intermediacy of (indenyl)Fe(CO)$_2$ which abstracts Cl from CCl$_4$. Analogous photochemistry occurs for $(\eta^5$-C$_5$R$_5)_2$Fe$_2$(CO)$_4$.[9] The photochemical cross-coulping process in eq 3 provides further evidence supporting the photogeneration of the radical (indenyl)Fe(CO)$_2$ from $(\eta^5$-indenyl)$_2$Fe$_2$(CO)$_4$. Low-temperature ($\sim$77 K) irradiation of $(\eta^5$-indenyl)$_2$Fe$_2$(CO)$_4$ in a rigid matrix results in relatively slow (compared to $(\eta^5$-C$_5$H$_5)_2$Fe$_2$(CO)$_4$) CO loss from only the trans isomer ($\sim$20% conversion in $\sim$1 h), according to eq 4, as found for $(\eta^5$-C$_5$R$_5)_2$Fe$_2$(CO)$_4$.[9b,d] The two IR peaks for

$$(\eta^5\text{-indenyl})_2\text{Fe}_2(\text{CO})_4 \xrightarrow[\text{alkane, 77 K}]{h\nu,\ \text{near-UV}}$$
(trans isomer)

$$(\eta^5\text{-indenyl})_2\text{Fe}_2(\mu\text{-CO})_3 + \text{CO} \quad (4)$$
$$\nu_{\text{CO}} = 1810, 1826\ \text{cm}^{-1}$$
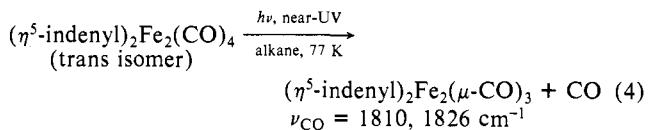
the CO loss product(s) suggest the presence of two isomers (presumably due to different orientations of the η^5-indenyl rings) or due to the less than D_{3h} symmetry of any of the CO loss products. A new finding is that the CO loss is not effected upon long wavelength ($\lambda > 500$ nm) excitation; near-UV is qualitatively more efficient in effecting CO loss at low temperature. In all respects the photochemistry of $(\eta^5$-indenyl)$_2$Fe$_2$(CO)$_4$ closely parallels that found for the related $(\eta^5$-C$_5$R$_5)_2$Fe$_2$(CO)$_4$ (R = H, Me).[9]

Results above indicate that long wavelength ($\lambda > 500$ nm) excitation of $(\eta^5$-indenyl)$_2$Fe$_2$(CO)$_4$ results mainly in formation of (indenyl)Fe(CO)$_2$ in fluid solution. In the absence of added ligands irradiation of $(\eta^5$-indenyl)$_2$Fe$_2$(CO)$_4$ in hydrocarbon solutions results in slow decomposition. However, when the irradiation is carried out in hydrocarbon solvents containing L (L = CO, PPh$_3$, PPh$_2$H) IR and EPR data show that the (indenyl)-Fe(CO)$_2$ radical can be trapped, eq 5. The resulting adducts back react thermally at 298 K to regenerate the starting $(\eta^5$-indenyl)$_2$Fe$_2$(CO)$_4$, eq 6. Most work has been done for L = CO

$$(\text{indenyl})\text{Fe}(\text{CO})_2 \xrightarrow[\text{alkane, 298 K}]{\text{L}} (\text{indenyl})\ \text{Fe}(\text{CO})_2\text{L} \quad (5)$$

