site since the orbital contribution to the magnetic moment is quite different for d_{z^2}. It is interesting to note that even though the chemistry of the binuclear complex reported here shows marked differences from the complexes reported by Hatfield and Hodgson,[30] the magnetic coupling is in agreement with their prediction.

(D) Summary and Conclusions. We have prepared a new type of binucleating ligand that provides three nitrogen donors for binding each metal ion in addition to a phenolate group to bridge the two metals. When the metal ion is copper(II), an additional bridging ligand can be accommodated and each copper center is five-coordinate. We have characterized the μ-hydroxo complex **2** crystallographically and find that the copper ions are in different coordination environments. The geometry of one copper ion is square pyramidal while that for the other copper center is more distorted, falling between square pyramidal and trigonal bipyramidal. In addition, we have examined the magnetic susceptibility of **2** and find that the two copper(II) centers are strongly antiferromagnetically coupled ($2J = -420$ cm^{-1}).

The complex described herein *may* provide a structural model for the active site in type-3 copper proteins. It meets the salient structural requirements of two *pentacoordinate* Cu(II) ions bridged by an "endogenous" phenolate ion in addition to having the appropriate strong antiferromagnetically coupled metal centers. No other single complex encompasses all three of these features,[31] suggesting the need for further investigation of complexes of this type.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the National Science Foundation, to the Research Council of The University of North Carolina, and to the University of New Orleans Graduate Research Council for support of this research. The automated diffractometer was purchased through NSF Grant No. CHE-7803064. Professor Derek Hodgson and his group generously assisted us with the crystallographic work presented herein.

Registry No. **2**, 88106-60-9; **3**, 88130-57-8; bpea, 88106-61-0; pyrazole, 288-13-1; bis(2-chloroethyl)amine hydrochloride, 821-48-7; 2,6-bis(chloromethyl)-*p*-cresol, 5862-32-8; *p*-cresol, 106-44-5; paraformaldehyde, 30525-89-4.

Supplementary Material Available: Tables S1–S6, listing magnetic susceptibility data, ligand and anion distances and angles, final hydrogen atom positions, final thermal parameters, and observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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(31) Karlin's complex[15] has the same structural features as the complex reported here, but it has not yet been magnetically characterized. We have recently prepared a new type of binucleating ligand in which the aliphatic nitrogen donors are bound directly to the phenol ring (ligand 3 minus the benzylic carbons) and the (μ-azido)dicopper(II) complex of that ligand is diamagnetic: Sorrell, T. N.; O'Connor, C. J., submitted for publication in *Inorg. Chem.*

Contribution from the Solar Energy Research Group,
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Wavelength-Dependent Photochemical Reaction of (μ-Tetraphenylporphinato)bis[dicarbonylrhodium(I)]. Locking of Metal Ion into Ligand

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(μ-Tetraphenylporphinato)bis[dicarbonylrhodium(I)], $TPP[Rh^{I}(CO)_2]_2$, in benzene solutions undergoes photochemical reaction to produce rhodium(II) tetraphenylporphyrin, $Rh^{II}TPP$, which forms its diamagnetic dimer, $[Rh^{II}TPP]_2$. The quantum yields of the photoreaction depend strongly on the irradiation wavelengths: $\Phi \sim 0$ at $\lambda > 420$ nm, $\Phi = 0.025$ in the range 350 nm $< \lambda <$ 400 nm, and $\Phi = 0.057$ at $\lambda = 300$ nm. The laser photolysis study using the fundamental (694 nm) of a ruby laser and the second (532 nm) and the third (355 nm) harmonics of a Nd-YAG laser revealed that neither the lowest excited singlet nor the triplet state of $TPP[Rh^{I}(CO)_2]_2$ is concerned with the photochemical reaction. Higher excited singlet states, S_n (probably $n > 2$), are assumed to be responsible for the reaction. The homolytic cleavage of one of the Rh–N bonds of $TPP[Rh^{I}(CO)_2]_2$ in S_n is considered to be involved in the reaction pathway.

