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Photocatalytic reduction of carbon dioxide using [*fac*-Re(bpy)$(CO)_3$(4-Xpy)]$^+$ (Xpy = pyridine derivatives)

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Abstract

Photocatalytic reduction of CO_2 using [*fac*-Re(bpy)$(CO)_3$(4-Xpy)]$^+$ [bpy = 2,2′-bipyridine, py = pyridine, X = *tert*-Bu, Me, H, MeCO, CN] in a triethanolamine (TEOA)–dimethylformamide (DMF) solution was examined. The quantum yields for CO formation were almost identical for each (0.03 to 0.04), except for the 4-CNpy complex. Irradiating the solutions caused ligand substitution of these complexes with solvent molecules to produce [*fac*-Re(bpy)$(CO)_3$(TEOA)]$^+$ and [*fac*-Re(bpy)$(CO)_3$(DMF)]$^+$, followed by formation of the formate complex [*fac*-Re(bpy)$(CO)_3${OC(O)H}], which acts as the real catalyst for CO formation. On the other hand, the much higher CO formation ability observed for the 4-CNpy complex (quantum yield for CO formation = 0.13) was due to the participation of the cyano complex [*fac*-Re(bpy)$(CO)_3$CN], which is converted from the 4-CNpy complex during irradiation. The photochemical substitution of the initial complexes with the solvent molecules is very rapid (quantum yields >1). This phenomenon is explained by a chain mechanism.

Keywords: Rhenium bipyridine complex; Pyridine; CO_2-reduction; Photocatalyst

1. Introduction

Rhenium bipyridine complexes have received a great deal of attention with regard to their photophysical and photochemical properties [1]. They show unique excited-state properties such as long lifetimes and high emission quantum yields [1–4]. Furthermore, they can act as photocatalysts for the selective reduction of CO_2 to CO in the presence of amines, for example, triethanolamine (TEOA) [5–10]. Although there have been numerous studies on their emission and related photoelectron-transfer properties, relatively few reports have focused on their CO_2-photoreduction catalysis. It has been generally accepted that the initiation process of their photocatalysis is an electron transfer from the amine to the excited complexes [3–12]. However, the following processes have not been explored for many years. From this point of view, we recently examined photocatalytic CO_2-reduction by rhenium bipyridine complexes having phosphorus ligands [*fac*-Re(bpy)$(CO)_3$L]$^+$ [bpy = 2,2′-bipyridine, L = phosphine, phosphite]. We found that the dark reaction between CO_2 and the one electron-reduced species of these complexes, which are generated by the photoelectron transfer, plays an important role in the catalytic CO formation [8]. We also reported that a photoinduced chain reaction of ligand substitution with solvent molecules occurs in the CO_2-photoreduction system of [*fac*-Re(bpy)$(CO)_3PPh_3$]$^+$ [9]. In the present work, we examine CO_2-photoreduction by a series of complexes having pyridine (py) derivatives: [*fac*-Re(bpy)$(CO)_3$(4-{*tert*-Bu}py)]$^+$ (**1**); [*fac*-Re(bpy)$(CO)_3$(4-Mepy)]$^+$ (**2**); [*fac*-Re(bpy)$(CO)_3$(py)]$^+$ (**3**); [*fac*-Re(bpy)$(CO)_3$(4-MeCOpy)]$^+$ (**4**); and [*fac*-Re(bpy)$(CO)_3$(4-CNpy)]$^+$ (**5**). The reaction mechanisms were elucidated using in situ UV–Visible (UV–Vis) spectral, high-performance liquid chromatographic (HPLC) and electrospray (ES) mass spectrometric techniques.

2. Experimental details

2.1. Materials

All reagents and solvents were of high purity and were commercially available from Kanto Chemical Co. and

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Table 1
Analytical and spectral data for [fac-Re(bpy)(CO)3(4-Xpy)][SbF_6]

Complex	X	Found (calculated) (%)			ν_{Co} (cm^{-1})[a]	m/z[b]
		C	H	N		
1	*tert*-Bu	33.28 (33.14)	2.60 (2.65)	5.09 (5.27)	2035, 1930	562
2	Me	30.14 (30.21)	1.90 (2.00)	5.43 (5.56)	2036, 1931	520
3	H	29.17 (29.17)	1.76 (1.77)	5.43 (5.67)	2036, 1932	506
4	MeCO	30.68 (3067)	1.89 (1.93)	5.23 (5.36)	2037, 1934	548
5	CN	29.97 (29.78)	1.47 (1.58)	6.98 (7.31)	2038, 1937	531

[a] Measured in an MeCN solution.

