necessarily requires a shorter separation between Rh and the strongly scattering W atoms and adds a higher frequency component to the EXAFS due to tungsten backscattering. Calculations and experiments with model compounds such as $(n\text{-}Bu_4N)[(Me_5C_5Rh)W_5O_{18}(TiC_5H_5)]$ indicate that a Rh–W contact of ≤4 Å can be detected by EXAFS, cf. *d*(Rh–O) = 2.20 Å in $(n\text{-}Bu_4N)_2[(Me_5C_5Rh)Nb_2W_4O_{19}]$ in which *d*(Rh–W) = 3.26 Å.[3] We propose that, instead, coordinatively unsaturated $(Ph_3P)_2Rh(CO)$ units are located in *interstitial* sites, between the $SiW_{12}O_{40}$ cages. In this regard, compounds such as **5** may be regarded as inverse zeolites in that they can exhibit inter- rather than intracluster chemistry.

These results establish that members of the two new rhodium oxometalate classes $[(Ph_3P)_2Rh(CO)(CH_3CN)]_{8-n}XM_{12}O_{40}$ and $[(Ph_3P)_2Rh(CO)]_{8-n}XM_{12}O_{40}$ are bifunctional catalysts capable of activating carbon monoxide and hydrogen at the rhodium centers as well as oxygen[22] at tungsten or molybdenum. This latter property is shared with bulk tungsten oxide surfaces.[23] In addition, the catalytic activity of rhodium is modified when $(Ph_3P)_2Rh(CO)^+$ units are associated with the $SiW_{12}O_{40}$ cluster in **1** and **5** in that selectivity for olefin hydroformylation vs. hydrogenation is significantly decreased relative to $[(Ph_3P)_3Rh(CO)][HC(SO_2CF_3)_2]$.

Acknowledgment. X-ray absorption data were recorded at the Stanford Synchrotron Radiation Laboratory, which is supported by the U.S. Department of Energy and the Research Resources Division of the National Institutes of Health. Research at Stanford University is supported in part by a grant from the 3M Corporate Research Laboratories. We are grateful to Prof. Walter Klemperer for gifts of model compounds and to Manfred Riechert for performing the high-pressure reactions.

Supplementary Material Available: Figure 1, Fourier transforms of background-subtracted Rh EXAFS spectra of **1** and **5**, and Figure 2, normalized edge spectra of **1** and **5** (2 pages). Ordering information is given on any current masthead page.

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(22) Oxygen is activated in the sense that it appears in the reaction product. The actual mechanism of oxidation is not yet established and could involve electron transfer or C–H bond cleavage. See: Gates, B. C.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979; pp 336–388.

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Lifetimes and Spectra of the Excited States of *cis*-Dicyanobis(2,2′-bipyridine)iron(II) and -ruthenium(II) in Solution

Sir:

The excited-state manifolds of the tris(polypyridine) complexes of iron(II), ruthenium(II), and osmium(II) are fairly well characterized.[1,2] The metal centers in these complexes possess $(d\pi)^6$ electronic configurations while the polypyridine complexes possess empty, low-lying π^* orbitals. The metal-to-ligand charge-transfer (MLCT) transitions are therefore intense and also of relatively low energy: this accounts for the very strong absorption of the polypyridine complexes in the visible region of the spectrum. The photophysics and photochemistry of these complexes are, however, complicated by the presence of ligand field (LF) excited states. These states arise from population of the empty metal $d\sigma^*$ orbitals. Although optical transitions to yield the LF excited states are not dipole-allowed and are therefore of low probability, the LF states can become populated by crossing from the MLCT states. This occurs readily in FeL_3^{2+} (L is 2,2′-bipyridine or 1,10-phenanthroline) where the LF state lies below the MLCT state and also in RuL_3^{2+} where the LF and MLCT states are of comparable energies but not in OsL_3^{2+} where the LF state lies well above the MLCT state.[1,2] This ordering parallels the increasing ligand field splitting for this triad.

