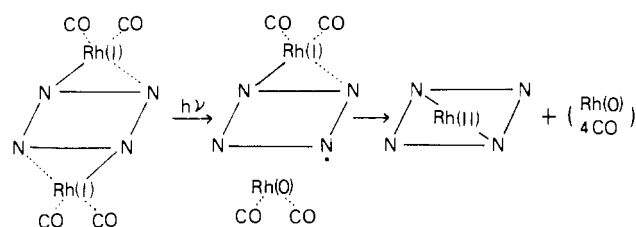


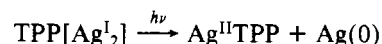
Scheme 1



reaction of $\text{TPP}[\text{Rh}^{\text{I}}(\text{CO})_2]_2$. 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 $\Phi_{\text{ST}}(355 \text{ nm})/\Phi_{\text{ST}}(532 \text{ nm}) \sim 1$.

Above discussions lead to the reaction mechanism by which $\text{Rh}^{\text{II}}\text{TPP}$ is formed via S_n . We consider that the initial process is the homolytic cleavage of one of the Rh-N bonds in $\text{TPP}[\text{Rh}^{\text{I}}(\text{CO})_2]_2$ followed by the locking of a Rh atom in the center of the porphyrin ligand as represented by Scheme 1.

It is noteworthy that the disilver salt of TPP, $\text{TPP}[\text{Ag}^{\text{I}}]_2$, formed in a pyridine solution¹ was found to undergo photochemical reaction producing the divalent silver salt of TPP, $\text{Ag}^{\text{II}}\text{TPP}$:



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

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

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Trans \rightarrow 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 $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ -biL systems (biL = 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and their derivatives) upon irradiating with visible light ($>390 \text{ nm}$). The activity of these Cu(I) catalysts depends on the $[\text{biL}]/[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ mole ratio and the concentration of $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$; the greatest activity was obtained at $[\text{biL}]/[\text{Cu}(\text{CH}_3\text{CN})_4]^+ = 0.5$ and $[\text{Cu}(\text{CH}_3\text{CN})_4]^+ = 5 \times 10^{-3} \text{ mol/dm}^3$. The quantum yield of the *cis*-stilbene formation, ϕ_{cis} , is 0.11 for biL = phen at $[\text{trans-stilbene}] = 5 \times 10^{-2} \text{ mol/dm}^3$, while ϕ_{cis} becomes remarkably large at high concentration of *trans*-stilbene; $\phi_{\text{cis}} = 0.55$ at $[\text{trans-stilbene}] = 4 \times 10^{-1} \text{ mol/dm}^3$. The *trans*-stilbene/*cis*-stilbene mole ratio at the photostationary state, $(c/t)_{\text{ps}}$, is 9.9 for biL = phen and 9.2 for biL = 4,7-dimethyl-1,10-phenanthroline. These $(c/t)_{\text{ps}}$ values are about half of the $(c/t)_{\text{ps}}$ value obtained in the $[\text{Ru}(\text{bpy})_3]^{2+}$ photocatalytic isomerization but substantially larger than the $(c/t)_{\text{ps}}$ values obtained in the photocatalytic isomerization with $\text{W}(\text{CO})_6$ 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 ($\geq 313 \text{ nm}$) irradiation and no catalytic reaction is known to proceed under visible-light irradiation; a visible-light-induced electron transfer from $[\text{Cu}(\text{dmp})_2]^+$ (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 $[\text{Cu}(\text{dmp})_2]^+$, have a large absorption at 440-460 nm,² perhaps due to the charge-transfer to ligand (CTTL) transition from the Cu $d\pi$ 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 $[\text{Cu}(\text{dmp})_2]^+$ has been reported to be photochemically inert.⁶

Experimental Section

Materials. Tetrakis(acetonitrile)copper(I) perchlorate, $[\text{Cu}(\text{C}_2\text{H}_3\text{N})_4]\text{ClO}_4$, and $[\text{Cu}(\text{biL})_2]\text{ClO}_4$ (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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(6) Wehry, E. L.; Sundararajan, S. *J. Chem. Soc., Chem. Commun.* **1972**, 1135.

(7) Hemmerich, P.; Sigwart, C. *Experientia* **1963**, *19*, 488.

Table I. Absorption Maxima and Molar Extinction Coefficients of Various Cu(I) Complexes

complexes	λ_{\max} , nm	$10^3 \epsilon$, mol ⁻¹ dm ²
[Cu(CH ₃ CN) ₄] ⁺ ClO ₄ ⁻	230	10.0
[Cu(bpy) ₂] ⁺ ClO ₄ ⁻	440	4.8 ^a
[Cu(phen) ₂] ⁺ ClO ₄ ⁻	440	6.6 ^a
[Cu(2,9-dmp) ₂] ⁺ BF ₄ ⁻	454	7.95 ^b
[Cu(CH ₃ CN) ₄] ⁺ ClO ₄ ⁻ + bpy	440	2.2 ^c
[Cu(CH ₃ CN) ₄] ⁺ ClO ₄ ⁻ + phen	440	1.0 ^c
[Cu(CH ₃ CN) ₄] ⁺ ClO ₄ ⁻ + 2,9-dmp	460	1.7 ^c
[Cu(CH ₃ CN) ₄] ⁺ ClO ₄ ⁻ + 4,7-dmp	460	3.3 ^c
[Cu(CH ₃ CN) ₄] ⁺ ClO ₄ ⁻ + 4,7-dpp	460	3.3 ^c

^a Kitagawa, S.; Munakata, M. *Inorg. Chem.* 1981, 20, 2261.