[b] Positive ion ESMS. The *m/z* values are corresponding to the cation [*fac*-Re(bpy)$(CO)_3$(4-Xpy)]$^+$.

Aldrich Chemical Company. The solvents TEOA and DMF were distilled under reduced pressure and kept under an argon atmosphere. The complex [*fac*-Re(bpy)$(CO)_3$-(MeCN)][SbF_6] was prepared by a reported method [4]. The complex [*fac*-Re(bpy)$(CO)_3$(4-Xpy)][SbF_6] was synthesized using a procedure analogous to the reported method for [*fac*-Re(bpy)$(CO)_3$(py)][PF_6] [4], with some modifications as follows. The MeCN complex [*fac*-Re(bpy)$(CO)_3$(MeCN)][SbF_6] (0.20 g, 0.28 mmol) and a 50-fold molar excess of the appropriate 4-Xpy ligand were dissolved in THF (50 ml). The solution was heated at reflux under an argon atmosphere for 8 h in dim light. After cooling to room temperature, the solution was evaporated to dryness and recrystallized from MeCN-Et_2O or CH_2Cl_2-Et_2O to give [*fac*-Re(bpy)$(CO)_3$(4-Xpy)][SbF_6]. The purity of these complexes was checked by elementary analysis, IR (ν_{CO}) and ES-mass spectra (summarized in Table 1).

2.2. Photochemical procedures

A high pressure Hg lamp (500 W) with a band pass filter (365 nm) was used to produce 365 nm monochromatic light. Neutral density (ND) filters were added to the irradiation system to adjust light intensity. The incident light intensity was determined by a $K_3[Fe(C_2O_4)_3]$ actinometer. A TEOA–DMF (1 : 5, v/v) solution (4 ml) containing the complex was placed in an 8 ml cubic quartz cell. The solution was purged with CO_2 for 20 min, then sealed with a rubber septum (Aldrich). Finally, the sample solution was irradiated while stirring at 20°C. In all runs, the stirring speed was kept constant.

2.3. Measurements

Emission lifetimes of the complexes and the TEOA quenching rate constants were measured using the previously reported flash photolysis technique [7–10]. In situ UV–Vis spectra were measured by a Photal MCPD-1000 spectrometer connected by optical fiber to the reaction cell. We used a reversed-phase HPLC system consisting of a JASCO PV-980 pump, a Nakalai 5C18-ODS column, a JASCO UV-970 detector (wavelength: 360 nm) and a Rheodyne 7125 injector. The mobile phase was a mixture of MeOH and KH_2PO_4–NaOH buffer (0.05 M, pH = 5.9). Positive-ion ES mass spectra of the reaction solutions were measured following a previously reported procedure [13,14]. The drift voltage was set at 10 V, where no fragment ions were detected. The CO produced was analyzed with a Yanaco G-3800 gas chromatograph using an active carbon column (2 m) and a thermal conductivity detector.

3. Results and discussion

3.1. Photophysical properties of the complexes and reaction with TEOA

All of the complexes presented here had an absorption maximum around 340 to 350 nm. The absorption bands were solvent sensitive; a red-shift was caused by changing from a polar to less polar solvent. This phenomenon is often observed in the metal-to-ligand charge transfer (MLCT) absorption of metal–polypyridine complexes, including other rhenium-bpy complexes [3–12,15,16]. A broad emission of around 540 to 550 nm was observed from the ^{3}MLCT excited state at room temperature. The photophysical properties of these complexes (summarized in Table 2) were similar to those for other reported rhenium-bpy complexes[3–12,15,16]. As for the effect of the pyridine substituents on the absorption and emission properties, an increase in the electron accepting strength of the substituent caused shorter MLCT absorption and emission wavelengths (λ_{MLCT} and λ_{em}). This tendency indicates that an electron

