Significant Phosphine Ligand Effect on the Photochemical Reactivity of $[Cu(N\text{-}N)L_2]^+$ (N–N = 1,10-phenanthroline or 2,9-dimethyl-1,10-phenanthroline; L = tertiary phosphine)

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Photo-induced electron-transfer reactions between $[Co(edta)]^-$ and $[Cu(N\text{-}N)L_2]^+$ [N–N = 1,10-phenanthroline (phen) or 2,9-dimethyl-1,10-phenanthroline (dmphen), L = tertiary phosphine, edta = ethylenediaminetetra-acetate] have been investigated. Although $[Cu(N\text{-}N)(PPh_3)_2]^+$ exhibits rather low photochemical reactivity, substituting PPh_3 by a bulky and/or donative phosphine significantly enhances the reactivity. In the case of N–N = dmphen, introducing a donative phosphine, $P(C_6H_4OMe\text{-}p)_3$, instead of PPh_3 remarkably increases the photochemical reactivity, but in the case of N–N = phen, substituting PPh_3 by a donative and bulky phosphine such as $P(C_6H_{11})_3$ much improves the photochemical reactivity. A kinetic study has also been carried out and it is concluded that this reaction proceeds *via* a dynamic quenching mechanism. Phosphine ligand effects are discussed in terms of the lifetime of the excited copper(I) complexes and the facility of formation of the encounter complex.

Copper(I) complexes including heteroaromatic ligands (N–N)* such as 1,10-phenanthroline and its derivatives exhibit a metal-to-ligand charge-transfer (m.l.c.t.) absorption band around 360—460 nm and an m.l.c.t. triplet as their lowest-energy excited state[1] like $[Ru(bipy)_3]^{2+}$.[2] However, applying these complexes to the photochemical reduction of various substrates is rather difficult and only one pioneering work has been reported,[3] whereas $[Ru(bipy)_3]^{2+}$ and its analogues have been successfully applied to various photocatalytic reductions.[4] This might be because the lifetime of the excited state of the copper(I) complexes is shorter than that of $[Ru(bipy)_3]^{2+}$. Some latitude is, however, expected, because the lifetime of the excited states of copper(I) complexes can be lengthened by chemical modification of the ligands:[1,3,5,6] for instance, introducing substituents at the 2 and 9 positions of 1,10-phenanthroline inhibits the solvation of the Cu^I and slows non-radiative decay of the excited state of copper(I) complexes by suppressing the electronic-to-vibrational energy conversion, leading to a considerably long-lived excited state of $[Cu(N\text{-}N)L_2]^+$ (ref. 1) and $[Cu(N\text{-}N)_2]^+$ in solution.[3,5,6]

Very recently, we successfully applied $[Cu(N\text{-}N)(PPh_3)_2]^+$ to photocatalytic reduction of several cobalt(III) complexes[7a] and methyl viologen (1,1′-dimethyl-4,4′-bipyridinium).[7b,c] Unfortunately, however, $[Cu(N\text{-}N)(PPh_3)_2]^+$ provides a much smaller quantum yield for methyl viologen reduction than does $[Ru(bipy)_3]^{2+}$. In this context, we need to improve the photoreactivity of $[Cu(N\text{-}N)(PPh_3)_2]^+$.

In the present work we tried to improve the photochemical reactivity of $[Cu(N\text{-}N)L_2]^+$ (N–N = phen or dmphen) by introducing a bulky and/or donative phosphine instead of PPh_3, expecting that such phosphines sterically and/or electronically inhibit the solvation of the Cu^I and thereby lengthen the lifetime of excited $[Cu(N\text{-}N)L_2]^+$. The photoreduction of $[Co(edta)]^-$ by $[Cu(N\text{-}N)L_2]^+$ was examined as a test reaction, since both $[Cu(phen)L_2]^+$ and the dmphen analogues exhibit comparable photochemical reactivity for this reaction.† One purpose of this work is to elucidate what type of phosphine is best for the copper(I) complexes used as photosensitizers. It is also our intention to elucidate the reaction mechanism, because two kinds of mechanism, the static quenching mechanism and the dynamic one, have been proposed for the photo-induced electron transfer reactions of these copper(I) complexes and which of them actually occurs has not been unambiguously determined.[7,8]

