same sign is also observed for the n → π*. The cyclopentanone shows a negative signal opposite to the observed n → π*. It is therefore difficult to conclude whether a consignate or a dissignate octant rule is valid for the n → 3s transition.

This study provides a comprehensive assignment of the high-energy transitions observed in the CD and absorption spectra of camphor, it also explains the change in CD sign of the 190-nm band in TFE of many ketones.

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Intramolecular Shielding of Charge-Transfer Excited States of Surfactant-Active Rhenium(I) Photosensitizers

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Excited-state electron-transfer processes involving organized assemblies are currently under active study.[1] Such systems show promise for increasing the efficiency of energy-storage reactions. In particular, surfactant-active analogues of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) with long hydrophobic alkyl chains have been used to modify sensitizer chemistry and photophysics.[2]

We are studying a new series of surfactant-active Re(I) photosensitizers:

$$fac\text{-}[(bpy)Re^I(CO)_3L]^+ \quad (L = NC(CH_2)_nCH_3,\ n = 0,2,5,6,7,9,10,13,17)$$

These systems exhibit intense d–π* metal to ligand charge-transfer (MLCT) emissions in fluid solutions similar to the parent acetonitrile complex ($n = 0$).[3] We wish to report a dramatic example of an intramolecular perturbation of CT excited-state properties by the electronically passive alkyl chain.

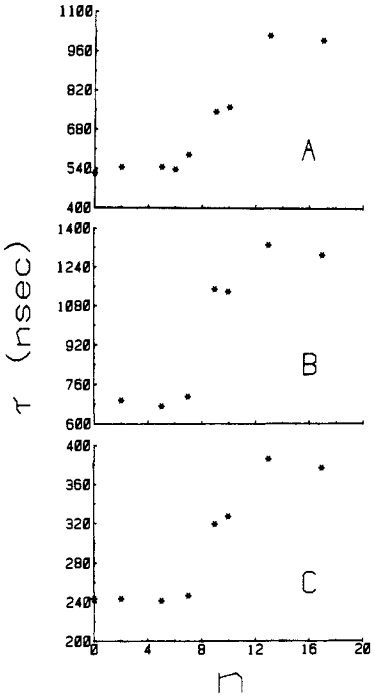

Figure 1. Excited-state lifetime of $[(bpy)Re^I(CO)_3NC(CH_2)_nCH_3]^+$ vs. n in deoxygenated solvents at 298 K°. (A) acetonitrile; (B) toluene; (C) pyridine.

Figure 1 shows the excited state lifetimes (τ) vs. chain length, n, for acetonitrile, toluene, and pyridine. Methanol and methylene chloride exhibit similar behavior. For the shorter alkyl chains, τ is essentially independent of chain length. There is an abrupt increase in τ over the range $6 \leq n \leq 13$, and τ then becomes essentially constant for $n \geq 13$. The differences among solvents are in the initial and final lifetimes and the ratio of these lifetimes. The ratio can exceed a factor of 3.

This dramatic change in τ must arise from changes in the radiative or radiationless rate constants. In either case, such changes may arise from perturbations of the excited-state electronic properties due to changes in molecular structure or to environmental factors.

Our lifetime changes cannot be attributed to a direct intramolecular electronic effect. The alkyl chain of the nitrile is not directly involved in the CT excited state. The nitrile does perturb the CT excited state by π-back-bonding of the CN.[4] While one might expect a small change in the degree of back-bonding on changing from CH_3CN to a $\text{-}CH_2CN$, it is inconceivable that any appreciable inductive effect could be propagated through more than one or two CH_2's. This is verified experimentally by the essential invariance of τ on going from $n = 0$ to 2 and 5. This result indicates that the radiative and radiationless rate constants are essentially invariant for the shorter chain nitriles.

We conclude that the dependence on n must reflect a change in the environment felt by the MLCT excited state. The excitation resides in the metal–bipyridine portion of the molecule, and for an environmental effect to be operative, the local environment in this region must be altered with changes in n. We propose that the observed τ dependence arises from foldback of the longer alkyl chains onto one face of the bpy ligand. The resultant displacement of the solvent from the vicinity of the excited state yields a difference in decay constants, particularly the nonradiative one, with a concomitant change in τ. Short chains cannot fold back and

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[1] (1) For recent reviews, see: (a) Thomas, J. K. *The Chemistry of Excitation at Interfaces*; ACS Monograph 181; American Chemical Society: Washington, DC, 1984. (b) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (c) Fendler, J. H. *Membrane Mimetic Chemistry: Characterization and Applications to Micelles, Microemulsions, Monolayers, Bilayers, Vesicles, Host–Guest Systems and Polyions*; Wiley-Interscience: New York, 1982. (d) Grätzel, M. *Acc. Chem. Res.* **1981**, *14*, 376. (e) Thomas, J. K. *Chem. Rev.* **1980**, *80*, 283. (f) Turro, N. J.; Grätzel, M.; Braun, A. M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 675. (g) Fendler, J. H. *Acc. Chem. Res.* **1980**, *13*, 7. (h) Hinze, W. L. In *Solution Chemistry of Surfactants*; Mittal, K. L., Ed.; Plenum: New York, 1979; Vol. 1. (i) Whitten, D. G.; DeLaive, P. J.; Foreman, T. K.; Mercer-Smith, J. A.; Schmehl, R. H.; Giannotti, C. In *Solar Energy: Chemical Conversion and Storage*; Hautala, R. R., King, R. B., Kutal, C., Eds.; *The Humana Press Inc.*: NJ, 1979; p 117.

