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Novel Photoisomerization Behavior of Rh Binuclear Complexes Involving an Azobenzene-Bridged Bis(terpyridine) Ligand. Strong Effects of Counterion and Solvent and the Induction of Redox Potential Shift

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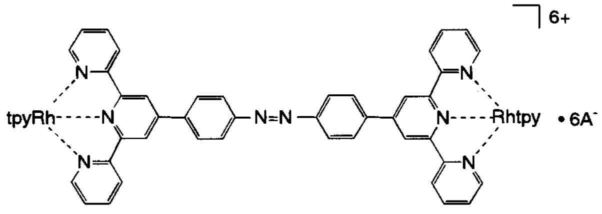
Oligonuclear polypyridyl complexes have attracted much recent attention because they can provide pliant systems for fundamental investigations into the electronic interaction between metal centers, photoinduced energy, and electron transfer.[1] The conjunction of such oligonuclear complexes with the azo group, which introduces photochemically and thermally responsive changes in the cis−trans configuration[2] and electronic interactions between the functional sites through π-conjugation,[3] provides a useful tool in the construction of molecular-switching and information-storage systems.[4] However, only a few reports regarding the photoisomerization of the azobenzene-bridged metal complexes are available,[5] while numerous publications have appeared on the photoisomerization of organic compounds as well as their mechanisms[6] and utilization.[2,4]

We have recently carried out a study on the synthesis and physical properties of an azobenzene-bridged bis(terpyridine) ligand (tpy−AB−tpy) and its Ru(II) binuclear complexes and have observed that the ligand loses its photoisomerization ability in response to complexation to Ru.[7] This crucial effect of the metal center on the photoisomerization of the azobenzene moiety prompted us to determine the factors dominating the photochemical behavior of azobenzene-bridged metal complexes. Here, we report that Rh(III) binuclear complexes of tpy−AB−tpy readily undergo photoisomerization, the kinetics of which depends markedly on the counterion and solvent. The alteration of the redox potential of Rh(III)/Rh(I) due to the photoinduced trans-to-cis isomerization is also presented.

Rh(III) binuclear complexes of [(tpy)Rh(tpy−AB−tpy)Rh(tpy)]$^{6+}$ ($\mathbf{1}^{6+}$; Chart 1) with different counterions $\mathbf{1}\cdot 6PF_6$, $\mathbf{1}\cdot 6BF_4$, and $\mathbf{1}\cdot 6BPh_4$ were obtained by reacting tpy−AB−tpy,[7] Rh(III)-Cl_3(tpy),[8] and $AgCF_3SO_3$ in refluxing *N*,*N*-dimethylacetamide, followed by precipitation with the addition of NH_4PF_6, NH_4BF_4, and $NaBPh_4$, respectively, and then recrystallization.

Chart 1



[tpyRh(tpy-AB-tpy)Rhtpy]$^{6+}$ • 6A$^-$
(1•A; A$^-$ = BF_4^- , PF_6^-, BPh_4^-)

In the UV−vis absorption spectrum of $\mathbf{1}\cdot 6PF_6$ in MeCN, the π−π* band of the azo group is observed at 370 nm as a relatively clear shoulder peak (Figure 1). While a small red shift of the π−π* band of tpy−AB−tpy from 358 to 370 nm occurs by complexation (Figure 1, inset), the spectrum of $\mathbf{1}\cdot 6PF_6$ is essentially interpreted as a superposition of the spectra of the tpy−AB−tpy ligand and $[Rh(tpy)_2]^{3+}$,[9] suggesting that the electronic states of the azobenzene moiety are insignificantly affected by the Rh(III) complex units. This spectrum is quite different from that of a Ru(II) complex with a similar structure, for which the UV−vis absorption band due to the N═N unit is significantly smaller in intensity than those of tpy−AB−tpy.[7]

Upon photoirradiation with light at λ_{max} = 360 nm,[10] changes in the absorption spectrum of $\mathbf{1}\cdot 6PF_6$ occur in MeCN, as shown in Figure 1. The spectral changes are very similar to those of tpy−AB−tpy, indicative of the occurrence of a trans-to-cis photoisomerization of the azobenzene moiety in the complex. This is also supported by the ^{1}H NMR spectral change of $\mathbf{1}\cdot 6BF_4$ in response to photoirradiation. The difference between the photochemical behavior of the Rh(III) complex and the Ru(II) complex is likely due to the electronic states of the azobenzene moiety being less affected by Rh(III) than by Ru(II), as is indicated by the differences in the UV−vis spectra as noted above.