Table 2
UV–Visible absorption, emission and quencing data for [*fac*-Re(bpy)-$(CO)_3$(4-Xpy)]$^{+a}$

Complex	X	λ_{MLCT} (nm)	λ_{em} (nm)	τ_{em} (ns)	k_q[b] (10^8 $M^{-1}s^{-1}$)
1	*tert*-Bu	349	550	206	3.00
2	Me	350	549	210	2.70
3	H	345	545	250	3.46
4	MeCo	344, sh	541	308	4.31
5	CN	342, sh	540	418	6.62

[a] Measured in an MeCN solution.

[b] Quenching rate constant by TEOA.

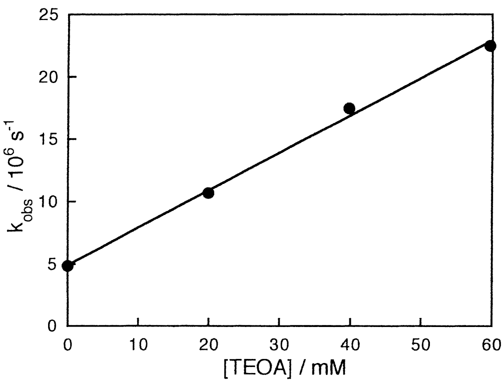

Fig. 1. Stern–Volmer plot for the quenching of the luminescence of the 4-(*tert*-Bu)py complex **1** by TEOA in an argon saturated MeCN solution. k_{obs} = observed rate constant of luminescence decay of **1**.

should locate on the bpy ligand, but not on the 4-Xpy ligand in both the singlet and triplet MLCT excited states of these complexes. Comparing the emission lifetimes (τ_{em}) observed here in MeCN with those of some complexes in CH_2Cl_2 [16], the values in CH_2Cl_2 are about twice those in MeCN. This agrees well with the tendency observed for [*fac*-Re(LL)$(CO)_3$Cl] (LL = bpy, phenanthroline) [3]. The shorter τ_{em} in the more polar solvent is attributed to an increase in non-radiative decay rate from the excited state. The τ_{em} values increase with a decrease in λ_{em}. This fact is consistent with the energy gap low [4]; an increase in the energy of an excited state decreases its non-radiative decay rate.

It has been reported that emission from some rhenium-bpy complexes having pyridine-derivative ligands is quenched by oxygen [16]. However, there have been no reports of the reductive quenching of these excited states. Fig. 1 shows a Stern–Volmer plot for the quenching of the luminescence of the 4-(*tert*-Bu)py complex **1** by TEOA. The quenching rate constant (k_q) was 3.00×10^8 $M^{-1}s^{-1}$. The k_q values of all these complexes are in the order of 10^8 M^{-1} s^{-1} (Table 2), which are similar to those of reductive quenching by TEOA of other excited rhenium-bpy tricarbonyl complexes [3,5–9,11,12]. The k_q value increases with an increase in the electron accepting strength of the pyridine substituent.

3.2. CO_2-photoreduction

Irradiating TEOA–DMF solutions containing complexes **1** to **5** caused catalytic reduction of CO_2 to CO. Fig. 2 shows the dependence of CO formation on irradiation time. The 4-CNpy complex **5** shows a relatively long induction period of CO formation (approximately 3 h), in contrast to other complexes. Table 3 lists the quantum yields for CO formation (Φ_{CO}) together with the quantum yields for decrease of the initial complexes (Φ_I) described in the following section. No significant differences were observed between the Φ_{CO} values of the complexes **1** to **4**. However, the value of complex **5** was exceptionally higher than the others.