Experimental

The complexes $[Cu(N\text{-}N)L_2]X$ (X = ClO_4 or NO_3) were synthesized as before.[9] Their purities were ascertained by elemental analysis, and absorption maxima are listed in the Table. In typical runs, $[Cu(N\text{-}N)L_2]X$ (1.0×10^{-3} mol dm^{-3}) and K[Co(edta)] (0.5×10^{-3}—2.0×10^{-3} mol dm^{-3}) were dissolved in either ethanol–water (70:30 v/v) (for the phen complexes) or acetone–water (70:30 v/v) (for the dmphen complexes),‡ and irradiated at 30 °C in a 1-cm Pyrex cell under a nitrogen atmosphere by using a 400-W high-pressure mercury-arc lamp (Toshiba H-400P). Four equivalents of phosphines were added to the solution to suppress the dissociation of phosphine from $[Cu(dmphen)L_2]^+$.[1,7]§ The incident light

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* Abbreviations: N–N = heteroaromatic ligand; bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline; dmphen = 2,9-dimethyl-1,10-phenanthroline; L = tertiary phosphine; edta = ethylenediaminetetra-acetate.

† Our goal is to find copper(I) complexes which can efficiently photoreduce various substrates including methyl viologen. Unfortunately, $[Cu(phen)L_2]^+$ hardly photoreduces methyl viologen, and thereby it is not easy to compare the photochemical reactivity of these complexes in such a reduction. This is the reason why not methyl viologen reduction but $[Co(edta)]^-$ reduction is examined.

‡ In our previous study of the photo-induced electron-transfer reaction between cobalt(III) complexes and $[Cu(N\text{-}N)(PPh_3)_2]^+$,[7a] the ethanol–water solvent was used. Although we tried to use the same solvent system in this work, it was very difficult because of the low solubility of $P(C_6H_4OMe\text{-}p)_3$ which must be added in excess to the solution of $[Cu(dmphen)L_2]^+$ to suppress the dissociation of phosphine from this complex.[1] The solvent effect on the photochemical reactivity, of course, cannot be neglected. In this work, however, the photoreactivity of the dmphen complexes (acetone–water solvent) is not compared with that of phen complexes (ethanol–water solvent), but within each series of complexes, *i.e.* in the same solvent system.

§ For the phen complexes, excess of phosphine was not added because phosphine dissociation has been reported only in the case of dmphen complexes.[1b]

Table. The quantum yield for $[Co(edta)]^-$ reduction, $\varphi(Co^{2+})$, by $[Cu(N\text{-}N)L_2]^+$ [N–N = phen or dmphen; L = PPh_3, $P(C_6H_{11})Ph_2$, $P(C_6H_{11})_3$, or $P(C_6H_4OMe\text{-}p)_3$]

Complex	$\lambda_{max.}$/nm	$10^3\varepsilon$/dm^3 mol^{-1} cm^{-1}	$10^2\varphi(Co^{2+})$	$10^3(k_d/k_r)$	$(k_r)_{rel.}$ [a]
$[Cu(phen)(PPh_3)_2]ClO_4$	365	3.7	*ca.* 0		*b*
$[Cu(phen)\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$	380	3.0	0.5	21	
$[Cu(phen)\{P(C_6H_{11})Ph_2\}_2]ClO_4$	369	3.3	6.3	4.7	
$[Cu(phen)\{P(C_6H_{11})_3\}_2]ClO_4$	376	2.2	11.0	2.1	
$[Cu(dmphen)(PPh_3)_2]NO_3$	364	3.1	0.4	106	1
$[Cu(dmphen)\{P(C_6H_{11})Ph_2\}_2]ClO_4$	365	3.1	8.8	4.7	6
$[Cu(dmphen)\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$	369	2.5	23.8	2.8	7

[a] Relative value of k_r; the k_r value of $[Cu(dmphen)(PPh_3)_2]^+$ is taken as a standard. [b] The $(k_r)_{rel.}$ value cannot be estimated, because the τ value has not been measured.

