resembles the corresponding chair borinate **9**. The 2.5 kcal/mol preference for the twist-boat will be overcome by the *Z* enolate 4.0 kcal/mol preference for the chair transition structure. However, the *E* enolate will still prefer the twist-boat. This is the origin of the (*Z*) → (chair) → syn and (*E*) → (twist-boat) → *syn* stereochemistry for borates.[8,9] The larger preference for the twist-boat transition structure by the borate is related both to the small size of the alkoxy substituent and to the greater preference for planarity of the enol borate than the enol borinate (3.0 kcal/mol versus 2.0 kcal/mol, respectively, to rotate to a 90° conformation at the 3-21G level). This conclusion is probably applicable to other cases, such as titanium and zirconium enolates, where the chair is favored for *Z* enolates, but the twist-boat is favored for *E* enolates.

Finally, as shown in Table I, Dunitz–Bürgi attack angles of 101–108° are observed in both Li and BH_2 reactions, similar to what is found for other nucleophilic additions to carbonyls.[16]

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(16) Wu, Y.-D.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 908.

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cis-Diaquabis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) Sensitizes Wide Band Gap Oxide Semiconductors Very Efficiently over a Broad Spectral Range in the Visible

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Trisbipyridylruthenium(II) and its homologues are extensively employed as redox sensitizers.[1] By contrast, very little is known about the excited-state electron-transfer properties of bis(bipyridyl)ruthenium(II) complexes. Apart from $Ru(bipy)_2(CN)_2$, for which the emission lifetime in methanol is ca. 100 ns,[2] the excited state of this class of compounds is too short-lived[3] to allow for the occurrence of bimolecular solution reactions. In addition, photoinduced ligand loss and cis–trans isomerization[4] constitute frequently the preferred pathway of electronic deactivation. We report here on the surprisingly effective, broad band sensitization of TiO_2 to visible light by *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$ (L = 2,2′-bipyridyl-4,4′-dicarboxylate).

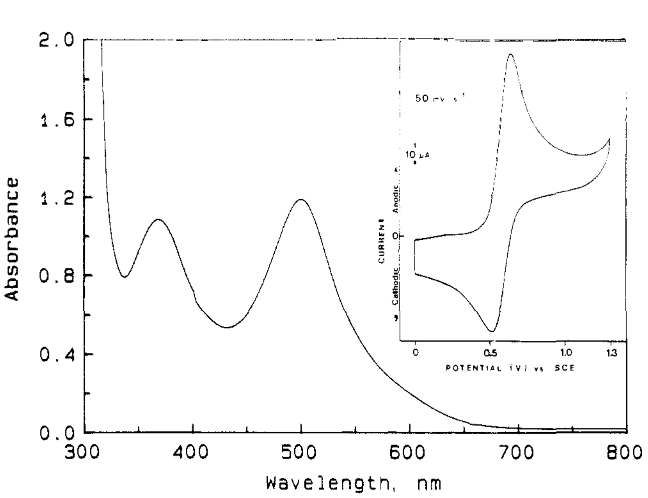

Figure 1. UV–vis absorption spectrum of 10^{-3} M *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$ in water at pH 4.85. Optical pathlength 0.1 cm. Inset: cyclic voltammogram of the same solution; working electrode: In-doped SnO_2.

cis-$Ru^{II}L_2Cl_2 \cdot 2H_2O$ was obtained by refluxing under Ar 60 mg (0.229 mmol) of $RuCl_3 \cdot 3H_2O$ (Fluka, 38–40% Ru) and 113 mg (0.463 mmol) of ligand (Aldrich) in 20 mL of DMF for 8 h. After cooling, traces of RuL_3 were filtered. Most of the DMF solvent was evaporated under vacuum, and *cis*-$Ru^{II}L_2Cl_2$ was precipitated with acetone. The crystals were filtered off and dried in vacuum. Elemental analysis corresponded to $C_{24}H_{16}N_4O_8Cl_2Ru \cdot 2H_2O$.

cis-$Ru^{II}L_2(H_2O)_2$ was prepared by hydrolysis of the dichloro complex at pH 4.5 and precipitation at its isoelectric point (pH 2.8) with 0.1 M CF_3SO_3H (Fluka, further purified by vacuum distillation) for acidification. Crystallization in the dark for 24 h at 4 °C gave shining crystals dried in vacuum (yield 70%). In air, this compound adds three lattice water molecules. This procedure was repeated twice for purification. Elemental analysis for $C_{24}H_{18}N_4O_{10}Ru \cdot 3H_2O$ gave (calculated values in parentheses) C, 42.79 (42.55); H, 2.95 (2.68); N, 8.40 (8.27); Ru, 14.84 (14.91). Chloride was undetectable.