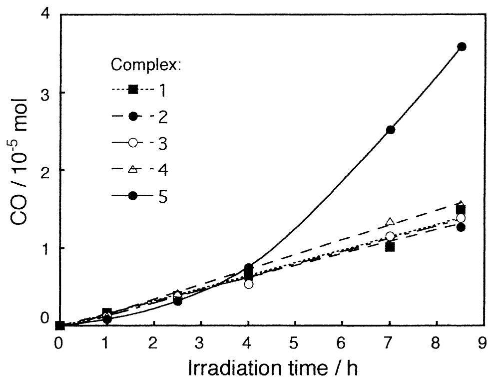

Fig. 2. Variations of CO formation with irradiation time. A CO_2-saturated TEOA–DMF solution (1 : 5, v/v) containing each complex (2.60 mM) was irradiated (365 nm, light intensity = 8.05×10^{-7} einstein min^{-1}; 1 einstein $\cong 6.022 \times 10^{23}$ photons)

Table 3
Quantum yields of CO formation (Φ_{CO})[a] and decomposition of [*fac*-Re(bpy)$(CO)_3$(4-Xpy)$]^+$(Φ_I)[b]

Complex	X	Φ_{CO}	Φ_I
1	*tert*-Bu	0.03	8.5
2	Me	0.03	12.5
3	H	0.03	50.3
4	MeCO	0.04	1.2
5	CN	0.13	9.9

[a] Measured after the induction period; calculated by the following equation: amount of CO/light intensity.

[b] Measured by HPLC; the mixing ratios (MeOH : KH_2PO_4-NaOH buffer) of mobile phase were 40 : 60, 50 : 50, and 60 : 40 (v/v) for the complexes (**3** and **4**), (**2** and **5**), and **1**, respectively.

3.3. Reaction monitoring

Fig. 3 shows the in situ UV–Vis spectral changes for a CO_2-saturated TEOA–DMF solution of the 4-Mepy complex **2** during 365 nm irradiation. The spectrum taken after irradiating for 119 s had an absorption maximum at approximately 490 nm [Fig. 3(b)]. This absorption is assigned to the

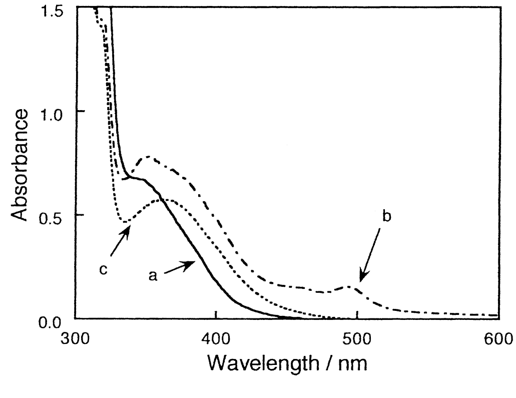

Fig. 3. In situ UV–Visible spectral changes for a CO_2-saturated TEOA–DMF solution (1 : 5, v/v) of the 4-Mepy complex **2** (0.17 mM) during 365 nm irradiation for (a) 0, (b) 119, and (c) 383 s. Light intensity was 1.12×10^{-7} einstein min^{-1}