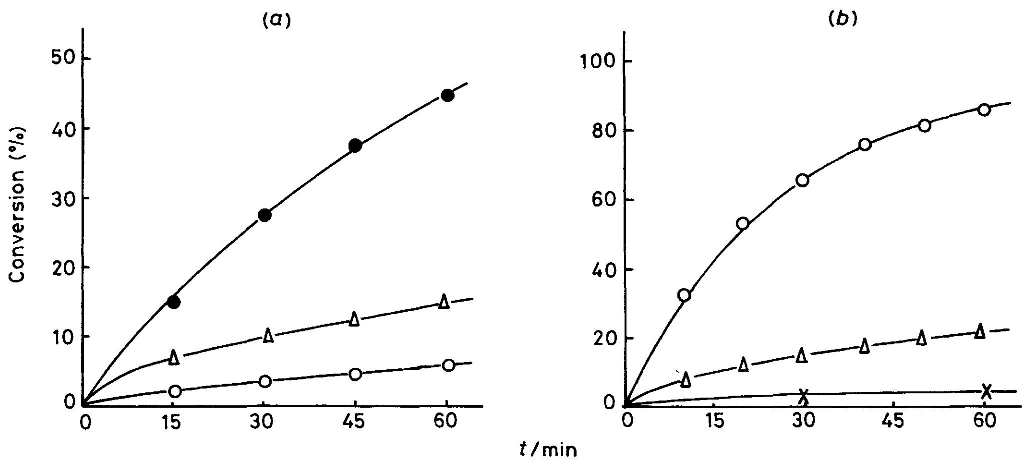

Figure 1. Time *vs.* conversion (with respect to Cu^I) curves for $[Co(edta)]^-$ photo-reduced with $[Cu(N\text{-}N)L_2]^+$ [N–N = phen (*a*) or dmphen (*b*); L = PPh_3 (×), $P(C_6H_{11})Ph_2$ (△), $P(C_6H_{11})_3$ (●), or $P(C_6H_4OMe\text{-}p)_3$ (○)]

(360—400 nm), corresponding to the m.l.c.t. absorption band of $[Cu(N\text{-}N)L_2]^+$ (see Table), was selected with a combination of cut-off filters (Toshiba UV35 ×2 and UV-D35). The light intensity absorbed by the reaction solution was measured as the difference in the light intensity transmitted by the reaction and the reference cells by using Reineckate chemical actinometry.[10,*] The decrease in $[Co(edta)]^-$ concentration was measured spectrophotometrically at its *d–d* band (539 nm).[11]

Results and Discussion

The ion $[Co(edta)]^-$ is efficiently photoreduced by $[Cu(N\text{-}N)L_2]^+$, as clearly shown by the time *vs.* conversion curves of Figure 1, and the quantum yields $\varphi(Co^{2+})$ are compiled in the Table. In $[Cu(dmphen)L_2]^+$, substituting PPh_3 by $P(C_6H_4OMe\text{-}p)_3$ significantly increases the photochemical reactivity of the copper(I) complexes, while substituting PPh_3 by $P(C_6H_{11})Ph_2$ only slightly enhances the photochemical reactivity.[†] In the phen analogues, on the other hand, introducing $P(C_6H_{11})_3$ instead of PPh_3 leads to a remarkable enhancement in the photochemical reactivity of the copper(I) complex, while substituting PPh_3 by either $P(C_6H_{11})Ph_2$ or $P(C_6H_4OMe\text{-}p)_3$ only slightly enhances the photochemical reactivity. It is of much interest that although $[Cu(phen)L_2]^+$ and the dmphen analogues are very similar to each other, the ligand effects of phosphines are quite different in these two kinds of copper(I) complexes.

Before starting to discuss the phosphine ligand effects on the photochemical reactivity, the nature of tertiary phosphine derivatives will be discussed briefly. The bulkiness of phosphines is an important factor in the co-ordination chemistry of phosphines.[11] Also, in the photochemistry of $[Cu(N\text{-}N)L_2]^+$, the bulkiness of the ligand is expected to be important, because a bulky ligand would inhibit the solvation of the Cu^I and thereby slow the non-radiative decay of the excited state by suppressing the electronic-to-vibrational energy conversion.[1,5,6] The bulkiness of phosphines is usually expressed by the cone angle which increases in the order PPh_3 (145) ≈ $P(C_6H_4OMe\text{-}p)_3$ (145) < $P(C_6H_{11})Ph_2$ (153) < $P(C_6H_{11})_3$ (170°).[12] Thus, introducing $P(C_6H_{11})_3$ instead of PPh_3 is expected to enhance significantly the photochemical reactivity of $[Cu(N\text{-}N)L_2]^+$. Another property important to the photochemistry is the donor ability of the phosphine derivatives. Because solvation involves electrostatic interaction between the solvent and the Cu^I, a donative phosphine would weaken the solvation by decreasing the positive charge on the Cu^I, leading to a longer-lived excited

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[*] The ion $[Co(edta)]^-$ absorbs incident light at 360—400 nm. The light intensity absorbed by $[Cu(N\text{-}N)L_2]^+$ was determined by numerically integrating absorption curves of $[Co(edta)]^-$ and $[Cu(N\text{-}N)L_2]^+$. In the kinetic work, the reaction was stopped when the conversion of $[Co(edta)]^-$ reached 5—7%.

