already found low activation barriers for elimination of ethylene from metallacyclobutanes (eq 7 with only one X a metal).[24]

The results reported herein may well be related to the recently reported retention of stereochemistry upon chemisorption of *cis*- and *trans*-2-butene on Pt(111).[25]

Acknowledgment. We are grateful to Prof. K. P. C. Vollhardt for suggesting that we investigate the stereochemistry of ethylene extrusion from **1** and to Prof. G. Drobny for advice on the practical aspects of liquid-crystal NMR spectroscopy. We thank Colonial Metals, Inc., for a generous loan of OsO_4. This work was funded by Department of Energy Grant DE-FG02-84ER13299.A003.

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Solvent Tuning of the Excited-State Properties of (2,2′-Bipyridine)tetracyanoferrate(II): Direct Observation of a Metal-to-Ligand Charge-Transfer Excited State of Iron(II)

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In contrast to $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) the lowest excited state of $Fe(bpy)_3^{2+}$ is LF (ligand field) rather than MLCT (metal-to-ligand charge transfer) in character.[1] Replacement of a bpy by two stronger field CN^- ligands to give $Fe(bpy)_2(CN)_2$ does not alter this ordering.[2] Here we report observations that show that in water this ordering is retained for $Fe(bpy)(CN)_4^{2-}$ even with its stronger ligand field but that the extraordinary solvent sensitivity of this complex[3,4] can be used to access the MLCT state: the MLCT state is observed in the weak acceptor solvent[5] acetone.

The two MLCT maxima of $(TBA)_2[Fe(bpy)(CN)_4]$ (TBA = tetrabutylammonium ion) shift from 346 and 482 nm in water to 455 and 725 nm in acetone, respectively—a shift of 7000 cm^{-1} or 20 kcal mol^{-1}.[3] This solvent dependence has been attributed to donor–acceptor interactions.[3-5] Strong acceptor solvents remove electron density from the metal center via interaction with the lone-pair electrons of the cyanide ligands thereby stabilizing the Fe(II) state of the complex with respect to the Fe(III) state. Thus the MLCT transitions occur at higher energies in strongly accepting solvents such as water than in weakly accepting solvents such as acetone.[6] The $Fe(bpy)(CN)_4^{2-}$ ion with its relatively strong ligand field[7] is therefore a good candidate for a complex in which solvent might be used to reverse the order of the MLCT and LF states.[9]

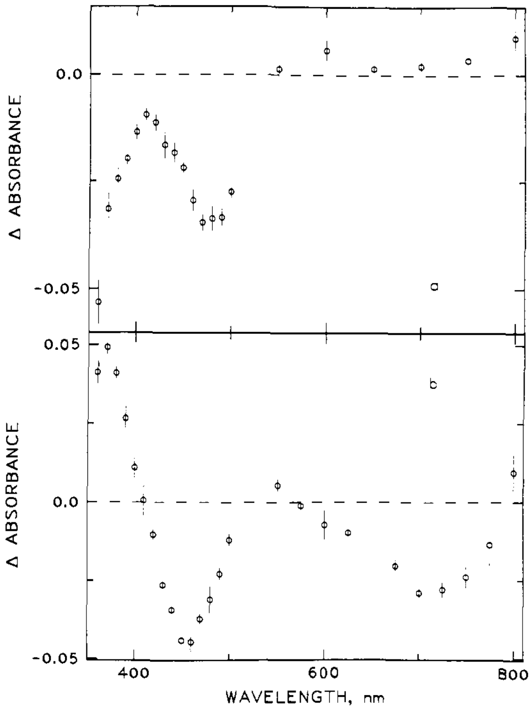

Figure 1. Difference spectra recorded during 532-nm excitation of $Fe(bpy)(CN)_4^{2-}$ in H_2O (a) and acetone (b). The spectra were determined with 6 × 10^{-4} M solutions in 2-mm path length cells.