[2] (2) (a) Kaizu, Y.; Ohta, H.; Kobayashi, K.; Kobayashi, H.; Matsuo, T. *J. Photochem.* **1985**, *30*, 93. (b) Schmehl, R. H.; Whitesell, L. G.; Whitten, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 3761. (c) Schmehl, R. H.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 1938. (d) Gaines, G. L., Jr. *Inorg. Chem.* **1980**, *19*, 1710. (e) Infelta, P. P.; Grätzel, M.; Fendler, J. H. *J. Am. Chem. Soc.* **1980**, *102*, 1479. (f) Memming, R.; Schroppel, F. *Chem. Phys. Lett.* **1979**, *62*, 207. (g) Tsutsui, Y.; Takuma, K.; Nishijima, T.; Matsuo, T. *Chem. Lett.* **1979**, 617. (h) Ford, W. E.; Otvos, J. W.; Calvin, M. *Nature (London)* **1978**, *274*, 507. (i) Gaines, G. L., Jr.; Behnken, P. E.; Valenty, S. J. *J. Am. Chem. Soc.* **1978**, *100*, 6549. (j) Seefeld, K. P.; Möbius, D.; Kuhn, H. *Helv. Chim. Acta* **1977**, *60*, 2608. (k) DeLaive, P. J.; Lee, J. T.; Sprintschnik, H. W.; Abrũna, H.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 7094. (l) Sprintschnik, G.; Sprintschnik, H. W.; Kirsch, P. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 4947.

[3] (3) (a) Fredericks, S. M.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 7415. (b) The Re(I) complexes studied were prepared with slight modifications by the method of ref 3a.

[4] (4) (a) Kober, E. M.; Marshall, J. L.; Dressick, W. J.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2755. (b) Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2098.

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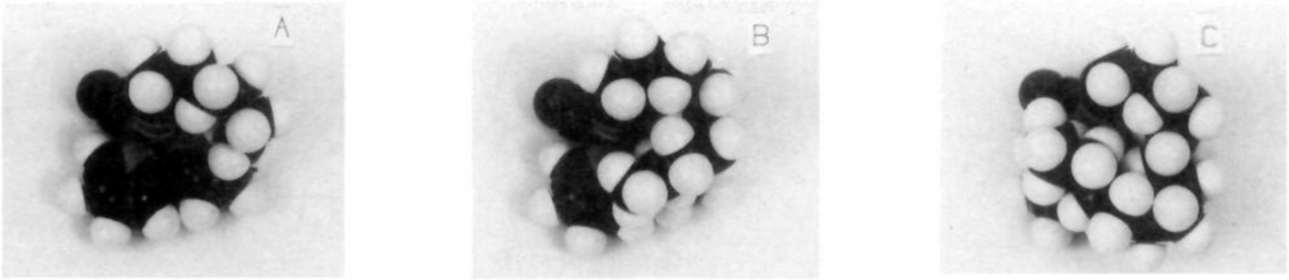

Figure 2. Space-filling models of $[(\mathrm{bpy})\mathrm{Re}^{\mathrm{I}}(\mathrm{CO})_3\mathrm{NC}(\mathrm{CH}_2)_n\mathrm{CH}_3]^+$ showing the maximal degree of overlap between the alkyl chain and the bpy ligand. (A) $n = 5$; (B) $n = 9$; (C) $n = 13$. The view in all cases is from the top along the CN–Re axis. The bpy is at the bottom of the figure and one of the CO's is visible on the upper left.

make contact with the bpy; thus, no perturbation of the decay results. Medium-length chains can interact to varying degrees depending on the chain length. Longer chains can completely cover one bpy face.

Solvent shielding by intramolecular foldback is supported by examination of space-filling molecular models. Figure 2A shows a model for the $n = 5$ case where the alkyl chain was folded to give maximum proximity or contact with the exposed bpy face. In this case there is little or no actual contact between the two portions, and the degree of shielding is minimal. Figure 2B shows the same view for $n = 9$ where roughly 50% of the face is shielded from solvent contact. Finally, Figure 2C shows the $n = 13$ case where the one bpy face is virtually completely shielded from the solvent. Further increases in n have no appreciable effect on the degree of solvent shielding of the bpy.

The changes in τ exactly mirror the degree of solvent shielding predicted by the molecular models. For $n \leq 5$, there is no shielding, and τ is independent of n. Starting around n equal 6 to 7, shielding can occur and τ increases. For $n \geq 13$, 100% coverage of one face can occur and τ is again independent of n, but at a different value than for the earlier plateau. For intermediate n's where the degree of coverage depends on chain length, τ varies rapidly with n. For example, at $n = 9$, the models show that about half of the bpy face is covered, and the τ's for acetonitrile and pyridine are almost exactly halfway between the unshielded and fully shielded plateaus.