^b Reference 2d. ^c Because equilibria of these solution are unknown, we cannot obtain molar extinction coefficients per chemical species. These values are merely apparent molar extinction coefficients per mole of Cu(I) ion.

materials, such as bpy, phen, dmp, 4,7-dimethyl-1,10-phenanthroline (4,7-dmp), and 4,7-diphenyl-1,10-phenanthroline (4,7-dpp) (extra-pure grade purchased from Tokyo Kasei Co. Ltd.), were used without further purification.

Photoreaction and Analysis. All solutions were prepared under a nitrogen atmosphere, where the solvent was carefully deoxygenated by a nitrogen stream before use. In a typical run, [Cu(CH₃CN)₄]⁺ClO₄⁻ (5×10^{-3} mol/dm³), biL (2.5×10^{-3} mol/dm³), and *trans*-stilbene (5×10^{-2} mol/dm³) were dissolved in dichloromethane and irradiated in a 1-cm quartz cell with a 400-W high-pressure mercury-arc lamp (Toshiba H-400P). When [Cu(CH₃CN)₄]⁺ClO₄⁻ or [Cu(biL)₂]⁺ClO₄⁻ was used as a catalyst, the same reaction conditions were adopted except that further biL was not added to the solution. The irradiated solution was thermostated at 25 °C during the reaction.

Incident light above 390 nm was isolated with a Model L-39 cutoff filter (Toshiba; transmittance at 390 nm, 50%). When the quantum yield was measured, light of 390–460 nm was isolated with a combination of L-39 and C-40C cutoff filters (the latter filter cuts off the light of wavelengths longer than 460 nm). The light intensity absorbed by the reaction system was measured as the difference in the light intensity transmitted by the reaction and the reference cells by using Reinecke's actinometry.⁸

Aliquots of the irradiated solutions were analyzed for *trans*- and *cis*-stilbene by gas chromatography (Shimadzu GC-3AH equipped with a 1-m column of ethylene glycol adipate (15%) supported on Uniport B (purchased from Gaskuro Kogyo Co. Ltd.)).

Results and Discussion

Active Catalysts. Absorption maxima of various Cu(I) complexes are listed in Table I. All [Cu(biL)₂]⁺ complexes have an intense large absorption band at 440–450 nm, which has been assigned as a CTTL transition from the Cu dπ to the biL π* orbital.^{2d} Though [Cu(CH₃CN)₄]⁺ has no absorption band in the visible region, addition of biL causes the appearance of a new absorption band at 440–460 nm, suggesting the complexation of biL to Cu(I). This new band can be assigned to the Cu dπ → biL π* CTTL transition, because the absorption maximum is similar to those of [Cu(biL)₂]⁺. Thus, [Cu(biL)₂]⁺ and [Cu(CH₃CN)₄]⁺-biL systems are expected to act as efficient photocatalysts upon irradiating the CTTL band in the visible region.

The *trans* → *cis* isomerization of stilbene was examined by using these Cu(I) systems, as shown in Figure 1. [Cu(CH₃CN)₄]⁺ offers little catalytic activity, as expected from the absence of the absorption band in the visible region. [Cu(biL)₂]⁺ also hardly catalyzes the photoisomerization of *trans*-stilbene, despite the presence of the strong CTTL band at 440–450 nm. On the other hand, [Cu(CH₃CN)₄]⁺-biL

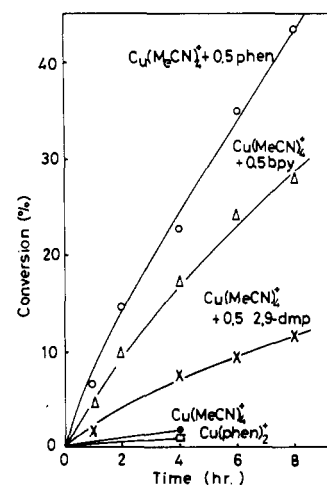


Figure 1. Time-conversion curve in the *trans* → *cis* isomerization of stilbene catalyzed by various Cu(I) complexes; [*trans*-stilbene] = 5×10^{-2} mol/dm³, [[Cu(CH₃CN)₄]⁺] = 5×10^{-3} mol/dm³, [biL] = 2.5×10^{-3} mol/dm³, and the L-39 cutoff filter was used.

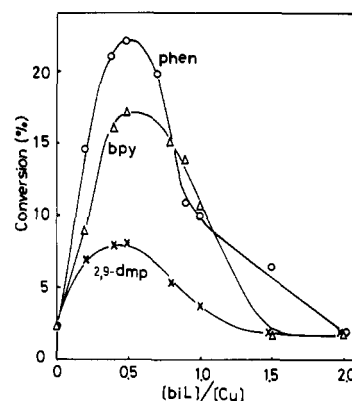
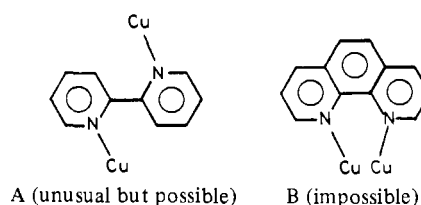


Figure 2. Effect of the [biL]/[Cu(CH₃CN)₄]⁺ mole ratio on the *trans* → *cis* isomerization of stilbene; [*trans*-stilbene] = 5×10^{-2} mol/dm³, [[Cu(CH₃CN)₄]⁺] = 5×10^{-3} mol/dm³, the reaction time was 4 h, and the L-39 cutoff filter was used.

Chart I



systems offer remarkably high catalytic activity; in Figure 1, examples of biL = phen, bpy, and 2,9-dmp are given, and all of them show high conversion of *trans*-stilbene to the *cis* form. It should be noted that these catalytic systems, [Cu(CH₃CN)₄]⁺-biL, are the first examples of Cu(I) photocatalysts efficient upon irradiating with visible light.