Figure 1 shows the absorption of *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$ in water at pH 4.85. There are three bands with maxima at 500 nm ($\epsilon = 11\,900$ M^{-1} cm^{-1}), 370 nm ($\epsilon = 10\,900$ M^{-1} cm^{-1}), and 306 nm ($\epsilon = 49\,200$ M^{-1} cm^{-1}). This differs markedly from the spectrum of *cis*-diaquabis(2,2′-bipyridyl-5,5′-dicarboxylate)ruthenium(II) which has maxima at 550, 365, and 300 nm.[5]

The inset shows a cyclic voltammogram of *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$ at pH 4.85. Oxidative and reductive peaks at 0.64 and 0.52 (SCE), respectively, are obtained indicating quasi-reversible behavior. The midpoint potential is at 0.58 V. In 0.5 M H_2SO_4 reversible one-electron oxidation occurs at 0.83 V. The unsubstituted analogue, $[cis\text{-}Ru(bpy)_2(H_2O)_2]^{3+/2+}$, exhibits a formal potential of 0.53 V (versus SCE) at pH 4 which increases to $E° = 0.65$ V in 1 M $HClO_4$.[6] The pH dependence was attributed to the deprotonation of one aqua ligand of the complex.[7]

cis-$Ru^{II}L_2(H_2O)_2^{2-}$ in acidic aqueous solution is strongly adsorbed to the surface of TiO_2. When TiO_2 powder is introduced into $3 \leq pH \leq 5$ solutions of *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$, an intense violet color develops onto the particles, while the supernatant spectrum shows simply the disappearance of the dye. The ability of the surface-bound *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$ to sensitize electron injection

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(1) (a) Gafney, H. D.; Adamson, A. W. *J. Am. Chem. Soc.* **1972**, *94*, 8238. (b) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 83. (c) Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* **1981**, *103*, 512. (d) Sutin, L. *Acc. Chem. Res.* **1982**, *15*, 275. (e) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (f) Balzani, V.; Scandola, F. In *Energy Resources through Photochemistry and Catalysis*; Grätzel, M., Ed.; Academic Press: New York, 1983; p 1. (g) Adamson, A. W. *J. Chem. Ed.* **1983**, *60*, 803. (h) Meyer, T. G. *Prog. Inorg. Chem.* **1983**, *30*, 389. (i) Aken, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613. (j) Fuchs, Y.; Lofters, S.; Dieter, T.; Shi, W.; Morgan, R.; Strekas, T. C.; Gafney, H. D.; Baker, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 2681. (k) Juris, A.; Barigelletti, F.; Campagna, S.; Balzani, V.; Belzer, P.; von Zelewsky, A. *Coord. Chem. Rev.*, in press and references cited therein.

(2) Balzani, V.; Juris, A.; Barigelletti, F.; Belzer, P.; von Zelewsky, A. *Sci. Papers I.P.C.R.* **1984**, *78*, 78.

(3) (a) Klassen, D. M.; Crosby, G. A. *J. Chem. Phys.* **1968**, *48*, 1853. (b) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 2841. (c) Krause, R. A.; Ballnausen, C. J. *Acta Chem. Scand. Ser. A* **1977**, *31*, 535.

(4) Durham, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 600.

(5) Rotzinger, F. P.; Munavalli, S.; Comte, P.; Hurst, J. K.; Grätzel, M.; Pern, F. J.; Frank, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 6619.

(6) Takenuchi, K. J.; Samuels, G. J.; Gersten, S. W.; Gilbert, J. A.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1407.