The situation is much more complicated for mixed-ligand complexes. Because of their lower symmetry, there are more excited states in such systems. In addition the relative ordering of the LF and MLCT transitions can be tuned by a suitable choice of the ligands and solvent. This communication is concerned with the excited states of *cis*-dicyanobis(2,2′-bipyridine)iron(II). There is very good evidence[3] that in $Ru(bpy)_2(CN)_2$ the MLCT excited state lies below the LF excited state, and it has recently been proposed[4] that a similar situation may also obtain in $Fe(bpy)_2(CN)_2$. On the basis of sensitization studies, a lifetime of ≥56 ns was calculated for the lowest energy excited state of $Fe(bpy)_2(CN)_2$. This lifetime is considerably longer than the 0.81-ns lifetime reported for the LF excited state of $Fe(bpy)_3^{2+}$.[1a] The relatively long $Fe(bpy)_2(CN)_2$ lifetime implicated by the sensitization studies was rationalized[4] by proposing that the LF excited state in $Fe(bpy)_3^{2+}$ is raised in energy upon replacement of a bpy by $2CN^-$ so that the lowest excited state in $Fe(bpy)_2(CN)_2$ is the MLCT state. In order to obtain further information on this question we undertook a study of $Fe(bpy)_2(CN)_2$ by picosecond flash-photolysis techniques.[5] The longest lived excited state of $Fe(bpy)_2(CN)_2$ detected in this study has a lifetime of more than 2 orders of magnitude shorter than that estimated in the sensitization studies[4] and the absorption spectrum of this excited state is not consistent with a MLCT assignment.

$Fe(bpy)_2(CN)_2 \cdot 3H_2O$ was synthesized according to a published procedure.[6] As previously noted,[6,7] the visible absorption spectrum of the complex is very solvent dependent, a result that can be rationalized in terms of specific solvent effects on the redox potential of the Fe(II)/Fe(III) center and, to a lesser extent, the change in dipole moment associated with the $d\pi \rightarrow \pi^*(bpy)$ MLCT transition. In ethanol the absorption maxima were determined to be 570 nm ($\epsilon = 6.83 \times 10^3\ M^{-1}\ cm^{-1}$) and 373 nm ($\epsilon = 6.68 \times 10^3\ M^{-1}\ cm^{-1}$), in good agreement with the values reported by Schilt.[6] A single excited state can be detected by transient absorption spectroscopy following 532 nm (25–30 ps) excitation of $Fe(bpy)_2(CN)_2$ in methanol. This excited state decays with greater than 98% recovery of the initial absorbance and is well fit by a single exponential function with a lifetime of 0.33 ns at room temperature, very similar to the lifetime of the LF excited state of $Fe(bpy)_3^{2+}$ [1a] but considerably shorter than the 0.39-μs lifetime (methanol, 293 K) of the MLCT excited state of $Ru(bpy)_2(CN)_2$.[3a] Moreover the lifetime of the MLCT state of $Ru(bpy)_2(CN)_2$ *decreases* from 0.39 to 0.22 μs when the solvent is changed from methanol to DMF[3a] while the lifetime of the excited state of $Fe(bpy)_2(CN)_2$ *increases* from 0.33 to 0.78 ns upon

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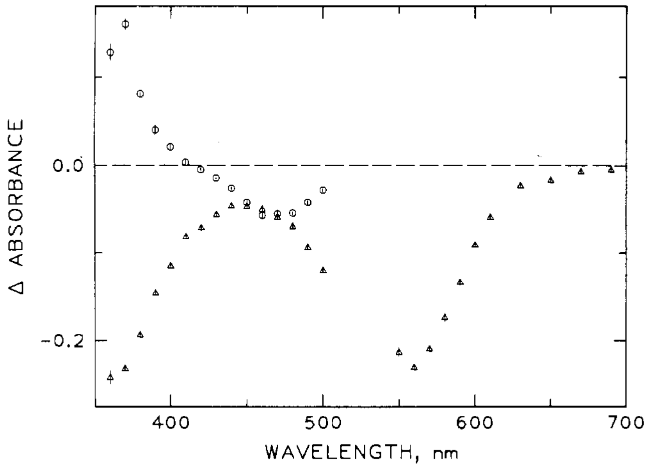

