Inorg. Chem. **1987**, *26*, 1817-1819

Notes

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Improvement of the Photochemical Reactivity of $[Cu(dmp)P_2]^+$ (dmp = 2,9-Dimethyl-1,10-phenanthroline; P = Tertiary Phosphine) by Substituting PPh_3 with Larger Phosphines: Application to Photoreduction of Methylviologen

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Received May 8, 1986

Cu(I) complexes containing heteroaromatic ligands such as 2,2′-bipyridine (bpy) or 1,10-phenanthroline exhibit a metal-to-ligand charge-transfer (MLCT) band in the visible to near-ultraviolet spectral region and have a triplet MLCT state as the lowest energy excited state[1] like $[Ru(bpy)_3]^{2+}$ which has been applied extensively to the photochemical reduction of water to hydrogen gas.[2] Nevertheless, application of those Cu(I) complexes to the photochemical reduction of water has not been carried out, excepting only one report of Sauvage et al.[3]

Recently, we reported that Cu(I) complexes containing a heteroaromatic ligand, $[Cu(NN)(PPh_3)_2]^+$ (NN = 2,9-dimethyl-1,10-phenanthroline (dmp) or 4,4′,6,6′-tetramethyl-2,2′-bipyridine), found application as a sensitizer in photocatalytic reduction of methylviologen (MV^{2+}) upon near-UV-light irradiation.[4] Unfortunately, however, the quantum yield for MV^{2+} reduction (ϕ_{MV^+}) is lower than that of $[Ru(bpy)_3]^{2+}$. In this work, we have succeeded in improving the photoreducing activity of $[Cu(dmp)(PPh_3)_2]^+$ by using such bulky and/or donating tertiary phosphines as cyclohexyldiphenylphosphine, $PCyPh_2$, and tris(*p*-methoxyphenyl)phosphine, $P(p\text{-}C_6H_4OMe)_3$, instead of PPh_3. Another emphasis presented here lies in investigating the phosphine ligand effect on the photoreactivity of Cu(I) complexes, because such investigation has not been carried out yet to our knowledge.

Experimental Section

Materials. $PCyPh_2$ and $P(p\text{-}C_6H_4OMe)_3$ were prepared by literature methods.[5] The other ligands, PPh_3 and dmp, were obtained commercially (extra pure grade) and used without further purification. $[Cu(dmp)P_2]^+$ complexes (P = $PCyPh_2$, $P(p\text{-}C_6H_4OMe)_3$) were synthesized by adding dmp and the corresponding tertiary phosphine to $[Cu(CH_3CN)_4]ClO_4$ in absolute ethanol under nitrogen atmosphere.[6] Their purity was successfully ascertained by elemental analysis. Commercially available MV^{2+} (extra pure grade) was used without further purification.

Photoreaction. In typical runs, the copper(I) complex (1.0×10^{-4} mol·dm^{-3}) and MV^{2+} (0.5×10^{-4}–3.0×10^{-3} mol·dm^{-3}) were dissolved in 60 vol % ethanol–water mixed solvent and irradiated at 30 °C in a 1-cm Pyrex cell under nitrogen atmosphere by using a 400-W high-pressure mercury arc lamp (Toshiba H-400F). Five equivalents of excess tertiary phosphine was added to the solution to suppress the dissociation of tertiary phosphine from the Cu(I) complex, except for the $P(p\text{-}C_6H_4OMe)_3$ analogue, in which only an equimolar excess of $P(p\text{-}C_6H_4OMe)_3$ was added to the solution because of the low solubility of this phosphine.[7] The incident light (360–400 nm) was selected with a combination of cutoff filters (Toshiba UV-35 and UV-D35). The light intensity absorbed by the reaction system was measured as the difference in the light intensities transmitted by the reaction and reference cells with the use of Reineckate chemical actinometry. The appearance of reduced product, methylviologen radical ($^{\bullet}MV^+$), was monitored spectroscopically at 605 nm.

