the configuration of the aglycon portion of the molecule to be as drawn.[16]

Acknowledgment. We thank Professors K. L. Rinehart, Jr., K. Nakanishi, and C. Townsend and Dr. N. Colthup for helpful discussions; J. K. Manning and L. Barbieri for technical assistance; and M. Pastel for GCMS identification of methyl mercaptan.

Supplementary Material Available: Tables of ^{13}C NMR shifts of **3–5** and **9**, summary of crystal data, computer-generated perspective drawing with atom numbering scheme, and table of the atomic positional and thermal parameters of **11** (7 pages). Ordering information is given on any current masthead page.

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[16] (a) Liu, H.-W.; Nakanishi, K. *J. Am. Chem. Soc.* **1982**, *104*, 1178–1185. (b) A negative first and positive second Cotton effect (311 nm, $\Delta\epsilon$ −370; 272 nm, $\Delta\epsilon$ +370) was observed for calichemicin $\gamma_1{}^1$, suggesting a negative chirality of the enediyne/dienone chromophoric system as drawn.

Reversible Stereospecific Extrusion of Ethylene from a 1,2-Diosmacyclobutane. Determination of Stereochemistry by Liquid-Crystal NMR

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In a reaction analogous to the desorption of an olefin from a metal surface, (μ-1,2-ethanediyl)octacarbonyldiosmium[1] (**1**) undergoes facile ethylene loss. As **1** is related to cyclobutane by the isolobal analogy[2] between $Os(CO)_4$ and CH_2, the loss of ethylene from **1** can be compared to the fragmentation of cyclobutane into two ethylenes—a classic example of a reaction "forbidden" by orbital symmetry as a concerted process. One would, therefore, expect the loss of ethylene from **1** to be forbidden as a concerted process[3] and to occur by a diradical mechanism leading to loss of stereochemistry. We now report that, to the contrary, the loss of ethylene from **1** is stereospecific.

Elegant experimental studies of $[2_\pi + 2_\pi]$ thermal cycloreversions[4] in organic systems have demonstrated that the most sensitive stereochemical test for diradical intermediacy is the observation of retention or loss of stereochemistry at a primary radical center.[5] A sensitive test for diradical intermediacy in the fragmentation of **1** is thus the observation of retention or loss of stereochemistry in the evolution of ethylene from **1**-*3,4*-d_2. It seemed likely that stereochemically pure *cis*- and *trans*-**1**-*3,4*-d_2 would be available from the reaction of $Na_2[Os_2(CO)_8]$[1a,7] (**2**) with *meso*- and *dl*-ethanediyl-*1,2*-d_2 bis(trifluoromethanesulfonate)[8] (**3**), respectively, on the assumption that the reaction would occur with inversion at both chiral centers and therefore with retention of their relative stereochemistry.

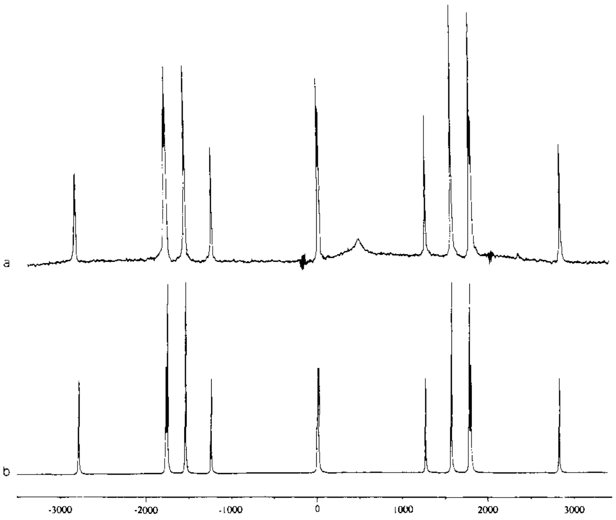
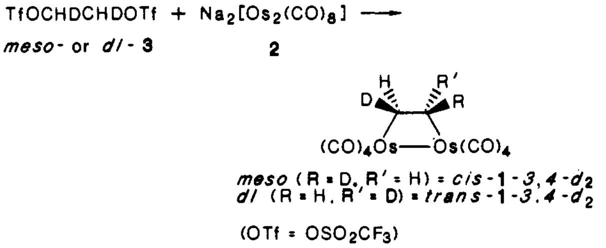


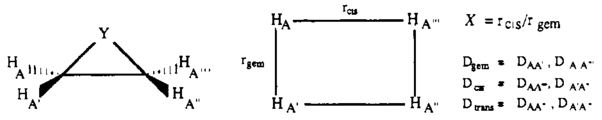
Figure 1. ^1H NMR spectrum, 200 MHz, of partially oriented **1**: (a) experimental, <3.0 wt% **1** in E. Merck, Licristal TNC-1565, t = 23 °C, 660 scans, sweep width = 15 kHz; (b) calculated, D_1 = −520.5 Hz, D_2 = −934.4 Hz, D_3 = +418.5 Hz.