The photoisomerization reaction kinetics of $\mathbf{1}\cdot 6PF_6$ estimated from the UV−vis spectral change is first-order, as is that of tpy−AB−tpy and azobenzene. We measured the rate of the trans-to-cis photoisomerization of the Rh complexes with different anions in various solvents such as benzonitrile (PhCN), MeCN, *N*,*N*-dimethylacetamide (DMA), DMSO, and propylene carbonate (PC) and of tpy−AB−tpy and azobenzene in PhCN. The results thus obtained are given in Table 1. The relative rate constant values of Rh complexes are much smaller than those of tpy−AB−tpy

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(9) $[Rh(tpy)_2](PF_6)_3$ was prepared by heating 2 equiv of tpy and $RhCl_3$ in methanol containing triethylamine, followed by precipitating with NH_4PF_6.

(10) The light source was a superhigh-pressure 500 W Hg lamp, and the isolation of 360 nm radiation was achieved by a UV-D35 Toshiba color filter. The light intensity at the cell position was regulated in the range between 0.11 and 0.45 W according to the rate of photoisomerization.

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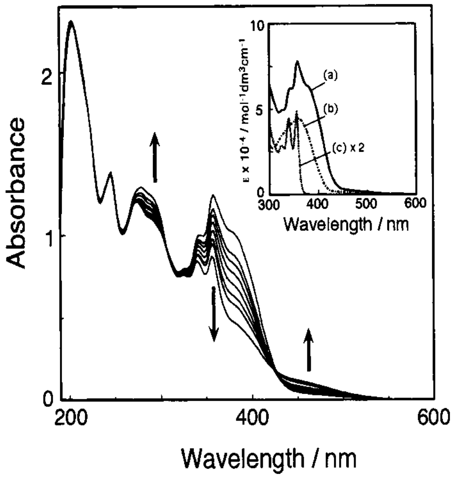

Figure 1. UV−vis absorption spectral change of **1**·$6PF_6$ in MeCN (1.6 × 10^{-4} M) upon irradiation at 360 nm. Inset: the spectra of (a) **1**·$6PF_6$, (b) tpy-AB-tpy, and (c) $[Rh(tpy)_2]^{3+}$.

Table 1. Relative Photoisomerization Rate Constant Data of the Rh(III) Complexes

solvent	dielectric constant[a] (ε)	relative rate constant		
		1·$6BF_4$	**1**·$6PF_6$	**1**·$6BPh_4$
PhCN[b]	25.9	3.2	0.58	37
MeCN	36.6	0.15	0.10	48
DMA	38.9	33	41	51
DMSO	47.2	5.4	15	31
PC	68.8	0.49	1	14

[a] Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 79th ed.; CRC Press: Boca Raton, FL, 1998. [b] Relative rate constant values of tpy−AB−tpy and azobenzene in PhCN are 165 and 174, respectively.

and azobenzene, which is probably due to the enlargement of the rotor volume for the motion of isomerization that occurs in response to complexation and/or the difficulty to achieve the cis form due to steric repulsion.[11]

A remarkable finding of this study is that the rate of the trans-to-cis photoisomerization of Rh complexes depends significantly on the nature of the counterion and solvent, as seen in Table 1. To our knowledge, there have been no reports regarding the role of the counterion in the photoisomerization reaction of ionic complexes. Many papers have appeared on the thermal cis-to-trans isomerization kinetics of donor−acceptor substituted azobenzenes,[12] while studies of the solvent effects have been limited to the trans-to-cis photoisomerization kinetics.