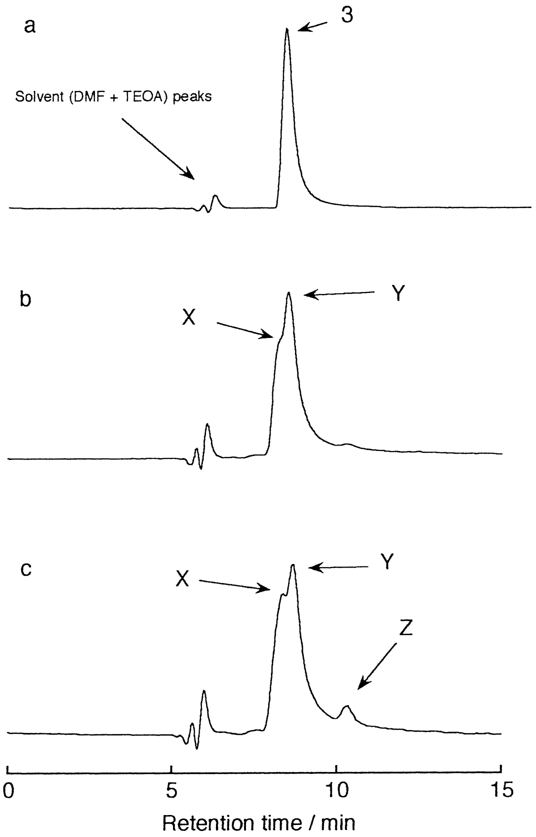

Fig. 4. Changes in HPLC chromatograms of a CO_2-saturated TEOA–DMF solution (1 : 5, v/v) of the py complex **3** (2.60 mM) before and after 365 nm irradiation. Light intensity was 8.05×10^{-7} einstein min^{-1}. Irradiation time was (a) 0, (b) 1, and (c) 4 h. The mobile phase composition was 60 : 40 (v/v) of MeOH / KH_2PO_4-NaOH buffer (0.05 M, pH = 5.9). It is clear that the irradiated samples (b, c) included no initial complex **3** because the corresponding ES-mass spectra showed no peak of **3** ($m/z = 506$). See Fig. 5(b) and (c).

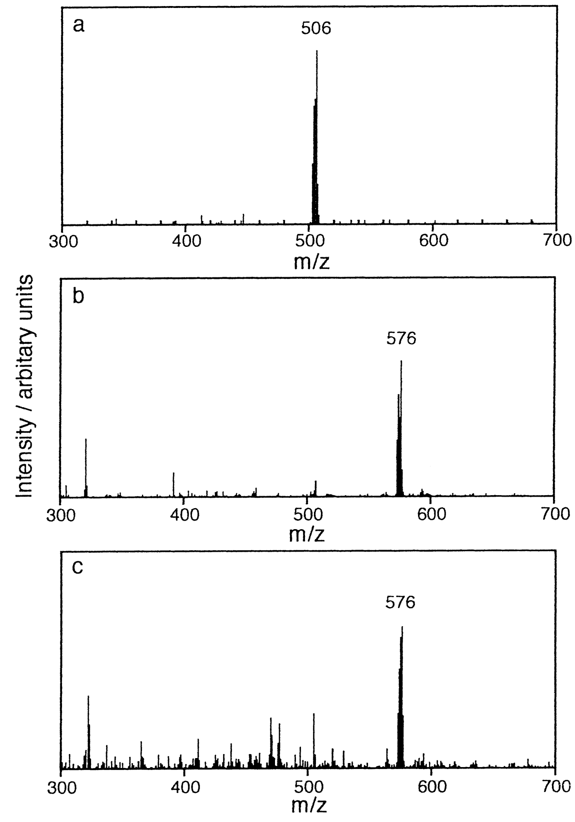

Fig. 5. Changes in ES-mass spectra of a CO_2-saturated TEOA–DMF solution (1 : 5, v/v) of the py complex **3** (2.60 mM) before and after 365 nm irradiation. The light intensity was 8.05×10^{-7} einstein min^{-1}. Irradiation time was (a) 0, (b) 1, and (c) 4 h. The neutral complex **6** shows no signal because complexes with no charges are hard to detect by ES-mass spectrometry unless ionized by addition of some ionization agent [14].

one-electron reduced species of **2** [7–12]. Further irradiation caused a decrease in the absorption of the one- electron reduced species and gave a new absorption maximum at approximately 370 nm [Fig. 3(c)]. No further changes occurred after 383 s irradiation. The spectral changes for complexes **1**, **3**, and **4** were very similar to those for **2**. We have previously reported similar spectral changes for the photocatalytic reduction of CO_2 using [*fac*-Re(bpy)$(CO)_3PPh_3]^+$ [9], where the final product having an absorption maximum at approximately 370 nm is the formate complex, [*fac*-Re(bpy)$(CO)_3\{OC(O)H\}$] (**6**).