Factors Influencing the Catalytic Activity. The effect of the [biL]/[Cu(CH₃CN)₄]⁺ mole ratio was investigated. As shown in Figure 2, the conversion of *trans*-stilbene into *cis*-stilbene becomes larger with increasing the [biL]/[Cu(CH₃CN)₄]⁺ ratio from 0.0 to 0.5, and the conversion arrives at the maximum value at [biL]/[Cu(CH₃CN)₄]⁺ ≈ 0.5 but then decreases with increasing the [biL]/[Cu(CH₃CN)₄]⁺ ratio from 0.5 to 2.0. Finally, the photoisomerization hardly proceeds at [biL]/[Cu(CH₃CN)₄]⁺ ≈ 2.0, which is in accordance with little activity of the [Cu(biL)₂]⁺ complexes. There are three possible explanations why the maximum activity is attained at [biL]/[Cu(CH₃CN)₄]⁺ ≈ 0.5: First, a binuclear Cu(I)

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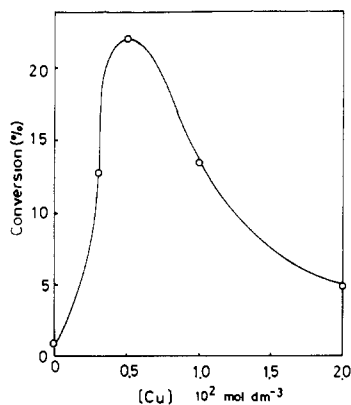
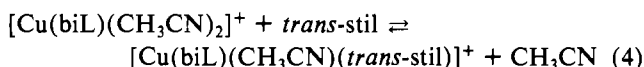
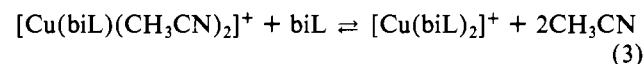
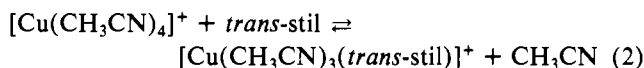
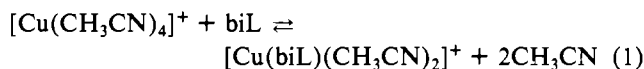


Figure 3. Effect of the Cu(I) complex concentration on the *trans* → *cis* isomerization of stilbene. The $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ -phen catalytic system was employed, where $[\text{biL}]/[\text{Cu}(\text{CH}_3\text{CN})_4] = 0.5$. $[\text{trans-stilbene}] = 5 \times 10^{-2} \text{ mol/dm}^3$, the irradiation time was 4 h, and the L-39 cutoff filter was used.

complex bridged by biL is an active species. The bpy ligand can play the role of bridging ligand (see structure A in Chart I), although such coordination is unusual. However, phen and its derivatives seem unable to act as bridging ligands (structure B in Chart I). Thus, this explanation seems difficult. Second, the catalytic system requires coexistence of a Cu(I) complex with biL and a Cu(I) complex without biL; at $[\text{biL}]/[\text{Cu}(\text{CH}_3\text{CN})_4]^+ = 0.5$, about half of the $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ added into the solution coordinates with biL through eq 1 and the



remaining $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ without biL coordinates with *trans*-stilbene (*trans-stil*) through eq 2. This explanation requires that the contribution of further equilibria such as eq 3 be small. In the third explanation, an active species is considered to be $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})(\text{trans-stil})]^+$, which would be formed through eq 4, as will be discussed below. When the equilibrium (3) cannot be neglected even at $[\text{biL}]/[\text{Cu}(\text{CH}_3\text{CN})_4]^+ = \sim 0.5$ –1.0, the increasing biL concentration above half of that of $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ would probably lead to the increasing concentration of $[\text{Cu}(\text{biL})_2]^+$ and to the decreasing concentration of the active species. Thus, the maximum conversion would be attained at $[\text{biL}]/[\text{Cu}(\text{CH}_3\text{CN})_4]^+ \approx 0.5$. These second and third explanations remain as possible ones; as will be described, the reaction mechanism based on the second explanation would include energy transfer from the excited Cu(I)-biL complex to $[\text{Cu}(\text{CH}_3\text{CN})_3(\text{trans-stilbene})]^+$, and the mechanism based on the third explanation would need intersystem crossing or internal conversion from the initially formed Cu $d\pi \rightarrow \text{biL} \pi^*$ photoexcited state to the reactive excited state.

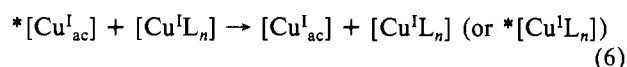
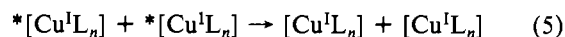
The effect of the $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ concentration was examined for the $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ -phen system, as shown in Figure 3, where the $[\text{phen}]/[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ ratio was kept at 0.5. The conversion increases with increasing Cu(I) concentration and arrives at the maximum value at $[\text{Cu}(\text{CH}_3\text{CN})_4]^+ \sim 5 \times 10^{-3} \text{ mol/dm}^3$, but then the conversion becomes small with increasing Cu(I) concentration ($[\text{Cu(I)}] > 5 \times 10^{-3} \text{ mol/dm}^3$). Although the mutual collision of the

Table II. Quantum Yield for the *cis*-Stilbene Formation, ϕ_{cis} , and the *cis*-Stilbene/*trans*-Stilbene Mole Ratio at the Photostationary State, $(c/t)_{\text{ps}}^a$

catalysts	ϕ_{cis}	$(c/t)_{\text{ps}}$
$[\text{Cu}(\text{CH}_3\text{CN})_4]^+ + 4,7\text{-dmp}$	0.18	9.2
+ phen	0.11	9.9
	0.55 ^b	
+ 4,7-dpp	0.10	6.1
+ bpy	0.09	9.0
+ 2,9-dmp	0.02	8.6
benzophenone ^c	0.5	1.5
$[\text{Ru}(\text{bpy})_3]^{2+ d}$	0.21 ($\phi_{\text{lim}} = 0.44$)	19.0
$\text{W}(\text{CO})_6^e$	0.02	1.5
thermal equilibrium state ^f		2.1×10^{-3}