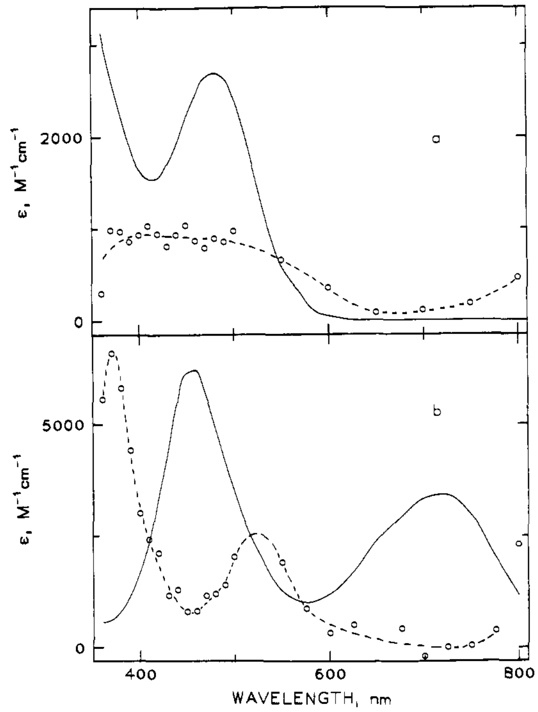

Figure 2. Ground-state (solid line) and approximate excited-state (circles) absorption spectra of $Fe(bpy)(CN)_4^{2-}$ in H_2O (a) and acetone (b).

The excited-state lifetimes and spectra of $(TBA)_2$[Fe(bpy)-

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(6) Since the ligand field strength of the cyanide ligands is likely to be reduced upon interaction with an electron-accepting solvent, the LF transitions could be shifted to lower energies in strongly accepting solvents. This shift, which is probably not large, would be in the opposite direction to the shift of the MLCT states.

(7) (a) The lowest energy excited state in $Fe(CN)_6^{4-}$ is the $^3T_{1g}$ LF state and the minimum of this state is estimated to lie about 18 600 cm^{-1} above the ground state.[7b,8] (b) Gray, H. B.; Beach, N. A. *J. Am. Chem. Soc.* **1963**, *85*, 2922.

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(9) (a) From the absorption and (uncorrected) emission data recently reported for the MLCT state of $Ru(bpy)(CN)_4^{2-}$ in water[10] and the estimated singlet–triplet splitting of 3000 cm^{-1},[9b] the Stokes shift for $Ru(bpy)(CN)_4^{2-}$ in water is calculated to be about 5600 cm^{-1}, corresponding to an excited-state distortion energy of ~2800 cm^{-1}. Assuming a similar distortion energy for the MLCT state of $Fe(bpy)(CN)_4^{2-}$ and a singlet–triplet splitting of 2000 cm^{-1},[9b] the minimum of the triplet MLCT state of $Fe(bpy)(CN)_4^{2-}$ is estimated to lie ~9000 cm^{-1} above the ground state in acetone (in contrast to ~16 000 cm^{-1} in water). (b) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3697.

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$(CN)_4]$ in water and acetone were determined by picosecond transient absorption spectroscopy.[8,11] In both solvents transient absorption kinetics were pulse-width limited, indicating excited-state lifetimes shorter than 25–30 ps. Although the decay kinetics for the complex in the two solvents appeared similar, the spectra of the transient species were not. The difference spectrum recorded during 532-nm (25-ps) excitation of $Fe(bpy)(CN)_4^{2-}$ in H_2O is shown in Figure 1a and that recorded during 532-nm excitation of the same complex in acetone is shown in Figure 1b; similar results were observed for excitation at 650 nm.[12]