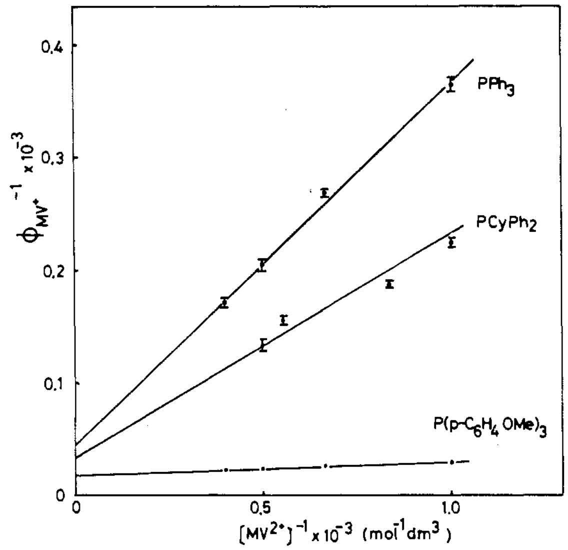

Figure 1. Stern–Volmer relation for the MV^{2+} photoreduction with $[Cu(dmp)P_2]^+$ (P = PPh_3, $PCyPh_2$, or $P(p\text{-}C_6H_4OMe)_3$). Error limits for the $P(p\text{-}C_6H_4OMe)_3$ complex cannot be displayed here, because of their smallness.

Results and Discussion

The 360–400-nm irradiation of the solution containing $[Cu(dmp)(PPh_3)_2]^+$ and MV^{2+} induces an electron transfer from the Cu(I) complex to MV^{2+} and yields the $^{\bullet}MV^+$ radical according to eq 1, as described in ref 4.[8] Substitution of PPh_3 by $P(p\text{-}$

$$[Cu^I(dmp)P_2]^+ + MV^{2+} \rightarrow [Cu^{II}(dmp)P_2]^{2+} + {}^{\bullet}MV^+ \qquad (1)$$

$C_6H_5OMe)_3$ in $[Cu(dmp)(PPh_3)_2]^+$ significantly accelerates the photoreduction of MV^{2+}, leading to a considerable increase in the quantum yield for the MV^{2+} reduction, ϕ_{MV^+}, as shown in Table I, whereas an increase in the ϕ_{MV^+} value that occurs on substitution of PPh_3 by $PCyPh_2$ is rather small. First, the above-described ligand effects of tertiary phosphine will be examined on the basis of kinetic study. Two limiting reaction mechanisms, the static and the dynamic mechanisms, are conceivable in the photoinduced electron-transfer reaction of transition-metal complexes.[9] In the

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(1) For example: (a) Blaskie, M. W.; McMillin, D. R. *Inorg. Chem.* **1980**, *19*, 3519. (b) Rader, R. A.; McMillin, D. R.; Buckner, M. T.; Matthews, T. G.; Casadonte, D. J.; Lengel, R. K.; Whittaker, S. B.; Darmon, L. M.; Lytle, F. E. *J. Am. Chem. Soc.* **1981**, *103*, 5906.

(2) For example: Lee, L.; Hurst, J. K.; Politi, M.; Kurihara, K.; Fendler, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 270. Brown, G. M.; Brunschwig, B. S.; Creutz, C.; Endicott, J. F.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 1298.

(3) Edel, A.; Marnot, P. A.; Sauvage, J. P. *Nouv. J. Chim.* **1984**, *8*, 495.

(4) Sakaki, S.; Koga, G.; Ohkubo, K. *Inorg. Chem.* **1986**, *25*, 2330.

(5) (a) Bianco, V. D.; Doronzo, S. *Inorg. Synth.* **1976**, *16*, 159. (b) Issleib, von K.; Brack, A. *Z. Anorg. Allg. Chem.* **1954**, *277*, 258.