Introduction

In recent decades, several unusual metalloporphyrins that have two metal ions in a molecule have been detected spectroscopically[1] and sometimes isolated as stable products.[2-5] The X-ray structure analysis carried out for some of these binuclear complexes revealed that one metal ion is located on each side of the porphyrin plane.[6,7] These complexes are expected to show photochemical behavior characteristically different from usual mononuclear metalloporphyrins.

We have carried out systematic studies on the photochemistry of binuclear metalloporphyrins for an understanding of their nature in their electronically excited states. The present paper reports the photochemistry of (μ-tetraphenylporphinato)bis[dicarbonylrhodium(I)] ($TPP[Rh^{I}(CO)_2]_2$) studied by steady-light and laser-flash photolysis.

Experimental Section

(μ-Tetraphenylporphinato)bis[dicarbonylrhodium(I)] was prepared according to the literature.[3] The absorption peaks of $TPP[Rh^{I}(CO)_2]_2$ in benzene solution are located at 700, 460, and 370 nm with molar absorption coefficients of 6.0×10^3, 6.45×10^4, and 5.55×10^4 M^{-1} cm^{-1}, respectively. Sample solutions were degassed by freeze–pump–thaw cycles.

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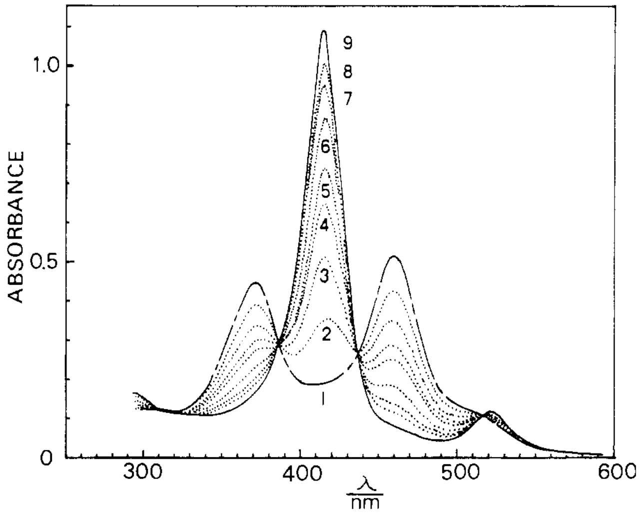

Figure 1. Absorption spectral change by 355-nm irradiation observed for 8.1 × 10^{-6} M TPP[$Rh^I(CO)_2]_2$ solution in degassed benzene: 1, before irradiation; 2, after 5 min; 3, after 10 min; 4, after 15 min; 5, after 20 min; 6, after 30 min; 7, after 40 min; 8, after 50 min; 6, after 84 min.

Absorption and fluorescence spectra were recorded on a Hitachi 200-20 spectrophotometer and a Hitachi MPF-4 spectrofluorimeter, respectively. X-band ESR spectra were measured by a JEOL JES-FE 3AX spectrometer.

Monochromatic light for steady-light photolysis was obtained by using a xenon lamp and a monochromator incorporated in the spectrofluorimeter. A relative light intensity distribution of the xenon lamp between 290 and 600 nm was determined by measuring the fluorescence excitation spectrum of the rhodamin B solution in ethylene glycol (8 g/L).[8] The number of photons at 310 nm was determined by using *N*-methyldiphenylamine (NMD) as a chemical actinometer; NMD in aerated methylcyclohexane solution has been established to form *N*-methylcarbazole by UV light irradiation with a quantum yield of 0.42.[9] From the relative light intensity distribution and the number of photons at 310 nm, we obtain the absolute numbers of photons at given wavelengths between 290 and 600 nm. Changes in concentration of TPP[$Rh^I(CO)_2]_2$ upon irradiation were measured by monitoring the absorbance at 700 nm.