Approximate absorption spectra of the transient species generated from the difference spectra are shown in Figure 2.[13] The excited-state absorption spectrum for $Fe(bpy)(CN)_4^{2-}$ in water (Figure 2a) exhibits only weak, featureless absorption from 360 to 800 nm. By contrast, the spectrum of the transient formed in acetone (Figure 2b) has two major absorption features: a sharp band at 370 nm and a weaker one maximizing near 525 nm. The spectrum in Figure 2b bears a close resemblance to that of the 2,2′-bpy radical anion[1,14] and is very strong evidence that the transient generated by 532- or 650-nm excitation of $Fe(bpy)(CN)_4^{2-}$ in acetone is an MLCT ($Fe^{III}(bpy^-)$) state.[15] The absence of bands at 370 and 525 nm in Figure 2a and the resemblance to the transient spectra of $Fe(bpy)_3^{2+}$ and $Fe(bpy)_2(CN)_2$ demonstrate that a LF state is produced when $Fe(bpy)(CN)_4^{2-}$ is excited at 532 nm in water.

These results demonstrate the dramatic effect of solvent on the photophysical properties of a solute molecule.[16] The coarse tuning of MLCT excited-state energies by modifying the ligands has been fairly widely exploited.[4,11,16,17] The additional dimension of solvent variation permits a continuous fine tuning of MLCT state energies over a comparable range. When used together, ligand and solvent tuning of excited-state energies creates an extraordinary degree of flexibility in selecting the properties of a photosensitizer.

Acknowledgment. We thank Mei H. Chou for preparing the $Fe(bpy)(CN)_4^{2-}$ used in this study. This work was performed at Brookhaven National Laboratory under Contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

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(11) (a) $H_2Fe(CN)_4(bpy)$ was prepared using the procedure described by Schilt[11b] and the complex was converted to its tetrabutylammonium salt as described by Toma and Takasugi.[3] (b) Schilt, A. A. *J. Am. Chem. Soc.* **1960**, *82*, 3000.

(12) Although similar difference spectra were obtained for both 532-nm and 650-nm excitation of $Fe(bpy)(CN)_4^{2-}$ in acetone, complete recovery of the initial absorbance was only observed with 650-nm excitation, perhaps because of photochemistry or multiphoton effects with 532-nm excitation.[8] The 650-nm excitation was of lower intensity and was predominantly into the lower energy MLCT band of $Fe(bpy)(CN)_4^{2-}$ (Figure 2b). By contrast, excitation with 532 nm was into both the higher and the lower energy MLCT bands.

(13) The absorption spectra of the transient species were estimated from their difference spectra by adding to the latter sufficient ground-state absorption to produce nonnegative, smoothly varying molar absorptivities throughout the observation region.[2]

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(15) (a) The molar absorptivities of the 370- and 525-nm bands in Figure 2b are about half as great as the values reported for the corresponding transitions in $Ru(bpy)(CN)_4^{2-}$.[10] A low molar absorptivity for the MLCT state of $Fe(bpy)(CN)_4^{2-}$ would be calculated if the difference spectrum in Figure 1a does not arise solely from the MLCT state but rather from two excited states (MLCT and LF) which decay serially or in parallel with comparable rates. If this is the case the MLCT state need not necessarily be lower in energy than the LF state, but the two states must be close enough in energy to retard the MLCT to LF transition. (b) The very short lifetime of the MLCT state in acetone could be due to the proximity of the LF state and/or the fact that the MLCT state is relatively low lying[9] (energy-gap law).

(16) (a) To our knowledge this is the first transient measurement demonstrating solvent tuning of the excited state. However, Malouf and Ford[16b] discussed the possibility of solvent tuning in steady-state photolyses of the comparably solvent-dependent $Ru(NH_3)_5L^{2+}$ (L a pyridine derivative) series. In addition, the solvent-sensitive carbonyls[16c] afford the same opportunity for certain metal–ligand combinations. (b) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 7213. (c) See: Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 572 and references cited therein.