Figs. 4 and 5 show the changes of HPLC chromatograms and ES-mass spectra for a CO_2-saturated TEOA-DMF solution of the py complex **3** during the 365 nm irradiation. Before irradiation, **3** was stable in the solution and no other complexes were detected [Fig. 4(a) and Fig. 5(a)]. When irradiation started, the initial complex vanished rapidly and two new peaks marked X and Y appeared in the HPLC chromatogram [Fig. 4(b)]. Further irradiation caused decreases in X and Y, which resulted in the appearance of a peak marked Z [Fig. 4(c)]. Other complexes **1**, **2**, and **4** showed almost the same pattern. The species that gave peak Z was isolated by extraction with CH_2Cl_2–water. It was identified as the formate complex **6** because its ES-mass spectrum, using sodium ion as an ionization agent, gave the sole peak corresponding to $[\mathbf{6} + Na]^+$ ($m/z = 495$). The intermediates that gave peaks X and Y appeared not only under CO_2, but also under an argon atmosphere. These species easily changed to [*fac*-ClRe(bpy)$(CO)_3$] when an excess NEt_4Cl was added and then warmed. Therefore, they were suggested to be complexes having an easily removable ligand, such as a solvent molecule. Actually, a DMF complex [*fac*-Re(bpy)$(CO)_3(DMF)]^+$ (**7**), which was prepared by a reaction of [*fac*-ClRe(bpy)$(CO)_3$] and Ag^+ in a DMF solution, showed the same retention time as that of X. Furthermore, the ES-mass spectra of irradiated solutions of **1** to **4** revealed a peak of $m/z = 576$ for a single positively charged species, which is attributable to a TEOA complex [*fac*-Re(bpy)$(CO)_3(TEOA)]^+$ (**8**) [Fig. 5(b and c)]. Unfortunately, no peak corresponding to the DMF complex **7** was detected in the ES-mass spectra. Complex **7** should be decomposed during the ES-mass spectral measurements

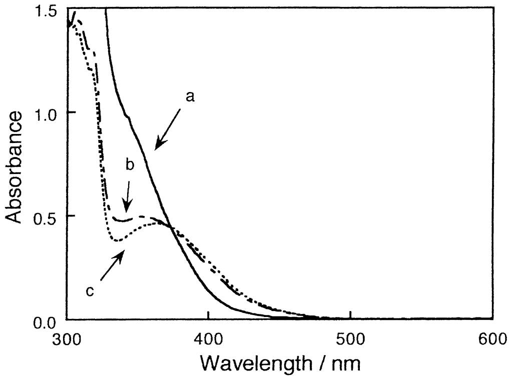

Fig. 6. In situ UV-Vis spectral changes for a CO_2-saturated TEOA–DMF solution (1 : 5, v/v) of the 4-CNpy complex **5** (0.17 mM) during 365 nm irradiation for (a) 0, (b) 89, and (c) 383 s. Light intensity was 1.12×10^{-7} einstein min^{-1}

as described in Hori et al [9]. Therefore, Y was identified as **8** and X was supposed to be derived from the DMF complex **7**.

Lehn and co-workers reported that the formate complex **6** photocatalyzes selective reduction of CO_2 to CO in the similar reaction condition to our systems [6]. Because complexes **7** and **8** do not produce CO by themselves [9], the CO formation using complexes **1** to **4** should be caused by the photocatalysis[2] of the formate complex **6**, which is photochemically produced from **7** and/or **8**. In fact, the Φ_{CO} values for **1** to **4** (Table 3) are similar to that for complex **6** (~0.04, which was calculated using Lehn's data) [6].

Spectroscopic and chromatographic changes of the 4-CNpy complex **5** during irradiation were much different from those of **1** to **4**. Fig. 6 shows the in situ UV–Vis spectral changes for a CO_2-saturated TEOA–DMF solution of **5** during 365 nm irradiation. Only a very small amount of the one-electron reduced species, which shows an absorption maximum at approximately 490 nm, was accumulated and then the absorption maximum in the spectrum, which did not change during further irradiation, was observed. This final product was extracted with CH_2Cl_2–water and then purified by silica-gel chromatography using MeOH–ethyl acetate as an eluent. Finally, the resulting species were identified as the formate complex **6** and the cyano complex [*fac*-Re(bpy)$(CO)_3$CN] (**9**) by comparing their NMR, IR and UV–Vis spectra with those of authentic samples prepared by reported methods [6,17,18]. We have previously reported the photoinduced cyano group rearrangement from **5** to **9** in the presence of TEOA [19]. The same phenomenon occurs in the present photocatalytic reaction. Fig. 7 shows the changes in HPLC chromatograms for a CO_2-saturated TEOA–DMF solution of the 4-CNpy complex **5** during irradiation. When irradiation started, peaks X and Y appeared similar to those of complexes **1** to **4** [Fig. 7(b)]. Further irradiation caused peaks Z and U, which correspond to the formate complex **6** and the cyano complex **9**, respectively [Fig. 7(c)].