[†] Unfortunately, $[Cu(dmphen)\{P(C_6H_{11})_3\}_2]^+$ could not be synthesized, probably because of a large steric repulsion between dmphen and the bulky $P(C_6H_{11})_3$ ligands.

state. Also, an increase in the donor ability of the phosphine would improve the redox property of the copper(I) complex. The donor ability is considered to increase in the order $PPh_3 < P(C_6H_4OMe\text{-}p)_3 < P(C_6H_{11})Ph_2 < P(C_6H_{11})_3$, according to the ν(CO) value of $Ni(CO)_3L$ which decreases in the order PPh_3 (2 069) > $P(C_6H_4OMe\text{-}p)_3$ (2 066.3) > $P(C_6H_{11})Ph_2$ (2 064.8) > $P(C_6H_{11})_3$ (2 056.4 cm^{-1}).[11] Again, the ligand $P(C_6H_{11})_3$ is expected to be best to improve the photochemical reactivity of $[Cu(N\text{-}N)L_2]^+$.

In the case of phen complexes, the photochemical reactivity increases in the order $PPh_3 < P(C_6H_4OMe\text{-}p)_3 < P(C_6H_{11})Ph_2 < P(C_6H_{11})_3$ (see Table), as expected above. This order seems reasonable, because both the cone angle and the donor ability of the phosphine derivatives increase in the same order. In the case of dmphen complexes, however, the photochemical reactivity increases in the order $PPh_3 < P(C_6H_{11})Ph_2 < P(C_6H_4OMe\text{-}p)_3$. This is contrary to expectation, because this does not agree with the increasing order of the cone angle or with the increasing order of the donor ability. The only difference between $[Cu(phen)L_2]^+$ and the dmphen analogues is that the latter have two methyl substituents at positions 2 and 9 of phen. These substituents are believed sterically to suppress the solvation of the Cu^I.[1,5,6] Thus, the difference in the phosphine ligand effect between the phen and dmphen complexes suggests that when a N–N ligand, like phen, has no substituent sterically to suppress the solvation of the Cu^I the bulkiness and donor ability of the phosphine derivatives is important in enhancing the photochemical reactivity, and that when a N–N ligand, like dmphen, has substituents suppressing the solvation other factors are important.

To investigate these interesting phosphine ligand effects in more detail, the reaction mechanism must be elucidated. Two types of reaction schemes, the dynamic quenching mechanism [(*a*) in the Scheme][7a,b] and the static quenching mechanism [(*b*) in the Scheme],[8,13] have been proposed in the photochemistry of copper(I) complexes involving N–N ligands. In the dynamic mechanism, the Stern–Volmer equation (1) is derived by

$$1/\varphi(Co^{2+}) = \eta^{-1}\cdot\frac{k_p + k_b}{k_p}\left(\frac{k_d}{k_r}[Co^{III}]^{-1} + 1\right) \quad (1)$$

assuming steady-state conditions for the concentration of the excited $*[Cu(N\text{-}N)L_2]^+$ and the successor complex $\{Cu^{II}(N\text{-}N)L_2\cdots Co^{II}\}$. In the static mechanism a similar equation (2) is obtained by assuming steady-state conditions for

$$1/\varphi(Co^{2+}) = \eta^{-1}\cdot\frac{k_p' + k_b'}{k_p'}\cdot\frac{k_r' + k_d'}{k_r'}\cdot\left(\frac{1}{K}[Co^{III}]^{-1} + 1\right) \quad (2)$$