$$2(\text{indenyl})\text{Fe}(\text{CO})_2\text{L} \xrightarrow[\text{alkane, 298 K}]{\Delta} (\eta^5\text{-indenyl})_2\text{Fe}_2(\text{CO})_4 + 2\text{L} \quad (6)$$
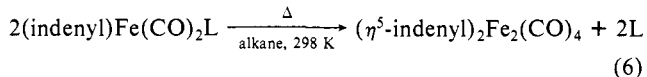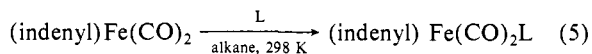
or PPh$_3$, and Figure 1 shows IR and EPR data relating to the radicals. The IR spectra in the CO region are remarkably similar to those reported for $(\eta^3$-C$_3$H$_5)$Fe(CO)$_2$L (ν_{CO} L = CO: 2045, 1969, 1963 cm^{-1}; L = PPh$_3$: 1956, 1893 cm^{-1}).[6] The splitting of the features for L = PPh$_3$ is likely due to the presence of endo and exo isomers as known for species such as $(\eta^3$-C$_3$H$_5)$Fe-(CO)$_3$X[10,11] and suggested for $(\eta^3$-C$_3$H$_5)$Fe(CO)$_2$PPh$_3$.[6c] The EPR ($g = 2.0103$) for L = CO shows no splitting and, in particular, no hyperfine splitting from H's in the indenyl ligand. For L = PPh$_3$ the EPR ($g = 2.0054$) shows splitting due to coupling with ^{31}P ($A = 68$ G), and when L = PPh$_2$H is used, there is no additional splitting associated with the H bonded to the P. When L = ^{13}CO is used, there is splitting attributed to coupling with ^{13}CO and evidence for multiple substitution to form (indenyl)-Fe(CO)$_n$(^{13}CO)$_{3-n}$ ($n = 0, 1, 2$) with n depending on the reaction time.[12] The (indenyl)Fe(CO)$_2$L radicals back react to regenerate $(\eta^5$-indenyl)$_2$Fe$_2$(CO)$_4$ with a rate that is proportional to the square of the concentration of the radical. In the case of L = PPh$_3$ it has been demonstrated that reaction of (indenyl)Fe(CO)$_2$L to regenerate $(\eta^5$-indenyl)$_2$Fe$_2$(CO)$_4$ is suppressed by added L, consistent with loss of L as the first step followed by coupling of (indenyl)Fe(CO)$_2$ radicals. We do not observe any IR bands assignable to the unknown $(\eta^3$-indenyl)$_2$Fe$_2$(CO)$_6$ from reaction of (indenyl)Fe(CO)$_3$ that would be an analogue of $(\eta^3$-C$_3$H$_5)_2$Fe$_2$(CO)$_6$.[6d]
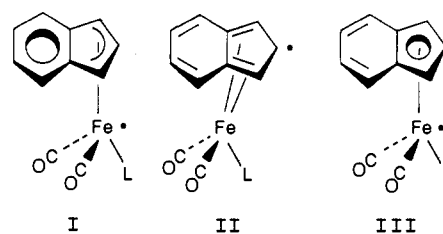
We proposed formulation of the photogenerated radicals from $(\eta^5$-indenyl)$_2$Fe$_2$(CO)$_4$ in the presence of L as 17e$^-$ species having

an η^3-indenyl ligand I. EPR shows the odd e$^-$ to be Fe-localized,

I   II   III

ruling out II, a C-centered radical with a (η^4-1,3-diene) ligand to make the Fe center electron precise. Formulation of the radicals as 19e$^-$ species III with an η^5-indenyl ligand is not likely based on the IR spectral data in the CO region which are nearly the same as reported for the 17e$^-$ (η^3-C$_3$H$_5$)Fe(CO)$_2$L species.[6] The structure I proposed for the radicals from irradiation of (η^5-indenyl)$_2$Fe$_2$(CO)$_4$ in the presence of CO is the same as found by crystallography for the electron precise [(η^3-indenyl)Fe(CO)$_3$]$^-$.[7] The spectroscopic data for (indenyl)Fe(CO)$_2$L radicals, however, do not unambiguously rule out III, and further structural characterization of the radicals is under way.

A species analogous to II has been suggested[5] to account for the formation of (η^4-C$_5$R$_5$R')Fe(CO)$_2$L from irradiation of (η^5-C$_5$R$_5$)Fe(CO)$_2$R' in the presence of L, e.g., for R = Me, R' = benzyl. Our new results establishing the formation of Fe-centered radicals from irradiation of (η^5-indenyl)$_2$Fe$_2$(CO)$_4$ suggest that it is possible that the photochemistry of (η^5-C$_5$R$_5$)Fe(CO)$_2$R' in the presence of L proceeds via the intermediacy of a Fe-centered radical (C$_5$R$_5$)Fe(CO)$_2$L. Work is in progress to characterize the reactivity of (indenyl)Fe(CO)$_2$L radicals toward R'.

The Effect of Hydrophobic–Lipophilic Interactions on Chemical Reactivity. 8. Large-Ring Intramolecular Excimer Formation Brought About by Hydrophobic Forces

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Received July 17, 1986

It has been demonstrated recently by kinetic methods that we may deliberately make use of hydrophobic–lipophilic interactions to force the two ends of 13-, 16-, and 17-carbon-chain esters to meet and interact.[1] The same result has also served as the first direct evidence for self-coiling or hairpin looping of monomeric organic molecules and may lead to synthetic applications.[2] Therefore, a demonstration of this hydrophobicity-enforced chain folding by some physical method would be most desirable. This has now been achieved by using fluorescence spectrometry.