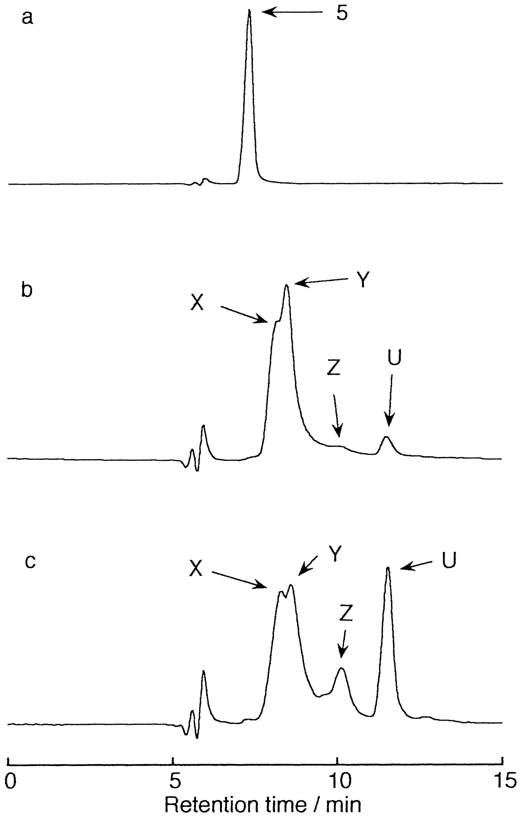

Fig. 7. Changes in HPLC chromatograms of a CO_2-saturated TEOA–DMF solution (1 : 5, v/v) of the 4-CNpy complex **5** (2.60 mM) before and after 365 nm irradiation. Light intensity was 8.05×0^{-7} einstein min^{-1}. Irradiation time was (a) 0, (b) 1, and (c) 4 h. The mobile phase composition was 60 : 40 (v/v) of MeOH/KH_2PO_4–NaOH buffer (0.05 M, pH = 5.9).

The sole use of **9** instead of **5** also produced catalytic CO_2-reduction to CO, where the Φ_{CO} value was 0.20. Although the mechanism of the photocatalytic reaction by **9** has not been known yet, complex **9** should play an important role in the photocatalytic CO formation using **5**. Actually, the photoreaction system of **5** showed the high Φ_{CO} value of 0.13 (Table 3), while that by the sole use of **6** was ~0.04 as described above.

3.4. Pyridine-ligand substitution reaction with a solvent molecule: participation of a chain reaction mechanism

As described above, complexes **1** to **5** changed to the solvent complexes **7** and **8** during irradiation in the presence of TEOA. Fig. 8 shows the decrease of the 4-(*tert*-Bu)py complex **1** in a CO_2-saturated TEOA–DMF solution by 365 nm irradiation. The photochemical formation of **7** and **8** should be proceed via chain reactions because the quantum yield for decrease of **1** (Φ_I) was estimated to be 8.5 and those of complexes **2** to **5** also exceeded unity (Table 3). Wrighton and co-workers reported the chain ligand substi-

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[2] Small difference of the quantum yields between our systems and the reported photocatalytic system using **6** may arise from inner-filter effects by decomposition products from the rhenium complexes during irradiation

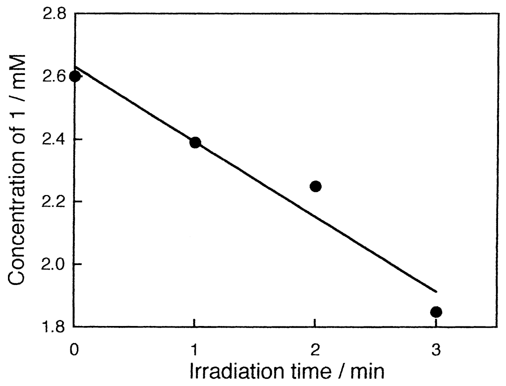

Fig. 8. Decrease of the 4-(*tert*-Bu)py complex **1** in a CO_2-saturated TEOA–DMF solution (1 : 5, v/v) during 365 nm irradiation. Light intensity was 1.12×10^{-7} einstein min^{-1}.