(1)

Determination of both the stereochemistry (cis or trans) and stereochemical purity of **1**-*3,4*-d_2 poses an interesting spectroscopic problem, for which the dipolar couplings observable in liquid-crystal ^1H NMR spectra[9] provide a unique solution. The magnitude of this coupling is directly dependent on the magnetic moments of the nuclei and on the degree of molecular orientation, and is inversely dependent on r^3, where r is the internuclear separation. The C_{2v} symmetry of **1**[10] means that two parameters are required to describe its orientation;[9d] the observed dipolar couplings in such a four-spin system are, therefore, not a simple function of relative internuclear distance. However, in a four-proton system of this symmetry a useful relationship (eq 2) has

$$D_{trans} = (X^2 + 1)^{-5/2}\,[D_{cis}X^5 + D_{gem}] \qquad (2)$$



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[5] Complete loss of stereochemistry due to bond rotation in an intermediate diradical is often not observed in stepwise cycloreversions.[6] However, in cases where comparisons can be made, primary radical centers confront the lowest rotational barriers and may rotate 2 orders of magnitude faster than tertiary radical centers: Dervan, P. B.; Santilli, D. S. *J. Am. Chem. Soc.* **1980**, *102*, 3863.

[6] (a) Chickos, J. S.; Al-Nawwar, K. *Tetrahedron Lett.* **1985**, *26*, 1127. (b) Aalbersberg, W. G. L.; Vollhardt, K. P. C. *Isr. J. Chem.* **1981**, *21*, 145. (c) Koniz, R. F. Ph.D. Thesis, Cornell University, 1980. (d) Doering, W. v. E.; Guyton, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 3229. (e) Srinivasan, R.; Hsu, J. N. C. *J. Chem. Soc., Chem. Commun.* **1972**, 1213. (f) Paquette, L. A.; Thompson, G. L. *J. Am. Chem. Soc.* **1971**, *93*, 4920. (g) Paquette, L. A.; Leichter, L. M. *Ibid.* **1971**, *93*, 4922. (h) Baldwin, J. E.; Ford, P. W. *Ibid.* **1969**, *91*, 7192.

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[9] Informative general discussions of liquid-crystal NMR spectroscopy may be found in: (a) Khetrapal, C. L.; Kunwar, A. C. *Adv. Liq. Cryst.* **1983**, *6*, 173. (b) Emsley, J. W.; Lindon, J. C. *NMR Spectroscopy Using Liquid Crystal Solvents*; Pergamon: Oxford, 1975. (c) Diehl, P.; Khetraphal, C. L. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1969, Vol. 1. (d) Snyder, L. C. *J. Chem. Phys.* **1965**, *43*, 4041. A review of the application of this technique to the study of inorganic molecules is also available: (e) Khetrapal, C. L. *J. Indian Chem. Soc.* **1982**, *59*, 164.

[10] Although the diosmacyclobutane ring of **1** is puckered in the solid state,[1a] a single, sharp ^1H NMR signal is observed down to −90 °C, reflecting a very low inversion barrier and justifying the assumption of effective C_{2v} symmetry in the liquid-crystal experiments.