^a $[\text{Cu}(\text{CH}_3\text{CN})_4]^+ = 5.0 \times 10^{-3} \text{ mol/dm}^3$, $[\text{biL}] = 2.5 \times 10^{-3} \text{ mol/dm}^3$, and $[\text{trans-stilbene}] = 5.0 \times 10^{-2} \text{ mol/dm}^3$; the L-390 and C-40C cutoff filters were used. ^b $[\text{trans-stilbene}] = 4.0 \times 10^{-1} \text{ mol/dm}^3$. ^c Reference 9. ^d Reference 10; 436-nm irradiation. ^e Reference 11; 366-nm irradiation. ^f At 27 °C. Fischer, G.; Muszkat, K. A.; Fischer, E. *J. Chem. Soc. B* 1968, 1156.

excited Cu(I) species is considered to suppress the reaction according to eq 5, this deactivation is not plausible here, be-



cause the present Cu(I) concentration is sufficiently high and the lifetime of the Cu(I) excited state is not always long. Rather than eq 5, the collision between the excited-state active species and the ground state of other Cu(I) complexes should be considered, which would lead to the deactivation of the excited active species through eq 6; such collision becomes more frequent with increasing Cu(I) concentration. Thus, too high concentration of Cu(I) would reduce the catalytic activity. Further discussion is omitted here, for there is no definitive evidence.

The quantum yield for the *cis*-stilbene formation, ϕ_{cis} , and the *cis*-stilbene/*trans*-stilbene mole ratio at the photostationary state, $(c/t)_{\text{ps}}$, are listed for various ligands, as shown in Table II. The ϕ_{cis} value decreases in the order 4,7-dmp > phen \approx 4,7-dpp \approx bpy > 2,9-dmp, and the $(c/t)_{\text{ps}}$ value decreases in the order phen > 4,7-dmp \approx bpy \approx 2,9-dmp > 4,7-dpp. A Saitiel plot shows that when the triplet excited-state photosensitizer (energy donor) lies at the same energy as the triplet excited-state *trans*-stilbene (energy acceptor) the $(c/t)_{\text{ps}}$ value is large but that the $(c/t)_{\text{ps}}$ value decreases when the energy level of the triplet excited-state photosensitizer becomes distant from the triplet excited-state energy of *trans*-stilbene.¹² Thus, the $(c/t)_{\text{ps}}$ value depends on the energy level of the photosensitizer, when the reaction mechanism includes the energy transfer. Here, two reaction mechanisms are considered to be possible; one includes energy transfer, and another possesses intersystem crossing and/or internal conversion. Even in the latter reaction mechanism, the $(c/t)_{\text{ps}}$ value is similarly expected to depend on the energy level of the initially formed photoexcited state.¹³ The energy level of the initial excited state also influences the probability of the reactive excited-state formation and, consequently, affects the ϕ_{cis} value; unless the initial excited state of the photosensitizer lies higher in energy

(12) Adams, B. K.; Cherry, W. R. *J. Am. Chem. Soc.* 1981, 103, 6904.

(13) Strictly speaking, a Saitiel plot has been proposed for a photoreaction including energy transfer. However, a similar discussion is considered to be applicable for the reaction in which the photoactive state is formed through intersystem crossing or internal conversion; when the initially formed Cu $d\pi \rightarrow \text{biL} \pi^*$ excited state is much higher in energy than the photoactive state, the highly energetic vibronic state of the photoactive state is formed through intersystem crossing or internal conversion, leading to the increased reverse *cis* → *trans* isomerization of stilbene and thus yielding the low $(c/t)_{\text{ps}}$ value.

than the reactive excited state of the energy acceptor, the energy transfer to the reactive excited state hardly proceeds, and unless the initial photoexcited state lies higher in energy than the reactive excited state, the intersystem crossing and/or internal conversion hardly yields the reactive excited state. Thus, in any reaction mechanism the energy level of the initially formed photoexcited state is suggested from ϕ_{cis} and $(c/t)_{ps}$. Because the $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ -phen system offers the highest $(c/t)_{ps}$ value, the Cu $d\pi \rightarrow \text{phen } \pi^*$ CTTL transition is the closest in energy to the reactive excited state of the energy acceptor or the active species. The $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ -4,7-dmp system presents lower $(c/t)_{ps}$ but higher ϕ_{cis} values than the $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ -phen system. Thus, the excited state of the 4,7-dmp complex is suggested to be higher in energy than the phen complex, which is attributable to two electron-donating CH_3 groups destabilizing the Cu $d\pi \rightarrow 4,7\text{-dmp } \pi^*$ CTTL excited state. Though 2,9-dmp also has two CH_3 groups, the $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ -2,9-dmp system offers a smaller ϕ_{cis} value. This ϕ_{cis} value may result from the presence of two CH_3 groups at the positions neighboring those of the coordinating N atoms; when the reaction mechanism includes the energy transfer from the excited Cu(I)-2,9-dmp complex to the energy acceptor, such CH_3 groups near the coordinating atom lead to the poor overlap between the d orbital of Cu and orbitals of the energy acceptor, suppressing the energy transfer.¹⁴ When the reaction mechanism includes the intersystem crossing or internal conversion from the Cu $d\pi \rightarrow \text{biL } \pi^*$ excited state of $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})(\text{trans-stil})]^+$ followed by the *trans* \rightarrow *cis* isomerization of stilbene in this complex, such CH_3 groups would disfavor the rotation of two phenyl groups about the C=C axis due to the steric repulsion. Thus, in any reaction mechanism, the presence of two such CH_3 groups is disadvantageous to the reaction. The $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ -4,7-dpp system offers low ϕ_{cis} and $(c/t)_{ps}$ values, suggesting that the excited state of this system lies lower in energy. Two electron-withdrawing phenyl groups of 4,7-dpp probably stabilize the excited state of the 4,7-dpp complex, leading to the decreased ϕ_{cis} and $(c/t)_{ps}$ values. The ϕ_{cis} and $(c/t)_{ps}$ values of the $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ -bpy system are similar to those of the phen system, suggesting that the excited state of the bpy complex lies at an energy similar to that of the phen complex. In fact, the bpy ligand has a coordinating site similar to that of phen, except it has less conjugation than phen.