tution of [*fac*-Re(phen)$(CO)_3$(MeCN)]$^+$ (phen = 1,10-phenanthroline) by pyridine or PPh_3 in the presence of an electron donor [20]. We have also observed a similar phenomenon in the CO_2-reduction system using [*fac*-Re(bpy)$(CO)_3PPh_3$]$^+$, that is, the initial complex rapidly changes to the solvent complexes **7** and **8** with a Φ_I of 16.9, which is attributable to a chain mechanism [9]. The ligand substitution from complexes **1–5** to complexes **7** and **8** should also proceed via the chain reaction, illustrated in the case of **1** as follows:

$$\mathbf{1} + h\nu \rightarrow \mathbf{1}^*(^3\mathrm{MLCT}) \qquad (1)$$

$$\mathbf{1}^* + \mathrm{TEOA} \rightarrow \mathbf{1}^- + \mathrm{TEOA}^{\bullet +} \qquad (2)$$

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$$\mathbf{1}^- + \mathrm{DMF\ or\ TEOA} \rightarrow \mathbf{7}^- \text{ or } \mathbf{8}^- + \mathbf{4}\text{-}(tert\text{-Bu})\text{ py} \qquad (3)$$

$$\mathbf{1} + \mathbf{7}^- \text{ or } \mathbf{8}^- \rightarrow \mathbf{1}^- + \mathbf{7} \text{ or } \mathbf{8} \qquad (4)$$

The excited species $\mathbf{1}^*$ generated by irradiation (Eq. (1)) is reduced by TEOA to the one-electron reduced species $\mathbf{1}^-$ (Eq. (2)), of which the (*tert*-Bu)py ligand is substituted with DMF or TEOA to give $\mathbf{7}^-$ or $\mathbf{8}^-$ (Eq. (3)). Subsequent electron exchange of $\mathbf{7}^-$ and $\mathbf{8}^-$ with another **1** leads to the formation of **7** and **8** accompanied by the regeneration of $\mathbf{1}^-$(Eq. (4)). The reduction potentials of **1–5** ($-1.11 \sim -1.27$ V versus $Ag/AgNO_3$) were more positive than that of [*fac*-Re(bpy)$(CO)_3PPh_3$]$^+$ (-1.40 V), of which chain ligand substitution to **7** and **8** has been reported in the similar reaction condition to this study [9]. Although the reduction potentials of **7** and **8** have not been known because of their difficulty to be isolated, the electron exchange shown in Eq. (4) should be reasonable.

4. Conclusion

Photochemical reduction of CO_2 using [*fac*-Re(bpy)-$(CO)_3$(4-{*tert*-Bu}py)]$^+$ (**1**), [*fac*-Re(bpy)$(CO)_3$(4-Mepy)]$^+$ (**2**), [*fac*-Re(bpy)$(CO)_3$(py)]$^+$ (**3**), [*fac*-Re(bpy) $(CO)_3$-(4-MeCOpy)]$^+$ (**4**) and [*fac*-Re(bpy)$(CO)_3$(4-CNpy)]$^+$ (**5**) in a TEOA–DMF solution was examined. All systems produced CO catalytically. The reaction mechanisms for complexes **1** to **4** were almost identical, that is, the initial complexes caused the ligand substitution with the solvent molecules to form [*fac*-Re(bpy)$(CO)_3$ (DMF)]$^+$ (**7**) and [*fac*-Re(bpy)$(CO)_3$(TEOA)]$^+$ (**8**), followed by the formation of the formate complex **6** which acted as the real catalyst for CO formation. On the other hand, in the case of the 4-CNpy complex **5**, the cyano complex [*fac*-Re(bpy)$(CO)_3$CN] (**9**) was formed in the initial stage of the reaction, which resulted in higher photocatalysis for CO_2 reduction.

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