Many elegant works have been done on intramolecular excimers or exciplexes.[3-12] Furthermore, it has been recently established

(10) Faller, J. W.; Adams, M. A. *J. Organomet. Chem.* **1979**, *170*, 71.
(11) In benzene solution, the two isomers of (indenyl)Fe(CO)$_2$PPh$_3$ have overlapping CO absorption near 1968 and 1909 cm^{-1}, similar to (η^3-C$_3$H$_5$)-Fe(CO)$_2$PPh$_3$ which has absorptions at 1956 and 1893 cm^{-1}.
(12) The (indenyl)Fe(^{13}CO)$_3$ has features at 1991, 1926, and 1918 cm^{-1}.

(1) (a) Jiang, X.-K.; Fan, W.-Q.; Hui, Y.-Z. *J. Am. Chem. Soc.* **1984**, *106*, 7202. (b) Jiang, X.-K.; Fan, W.-Q.; Hui, Y.-Z.; Gu, J.-H.; Cheng, M.-F. *Huaxue Xuebao* **1987**, *45*, 912; *Acta Chim. Sin.* **1987**, 99.
(2) Fourteenth paper of the series on "The Effect of Hydrophobic–Lipophilic Interactions on Chemical Reactivity"; Jiang, X.-K.; Hui, Y.-Z.; Fei, Z.-X., submitted for publication.
(3) (a) Zachariasse, K. A.; Duveneck, G.; Busse, R. *J. Am. Chem. Soc.* **1984**, *106*, 1045. (b) Zachariasse, K. A.; Busse, R.; Kuhnle, W. *Chem. Phys. Lett.* **1982**, *89*, 303. (c) Zachariasse, K. A.; Kuhnle, W. *Z. Physik. Chem. NF.* **1976**, *101*, 267.
(4) Chandross, E. A.; Dempster, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 3586.
(5) (a) Larson, J. R.; Petrich, J. W.; Yang, N.-C. *J. Am. Chem. Soc.* **1982**, *104*, 5000. (b) Cox, G. S.; Turro, N. J.; Yang, N.-C.; Chen, M.-J. *J. Am. Chem. Soc.* **1984**, *106*, 422. (c) Yang, N.-C.; Gerald, R.; Wasielewsk, M. R. *J. Am. Chem. Soc.* **1985**, *107*, 5531.
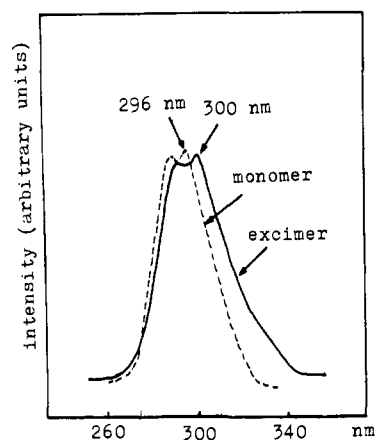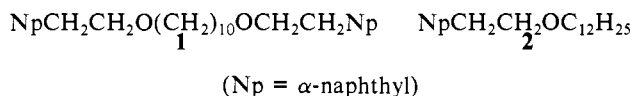
Figure 1. Normalized excitation spectra of **1** monitored at 337 nm (monomer) and at 400 nm (excimer) in $Me_2SO–H_2O$ ($\phi = 0.55$).

that for linear polymers, intramolecular excimer formation can be effected by hydrophobic interactions which change the conformations of the polymer chain.[6,7] For "small", monomeric species, however, large-ring intramolecular excimer formation brought about by hydrophobic forces has never been demonstrated. In this work we studied the fluorescence behaviors of 1,16-bis-(α-naphthyl)-3,14-dioxahexadecane (**1**)[13] and 1-(α-naphthyl)-3-oxapentadecane (**2**) in $Me_2SO–H_2O$ and dioxane–H_2O mixtures with different ϕ values, i.e., volume fractions, of the organic cosolvent at 15 °C in order to obtain yet another line of evidence for hydrophobicity-enforced aggregation as well as self-coiling of simple molecules.[14-16]

Emission spectra were recorded by a Shimadzu RF-510LC fluorescence spectrometer, by using the excitation wavelength of 300 nm. In agreement with the literature,[4,17] both **1** and **2** have

$$NpCH_2CH_2O(CH_2)_{10}OCH_2CH_2Np \qquad NpCH_2CH_2OC_{12}H_{25}$$
$$\mathbf{1} \qquad\qquad\qquad\qquad\qquad \mathbf{2}$$

(Np = α-naphthyl)

fluorescence λ_{max} at 337 nm (naphthalene ring) and 400 nm (excimer), thus the latter was used to monitor excimer formation from **1** and **2**. In $Me_2SO–H_2O$, when ϕ is >0.70, **1** ($10^{-5}–10^{-6}$ M) only shows 337-nm emission, but when ϕ is 0.65, the 400-nm emission begins to appear. Thus at low concentrations of **1**, aggregation occurs only when the medium is of sufficient hydrophobicity.