Conventional laser photolysis was carried out by using a ruby laser. Apollo's Model 5, and a Nd-YAG laser, J. K. Laser's Model HY 500, equipped with second, third, and fourth harmonic generators. Excitation of TPP[$Rh^I(CO)_2]_2$ was made by the fundamental (694 nm, fwhm 30 ns, ca. 200 mJ/pulse) of the ruby laser and the second (532 nm, fwhm 20 ns, ca. 100 mJ/pulse) and third harmonics (355 nm, fwhm 20 ns, ca. 40 mJ/pulse) of the Nd-YAG laser. Analyzing light beams from a xenon lamp (Ushio UXL-150D, 150W) were intensified by a factor of 20 during the detection of transient spectra. The transmitted light beam through a sample cell was led into a Ritsu monochromator (Model MC-20N), and the output from a photomultiplier attached to the exit slit of the monochromator was displayed on a Tektronix oscilloscope (Model 7904).

Results and Discussion

Figure 1 shows the absorption spectral change observed when a degassed benzene solution of TPP[$Rh^I(CO)_2]_2$ was irradiated with 355-nm light. The photoproduct, which has absorption peaks at 412 and 521 nm, was confirmed to be diamagnetic by ESR measurement. By aeration of the irradiated solution, the absorption spectrum gradually changed and ultimately new absorption peaks appeared at 420, 528, and 564 nm. The ESR spectrum revealed that the aeration gives rise to the formation of an oxygen adduct of rhodium(II) tetraphenylporphyrin, $Rh^{II}TPP(O_2)$,[10,11] which was once formulated erroneously as $Rh^{II}TPP$.[12] The absorption spectrum of $Rh^{II}TPP(O_2)$ prepared according to Wayland and Newman[11] is in good accord with that observed for the aerated solution. It is well recognized[10,11] that $Rh^{II}TPP$ forms a diamagnetic dimer, $[Rh^{II}TPP]_2$, which absorbs oxygen to produce $Rh^{II}TPP(O_2)$. The photochemical reaction taking place by steady-light irradiation, therefore, is represented as

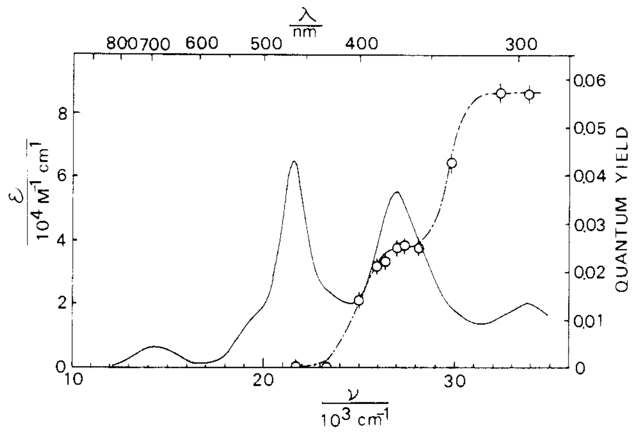

Figure 2. Absorption spectrum of TPP[$Rh^I(CO)_2]_2$ and the quantum yields of photodecomposition of TPP[$Rh^I(CO)_2]_2$ as a function of excitation wavelength.

$$TPP[Rh^I(CO)_2]_2 \xrightarrow{h\nu} Rh^{II}TPP + [Rh(0) + 4CO] \quad (1)$$

followed by

$$2Rh^{II}TPP \rightarrow [Rh^{II}TPP]_2 \quad (2)$$

The products of reaction 1 in brackets are assumed on the basis of the stoichiometry, although we could not isolate them from the reaction mixture owing to the low concentrations of the products. The absorption spectra in Figure 1 indicate that the photoproduct that has the porphyrin ligand is only $[Rh^{II}TPP]_2$. This fact supports the above reactions, which exclude the formation of TPP compounds other than $[Rh^{II}TPP]_2$.