(7) In formulating $Ru^{II}L_2(H_2O)_2^{2-}$ as a dianion, it is assumed that at pH 4–5 the carboxylic acid groups of the ligands are fully deprotonated, while the H_2O ligands in the Ru^{II} state are not dissociated. Acid–base titration shows the isoelectric point of the Ru(II) complex to be at 2.8. Hence, above this pH the molecule is anionic. Combined acid–base titration and spectral analysis indicate the first H_2O ligand to deprotonate above pH 9. This is in agreement with literature data for the unsubstituted complex $Ru^{II}(bipy)_2(H_2O)_2^{2+}$ and $Ru^{II}(bipy)_2(py)(H_2O)^{2+}$ for which the first pK_a values are 11[11] and 10.3,[12] respectively. The cis configuration of the complex was ascertained by precipitation as sulfato complex and subsequent IR analysis.[5]

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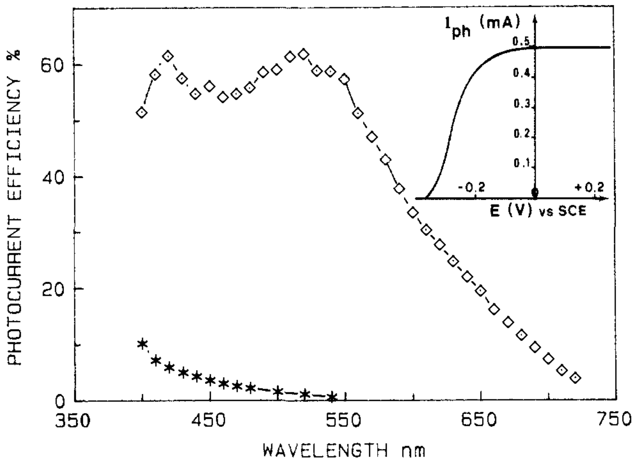

Figure 2. Photocurrent action spectrum for *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$-coated TiO_2 films in 0.1 M aqueous NaI (pH 4.6). Inset: photocurrent-potential curve obtained with the same system under white light ($\lambda > 420$ nm, intensity 23 W/m^2) illumination. Solutions are deaerated with Ar. The lower curve shows the photoresponse of the TiO_2 layer in the absence of sensitizer.

in the conduction band of TiO_2 was tested in photoelectrochemical experiments which employed a high surface area (roughness factor ca. 200) fractal anatase film deposited onto a 2 × 2 cm Ti sheet.[7] The dye was coated onto the TiO_2 layer by dipping the electrode for 4 h in an aqueous solution (pH 4.85) of 10^{-3} M *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$. The TiO_2 film assumed an intensely violet coloration due to adsorption of the dye. Photoelectrochemical experiments employed a standard cell equipped with a flat pyrex window. The regenerative photocell consisted of the dye-loaded TiO_2 sheet immersed in the electrolyte and a 3 × 3 cm-sized Pt flag as counterelectrode. All solutions were degassed with Ar. An Oriel 450 W Xe lamp served as a light source in conjunction with a water filter and a Bausch & Lomb 300 nm blaze high intensity monochromator. The incident photon flux was determined by a thermopile and by chemical actinometry with ferrioxalate.[8] The value at 420 nm was $(5 \pm 0.25) \times 10^{-10}$ Einstein $cm^{-2}\ s^{-1}$.

Figure 2 shows the photocurrent action spectrum for *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$-coated TiO_2 films in 0.1 M aqueous NaI (pH 4.6). For comparison, results obtained prior to dye coating are also presented. The incident monochromatic photon to current conversion efficiency (IPCE), defined as the ratio of the number of electrons generated by light in the external circuit divided by the number of incident photons, shows a wavelength dependency

$$\mathrm{IPCE}(\%) = \frac{[(1.24 \times 10^3) \times \text{photocurrent density } (\mu A/cm^2)]}{[\text{wavelength (nm)} \times \text{photon flux } (W/cm^2)]} \qquad (1)$$

matching the spectrum of *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$ except that the features are red-shifted and broadened. It attains values exceeding 60% close to the maximum and falls gradually toward longer wavelengths. Even with red light ($\lambda \approx 700$ m), sensitization currents are still clearly discernable.