In conclusion, conditions for an excellent catalyst are as follows: (i) $[\text{biL}]/[\text{Cu}(\text{CH}_3\text{CN})_4]^+ = 0.5$; (ii) $[\text{Cu}(\text{CH}_3\text{CN})_4]^+ = \sim 5 \times 10^{-3} \text{ mol/dm}^3$. (iii) $\text{biL} = \text{phen}$, from the viewpoint of $(c/t)_{ps}$, and $\text{biL} = 4,7\text{-dmp}$, from the viewpoint of ϕ_{cis} . Substituents near the coordinating atom are unfavorable.

Comparison of the Present Catalysts with the Previously Studied Catalysts. The ϕ_{cis} and $(c/t)_{ps}$ values of the present systems are compared with those of $[\text{Ru}(\text{bpy})_3]^{2+}$, benzophenone, and $\text{W}(\text{CO})_6$ in Table II. The present Cu(I) systems possess smaller $(c/t)_{ps}$ values than $[\text{Ru}(\text{bpy})_3]^{2+}$ but give larger ϕ_{cis} values than $[\text{Ru}(\text{bpy})_3]^{2+}$ at high concentration of *trans*-stilbene. Although benzophenone can offer the high value of ϕ_{cis} , this photocatalyst gives a small $(c/t)_{ps}$ value. $\text{W}(\text{CO})_6$ presents lower values of ϕ_{cis} and $(c/t)_{ps}$ than the Cu(I) systems. Because the high ϕ_{cis} and $(c/t)_{ps}$ values are requisites for a good catalyst, the present Cu(I) systems are as good as $[\text{Ru}(\text{bpy})_3]^{2+}$ and are better than benzophenone and $\text{W}(\text{CO})_6$. Thus, it is expected that the $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ -biL system can be applied to various photocatalytic reactions to a similar extent as $[\text{Ru}(\text{bpy})_3]^{2+}$.

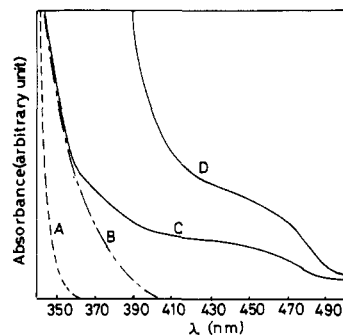


Figure 4. UV-vis spectra of various Cu(I) systems: (A) *trans*-stilbene; (B) $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ + *trans*-stilbene (1/5); (C) $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ + phen (1/0.5); (D) $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ + phen + *trans*-stilbene (1/0.5/5). $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ has no absorption in this region.

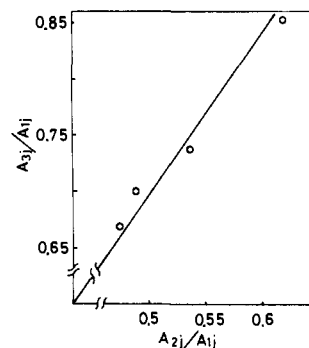
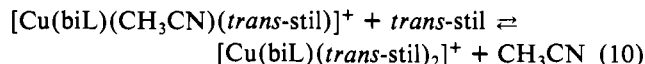
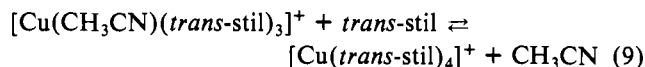
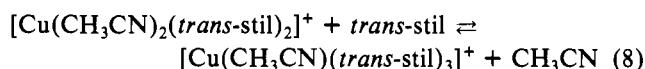
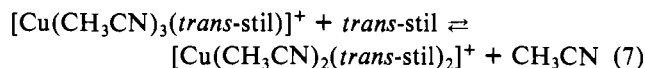


Figure 5. Graphical matrix rank test for two absorbing species; j = solution number, $[\text{Cu}(\text{CH}_3\text{CN})_4]^+ = (4-7) \times 10^{-3} \text{ mol/dm}^3$, $[\text{phen}] = (2-3.5) \times 10^{-3} \text{ mol/dm}^3$, and $[\text{trans-stilbene}] = (2-3.5) \times 10^{-2} \text{ mol/dm}^3$. Wavelength at measurement: 1, 410 nm; 2, 440 nm; 3, 470 nm.

Active Species and Reaction Mechanism. Let us consider the Cu(I) complexes present in the catalytic system. In addition to equilibria 1-4 described above, further substitutions by *trans*-stilbene are considered (eq 7-10). In order to as-



certain the coordination of *trans*-stilbene, the absorption spectra of $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ with and without *trans*-stilbene were examined. As is shown in Figure 4, the addition of *trans*-stilbene to the solution of $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ enlarges the absorption in the range of 350-400 nm, whereas no new absorption maximum appears. The addition of *trans*-stilbene to the solution containing $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ and biL ($[\text{biL}]/[\text{Cu}(\text{CH}_3\text{CN})_4]^+ = 0.5$) also makes the absorption in the visible region large, and the resulting absorption is larger than the sum of the absorption of the $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ -biL system and that of the $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ -*trans*-stilbene system (see Figure 4). These results indicate the coordination of *trans*-stilbene with $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ and $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})_2]^+$, i.e., the formation of $[\text{Cu}(\text{CH}_3\text{CN})_3(\text{trans-stil})]^+$ and $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})(\text{trans-stil})]^+$.