The quantum yield, Φ, of the photochemical decomposition of TPP[$Rh^I(CO)_2]_2$ was found to depend strongly on the irradiation wavelengths: $\Phi \sim 0$ at $\lambda > 420$ nm, $\Phi = 0.025 \pm 0.005$ at 350 nm $< \lambda < 400$ nm, and $\Phi = 0.057 \pm 0.005$ at 300 nm. Figure 2 shows the quantum yields as a function of the excitation wavelength together with the absorption spectrum of TPP[$Rh^I(CO)_2]_2$ in benzene solution. From the absorption spectral measurements of the irradiated solutions, we concluded that the photoproduct is $[Rh^{II}TPP]_2$ irrespective of the irradiation wavelengths. The result that the photodecomposition of TPP[$Rh^I(CO)_2]_2$ takes place at excitation wavelengths shorter than 420 nm, not by excitation of the first and the second major bands (700 and 460 nm), leads to the conclusion that the lowest excited singlet state, S_1, is not responsible for the photodecomposition of TPP[$Rh^I(CO)_2]_2$.

No fluorescence was observed for the benzene solution, indicating that TPP[$Rh^I(CO)_2]_2$ undergoes efficient radiationless transitions from S_1 to the ground state and/or the triplet state.

The photophysical and photochemical processes of TPP-[$Rh^I(CO)_2]_2$ in benzene solution were also studied by laser-flash photolysis. As shown in Figure 3, the transient spectrum observed at 20 ns after a 694-nm flash of the fundamental of a ruby laser or a 532-nm flash of the second harmonic of a Nd-YAG laser has absorption peaks at 580 and 800 nm. The spectrum decays according to first-order kinetics with a lifetime

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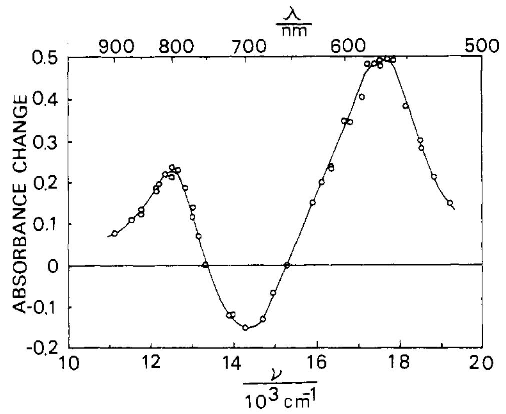


Figure 3. Transient spectrum observed immediately after a 532-nm flash.

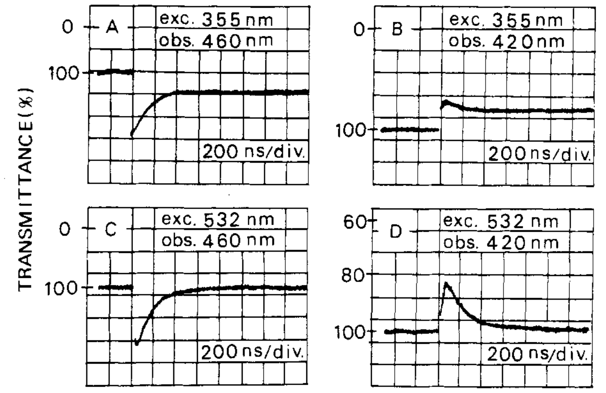


Figure 4. Oscilloscope traces observed in laser photolysis: A, monitored at 460 nm after a 355-nm flash; B, monitored at 420 nm after a 355-nm flash; C, monitored at 460 nm after a 532-nm flash; D, monitored at 420 nm after a 532-nm flash.

of 167 ns. Oxygen-saturated benzene solution gives the same transient spectrum as in the absence of oxygen, but the lifetime was found to be as short as 63 ns. No photoproduct was detected at all for both the degassed and oxygen-saturated solutions even after several laser flashes, indicating that stable photoproducts were not formed by 694- and 532-nm irradiation. Taking account of the lifetime and the quenching by oxygen, we concluded that the transient observed after laser flash is ascribed to the photoexcited triplet state of $\mathrm{TPP[Rh^I(CO)_2]_2}$, which is not concerned in the photochemical reaction, however.