(6) A similar method has been proposed by Sauvage and co-workers: Albrecht-Gary, A. M.; Saad, Z.; Dietrich-Buchecker, C. O.; Sauvage, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3205.

(7) Under the reaction conditions, $P(p\text{-}C_6H_4OMe)_3$ in more than equimolar excess to Cu(I) cannot be dissolved into the solution. The solution of $[Cu(dmp)\{P(p\text{-}C_6H_4OMe)_3\}_2]^+$ involving an equimolar excess of $P(p\text{-}C_6H_4OMe)_3$ exhibits little of a shoulder around 440 nm, which appears in the absence of excess $P(p\text{-}C_6H_4OMe)_3$.

(8) (a) In the case of $[Cu(dmp)(PPh_3)_2]^+$, the oxidized $[Cu^{II}(dmp)(PPh_3)_2]^{2+}$ is reduced photochemically by the solvent ethanol, under irradiation with near-UV light.[4,8b] In the case of the other donor phosphines such as $PCyPh_2$ and $P(p\text{-}C_6H_4OMe)_3$, the oxidized $[Cu^{II}(dmp)P_2]^{2+}$ would be reduced by the solvent ethanol and/or the excess phosphine, which will be examined in detail. (b) Sundarajan, S.; Wehry, E. L. *J. Phys. Chem.* **1972**, *76*, 1528.

(9) For example: (a) Ahn, B. T.; McMillin, D. R.; *Inorg. Chem.* **1981**, *20*, 1427. (b) Photochemical reactions of Cu(I) complexes involving heteroaromatic ligands have been analyzed on the basis of the dynamic mechanism in many cases.[9a,10]

(10) (a) Ahn, B. T.; McMillin, D. R. *Inorg. Chem.* **1978**, *17*, 2253. (b) Gamache, R. E.; Rader, R. A.; McMillin, D. R. *J. Am. Chem. Soc.* **1985**, *107*, 1141.

0020-1669/87/1326-1817$01.50/0

Table I. Quantum Yields for MV^{2+} Photoreduction (ϕ_{MV^+}) by $[Cu(dmp)P_2]^+$ (P = PPh_3, $PCyPh_2$, or $P(p\text{-}C_6H_4OMe)_3$) and Spectral Data for These Cu(I) Complexes

	MV^{2+} reduction		absorption		emission		
	$10^3\phi_{MV^+}$[a]	k_d/k_r	λ_{max}, nm	$10^{-3}\epsilon$, $mol^{-1}\cdot dm^3\cdot cm^{-1}$	$10^3\phi_{em}$	τ_{rel}[b]	$k_{r,rel}$[c]
$[Cu(dmp)(PPh_3)_2]^+$	2.9 ± 0.1	7.4×10^{-3}	365	3.09	1.4	1.0	1.0
$[Cu(dmp)(PCyPh_2)_2]^+$	4.5 ± 0.1	5.9×10^{-3}	366	2.73	5.1	3.6	0.33
$[Cu(dmp)\{P(p\text{-}C_6H_4OMe)_3\}_2]^+$	34.9 ± 0.3	5.3×10^{-4}	373	2.07	7.3	5.2	2.6

[a] Reaction conditions: $[Cu(I)] = 5.0 \times 10^{-4}$ $mol\cdot cm^{-3}$, $[MV^{2+}] = 1.0 \times 10^{-3}$, and 30 °C. [b] The relative-value lifetime of the excited state. [c] The relative value of k_r.