Then, the numbers of species absorbing the visible light (410-470 nm) were investigated with a graphical matrix rank method.¹⁵ As is shown in Figure 5, the linear relationship

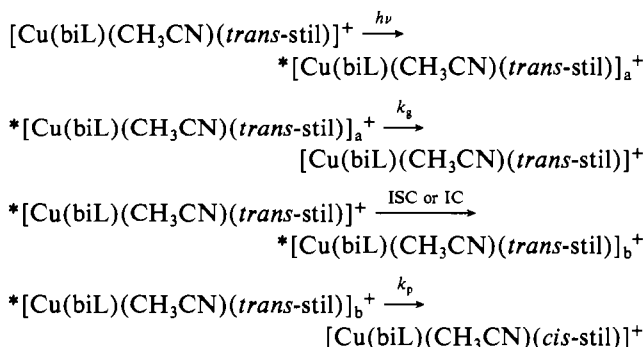
(14) A similar discussion has been presented by Balzani et al., where the donor is the aromatic triplet and the acceptors are Cr(III) complexes: Balzani, V.; Indelli, M. T.; Maestri, M.; Sandrini, D.; Scandola, F. *J. Phys. Chem.* **1980**, *84*, 852.

suggests the presence of two absorbing species in the solution. Because the Cu(I) complexes without biL show no absorption in this region (see Figure 4), two absorbing species are considered to be Cu(I)-biL complexes; four kinds of complexes, such as $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})_2]^+$, $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})(\text{trans-stil})]^+$, $[\text{Cu}(\text{biL})(\text{trans-stil})_2]^+$, and $[\text{Cu}(\text{biL})_2]^+$, are considered as candidates for two absorbing species.

The coordinating ability of *trans*-stilbene is examined here. The binding energy between Cu(I) and various ligands decreases in the order $\text{HCN} > (\text{CH}_3)_2\text{C}=\text{CH}_2 \gg (\text{CH}_3)\text{C}=\text{H}=\text{CH}_2$.¹⁶ This decreasing order indicates the importance of the σ -donating interaction in the olefin coordination with Cu(I), suggesting that *trans*-stilbene is a weaker ligand than $(\text{CH}_3)\text{C}=\text{H}=\text{CH}_2$ due to the electron-withdrawing phenyl group. On the other hand, CH_3CN can coordinate to Cu(I) more strongly than HCN, because of the presence of the electron-donating CH_3 group. Thus, the coordinating ability is expected to decrease in the order $\text{CH}_3\text{CN} > \text{HCN} > (\text{CH}_3)_2\text{C}=\text{CH}_2 \gg (\text{CH}_3)\text{C}=\text{H}=\text{CH}_2 > \text{trans-stilbene}$. Because of the above-mentioned weak coordinating ability of *trans*-stilbene, the presence of $[\text{Cu}(\text{biL})(\text{trans-stil})_2]^+$ and $[\text{Cu}(\text{CH}_3\text{CN})_m(\text{trans-stil})_{4-m}]^+$ ($m < 3$) seems unlikely, and all of the $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})_2]^+$ does not coordinate with *trans*-stilbene. Thus, $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})_2]^+$ and $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})(\text{trans-stil})]^+$ are coexistent as two absorbing species and $[\text{Cu}(\text{biL})_2]^+$ is present to a limited extent at $[\text{biL}]/[\text{Cu}(\text{CH}_3\text{CN})_4]^+ = 0.5$.

Results concerning the reaction mechanism can now be summarized: (i) The isomerization of *trans*-stilbene proceeds to a limited extent in the absence of biL. (ii) Both the $[\text{Cu}(\text{biL})_2]^+$ complex and the $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ -biL system possessing a twofold excess of biL ($[\text{biL}]/[\text{Cu}(\text{CH}_3\text{CN})_4]^+ = 2.0$) hardly catalyze the isomerization of *trans*-stilbene, whereas both systems have large CTTL absorptions in the visible region. (iii) The best condition is obtained at $[\text{biL}]/[\text{Cu}(\text{CH}_3\text{CN})_4]^+ \sim 0.5$. (iv) The equilibria (1)-(4) operate where $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$, $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})_2]^+$, $[\text{Cu}(\text{CH}_3\text{CN})_3(\text{trans-stil})]^+$ and $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})(\text{trans-stil})]^+$ are considered to be present. The result (i) means that the isomerization cannot proceed in the presence of only $[\text{Cu}(\text{CH}_3\text{CN})_3(\text{trans-stil})]^+$. From the result (ii), the energy transfer from the excited $[\text{Cu}(\text{biL})_2]^+$ complex to the uncomplexed *trans*-stilbene seems difficult in contrast to the photoisomerization of *trans*-stilbene catalyzed by $[\text{Ru}(\text{bpy})_3]^{2+}$ and benzophenone; if such energy transfer is possible, there is no reason why neither $[\text{Cu}(\text{biL})_2]^+$ nor $[\text{Cu}(\text{CH}_3\text{CN})_4]^+ - 2 \text{ biL}$ can catalyze the *trans* \rightarrow *cis* isomerization of stilbene. Here, two kinds of reaction mechanisms are considered to be possible as described above; in one (see Scheme I, where the subscript a denotes the Cu $d\pi \rightarrow$