The laser-flash photolysis of $\mathrm{TPP[Rh^I(CO)_2]_2}$ in benzene solution by 355-nm flash of the third harmonic of the Nd-YAG laser, on the other hand, provides a new aspect of the photochemistry. Parts A and B of Figure 4 show the oscilloscope traces monitored at 460 and 420 nm, respectively, after a 355-nm flash. The traces indicate that two species are produced by flash photolysis: one is a short-lived species having a lifetime of 167 ns, and the other, a long-lived one, will be discussed below. The short-lived species may be ascribed to the triplet state of $\mathrm{TPP[Rh^I(CO)_2]_2}$ on the basis of the same lifetime as that of the triplet state that was concluded above. The formation of the triplet $\mathrm{TPP[Rh^I(CO)_2]_2}$ by a 355-nm flash was confirmed from the transient spectrum appearing in the wavelength region from 500 to 900 nm; the spectrum and the lifetime were found to be in good agreement with those obtained with 532- and 694-nm flashes.

Parts C and D of Figure 4 show the oscilloscope traces monitored at 460 and 420 nm, respectively, after a 532-nm flash, in comparison with parts A and B of Figure 4. These traces show that the transient ascribed to the triplet $\mathrm{TPP[Rh^I(CO)_2]_2}$ regenerates the ground state $\mathrm{TPP[Rh^I(CO)_2]_2}$ completely. No long-lived species was detected to be formed with a 532-nm flash.

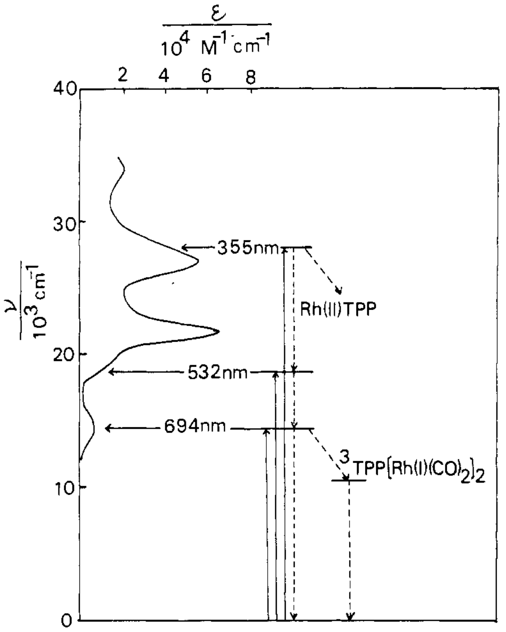


Figure 5. Absorption spectrum of $\mathrm{TPP[Rh^I(CO)_2]_2}$ in benzene solution and the photochemical and photophysical processes upon laser excitation.

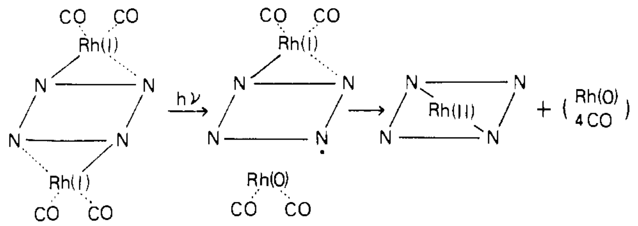
The laser photolysis using a 355-nm flash has revealed that both the triplet state of $\mathrm{TPP[Rh^I(CO)_2]_2}$ and the long-lived species are produced within the flash duration (20 ns). Since several 355-nm flashes give the absorption spectrum of $\mathrm{[Rh^{II}TPP]_2}$, the long-lived species is considered to be $\mathrm{Rh^{II}TPP}$, which undergoes dimerization to form $\mathrm{[Rh^{II}TPP]_2}$ according to reaction 2. We examined the flash-difference spectrum measured at 500 ns after a 355-nm flash and found that the spectrum is in accord with that obtained by steady-light photolysis of $\mathrm{TPP[Rh^I(CO)_2]_2}$. This fact leads to the assumption that the absorption spectrum of $\mathrm{Rh^{II}TPP}$ is similar to that of $\mathrm{[Rh^{II}TPP]_2}$. The assumption may be rationalized when the distance between two porphyrin planes in $\mathrm{[Rh^{II}TPP]_2}$ is short enought for the spin-pairing of the unpaired electron located in the $4d_{z^2}$ orbital of each Rh atom but not so short as it causes substantial difference in the absorption spectrum between $\mathrm{Rh^{II}TPP}$ and $\mathrm{[Rh^{II}TPP]_2}$.