static mechanism, the sensitizer forms a precursor complex with a substrate in the ground state, and this precursor absorbs incident light to yield an excited state, followed by an electron transfer to the substrate. In the dynamic mechanism, the sensitizer excited by absorption of incident light forms an encounter complex with a substrate, followed by electron transfer in the encounter complex. At present, we are unable to determine the mechanism unambiguously, because both mechanisms are consistent with linear plots of reciprocal quantum yield vs. reciprocal concentration of substrate. However, the static mechanism seems unlikely, since both MV^{2+} and $[Cu(dmp)(PR_3)_2]^+$ are positively charged. Thus, the kinetic study was carried out on the basis of the dynamic mechanism[9b] described in eq 2–6. In eq 2, η represents the

$$[Cu(dmp)(PR_3)_2]^+ \xrightarrow{\eta I_0/V} {}^*[Cu(dmp)(PR_3)_2]^+ \qquad (2)$$

$${}^*[Cu(dmp)(PR_3)_2]^+ \xrightarrow{k_d} [Cu(dmp)(PR_3)_2]^+ \qquad (3)$$

$${}^*[Cu(dmp)(PR_3)_2]^+ + MV^{2+} \xrightarrow{k_r} \{Cu(dmp)(PR_3)_2{}^{2+}\cdots{}^{\bullet}MV^+\} \qquad (4)$$

$$\{Cu(dmp)(PR_3)_2{}^{2+}\cdots{}^{\bullet}MV^+\} \xrightarrow{k_p} [Cu(dmp)(PR_3)_2]^{2+} + {}^{\bullet}MV^+ \qquad (5)$$

$$\{Cu(dmp)(PR_3)_2{}^{2+}\cdots{}^{\bullet}MV^+\} \xrightarrow{k_b} [Cu(dmp)(PR_3)_2]^+ + MV^{2+} \qquad (6)$$

efficiency of forming the photoreactive excited state. Assuming steady-state concentrations for ${}^*[Cu(dmp)(PR_3)_2]^+$ and $\{Cu(dmp)(PR_3)_2{}^{2+}\cdots{}^{\bullet}MV^+\}$, the Stern–Volmer relation of eq 7 is obtained. As predicted by this equation, a linear relation was

$$(\phi_{MV^+})^{-1} = \eta^{-1}\frac{k_p + k_b}{k_p}\left(\frac{k_d}{k_r}[MV^{2+}]^{-1} + 1\right) \qquad (7)$$

obtained between $(\phi_{MV^+})^{-1}$ and $[MV^{2+}]^{-1}$ (Figure 1). All of the Cu(I) complexes examined gave similar intercepts but significantly different slopes in Stern–Volmer plots, implying that the k_d/k_r values are considerably different in these complexes (note that the intercept and the slope are given by $\eta^{-1}(k_p + k_b)/k_p$ and $[\eta^{-1}(k_p + k_b)/k_p](k_r/k_d)$, respectively). In other words, the relative value of ϕ_{MV^+} is mostly determined by the k_d/k_r value.

The lifetime of the excited state, i.e., the reciprocal value of the decay rate constant (k_d), would approximately vary in parallel with the emission quantum yield (ϕ_{em}), in the present cases.[11] Thus, the relative k_d values might be estimated from ϕ_{em} given in Table I, and then the approximate relative k_r value can be obtained from the k_d/k_r value and the relative k_d value. Such relative k_r and k_d values, compiled in Table I, make clear the reason why $[Cu(dmp)(PCyPh_2)_2]^+$ and $[Cu(dmp)\{P(p\text{-}C_6H_4OMe)_3\}_2]^+$ give a larger ϕ_{MV^+} value than $[Cu(dmp)(PPh_3)_2]^+$ does: $[Cu(dmp)\{P(p\text{-}C_6H_5OMe)_3\}_2]^+$ has the longest lived excited state and the largest k_r value, leading to the greatest ϕ_{MV^+} value. $[Cu(dmp)(PCyPh_2)_2]^+$ exhibits a longer lived excited state but a smaller k_r value than those of the PPh_3 analogue, yielding the slightly larger ϕ_{MV^+} value.