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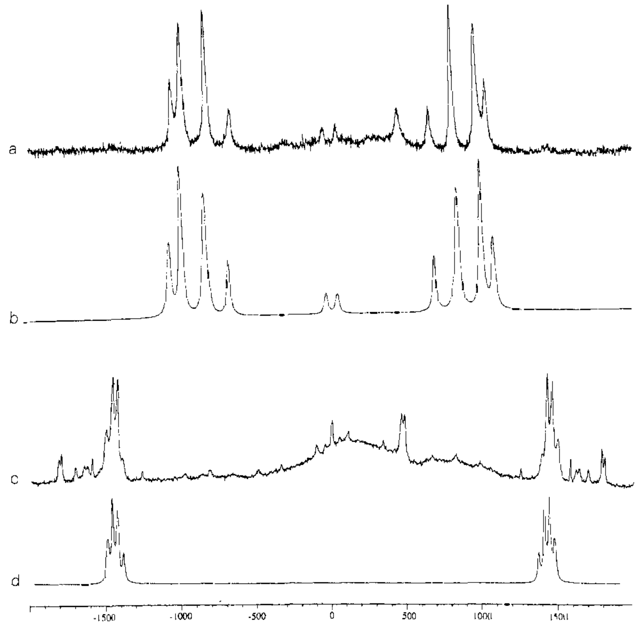


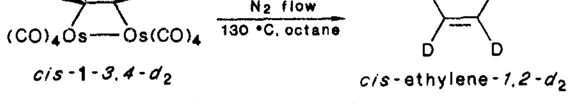
Figure 2. ^{1}H NMR spectra, 200 MHz, of *trans*-**1**-*3,4*-d_2 and *cis*-**1**-*3,4*-d_2: (a) experimental for trans, 5460 scans, sweep width = 10 kHz; (b) calculated for trans, $D_1 = -145.0$ Hz, $D_2 = -547.0$ Hz, $D_3 = 60.0$ Hz; (c) experimental for cis, 5280 scans, sweep width = 10 kHz; (d) calculated for cis, $D_1 = -947.0$ Hz, $D_2 = -78.0$ Hz, $D_3 = 60.0$ Hz.

been derived[11] between the three observed dipolar couplings D and the ratio X of the two unique distances r_{gem} and r_{cis}. This allows an unambiguous assignment of the three dipolar coupling constants observed for unlabeled **1** and provides a method for distinguishing *cis*- and *trans*-**1**-*3,4*-d_2.

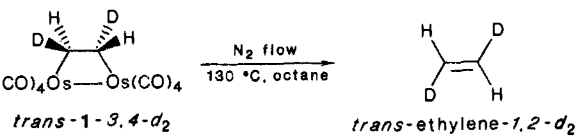
The 12-line pattern of an AA′A″A‴ system for the diosmacyclobutane **1** can be observed in Licristal TNC-1565 (Figure 1a). Simulation of this spectrum[12] (Figure 1b) confirms that the three dipolar couplings are $D_1 = -520.5$, $D_2 = -934.4$, and $D_3 = +418.5$ Hz. Attempts to fit all possible assignments of D_1, D_2, and D_3 to eq 2 show that a meaningful solution exists[13,14] only for the assignment $D_{\text{trans}} = D_1$, $D_{\text{cis}} = D_2$, and $D_{\text{gem}} = D_3$.

When the liquid-crystal NMR spectra of the products of reaction 1 are obtained under the same conditions used for **1** itself, their D values can be compared with those calculated for *cis*- and *trans*-**1**-*3,4*-d_2 by correcting the D values of **1** for the smaller magnetic moment of deuterium (Figure 2). These results unambiguously identify *cis*- and *trans*-**1**-*3,4*-d_2 and confirm that reaction 1 follows the predicted stereochemical course: *meso*-**3**-*1,2*-d_2 gives *cis*-**1**-*3,4*-d_2, and *dl*-**3**-*1,2*-d_2 gives *trans*-**1**-*3,4*-d_2.

The thermal extrusion of ethylene from both *cis*- and *trans*-**1**-*3,4*-d_2 at 130 °C under a flow of nitrogen occurs with retention of stereochemistry: *cis*-ethylene-*1,2*-d_2 (>99.75%) is formed from *cis*-**1**-*3,4*-d_2, and *trans*-**1**-*3,4*-d_2 yields *trans*-ethylene-*1,2*-d_2 (>99.20%) (eq 3 and 4).