The ratio of the triplet yield of $\mathrm{TPP[Rh^I(CO)_2]_2}$ obtained by 355-nm flashes to those by 532-mn flashes, Φ_{ST}(355 nm)/Φ_{ST}(532 nm), was found to be almost unity. This was estimated by evaluating the relative number of photons of the two laser flashes by measuring the absorbance at 490 nm of the triplet–triplet absorption spectrum of tetraphenylporphyrin, TPP, in benzene solution after laser excitation, on the assumption that the triplet yield of TPP does not depend on the excitation wavelength.

Figure 5 illustrates the photochemical and photophysical processes revealed by laser photolysis in connection with the absorption spectrum of $\mathrm{TPP[Rh^I(CO)_2]_2}$. The electronic excitation of $\mathrm{TPP[Rh^I(CO)_2]_2}$ by 532- or 694-nm laser flash gives rise to the formation of the triplet state without any stable photoproduct, while that by 355-nm laser flash, to the formation of $\mathrm{Rh^{II}TPP}$ as well as the triplet state. These results are in good accord with the fact that the photochemical reaction of $\mathrm{TPP[Rh^I(CO)_2]_2}$ occurs by irradiation of light whose wavelengths are shorter than 420 nm as revealed by the steady-light photolysis.

The present results on the wavelength dependence of the photochemistry provide evidence that neither the lowest excited singlet nor triplet state is responsible for the photochemical

Scheme I



reaction of $\mathrm{TPP[Rh^I(CO)_2]_2}$. We assume that the reaction occurs from higher excited singlet states, S_n (probably $n > 2$), in competition with the fast internal conversion. This assumption, together with the low quantum yields for the photodecomposition, gives a satisfactory account of the fact that $\Phi_{ST}(355\ \mathrm{nm})/\Phi_{ST}(532\ \mathrm{nm}) \sim 1$.

Above discussions lead to the reaction mechanism by which $\mathrm{Rh^{II}TPP}$ is formed via S_n. We consider that the initial process is the homolytic cleavage of one of the Rh–N bonds in $\mathrm{TPP[Rh^I(CO)_2]_2}$ followed by the locking of a Rh atom in the center of the porphyrin ligand as represented by Scheme I.

It is noteworthy that the disilver salt of TPP, $\mathrm{TPP[Ag^I{}_2]}$, formed in a pyridine solution[1] was found to undergo photochemical reaction producing the divalent silver salt of TPP, $\mathrm{Ag^{II}TPP}$:

$$\mathrm{TPP[Ag^I{}_2]} \xrightarrow{h\nu} \mathrm{Ag^{II}TPP} + \mathrm{Ag(0)}$$

This reaction may also involve the homolytic cleavage of one of the Ag–N bonds in $\mathrm{TPP[Ag^I{}_2]}$.

Registry No. $\mathrm{TPP[Rh^I(CO)_2]_2}$, 88083-36-7; $\mathrm{Rh^{II}TPP}$, 38856-19-8; $\mathrm{[Rh^{II}TPP]_2}$, 88083-37-8.