Finally, the above-mentioned ligand effects on the τ_{rel} and k_r values will be briefly discussed: (1) In Cu(I) complexes containing a heteroaromatic ligand, vibrational coupling to a solvated molecule is a key factor determining nonradiative decay rate.[12] Indeed, bulky substituents at the 2,9-positions of 1,10-phenanthroline slow the nonradiative decay by suppressing solvation at the Cu(I) center.[12a,b] A similar effect might be possible in the $PCyPh_2$ complex: because $PCyPh_2$ has a larger cone angle (153°) than PPh_3 has (145°),[13] the solvation to the $PCyPh_2$ complex would be sterically suppressed. The solvation is also influenced by the donating ability of phosphine, since the solvation would involve a donor interaction from solvent to Cu(I). The donating ability of phosphine is considered to increase in the order $PPh_3 < P(p\text{-}C_6H_4OMe)_3 < PCyPh_2$, because the estimated ν_{CO} of $Ni(CO)_3P$ (P = tertiary phosphine) decreases in the reverse order.[13] Thus, the importance of solvation would decrease in the order $PPh_3 > P(p\text{-}C_6H_4OMe)_3 > PCyPh_2$, leading to the longer lived excited state of the $P(p\text{-}C_6H_4OMe)_3$ and $PCyPh_2$ complexes than that of the PPh_3 complex. (2) However, the above discussion is not sufficient, because it does not explain why the excited state of $[Cu(dmp)\{P(p\text{-}C_6H_4OMe)_3\}_2]^+$ is longer lived than that of the $PCyPh_2$ analogue. This means that some other factors influence the lifetime of the excited state. One possible factor is the electronic-to-vibrational energy conversion: $PCyPh_2$ has many C–H vibrations near the coordinating atom. On the other hand, in $P(p\text{-}C_6H_4OMe)_3$, one C–H bond of the phenyl group is replaced by one C–O bond, which is less effective as an energy-acceptor vibrating mode because of the lower frequency of the C–O vibration. This factor would lead to the longer lived excited state of $[Cu(dmp)\{P(p\text{-}C_6H_4OMe)_3\}_2]^+$. (3) It is also noted that $[Cu(dmp)\{P(p\text{-}C_6H_4OMe)_3\}_2]^+$ exhibits the larger difference between emission and absorption maxima than the PPh_3 and $PCyPh_2$ analogues do; absorption and emission maxima of the former shift to longer wavelengths by ca. 6 and ca. 20 nm, respectively, compared to the corresponding maxima of the latter.[14] The larger difference between emission and absorption maxima would correspond to the greater difference in geometry between the triplet excited state and the ground state, suggesting the smaller Frank–Condon factor and thereby the less probability of nonradiative decay from the triplet excited state to the ground state. This again leads to the longer lived excited state of the $P(p\text{-}$

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(11) The emission quantum yield, ϕ_{em}, is represented by $\eta^{-1}k_{em}/(k_{em} + k_{nd})$, where k_{em} and k_{nd} are emitting and nonradiative decay rate constants, respectively. Because the photoreactive state of the Cu(I) complex is considered to be a triplet, η and k_{em} might be closely related to spin–orbit coupling interaction, which arises from heavy atoms such as Cu and P. All of the Cu(I) complexes examined include one Cu and two P atoms, and therefore k_{em} and η would not be very different in these complexes. Thus, $\phi_{em,A}/\phi_{em,B}$ is approximately represented by τ_A/τ_B, i.e., $k_{d,B}/k_{d,A}$. (Sakaki, S.; Koga, G.; Sato, F.; Ohkubo, K. *J. Chem. Soc., Dalton Trans.* **1985**, 1959.) Such-estimated τ_{rel} values agree well with the directly measured τ_{rel} values;[10b] $\tau = 0.48$ μs for $[Cu(dmp)(PPh_3)_2]^+$, 1.5 μs for the $PCyPh_2$ analogue, and 2.7 μs for the $P(p\text{-}C_6H_4OMe)_3$ analogue. (b) Sakaki, S.; Kawasaki, M., unpublished results. The measurement was carried out at room temperature; the solvent was methanol; the concentration of Cu(I) complexes was taken so that the OD at 337 nm (the wavelength of the exciting light) was ca. 0.5.