Figure 1. Difference spectra determined 40 ps and 1 ns after 532-nm excitation for Fe(bpy)$_2$(CN)$_2$ (Δ), and Ru(bpy)$_2$(CN)$_2$ (O), respectively, in methanol. The spectra were determined with 4×10^{-4} M solutions in 2-mm path length cells. The difference spectrum of Fe(bpy)$_2$(CN)$_2$ does not change significantly upon changing the solvent from methanol to DMF.

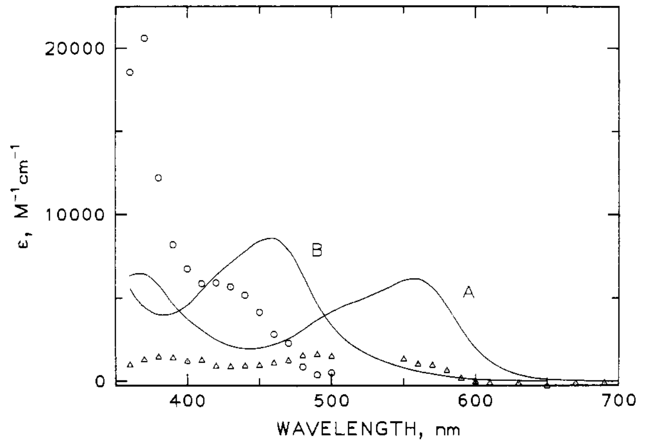

Figure 2. Ground-state absorption spectra of Fe(bpy)$_2$(CN)$_2$ (A), and Ru(bpy)$_2$(CN)$_2$ (B) and approximate excited-state absorption spectra of Fe(bpy)$_2$(CN)$_2$ (Δ) and Ru(bpy)$_2$(CN)$_2$ (O). All spectra were measured in methanol as solvent.

the same solvent change.[8] The lifetime measurements thus suggest that the lowest energy excited state of Fe(bpy)(CN)$_2$ in methanol is not a charge-transfer state.[9] This conclusion is further supported by the absorption spectra of the transients. It is apparent from Figure 1 (circles) that the Ru(bpy)$_2$(CN)$_2$ excited state absorbs much more strongly than the ground state in the 360–400-nm region (the measurements could not be extended beyond 500 nm because of the excited-state emission). By contrast, the Fe(bpy)$_2$(CN)$_2$ excited state (Figure 1, triangles) absorbs much less than the ground state in the 360–400-nm region and indeed throughout the visible region. The excited-state spectra presented in Figure 2 were obtained from the difference spectra by adding the minimum amount of ground-state absorbance necessary to produce nonnegative and smoothly varying molar absorptivities[10] and are therefore approximate only. Nevertheless, the data clearly show that the spectra of excited Ru(bpy)$_2$(CN)$_2$ and Fe(bpy)$_2$(CN)$_2$ are dramatically different. The spectrum of excited Ru(bpy)$_2$(CN)$_2$ features absorption maxima at 370 and 430 nm, wavelengths that are characteristic of species containing the bpy$^-$ chromophore.[11] This chromophore is clearly absent in the Fe(bpy)$_2$(CN)$_2$ transient spectrum.

On the basis of the present studies we conclude that the long-lived excited state of Fe(bpy)$_2$(CN)$_2$ is a LF state. Evidently replacement of a bpy by two CN$^-$ does not raise the LF state above the MLCT state of Fe(bpy)$_2$(CN)$_2$ in the solvents studied. The interpretation of the recent sensitization studies[4] is thus in need of revision.[12] The results of the present studies are also of interest in another connection. At room temperature the initially populated MLCT state of Fe(bpy)$_2$(CN)$_2$ crosses to the LF state in <<25 ps.[13] This crossing is very rapid and might be controlled, under suitable conditions, by the rate of solvent relaxation. Changing the solvent or lowering the temperature could slow down this relaxation process so that biphasic decay kinetics (MLCT → LF → ground state) might result.[14] The solvent and temperature dependence of the decay kinetics may thus shed light on the role of the solvent dynamics in determining the relaxation rate of Franck–Condon MLCT states.[3c,15] Studies along these lines are in progress.