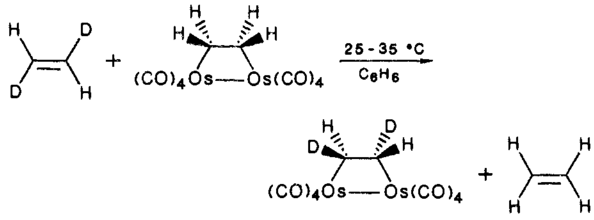


(3)



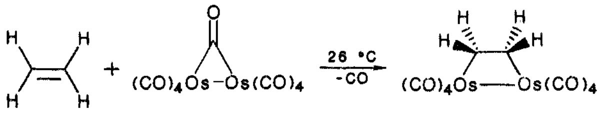
(4)

Ethylene extrusion from **1** is reversible. Under an atmosphere of C_2D_4, at 25–35 °C, the evolution of C_2H_4 can be observed while the tetradeuteriodiosmacyclobutane **1**-d_4 is formed. When isolated *cis*- or *trans*-**1**-*3,4*-d_2 is subjected to these exchange conditions under C_2H_4, IR analysis[15] of the ethylene over the solution shows only the evolution of *cis*- or *trans*-ethylene-*1,2*-d_2, respectively, demonstrating retention of stereochemistry in the exchange process. Pure *cis*- or *trans*-**1**-*3,4*-d_2 can be prepared by repeated treatment of unlabeled **1** with *cis*- or *trans*-ethylene-*1,2*-d_2 under exchange conditions (eq 5). Liquid-crystal spectra of samples prepared in this way show no scrambling of stereochemistry in the course of the ethylene exchange.



(5)

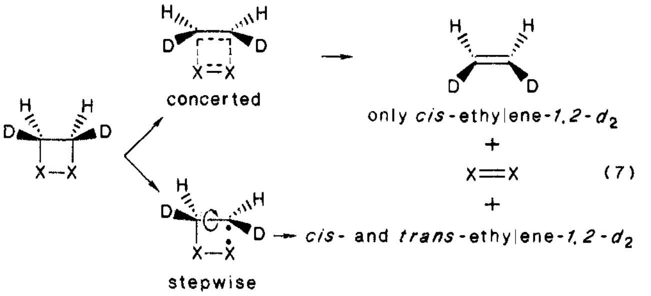
Under similarly mild conditions **1** reacts with CO to yield $Os_2(CO)_9$[16] and with H_2 to yield $H_2Os_2(CO)_8$.[17] In the former case the reaction is reversible; $Os_2(CO)_9$ may be converted to **1** under an atmosphere of ethylene (eq 6).



(6)

Preliminary kinetic data indicate that ethylene exchange occurs by a dissociative mechanism and support the proposition that these reactions occur through the intermediate formation of $Os_2(CO)_8$.[18]

The stereospecific elimination of ethylene from **1**-*3,4*-d_2 contrasts with the loss of stereochemistry observed for the elimination of ethylene from cyclobutane-*1,2*-d_2.[21] Our results suggest that concerted $[2_\pi + 2_\pi]$ processes may be possible when both of the participants X (eq 7) are metals.[22] Theoretical studies have



(7)

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[12] A computer program provided by IBM instruments, Inc., known as parameter adjustment in NMR by iteration calculation (PANIC) was used for spectral simulation on an Aspect 2000 computer.

[13] The present value of X, derived from the D values in the text without vibrational corrections, is 1.97.

[14] Exchanging the assignment of D_{cis} and D_{gem} results in a trivial permutation of the solution given, with X replaced by $1/X$.

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[18] The fact that the 32-electron Cp*Fe(μ-CO)$_3$FeCp* has a triplet ground state[19] raises the possibility that the 32-electron $Os_2(CO)_8$ may also. However, a triplet ground state for $Os_2(CO)_8$ is even harder to reconcile with the stereospecificity of reactions 3 and 4 than is a singlet ground state with an Os–Os double bond. The geometry observed for matrix-isolated $Fe_2(CO)_8$ implies that it has a singlet ground state.[20]

[19] Blaha, P. B.; Bursten, B. E.; Dewan, J. C.; Frankel, R. B.; Randolph, C. L.; Wilson, B. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 4561.

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[22] It is *possible* that elimination of ethylene from **1**-*3,4*-d_2 occurs via a diradical mechanism despite the observed stereospecificity: cleavage of the Os–C bond in the 1,4-diradical intermediate in eq 7 could *in principle* be much faster than rotation about the C–C bond. However, barriers to rotation about such C–CHD• are extremely low,[23] and the **1**-*3,4*-d_2 system, therefore, offers an extremely sensitive test for a diradical cycloreversion mechanism.