Inserted in Figure 2 is the current-potential curve measured under white light ($\lambda > 420$ nm) illumination under similar conditions as in Figure 1. The photocurrent onset is at –0.3 V from where it rises sharply reaching a plateau value at –0.1 V. Preliminary tests of the *cis*-$Ru^{II}L_2(H_2O)_2$-coated electrodes in a regenerative photoelectrochemical cell containing 0.1 M KI/10^{-3} M I_3^- redox electrolyte gave under white light ($\lambda > 420$ nm, incident photon flux 70 W/m^2) a short circuit current of 0.38 mA/cm^2, an open circuit potential of 0.52 V, and a fill factor of 0.7 corresponding to a light to electrical power conversion efficiency of 2%. The photocurrent remained stable during 4 days of illumination (turnover number of *cis*-$Ru^{II}L_2(H_2O)_2^{2-} > 50\,000$) confirming the high stability of this sensitizer.

The maximum IPCE value of 62% observed in Figure 2 corresponds to the product of the light harvesting efficiency of the *cis*-$Ru^{II}L_2(H_2O)_2$-loaded TiO_2 at 520 nm and the quantum yield for electron injection

$$\mathrm{IPCE}(\%) = 100\ (1 - I/I_0)\phi_{inj} \qquad (2)$$

Assuming that each adsorbed *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$ molecule occupies a surface of 100 Å^2, which is the area determined for $Ru^{II}L_3$,[8] and using $\epsilon = 11\,900\ M^{-1}\ cm^{-1}$, 60% light harvesting efficiency is derived. Thus, $\phi_{inj} \approx 1$. Admitting that multiple reflection in the TiO_2 layer may result in complete absorption of incident 520 nm photons by *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$, ϕ_{inj} would still be 0.62.

In view of the extremely short excited-state lifetime of *cis*-$Ru^{II}L_2(H_2O)_2$, such high efficiencies require injection rates in the picosecond domain, hence intimate contact of the dye with the semiconductor surface. Strong electronic coupling between electronically excited *cis*-$Ru^{II}L_2(H_2O)_2$ and the Ti-3d wave function manifold could be explained by the formation of Ru–O–Ti surface bonds. $Cu^{II}(bipy)_2$ complexes are bound in a similar fashion on silica.[9] The present discovery of efficient sensitization of TiO_2 by *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$ identifies a new class of heterogeneous redox sensitizers covering a broad spectral range in the visible which should be particularly useful for light energy conversion with oxide semiconductor devices.

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Registry No. *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$ (L = 2,2'-bipyridyl-4,4'-dicarboxylate), 114199-00-7; TiO_2, 13463-67-7.

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[8] (a) Desilvestro, J.; Grätzel, M.; Kavan, L.; Moser, J.; Augustynski, J. *J. Am. Chem. Soc.* **1985**, *107*, 2988. (b) Vlachopoulos, N.; Liska, P.; Augustynsky, Grätzel, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 1216.

[9] Furlong, D. N.; Wells, D.; Sasse, W. H. F. *J. Phys. Chem.* **1986**, *80*, 1107.

(10) von Zelewsky, A.; Bemtgen, J. M. *Inorg. Chem.* **1982**, *21*, 1771.

(11) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3601.

(12) Geselowitz, D. A.; Kutner, W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2015.

Criteria for Concertedness in Cycloadditions

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Discriminating between a concerted and a stepwise mechanism continues to be a significant challenge. Stereochemistry may not be a sufficiently sensitive probe, i.e., stereospecific reactions may involve nonconcerted processes. Kinetics offers an additional probe. Huisgen states that "the ratio of the trans/cis rates offers an elegant and theoretically clear criterion for concerted additions leading to five- and six-membered rings".[1,2] In our study of the palladium-catalyzed cycloadditions of 2-(trimethylsilylmethyl)allyl acetate (**1**) with electron-deficient olefins, we became concerned with the question of concertedness.[3] In this communication, we record our systematic study of this question with use of both the stereochemical and kinetic probes. These results suggest an ambiguity can arise regarding a conclusion of concertedness based upon the trans/cis rate ratio leading to five-membered carbocyclic rings.

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(1) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 633.

(2) (a) Huisgen, R.; Sturm, H. J.; Wagenhofer, H. *Z. Naturforsch.* **1962**, *176*, 202. (b) Sauer, J.; Wiest, H.; Mielert, A. *Ibid.* **1962**, *176*, 203. (c) Sauer, J.; Lang, D.; Wiest, H. *Ibid.* **1962**, *176*, 206.

(3) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1.