligands with either proteins or simple metal complexes.[7] We now report the fast geminate recombination of 1-methylimidazole (1-MeIm) and three isocyanides, methyl isocyanide (MeNC), *tert*-butyl isocyanide (*t*-BuNC), and tosylmethyl isocyanide (TMIC), to five-coordinate (1-methylimidazole)iron(II) protoheme dimethyl ester.

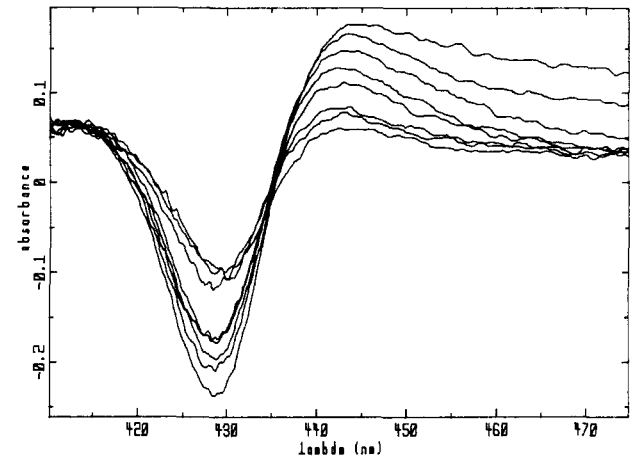

Figure 1. Transient difference spectra of (TMIC)(1-MeIm)iron(II) protoheme dimethyl ester. Successive traces were taken at 0, 1, 3, 5, 8, 15, 25, and 100 ps. Photolysis energy was 60 μJ at 314 nm.

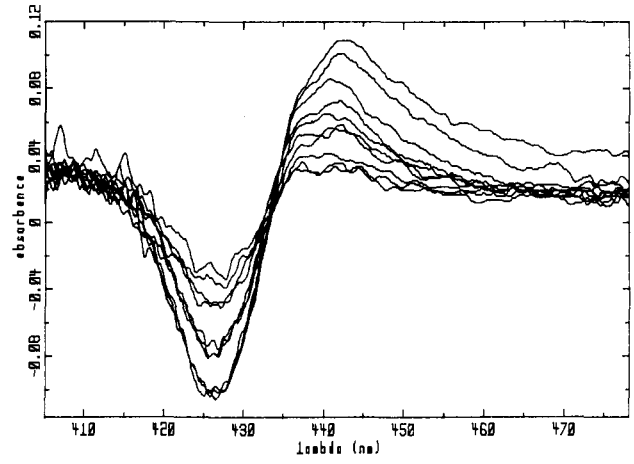

Figure 2. Transient difference spectra of bis(1-MeIm)iron(II) protoheme dimethyl ester. Successive traces were taken at 1, 2, 4, 6, 8, 9, 10, 15, 17, and 20 ps. Photolysis energy was 60 μJ at 314 nm.

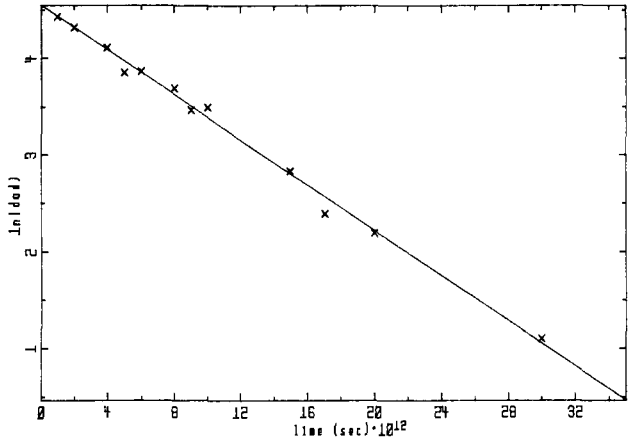

Figure 3. Kinetic plot of the transient absorbance at λ_{max} of bis(1-MeIm)iron(II) protoheme dimethyl ester.

The evolution of the difference spectra after subpicosecond laser photolysis[8] of (TMIC)(1-MeIm)iron(II) protoheme dimethyl ester (λ_{max} (Soret) = 428 nm) and bis(1-MeIm)iron(II) protoheme dimethyl ester (λ_{max} (Soret) = 426 nm) are shown in Figures 1

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(8) The instruments and the method of obtaining the spectra are described in ref 6 above.

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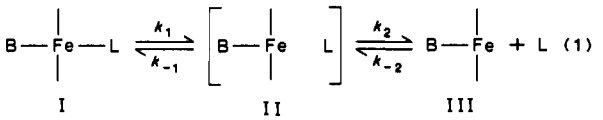
Table I. Rate Constants for Geminate Recombination and Diffusion in the Binding of Isocyanides and 1-Methylimidazole to the 1-Methylimidazole Complex of Protoheme Dimethyl Ester[c]

ligand	solvent	[L] (mM)	Γ^d	$k_{obsd} \times 10^{-10}$ (s^{-1})	k_1 (s^{-1})	$k_{-1} \times 10^{-10}$ (s^{-1})	$k_2 \times 10^{-10}$ (s^{-1})	$k_{-2} \times 10^{-8}$ (M^{-1} s^{-1})
MeNC	*a*	4.4	0.34 ± 0.03	11.3 ± 0.4	2.8	7.5	3.8	3.0
MeNC	*b*	4.0	0.45 ± 0.05	12.4 ± 0.7		6.8	5.6	
t-BuNC	*a*	1.8	0.36 ± 0.03	11.8 ± 0.4	2.3	7.6	4.2	2.2
t-BuNC	*b*	1.8	0.48 ± 0.03	12.0 ± 0.4		6.2	5.8	
TMIC	*a*	4.5	0.34 ± 0.03	10.3 ± 0.4	0.07	6.5	3.5	2.6
1-MeIm	*a*	*e*	0.20 ± 0.03	10.5 ± 0.5	7.3×10^3	8.4	2.2	2.3