If this model is correct anything that perturbs the degree of chain foldback should alter the excited-state lifetime. We reasoned that we should be able to pull the longer hydrophobic chains away from the bpy face by forming alkyl cyclodextrin (CD) inclusion complexes. The driving force for such complexation is displacement of water from the hydrophobic CD cavity.[5] We find that α- and β-CD Re(I) inclusion complexes do form, and the lifetime and degree of shielding of the excited state from external quenchers varies in a manner consistent with our model.

The good correspondence between τ and the fractional coverage of the bpy chromophore, assuming a maximal interaction of the alkyl chain, suggests a strong driving force for foldback. We would expect this driving force to depend on solvent hydrophobicity, and we do observe changes in the detailed shapes and breakpoints of the curves for different solvents, but the effect is not large. These results support a remarkably strong specific alkyl chain–bpy interaction even in such a nonpolar solvent as toluene.

In conclusion, we present evidence for an intramolecular shielding effect on excited-state properties for a transition-metal photosensitizer. This effect arises from self-foldback of long alkyl chain ligands onto the bpy chromophore, thereby shielding part or all of one bpy face from the solvent. This intramolecular hydrophobic sheath may prove useful in enhancing luminescence properties and in controlling excited-state electron- and energy-transfer processes as well as back-electron-transfer reactions.

Acknowledgment. We gratefully acknowledge support by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE 82-06279 and 86-00012). All lifetime measurements were carried out at the University of Virginia laser facility purchased in part through National Science Foundation Grant CHE 77-09296. We thank S. W. Snyder for many helpful discussions.

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(5) (a) Bender, M. L.; Komiyama, M. *React. Struct.: Concepts Org. Chem.* Springer-Verlag: Berlin, Heidelberg, 1978; Vol. 6. (b) Saenger, W. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 2. (c) Szejtli, J. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 3; 332. (d) Bergeron, R. J. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 3.

A Metal-Centered Radical-Pair Mechanism for Alkyne Hydrogenation with a Binuclear Rhodium Hydride Complex. CIDNP without Organic Radicals

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A radical pair mechanism for the hydrogenation of unsaturated substrates by mononuclear transition-metal hydrides has been demonstrated by the occurrence of chemically induced dynamic nuclear polarization (CIDNP).[1-4] In this mechanism, an $\overline{\mathrm{M}^\bullet,\mathrm{R}^\bullet}$ radical pair forms by H atom transfer, eq 1, and leads to the

$$\mathrm{MHL}_x + \rangle\!\!= \;\rightleftharpoons\; \mathrm{M}^\bullet,\mathrm{R}^\bullet \xrightarrow{\mathrm{MHL}_x} \mathrm{RH} + \mathrm{M}_2\mathrm{L}_{2x} \qquad (1)$$

observed CIDNP through singlet–triplet mixing and spin selective reactions. The reactant and product resonances in these reactions show *net* polarization which is explained by the difference in g values of the radical pair components, $\mathrm{M}^\bullet$ and $\mathrm{R}^\bullet$.[1] In this paper, we report that CIDNP also occurs in the hydrogenation of alkynes by $\mathrm{Rh}_2\mathrm{H}_2(\mathrm{CO})_2(\mathrm{dppm})_2$ (**1**)[5] but that the basis for CIDNP in this system is different, involving an extraordinary metal-centered biradical.[6]

Complex **1** reacts rapidly with $\mathrm{PhC{\equiv}CH}$ in $\mathrm{C}_6\mathrm{D}_6$ under H_2 to give ~1 equiv of styrene and an intense blue complex, **2**, which

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(1) Halpern, J.; Sweany, R. L. *J. Am. Chem. Soc.* **1977**, *99*, 8335.

(2) (a) Nalesnik, T. E.; Orchin, M. *Organometallics* **1982**, *1*, 222–223. (b) Nalesnik, T. E.; Orchin, M. *J. Organomet. Chem.* **1981**, *222*, C5.

(3) (a) Connolly, J. W. *Organometallics* **1984**, *3*, 1333. (b) Thomas, M. J.; Shackleton, T. A.; Wright, S. C.; Gillis, D. J.; Colpa, J. P.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1986**, 312.

(4) (a) Bockman, T. M.; Garst, J. F.; King, R. B.; Marko, L.; Ungvary, F. *J. Organomet. Chem.* **1985**, *279*, 165. (b) Garst, J. F.; Bockman, T. M.; Batlaw, R. *J. Am. Chem. Soc.* **1986**, *108*, 1689.

(5) Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1984**, *23*, 4207.

(6) A metal-centered biradical, $^\bullet(\mathrm{OC})_4\mathrm{Re}\overset{\frown}{\mathrm{P\;\;P}}\mathrm{Re}(\mathrm{CO})_4{}^\bullet$, has recently been proposed but its reaction chemistry is similar to that of related monoradicals. Lee, K.-W.; Hanckel, J. M.; Brown, T. L. *J. Am. Chem. Soc.* **1986**, *108*, 2266.

0002-7863/86/1508-5345$01.50/0 © 1986 American Chemical Society