Preassociation of chromophores can greatly facilitate excimer formation, and it can be detected by the slightly different excitation spectra of the monomer and excimer emission.[6,7,18] In Me_2SO–
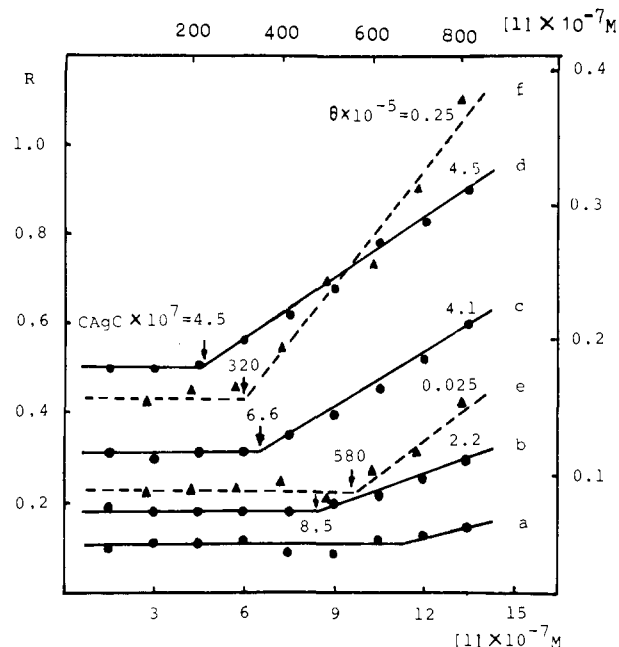

Figure 2. R (F-400/F-337) as a function of [**1**] at different volume fractions (ϕ). Values on the left are for the $Me_2SO–H_2O$ system and values on the right, the dioxane–H_2O system. θ = slope of the line. Solid lines a–d are for the $Me_2SO–H_2O$ system, and dashed lines e and f are for dioxane–H_2O. Molar concentration units in the bottom are for the $Me_2SO–H_2O$ system, and those on top are for dioxane–H_2O. The ϕ values for the six curves are the following: a, 0.65; b, 0.60; c, 0.55; d, 0.50; e, 0.40; f, 0.30.

H_2O with $\phi = 0.55$ ([**1**] = 5.8 × 10^{-7} M), excitation spectra of **1** (Figure 1) monitored at 337 nm (monomer) and at 400 nm (excimer) clearly show that preassociation of naphthalene end groups has occurred. Furthermore, at concentrations in the range of $10^{-5}–10^{-6}$ M, **1** has no excimer emission (15 °C) in the following pure solvents listed in the order of decreasing viscosity:[6a] Me_2SO, dioxane, EtOH, CCl_4, cyclohexane, methylcyclohexane, acetone. Therefore, under experimental conditions described in the present work, excimers are predominantly formed from preassociated naphthalenes.

In a particular aggregating binary solvent of constant composition ϕ, the degree of aggregation of large organic substrate molecules S increases with [S],[19,20] and below a certain critical aggregate concentration (CAgC), S exists only in its monomeric form. Oftentimes such CAgC values can be obtained from log k vs. initial [S] plots because the hydrolytic rates of long-chain esters will decrease suddenly at the CAgC.[1,19,21,22] Since below CAgC the relative population of coiled up[1,23] conformations which may lead to preassociation of the end groups is independent of [S] and the actual number of molecules involved in intramolecular excimer formation does depend on [S], we expect the following:
(1) Above CAgC, the total amount of excimers formed relative to uncomplexed **1**, as expressed by F-400/F-337 = R, will increase with decreasing ϕ because both inter- and intramolecular excimer

(6) (a) Cheung, S. T.; Winnik, M. A.; Redpath, A. E. C. *Makromol. Chem.* **1982**, *183*, 1815. (b) Winnik, F. M.; Winnik, M. A.; Tazuke, S.; Ober, C. K. *Macromolecules* **1987**, *20*, 38. (c) Winnik, F. M.; Winnik, M. A.; Tazuke, S. *J. Phys. Chem.* **1987**, *91*, 594.