Contribution from the Department of Synthetic Chemistry,
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Trans → Cis Isomerization of Stilbene Photocatalyzed by Copper(I) Complexes. The First Example of Copper(I) Photocatalysis Efficient under Visible-Light Irradiation

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The isomerization of *trans*-stilbene to its cis form was catalyzed by $\mathrm{[Cu(CH_3CN)_4]^+}$–biL systems (biL = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and their derivatives) upon irradiating with visible light (>390 nm). The activity of these Cu(I) catalysts depends on the $\mathrm{[biL]/[Cu(CH_3CN)_4]^+}$ mole ratio and the concentration of $\mathrm{[Cu(CH_3CN)_4]^+}$; the greatest activity was obtained at $\mathrm{[biL]/[Cu(CH_3CN)_4]^+} = 0.5$ and $\mathrm{[[Cu(CH_3CN)_4]^+]} = 5 \times 10^{-3}\ \mathrm{mol/dm^3}$. The quantum yield of the *cis*-stilbene formation, ϕ_{cis}, is 0.11 for biL = phen at [*trans*-stilbene] = $5 \times 10^{-2}\ \mathrm{mol/dm^3}$, while ϕ_{cis} becomes remarkably large at high concentration of *trans*-stilbene; $\phi_{\mathrm{cis}} = 0.55$ at [*trans*-stilbene] = $4 \times 10^{-1}\ \mathrm{mol/dm^3}$. The *trans*-stilbene/*cis*-stilbene mole ratio at the photostationary state, $(c/t)_{\mathrm{ps}}$, is 9.9 for biL = phen and 9.2 for biL = 4,7-dimethyl-1,10-phenanthroline. These $(c/t)_{\mathrm{ps}}$ values are about half of the $(c/t)_{\mathrm{ps}}$ value obtained in the $\mathrm{[Ru(bpy)_3]^{2+}}$ photocatalytic isomerization but substantially larger than the $(c/t)_{\mathrm{ps}}$ values obtained in the photocatalytic isomerization with $\mathrm{W(CO)_6}$ and benzophenone. Possible photosensitization mechanisms are presented and discussed.

Introduction

Recently, the photochemistry of Cu(I) systems has been a subject of increasing interest.[1-4] Especially, much attention has been received by photoisomerization of norbornadiene to quadricyclene catalyzed by Cu(I) complexes,[1a,5] because this isomerization can be applied to the storage of solar energy. Unfortunately, however, the photocatalysis by Cu(I) systems needs UV (≳313 nm) irradiation and no catalytic reaction is known to proceed under visible-light irradiation; a visible-light-induced electron transfer from $\mathrm{[Cu(dmp)_2]^+}$ (dmp = 2,9-dimethyl-1,10-phenanthroline) to Co(III) complexes has been reported,[2a,b] but this reaction is noncatalytic.

In this work, it is attempted to present a good Cu(I) photocatalyst efficient under visible-light irradiation. Here, photoinduced isomerization of *trans*-stilbene to the cis form was examined by using Cu(I) complexes with 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and their derivatives (these ligands are abbreviated as biL), considering the following: (1) Cu(I) complexes with biL, such as $\mathrm{[Cu(dmp)_2]^+}$, have a large absorption at 440–460 nm,[2] perhaps due to the charge-transfer to ligand (CTTL) transition from the Cu dπ orbital to the ligand π^* orbital. Thus, these Cu(I) complexes are considered to be useful as photocatalysts. (2) Though the endothermicity is small, the isomerization of *trans*-stilbene to the cis form is an uphill reaction and can store light energy (ca. 45 kJ/mol). The emphasis, a point of departure from previous works, is to present the first Cu(I) photocatalyst efficient under visible-light irradiation and to find a new catalytic ability of the Cu(I)–biL complexes, although the similar $\mathrm{[Cu(dmp)_2]^+}$ has been reported to be photochemically inert.[6]

Experimental Section

Materials. Tetrakis(acetonitrile)copper(I) perchlorate, $\mathrm{[Cu(CH_3CN)_4]ClO_4}$, and $\mathrm{[Cu(biL)_2]ClO_4}$ (biL = bpy, phen, or dmp) were prepared by literature methods.[2,7] Purities of these complexes were confirmed by elemental analysis. These complexes were stored under a nitrogen atmosphere in a desiccator.

All solvents were used after drying and purification. *trans*-Stilbene was also used after two recrystallizations from ethanol. The other

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