the concentration of the excited $\{*[Cu(N\text{-}N)L_2]^+\cdots Co^{III}\}$ and the successor complex $\{[Cu^{II}(N\text{-}N)L_2]^{2+}\cdots Co^{II}\}$. Both equations involve a linear relation between the reciprocal of $\varphi(Co^{2+})$ and the reciprocal of the cobalt(III) concentration. Certainly, such linear relations are found for all the copper(I) complexes examined, as shown in Figure 2. All the relations exhibit similar intercepts but very different slopes. This means that in the case of the dynamic mechanism the phosphine ligand effect on $\varphi(Co^{2+})$ mainly arises from the term k_d/k_r but hardly at all from the term $\eta^{-1}(k_p + k_b)/k_p$ and that in the case of the static mechanism the effect mainly results from the $1/K$ term but hardly at all from the term $\eta^{-1}(k_p' + k_b')/k_p' \times (k_r' + k_d')/k_r'$. The relative τ value significantly depends on the kind of phosphine ligands; taking the value for $[Cu(dmphen)(PPh_3)_2]^+$ as a standard, the τ_{rel} value of $[Cu(dmphen)\{P(C_6H_{11})Ph_2\}_2]^+$ is *ca.* 3.6 and that of $[Cu(dmphen)\{P(C_6H_4OMe\text{-}p)_3\}_2]^+$ is *ca.* 5.2.† If the static mechanism occurs, the intercept must be sensitive to the kind of phosphines through the k_d' ($= 1/\tau$) term, which does not seem in accord with the experimental result that not the intercept but the slope is sensitive to the kind of phosphines. Thus the static mechanism is ruled out here. On the other hand, the dynamic mechanism seems consistent with the experimental results, because this mechanism requires that the slope depends on the kind of phosphines through the k_d term.

(*a*) The dynamic quenching mechanism

$$[Cu(N\text{-}N)L_2]^+ \xrightarrow[\eta I_0/V]{h\nu} *[Cu(N\text{-}N)L_2]^+$$

$$*[Cu(N\text{-}N)L_2]^+ \xrightarrow{k_d} [Cu(N\text{-}N)L_2]^+$$

$$*[Cu(N\text{-}N)L_2]^+ + Co^{III} \xrightarrow{k_r} \{Cu^{II}(N\text{-}N)L_2\cdots Co^{II}\}$$

$$\{Cu^{II}(N\text{-}N)L_2\cdots Co^{II}\} \xrightarrow{k_p} [Cu(N\text{-}N)L_2]^{2+} + Co^{II}$$

$$\{Cu^{II}(N\text{-}N)L_2\cdots Co^{II}\} \xrightarrow{k_b} [Cu(N\text{-}N)L_2]^+ + Co^{III}$$

(*b*) The static quenching mechanism

$$[Cu(N\text{-}N)L_2]^+ + Co^{III} \overset{K}{\rightleftarrows} \{[Cu(N\text{-}N)L_2]^+\cdots Co^{III}\}$$

$$\{[Cu(N\text{-}N)L_2]^+\cdots Co^{III}\} \xrightarrow[\eta I_0/V]{h\nu} \{*[Cu(N\text{-}N)L_2]^+\cdots Co^{III}\}$$

$$\{\%[Cu(N\text{-}N)L_2]^+\cdots Co^{III}\} \xrightarrow[k_d']{} \{[Cu(N\text{-}N)L_2]^+\cdots Co^{III}\}$$

$$\{*[Cu(N\text{-}N)L_2]^+\cdots Co^{III}\} \xrightarrow{k_r'} \{[Cu(N\text{-}N)L_2]^{2+}\cdots Co^{II}\}$$

$$\{[Cu(N\text{-}N)L_2]^{2+}\cdots Co^{III}\} \xrightarrow{k_p'} [Cu(N\text{-}N)L_2]^{2+} + Co^{II}$$

$$\{[Cu(N\text{-}N)L_2]^{2+}\cdots Co^{III}\} \xrightarrow{k_b'} [Cu(N\text{-}N)L_2]^+ + Co^{III}$$

Scheme. η = Quantum efficiency with which the reactive excited state is formed from the Frank-Condon state reached upon excitation; I_0 = the number of photons absorbed by the photo-sensitizer per second

In the dynamic mechanism, the term k_d/k_r can easily be estimated from the slopes and intercepts of Figure 2, according to equation (1). The estimated values decrease with increasing photochemical reactivity, as clearly shown in the Table [note that the smaller is k_d/k_r the larger is $\varphi(Co^{2+})$]. This result indicates that the photochemical reactivity of $[Cu(N\text{-}N)L_2]^+$ depends on the tertiary phosphine through the k_d/k_r term. Furthermore, the relative value of k_r, $(k_r)_{rel}$, can be estimated from k_d/k_r and τ_{rel} [$=(1/k_d)_{rel}$]. As shown in the Table, $(k_r)_{rel}$ increases in the order $PPh_3 < P(C_6H_{11})Ph_2 < P(C_6H_4OMe\text{-}p)_3$. It is, therefore, reasonably concluded that introducing either $P(C_6H_{11})Ph_2$ or $P(C_6H_4OMe\text{-}p)_3$ into [Cu(dmphen)-