(7) Herkstroeter, W. G.; Martic, P. A.; Hartman, S. E.; Williams, J. L. R.; Farid, S. *J. Polym. Sci. Polym. Chem. Ed.* **1983**, *21*, 2473.

(8) Eisenthal, K. B. *J. Laser Chem.* **1983**, *3*, 145–167.

(9) Gastellan, A.; Desvergne, J.-P.; Bouas-Laurent, H. *Chem. Phys. Lett.* **1980**, *76*, 390.

(10) Beecroft, R. A.; Davidson, R. S. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1069.

(11) Todesco, D. R.; Gelan, J.; Martens, H.; Put, J.; Schryer, F. C. De. *J. Am. Chem. Soc.* **1981**, *103*, 7304.

(12) (a) Goldenberg, M.; Emert, J.; Morawetz, H. *J. Am. Chem. Soc.* **1978**, *100*, 7171. (b) Tung, C.-H.; Zhen, Z.; Xu, H.-J. *J. Photochem.*, in press.

(13) Prepared by KOH-promoted condensation of α,ω-dibromodecane with 2-(α-naphthyl)ethanol in Me_2SO and identified by NMR, MS, IR, and elemental analysis.

(14) Fan, W.-Q.; Jiang, X.-K. *J. Am. Chem. Soc.* **1985**, *107*, 7680.

(15) We would like to count Menger's work (ref 19b) as the 15th and the present work as the 16th line of evidene for aggregation and self-coiling.

(16) We presume that both the naphthalene end groups and the hydrocarbon chain in between are involved in hydrophobic–lipophilic interactions which bring about intra- and intermolecular excimer formation.

(17) Uoler, E.; Foster, T. *Z. Physik. Chem. NF.* **1962**, *31*, 274.

(18) We believe that in aggregating solvents many coiled up conformers with the naphthalene groups closely and properly aligned will live long enough to form excimers. These preassociated naphthalene pairs may be conceived as "intramolecular encounter pairs" with average lives much longer than those of the corresponding pairs in nonaggregating solvents.

(19) (a) Menger, F. M.; Portony, C. E. *J. Am. Chem. Soc.* **1968**, *90*, 1875. (b) Menger, F. M.; Venkataram, U. V. *J. Am. Chem. Soc.* **1986**, *108*, 2980. (c) Blyth, C. A.; Knowles, J. R. *J. Am. Chem. Soc.* **1971**, *93*, 3021. (d) Oakenfull, D. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1006. (e) Oakenfull, D.; Fenwick, D. E. *Aust. J. Chem.* **1974**, *27*, 2149.

(20) Jiang, X.-K.; Li, X.-Y.; Huang, B.-Z. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1987**, *98*, 409–434.

(21) Guthrie, J. P. *J. Chem. Soc., Chem. Commun.* **1972**, 897.

(22) Murakami, Y.; Aoyam, Y.; Kide, M. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1947.

(23) Jiang, X.-K.; Hui, Y.-Z.; Fan, W.-Q. *J. Am. Chem. Soc.* **1984**, *106*, 3839.

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.

(24) (a) Knowles, J. R.; Parsons, C. A. J. Chem. Soc., Chem. Communn. 1967, 755. (b) Fan, W.-Q.; Jiang, X.-K.; Hui, Y.-Z.; Li, M.-Z. Huaxue Xuebao 1985, 43, 839.

(25) Hui, Y.-Z.; Cheng, X.-E.; Gu, J.-H.; Jiang, X.-K. Sci. Sin. Ser. B: Engl. Ed. 1982, 25, 698.

(26) Cheng, X.-E.; Hui Y.-Z.; Gu, J. H.; Jiang, X.-K. J. Chem. Soc., Chem. Commun. 1985, 71.

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 iso-

(1) Collman, J. P.; Brauman, J. I.; Iverson, B. L.; Sessler, J. L.; Morris, R. M.; Gibson, Q. H. J. Am. Chem. Soc. 1983, 105, 3052–3064, and references therein.

(2) Traylor, T. G.; Koga, N.; Deardurff, L. A. J. Am. Chem. Soc. 1985, 107, 6504–6510, and references therein.

(3) Geoffroy, G. L.; Wrighton, M. S. Organometallic Photochemistry; Academic Press; New York, 1979.