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(14) The λ_{max} of the emission spectra is 520 nm for $[Cu(dmp)(PCyPh_2)_2]^+$ and $[Cu(dmp)(PPh_3)_2]^+$ but 540 nm for $[Cu(dmp)\{P(p\text{-}C_6H_4OMe)_3\}_2]^+$ (uncorrected value). The λ_{max} of the absorption spectra is almost the same in the PPh_3 and $PCyPh_2$ complexes (see Table I).

$C_6H_4OMe)_3$ analogue. (4) The phosphine effect on the k_r process is also interesting, because in $[Cu(dmp)\{P(p\text{-}C_6H_4OMe)_3\}_2]^+$ the largest k_r value is one of the important factors leading to the greatest ϕ_{MV^+} value. However, it is still ambiguous what type of factor is important in the k_r process. Previously, McMillin et al. suggested that the k_r step is sensitive to the self-exchange rate.[9a] Unfortunately, the self-exchange reaction rates of Cu(I) complexes examined have not been measured yet, and further discussion is omitted here. We need more detailed and systematic investigations to get a clear explanation about the phosphine ligand effect on the photochemical reactivity of Cu(I) complexes.

In conclusion, the activity of $[Cu(dmp)(PR_3)_2]^+$ in the photoreduction of MV^{2+} has been improved by substituting PPh_3 with $PCyPh_2$ or $P(p\text{-}C_6H_4OMe)_3$, because the lifetime of the excited state is lengthened and/or the oxidative quenching by MV^{2+} becomes faster.

Acknowledgment. The authors gratefully acknowledge the support of the Ministry of Education (Japan) through a Grant-in-Aid for Scientific Research (No. 59540397).

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Photochemistry of the Ion Pairs Rh(bpy)$^{3+}$M(CN)$_6^{4-}$ (bpy = 2,2'-Bipyridyl) with M = Fe, Ru, Os following Outer-Sphere Metal to Ligand Charge-Transfer Excitation

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Received July 17, 1986

Optical metal to ligand charge-transfer (MLCT) transitions play an important role in the photophysics and photochemistry of transition-metal complexes.[1-3] This electronic transition is an intramolecular (inner-sphere) process. It involves the promotion of a d electron of the metal to an empty orbital of a ligand coordinated to this metal. MLCT transitions occur at low energies if the metal is a reducing one and the ligand has available empty low-energy orbitals. Typical examples are the complexes Ru(bpy)$_3^{2+}$[4,5] (bpy = 2,2'-bipyridyl) and M(CN)$_6^{4-}$ (M = Fe, Ru, Os).[6,7] In the latter case MLCT excitation is associated with the generation of solvated electrons.[8-10] We report here on intermolecular (outer-sphere) MLCT transitions and the photochemistry following this type of CT excitation. In this case the optical transition involves the promotion of an electron from the metal of one complex to the ligand of another complex.

The ion pairs Rh(bpy)$_3^{3+}$M(CN)$_6^{4-}$ with M = Fe, Ru, Os were selected for this study. The colorless complex Rh(bpy)$_3^{3+}$ shows its longest wavelength absorption at λ_{max} = 320 nm (ϵ = 4.25 × 10^4).[11,12] This band is assigned to an intraligand $\pi\pi^*$ transition of the bpy ligand. Since Rh(III) is rather redox-inert, CT transitions of Rh(bpy)$_3^{3+}$ do not appear at low energies. The colorless complexes M(CN)$_6^{4-}$ which contain reducing metals do not absorb above 400 (Fe), 300 (Ru), and 300 nm (Os). Ligand field and MLCT bands occur at shorter wavelength.[6,7]