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† The relative τ values have been estimated for $[Cu(dmphen)L_2]^+$ from the emission quantum yield and from the direct measurement of the rate constant for decay of the excited state (S. Sakaki and M. Kawasaki, unpublished work). Very similar τ_{rel} values are obtained by both methods.[7c] In the case of phen complexes, neither the emission spectra nor the decay rate constant could be measured, unfortunately, probably because of the very short lifetime of the excited state.

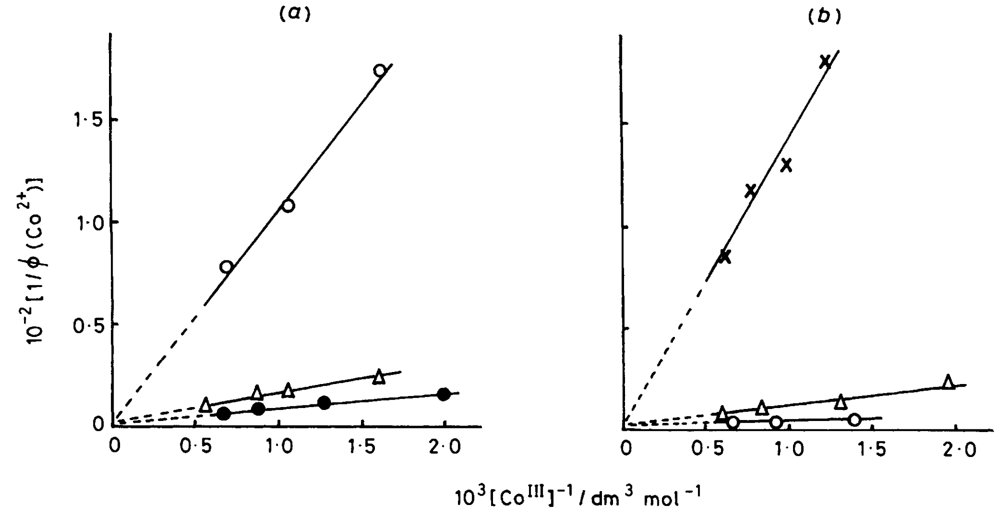

Figure 2. The Stern–Volmer relation between the quantum yield for the $[Co(edta)]^-$ reduction, $\varphi(Co^{2+})$, and the concentration of $[Co(edta)]^-$, $[Co^{III}]$. Details as in Figure 1

$L_2]^+$ lengthens the lifetime of the excited state and simultaneously facilitates the formation of the encounter complex, with which the photochemical reactivity of $[Cu(dmphen)L_2]^+$ complexes is enhanced. Such improvements in the lifetime and the k_r process are considered to result from an increase in the donor property of the phosphines, because $P(C_6H_4OMe\text{-}p)_3$ has almost the same cone angle as PPh_3 and only differs in donor strength. Unfortunately, however, it is still ambiguous why $[Cu(dmphen)\{P(C_6H_{11})Ph_2\}_2]^+$ is less reactive than the $P(C_6H_4OMe\text{-}p)_3$ analogue in spite of the slightly greater donor ability of $P(C_6H_{11})Ph_2$ than that of $P(C_6H_4OMe\text{-}p)_3$. A more systematic and detailed investigation to clarify the phosphine ligand effects is needed.

In conclusion, the dynamic quenching mechanism is considered to be plausible in the photoinduced electron-transfer reaction between $[Co(edta)]^-$ and $[Cu(N\text{–}N)L_2]^+$. The photochemical reactivity of the copper(I) complexes is significantly enhanced by using an appropriate bulky and/or donative phosphine instead of PPh_3. When the N–N ligand has no substituent able to suppress solvation of the Cu^I, a bulky and donative phosphine is the best. However, when the N–N ligand has bulky substituents, bulkiness of the phosphine does not seem important and $P(C_6H_4OMe\text{-}p)_3$ is the best. These results encourage us to apply $[Cu(N\text{–}N)L_2]^+$ to photoreduction of several substrates including methyl viologen.

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