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(8) A red shift of the Ru(bpy)$_2$(CN)$_2$ MLCT state upon changing solvent from methanol to DMF has been attributed to a donor–acceptor interaction between the lone pairs on the cyanide ligands and an acceptor solvent.[3a] Methanol is a better acceptor (acceptor number, AN = 41[3a]) than DMF (AN = 16[3a]); its stronger interaction with the cyanide ligands of Ru(bpy)$_2$(CN)$_2$ reduces the electron density at the metal center and leads to a higher energy MLCT state. The shorter MLCT-state lifetime of Ru(bpy)$_2$(CN)$_2$ in DMF compared with methanol is then consistent with simple "energy gap law" behavior for a direct nonradiative transition to the ground state. While stronger donor–acceptor interactions should produce higher energy MLCT states in M(bpy)$_2$(CN)$_2$ complexes, the weaker ligand field strength of the cyanide ligands in strongly accepting solvents should produce LF states lower in energy in methanol than in DMF. The smaller energy gap would tend to enhance the (nonradiative) decay rate of the LF state of Fe(bpy)$_2$(CN)$_2$ in methanol. Other factors, including, for example, changes in the coupling to the H-bonding modes, could also be important in determining the lifetime patterns.

(9) The LF states of Fe(bpy)$_2$(CN)$_2$ lie at lower energy and are probably more distorted than the MLCT states of the Ru complex. Both conditions favor faster decays for the LF states.

(10) The estimated molar absorptivities for the excited-state spectra shown in Figure 2 are obtained as follows. The molar absorptivity of the excited species at wavelength λ is given by the expression

$$\epsilon_{es}^{\lambda} = \Delta A^{\lambda}/l\Delta C + \epsilon_{gs}^{\lambda}$$

where ΔA^{λ} and ϵ_{gs}^{λ} are the change in absorbance and ground-state molar absorptivity, respectively, at wavelength λ, l is the optical path length, and ΔC is the change in ground-state concentration. Since a minimum amount of ground-state spectrum is added to the difference spectrum, the values chosen for ΔC are lower limits. Thus, in spectral regions where $\Delta A^{\lambda} > 0$, the estimated ϵ_{es}^{λ} values are upper limits to the correct values; lower limits for ϵ_{es}^{λ} obtain in regions where $\Delta A^{\lambda} < 0$.

(11) Creutz, C. *Comments Inorg. Chem.* **1982**, 1, 293.

(12) A possible explanation for the sensitization results reported in ref 4 is that a weak complex of the cobalt dihydride and Fe(bpy)$_2$(CN)$_2$ is present under the conditions used or perhaps that the sensitization is by an optically undetected, longer lived LF state of Fe(bpy)$_2$(CN)$_2$. Regardless of the detailed interpretation, the fact that in ref 4 sensitization by Fe(bpy)$_2$(CN)$_2$ was observed at less than millimolar quencher concentrations is noteworthy.

(13) Initial population of the MLCT state is inferred from the large molar absorptivity of the MLCT absorption band at 532 nm.

(14) (a) Although the observations were not interpreted in terms of solvent relaxation control (because no direct evidence for the formation of a relatively long-lived MLCT state was obtained), the decay of excited Fe(phen)$_3^{2+}$ in ethanol/methanol glass does become biphasic below 80 K.[14b] (b) Bergkamp, M. A.; Brunschwig, B. S.; Gütlich, P.; Netzel, T. L.; Sutin, N. *Chem. Phys. Lett.* **1981**, *81*, 147.

(15) See, for example: van der Zwan, G.; Hynes, J. T. *J. Phys. Chem.* **1985**, *89*, 4181.