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]

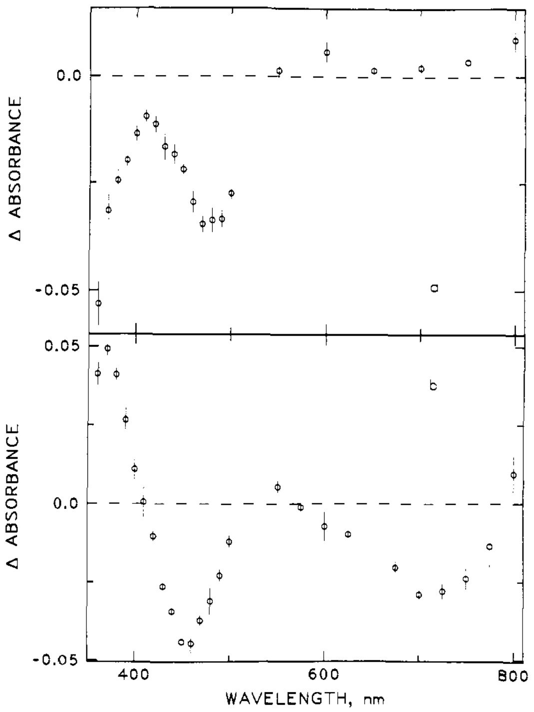

Figure 1. Difference spectra recorded during 532-nm excitation of $Fe(bpy)(CN)_4^{2-}$ in H_2O (a) and acetone (b). The spectra were determined with 6×10^{-4} M solutions in 2-mm path length cells.

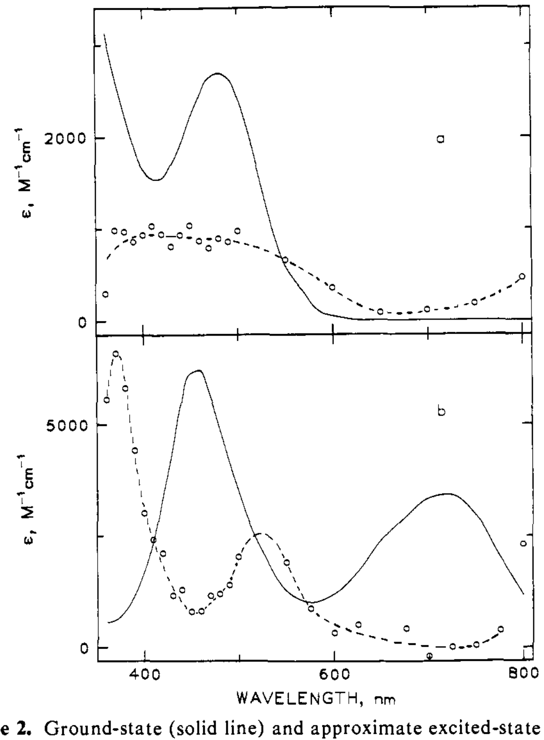

Figure 2. Ground-state (solid line) and approximate excited-state (circles) absorption spectra of $Fe(bpy)(CN)_4^{2-}$ in H_2O (a) and acetone (b).

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

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[1] Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 309. Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717. Sutin, N.; Creutz, C. *J. Chem. Ed.* **1983**, *60*, 809.

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[3] Toma, H. E.; Takasugi, M. S. *J. Soln. Chem.* **1983**, *12*, 547.

[4] (a) Remarkable solvent sensitivity is found for a number of CN^- complexes, cf. ref 4b,c. (b) Burgess, J. *Spectrochim. Acta, Part A* **1970**, *26*, 1369, 1957. Burgess, J.; Chambers, J. G.; Haines, R. I. *Trans. Met. Chem.* **1981**, *6*, 145. (c) Belser, P.; von Zelewsky, A.; Juris, A.; Barigelletti, F.; Balzani, V. *Gazz. Chim. Ital.* **1985**, *115*, 723. Barigelletti, F.; Belser, P.; von Zelewsky, A.; Juris, A.; Balzani, V. *J. Phys. Chem.* **1985**, *89*, 3680. Balzani, V.; Sabbatini, N.; Scandola, F. *Chem. Rev.* **1986**, *86*, 319.

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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.

[8] Winkler, J. R.; Netzel, T. L.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1987**, *109*, 2381.

[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.

[10] Bignozzi, C. A.; Chiorboli, C.; Indelli, M. T.; Rampi Scandola, M. A.; Varani, G.; Scandola, F. *J. Am. Chem. Soc.* **1986**, *108*, 7872.

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