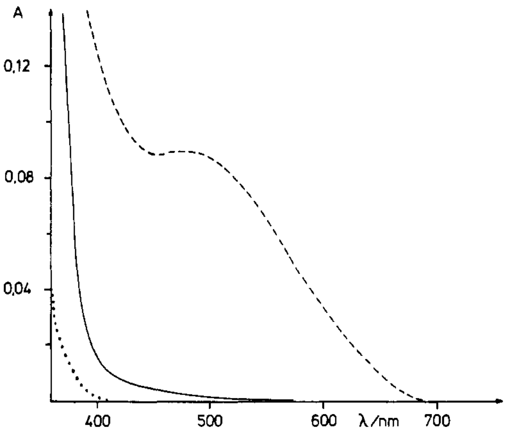

Figure 1. Electronic absorption spectra of aqueous 2.7 × 10^{-3} M [Rh(bpy)$_3$](ClO$_4$)$_3$ (···), 2.7 × 10^{-3} M K$_4$[Fe(CN)$_6$] (—), and a mixture of both solutions (---) (298 K, 1-cm cell).

When aqueous Rh(bpy)$_3^{3+}$ and M(CN)$_6^{4-}$ were mixed, the solutions turned immediately reddish for M = Fe (λ_{max} = 480 nm; Figure 1), yellow for Os (λ_{max} = 400 nm), and slightly yellow for Ru (λ_{max} = 379 nm). These colors are due to the appearance of new absorption bands (Figure 1). At fairly high equimolar concentrations (>10^{-3} M) of complex cations and anions these bands follow the Lambert–Beer law with ϵ = 61 (Fe), 110 (Ru), and 155 M^{-1} cm^{-1} (Os). It is assumed that at this concentration ion pairing was complete. The deviation from the Lambert–Beer law at much lower concentrations (<10^{-4} M) was used to estimate the ion-pair association constant (K = 3800 M^{-1} of Rh(bpy)$_3^{3+}$-Fe(CN)$_6^{4-}$.

We suggest that these new absorption bands are assigned to outer-sphere MLCT transitions from the reducing metals M(II) of M(CN)$_6^{4-}$ to the empty low-energy π^* orbitals of the bpy ligand of Rh(bpy)$_3^{3+}$. While M(CN)$_6^{4-}$ is oxidized at $E_{1/2}$ = 0.19 (Fe), 0.70 (Ru), and 0.40 V (Os),[13] the complex Rh(bpy)$_3^{3+}$ is reduced at $E_{1/2}$ = −0.7 V[14,15] vs. SCE. As expected, the outer-sphere MLCT bands shift to lower energies if the reducing power of M(CN)$_6^{4-}$ increases. However, these shifts do not match the potential differences exactly. The deviations can be caused by different reorganizational energies χ, which are associated with electron transfer. These energies, which are calculated according to the equation $\chi = E_{op} - \Delta E$,[16,17] are χ = 13 650 (Fe), 15 100 (Ru), and 16 130 cm^{-1} (Os).

Upon irradiation of the outer-sphere MLCT band of the ion pair Rh(bpy)$_3^{3+}$Fe(CN)$_6^{4-}$ (λ_{irr} = 546 nm) the cation Rh(bpy)$_3^{3+}$ underwent a photoaquation to Rh(bpy)$_2$(H$_2$O)$_2^{3+}$. At the irradiating wavelength both constituents of the ion pair do not absorb light. The formation of Rh(bpy)$_2$(H$_2$O)$_2^{3+}$ (λ_{max} = 318 nm, ϵ = 28 300)[15] led to a decrease of the optical density in the region of the $\pi\pi^*$ intraligand absorption of the coordinated bpy ligand. The release of bpy was detected by its fluorescence at λ_{max} = 325 nm. The quantum yield of photoaquation of Rh(bpy)$_3^{3+}$ was Φ = 2.4 × 10^{-3}.

We suggest that this photoaquation takes place according to the scheme

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