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A Novel Method for Determining Internuclear Distances and Correlation Times from NMR Cross-Relaxation Rates

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The development of NMR techniques for determining proton–proton distances, r_{ij}, from cross-relaxation rates, σ_{ij}, or NOE's has greatly enhanced our knowledge of the three-dimensional structure of molecules in solution.[1] To obtain quantitative distances from such experiments, however, one must also know the correlation time, τ_c, for the relaxation processes since $\sigma_{ij} = (\gamma^4\hbar^2/r_{ij}^6)f(\omega_0,\tau_c)$. Although τ_c may be obtained by measuring σ at different field strengths, $B_0 = \omega_0/\gamma$, a more common practice is to determine $f(\omega_0, \tau_c)$ by measuring σ for a pair of protons whose separation is known a priori. Unknown distances may then be calculated from the relation $r_{ij} = r_{std}(\sigma_{ij}/\sigma_{std})^{1/6}$. This approach requires that $f(\omega_0,\tau_c)$ is the same for all pairs of protons and that there is some proton pair suitably resolved for calibration purposes.

Here we show how τ_c, and thus internuclear distances, may be determined by a novel method involving measurements of both longitudinal ($\sigma_\parallel$) and transverse[2,3] ($\sigma_\perp$) cross-relaxation rates. The experiments may be done at a single field strength and require no calibration pair nor assumptions about $f(\omega_0,\tau_c)$ for different protons. The method is based on the fact that $\sigma_\parallel$ and $\sigma_\perp$ have different dependencies on τ_c.

As Bothner-By and co-workers first showed[2a] $\sigma_\perp$ for a pair of nonequivalent protons separated by r_{ij} which undergoes isotropic reorientation can be expressed as

$$(\sigma_\perp)_{ij} = (\gamma^4\hbar^2/10r_{ij}^6)(3/(1 + \omega_0^2\tau_c^2) + 2)\tau_c \qquad (1)$$

This equation may be compared with the well-known expression for $\sigma_\parallel$

$$(\sigma_\parallel)_{ij} = (\gamma^4\hbar^2/10r_{ij}^6)(6/(1 + 4\omega_0^2\tau_c^2) - 1)\tau_c \qquad (2)$$

For short τ_c ($\omega_0\tau_c \ll 1$), the ratio $\sigma_\parallel/\sigma_\perp$ has a limiting value of 1, while for long τ_c ($\omega_0\tau_c \ll 1$), the limit is –0.5. At intermediate values of τ_c in the range $-1 \leq \log \omega_0\tau_c \leq 1$, there is a smooth transition between these limits such that one can determine τ_c uniquely from the ratio of $\sigma_\parallel$ to $\sigma_\perp$. Once τ_c is known, r_{ij} can be calculated directly from eq 1 or 2.

Transverse cross-relaxation is observed in the rotating frame with the spins oriented along an effective spin-locking field, $\omega_e = \gamma B_{eff} = \gamma(\Delta^2 + B_{SL}^2)^{1/2}$, which makes an angle, $\beta = \sin^{-1}(B_{SL}/B_{eff})$ with the longitudinal component, Δ, of the applied field in the rotating frame.[2,4] In practice offsets, Δ cannot be ignored so that the cross-relaxation rate as observed in the rotating reference frame must be expressed as[5]

$$(\sigma_{RF})_{ij} = \cos\beta_i \cos\beta_j(\sigma_\parallel)_{ij} + \sin\beta_i \sin\beta_j(\sigma_\perp)_{ij} + (\gamma^4\hbar^2/10r_{ij}^6)\sin^2\beta_i \sin^2\beta_j((1 + 4\omega_e^2\tau_c^2)^{-1} - 1)\tau_c \qquad (3)$$

In solutions, $\omega_e^2\tau_c^2 \ll 1$ so the last term in eq 3 can safely be ignored. Clearly, when $B_{SL} \gg |\Delta|$, $\beta \approx \pi/2$ and $\sigma_{RF} \approx \sigma_\perp$.

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(3) The transverse cross-relaxation rate between two weakly coupled spins, I and S, is defined as the rate constant for the dipolar relaxation of the transverse (*x* and *y*) components of I-spin magnetization by those of spin S and is formally analogous to that for the dipolar cross-relaxation of the *z*- or longitudinal components. See ref 2b.

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