[a] Solvent: toluene/1-MeIm, 80:20 by volume. [b] Solvent: DMF/1-MeIm, 80:20 by volume. [c] Data for overall equilibria and kinetics from ref 9–12 are used to calculate k_1 and k_{-2}. [d] $\Gamma = \Delta A(t = \infty)/\Delta A(t = 0) = k_2/(k_{-1} + k_2)$. [e] The solvent is 2.5 M in 1-MeIm.

and 2, respectively. In the figures, the negative absorbance change, or bleaching, at 428 and 426 nm is due to the disappearance of the ground-state six-coordinate species as the ligands are photolzyed from the iron. The positive absorbance at about 440 nm is attributed to the absorption by the five-coordinate deligated species. As the relative delay between the pump and probe pulses is increased, the absolute magnitude of these two bands will decrease as rebinding of the geminate pair occurs. The spectral changes correspond closely with the titration spectra observed in static systems involving the species I and III.

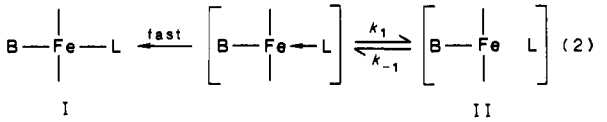


The observed relaxation rate constant, k_{obsd}, is the sum of k_{-1} (bond formation) and k_2 (diffusion). This, along with the fraction of absorption recovery at long time (yield for dissociation), affords k_{-1} and k_2. These, with published overall rate and equilibrium constants,[9-12] reveal all the rate constants in eq 1 for all of the ligands studied; see Table I. Figure 3 shows the first-order plot of the time dependence at λ_{max} (443 nm) of the five-coordinate species formed by the photolysis of bis(1-MeIm)iron(II) protoheme dimethyl ester.

In heme compounds, relaxation to the five-coordinate, high-spin "deoxy" state with the iron out-of-plane has been inferred from subpicosecond transient absorption[13] and Raman measurements[14] to occur in less than 1 ps. Therefore, we assume that the recombination rate k_{-1} characterizes a reaction between the singlet ligand and the high-spin iron(II) porphyrin. Since the bound species is diamagnetic, the spin change that accompanies recombination occurs with a rate in excess of 10^{10} s^{-1}.

The results we observe with all four ligands contrast with the behavior of CO, another diamagnetic ligand. We do not find any concentration independent recombination of carbon monoxide over the range from 10^5 to 10^{11} s^{-1}. Since we could have detected 10% geminate recombination of CO, we can use eq 1, with k_2 and k_{-2} taken to be the same as for methyl isocyanide, to estimate a maximum possible value k_{-1} of 10^9 s^{-1} for the rebinding of CO to model heme compounds. The recombination of CO is almost two orders of magnitude slower than other diamagnetic ligands.

There are several consequences of these results. First, the low quantum yields reported for transition-metal complex photodissociation should be reinvestigated for the possible occurrence of fast geminate rebinding. Second, steric effects in the binding of hemes, generally attributed to the bond making step, must be reevaluated. Finally, the differences between the rebinding of CO and the other diamagnetic ligands requires some rationalization. The alkyl isocyanides react at least 70 times faster with iron(II) porphyrin than does isoelectronic carbon monoxide. Both reactions require the conversion of high-spin iron(II) to the diamagnetic state. Since the diamagnetic isocyanides react just as rapidly as paramagnetic NO and O_2, we must look for some mechanism for spin change that is not available for CO but is accessible to the other ligands. One possibility is that the bases form transient high spin iron(II) complexes which rapidly relax to the diamagnetic complexes, eq 2. Such a reaction would be greatly accelerated by an increase in the basicity of L. This hypothesis prompted the study of the 1-MeIm reaction. The results in Table I are consistent with the mechanism.



These observations probably apply to a wide variety of transition-metal ligation reactions. Both the generality and the basicity dependence of these reactions are under further study.

Acknowledgment. This work was supported by NIH Grants HL13581 and RR02353-01 and NSF Grant CHE-8409642.

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Synthesis and Properties of a Series of Ruthenium Dihydrogen Complexes

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Since the initial discovery by Kubas,[1] dihydrogen complexes of the transition metals have been the subject of considerable interest since they may serve as models for the very important process of oxidative addition of dihydrogen.[2] In this context, Kubas has recently reported a tungsten complex in which a dihydride is in reversible equilibrium with a dihydrogen complex.[3] We now report further examples of such equilibria in cationic complexes of ruthenium.

Protonation (CH_2Cl_2 solutions) of the hydrides $CpRu(CO)(PR_3)H$((PR_3 = PPh_3 (**1a**), PMe_3 (**1b**), PMe_2Ph (**1c**), PCy_3 (**1d**))[4]

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(4) The hydride, $CpRu(CO)(PPh_3)H$, has been previously reported as the product of the reaction of $CpRu(CO)_2H$ and PPh_3.[5] Compounds **1b–d** were prepared similarly.

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