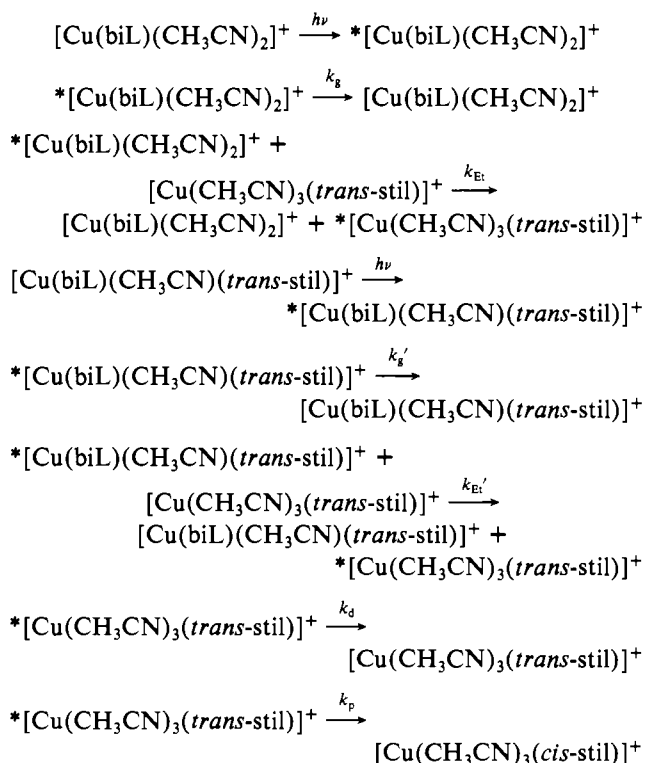
Scheme I



biL π^* CTTL excited state, the subscript b denotes perhaps the Cu $d\pi \rightarrow$ stilbene π^* or stilbene $\pi \rightarrow \pi^*$ excited state, and

ISC and IC are intersystem crossing and internal conversion, respectively), $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})(\text{trans-stil})]^+$ absorbs the visible light, yielding the Cu $d\pi \rightarrow$ biL π^* CTTL excited state. Then, internal conversion and/or intersystem crossing results in the reactive excited state, in which the *trans* \rightarrow *cis* isomerization proceeds perhaps through the alkyl complex as in the isomerization in $\text{W}(\text{CO})_5(\text{trans-stil})$.¹¹ The role of the Cu(I)-biL part is to absorb the visible light, and another role of Cu(I) is to stabilize the twisted structure of the stilbene intermediate between the *cis* form and the *trans* form by stilbene coordination to Cu(I), where the Cu-carbon σ bond is formed and the olefinic C=C bond character becomes small, leading to the easy rotation of the phenyl groups about the C-C bond. As a result, the *trans* \rightarrow *cis* isomerization becomes easier than in the uncomplexed stilbene. In another mechanism shown in Scheme II, *trans*-stilbene isomerizes to its *cis* form in $[\text{Cu}(\text{CH}_3\text{CN})_3(\text{trans-stil})]^+$, which cannot absorb the visible light by itself but receives the excitation energy from the excited Cu(I)-biL complex; $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})(\text{trans-stil})]^+$ and $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})_2]^+$ absorb the visible light ($> 390 \text{ nm}$), yielding the Cu $d\pi \rightarrow$ biL π^* CTTL excited state of these complexes, $[\text{Cu}(\text{CH}_3\text{CN})_3(\text{trans-stil})]^+$ in the ground state collides with the Cu(I)-biL complexes in the excited state to receive the excitation energy, leading to the excited state of $*[\text{Cu}(\text{CH}_3\text{CN})(\text{trans-stil})]^+$, and *trans*-stilbene isomerizes to the *cis* form in the excited state of $*[\text{Cu}(\text{CH}_3\text{CN})_3(\text{trans-stil})]^+$, perhaps through the alkyl complex. The role of $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})_2]^+$ and $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})(\text{trans-stil})]^+$ is to absorb the visible light and to transfer the absorbed light energy to $[\text{Cu}(\text{CH}_3\text{CN})_3(\text{trans-stil})]^+$. The role of $[\text{Cu}(\text{CH}_3\text{CN})_3(\text{trans-stil})]^+$ is probably to make the above-mentioned energy transfer possible by lowering the excited state of $[\text{Cu}(\text{CH}_3\text{CN})_3(\text{trans-stil})]^+$ relative to that of the uncomplexed *trans*-stilbene and to stabilize the twisted structure of the stilbene intermediate by stilbene coordination to Cu(I), as described in Scheme I.

Scheme II



Scheme II can interpret smoothly the result that the maximum catalytic activity is attained at $[\text{biL}]/[\text{Cu}(\text{CH}_3\text{CN})_4]^+ = 0.5$, where it is of course assumed that the contribution of

(15) Coleman, J. S.; Varga, L. P.; Mastin, S. H. *Inorg. Chem.* **1970**, *9*, 1015.

(16) Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2296.

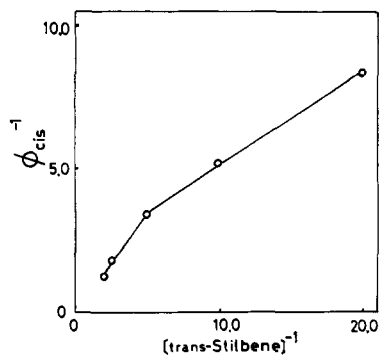


Figure 6. Stern-Volmer relationship in the *trans* → *cis* isomerization of stilbene catalyzed by the $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ -phen system; $[\text{Cu}(\text{CH}_3\text{CN})_4]^+ = 5 \times 10^{-3} \text{ mol/dm}^3$, $[\text{phen}] = 2.5 \times 10^{-3} \text{ mol/dm}^3$, and the L-39 and C-40C cutoff filters were used.

eq 3 is small. However, this mechanism needs the energy transfer between transition-metal complexes, which is usually considered to be novel. Scheme I does not require such energy transfer and seems more probable. However, this mechanism cannot explain the maximum activity at $[\text{biL}]/[\text{Cu}(\text{CH}_3\text{CN})_4]^+ = 0.5$, when eq 3 operates little at $[\text{biL}]/[\text{Cu}(\text{CH}_3\text{CN})_4]^+ = 0.5-1.0$.