(4) Martin, J. L.; Migus, A. ; Poyart, C.; Lecarpentier, Y.; Antonetti, A.; Orszag, A. Biochem. Biophys. Res. Commun. 1982, 107, 803–810.

(5) Cornelius, P. A.; Hochstrasser, R. M.; Steele, A. W. J. Mol. Biol. 1983, 163, 119–128.

(6) Jongeward, K. A.; Marsters, J. C.; Mitchell, M. J.; Magde, D.; Sharma, V. S. Biochem. Biophys. Res. Commmun. 1986, 140, 962–966.

(7) Dixon et al. (Dixon, D. W.; Kirmaier, C.; Holten, D. J. Am. Chem. Soc. 1985, 107, 808–813) studied the picosecond photolysis of bis(imidazole) complexes but did not have a short enough laser pulse to detect the geminate recombination.
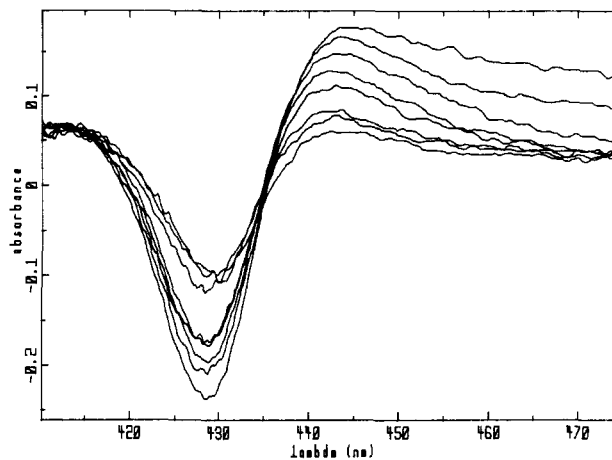
Figure 1. Transient difference spectra of (TMIC)(1-MeIm)iron(II) protoheme dimethyl ester. Successive traces were taken at 0, 1, 3, 5, 8, 15, 25, and 100 ps. Photolysis energy was 60 μJ at 314 nm.
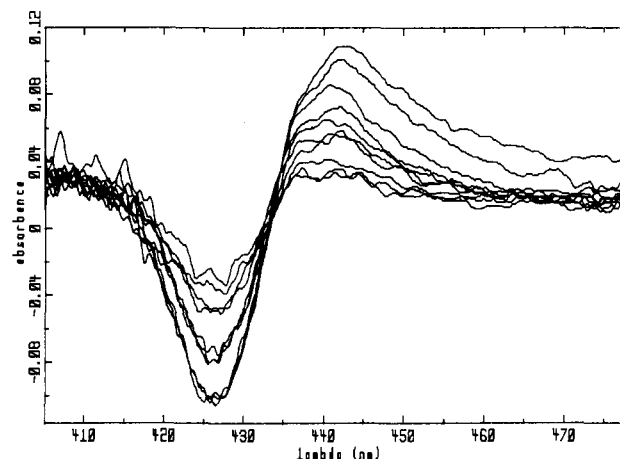

Figure 2. Transient difference spectra of bis(1-MeIm)iron(II) protoheme dimethyl ester. Successive traces were taken at 1, 2, 4, 6, 8, 9, 10, 15, 17, and 20 ps. Photolysis energy was 60 μJ at 314 nm.
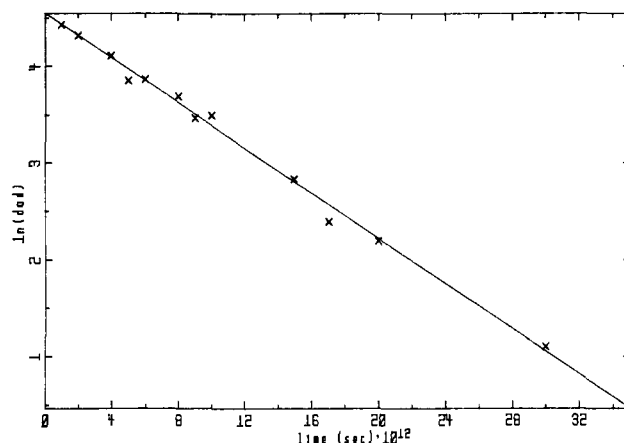

Figure 3. Kinetic plot of the transient absorbance at λ_{max} of bis(1-MeIm)iron(II) protoheme dimethyl ester.

cyanide (t-BuNC), and tosylmethyl isocyanide (TMIC), to five-coordinate (1-methylimidazole)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

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