The rate of **1**·$6BPh_4$ photoisomerization was found to be much higher than that of **1**·$6PF_6$ and **1**·$6BF_4$ in every solvent. This seems contradictory if we consider the size of the ion pair as the rotor volume. We deduce that BPh_4^-, which is much larger than PF_6^- and BF_4^-, prevents strong ion pairing with the complex cation, and consequently, the rotor volume corresponds to that of the complex cation, resulting in a faster photoisomerization. The weaker ion paring for **1**·$6BPh_4$ than for **1**·$6PF_6$ and **1**·$6BF_4$ is supported by the results of the ESI mass spectra. The ESI mass spectra of **1**·$6PF_6$ and **1**·$6BF_4$ in MeCN showed ion-pairing peaks corresponding to a successive loss of the counterions[13] $[\mathbf{1}\cdot 4PF_6]^{2+}$ and $[\mathbf{1}\cdot 3PF_6]^{3+}$ for **1**·$6PF_6$, and $[\mathbf{1}\cdot 4BF_4]^{2+}$, $[\mathbf{1}\cdot 3BF_4]^{3+}$, $[\mathbf{1}\cdot 2BF_4]^{4+}$, and $[\mathbf{1}\cdot BF_4]^{5+}$ for **1**·$6BF_4$. In contrast, no ion-pairing peaks were detected in the spectrum of **1**·$6BPh_4$ in MeCN, whereas successive reduction peaks of the complex cations $\mathbf{1}^{6+}$, $\mathbf{1}^{5+}$, $\mathbf{1}^{4+}$, $\mathbf{1}^{3+}$, and $\mathbf{1}^{2+}$, were observed. These results suggest that the ion pairing with the complex cation $\mathbf{1}^{6+}$ is weaker in **1**·$6BPh_4$ than in **1**·$6PF_6$ and **1**·$6BF_4$ in MeCN under the ESI mass conditions.

Table 1 also shows the strong effect of solvents on the photoisomerization rate. We here consider the tendency of the solvent effects on the basis of polarity (Table 1) because the solvent effect on the order of thermal cis-to-trans isomerization kinetics of donor−acceptor substituted azobenzenes has been rationalized mainly by polarity.[12] In the case of **1**·$6BPh_4$, there is a slight tendency for the rates to be higher in a less polar solvent. In the photoisomerization process **1**·$6BPh_4$ probably behaves as the complex cation $\mathbf{1}^{6+}$ in polar solvent, similar to MeCN, as mentioned above. The polarity effect of the solvent is understandable because the stronger solvation of the complex cations in more polar solvents enlarges the rotor volume of the complex, and consequently, the polarity acts as a negative factor for the photoisomerization rate. The slower isomerization in less polar PhCN than in MeCN or DMA might be due to the effects of ion pairing, which lead to an increase in the apparent rotor volume.

In contrast, the dependence of the rate on solvent for **1**·$6PF_6$ and **1**·$6BF_4$ shown in Table 1 is much keener and more complicated compared with that for **1**·$6BPh_4$. This larger solvent effect for the former is likely the consequence of strong ion paring, as indicated in the ESI mass spectra, since the electrostatic force of attraction between complex cations and counterions is affected by the ability of solvation.

It should be noted that the photochemical cis-to-trans isomerization occurs in response to irradiation at 440 nm for tpy−AB−tpy, but it has not been observed for the Rh(III) complexes. In contrast, thermal isomerization of the cis form of **1**·$6BPh_4$ occurs slowly at room temperature, whereas that of **1**·$6PF_6$ and **1**·$6BF_4$ is observable above 100 °C in DMSO and PC. A detailed study of the kinetics of the cis-to-trans isomerization is currently in progress.

Cyclic voltammograms and differential pulse voltammograms of **1**·$6BF_4$ in the trans and cis forms in Bu_4NBF_4−MeCN are shown in Figure 2 (Supporting Information). In the cyclic voltammograms in Figure 2a, both forms show irreversible reductions due to Rh(III)/Rh(I),[14] and the cathodic peak potentials of the trans and cis forms are −0.80 and −0.88 V vs Ag/Ag^+, respectively. The differential pulse voltammograms shown in Figure 2b also indicate the negative potential shift in response to the change from the trans ($E_p = -0.77$ V) to the cis form ($E_p = -0.84$ V). This shift demonstrates that a photochemical modulation in redox properties is achievable in the azobenzene-bridged metal complexes.

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Supporting Information Available: Data listing the characterization of the Rh complexes, experimental details of the photoisomerization data analysis, and Figure 2 showing the electrochemical data of *trans*- and *cis*-**1**·$6BF_4$. This material is available free of charge via the internet at http://pubs.acs.org.

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(11) According to semiempirical PM3 minimization, in the cis form of the Rh complex, a pyridine ring of a terminal tpy on one side of the Rh-$(tpy)_2$ units is sandwiched tightly between two tpy's on the other side, affording the closely packed structure.

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