Finally, the Stern-Volmer relationship was examined, by using the $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ -phen system. As is shown in Figure 6, the good linear relationship is found at low concentrations of *trans*-stilbene, but the downward deviation occurs at high concentrations of *trans*-stilbene. This feature of the Stern-Volmer relation generally suggests that the variance of the operating mechanism and/or the active species depends on the concentration of *trans*-stilbene. At low concentrations of *trans*-stilbene, equilibria 2-4 are operating, in which the concentration of $[\text{Cu}(\text{CH}_3\text{CN})_3(\text{trans-stil})]^+$ and $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})(\text{trans-stil})]^+$ increases with increasing concentration of *trans*-stilbene, leading to an increase of ϕ_{cis} values in either the mechanism of Scheme I or that of Scheme II. Thus, an increase in ϕ_{cis} with increasing *trans*-stilbene concentration, shown in Figure 6, is qualitatively explained.

At sufficiently high concentrations of *trans*-stilbene, equilibria 7-10 become operating. Resulting species, $[\text{Cu}(\text{biL})(\text{trans-stil})_2]^+$ and $[\text{Cu}(\text{CH}_3\text{CN})_m(\text{trans-stil})_{4-m}]^+$ ($m < 3$) are considered to be more effective for the *trans*-stilbene isomerization than $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})(\text{trans-stil})]^+$ and $[\text{Cu}(\text{CH}_3\text{CN})_3(\text{trans-stil})]^+$, for the increasing numbers of coordinating *trans*-stilbenes increase the probability that *trans*-stilbene participates in the excitation resulting from energy transfer, intersystem crossing, or internal conversion. Consequently, the ϕ_{cis}^{-1} value deviates downward at sufficiently high concentrations of *trans*-stilbene. A further discussion is omitted here, because the present system has complicated equilibria and the relation between ϕ_{cis}^{-1} and $[\text{trans-stilbene}]^{-1}$ cannot be derived here.

Concluding Remarks. New Cu(I) photocatalysts, prepared in situ from $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ and biL (biL = 2,2'-bipyridine, 1,10-phenanthroline, and their derivatives), are presented in this work. These catalysts are the first examples of Cu(I) photocatalysts efficient upon irradiating with visible light (>390 nm) and are as good as $[\text{Ru}(\text{bpy})_3]^{2+}$ if the quantum yield for *cis*-stilbene formation and the *cis*-stilbene/*trans*-stilbene mole ratio at a photostationary state are considered. Thus, further application to the other reaction is expected to be possible. Two kinds of reaction mechanisms are presented: In one, the active species is $[\text{Cu}(\text{biL})(\text{CH}_3\text{CN})(\text{trans-stil})]^+$ and the *trans* → *cis* isomerization of stilbene proceeds in the excited state of this complex resulting from the visible light absorption. In the other, the Cu(I)-biL complexes absorb the visible-light energy and transfer it to $[\text{Cu}(\text{CH}_3\text{CN})_3(\text{trans-stil})]^+$, in whose excited state the *trans* → *cis* isomerization proceeds. Experimental results are explainable for both mechanisms, but the former mechanism seems more probable, for this mechanism does not need the novel energy transfer between transition-metal complexes.

Acknowledgment. We wish to thank the reviewers for instructive suggestions about the reaction mechanism.

Registry No. $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$, 14057-91-1; bpy, 366-18-7; phen, 66-71-7; 2,9-dmp, 484-11-7; 4,7-dmp, 3248-05-3; 4,7-dpp, 1662-01-7; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0.

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Reaction of Nickel Electrode Surfaces with Anionic Metal-Cyanide Complexes: Formation of Precipitated Surfaces

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Anionic metalcyanide complexes ($\text{Fe}(\text{CN})_6^{3-}$, $\text{Ru}(\text{CN})_6^{3-}$, $\text{Mn}(\text{CN})_6^{3-}$, $[\text{Fe}(\text{CN})_{6-x}\text{L}_x]^{n-}$) ($\text{L} = \text{H}_2\text{O}$, NO, histidine, 1,2-cyclohexyldiamine) capable of precipitating aqueous Ni^{2+} are immobilized on Ni electrodes by potentiostating the electrode in aqueous solutions of the anions. The surface coverage obtained is shown to be a function of composition of derivatizing solution, nickel surface pretreatment, electrode potential, and the reaction time. Diffuse-reflectance FT IR spectra of derivatized Ni surfaces show a cyano-bridged bimetallic structure. The cyclic voltammograms of surface-immobilized $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Ru}(\text{CN})_6^{3-}$ show zero peak to peak separation and 110-mV peak width at half-height, close to the ideal case for surface-attached species. These surfaces are very stable with ~10% loss on >18 000 potential cycles between the Fe^{II} and Fe^{III} states. The $E_{1/2}$ value and the shape of the surface cyclic voltammetric wave are shown to depend strongly on the supporting electrolyte cation. These surfaces also show a cation selectivity, indicating an ordered structure. Such surfaces are shown to stabilize the Ni electrode surface against oxide formation while allowing various solution redox couples to react at the electrode. Thus, reaction specificity can be induced by this type of derivatization.

It is now well established that surface derivatization techniques can be employed to synthesize electrochemical interfaces having specific charge-transfer properties. Such techniques have been applied to both standard electroanalytical electrode materials¹ and various photosensitive semiconducting

electrodes.² Very little effort, however, has been exerted to apply these approaches to the modification and control of

(1) Murray, R. W. *Acc. Chem. Res.* 1980, 13, 135.

(2) Wrighton, M. S. *Acc. Chem. Res.* 1979, 12, 303.