Photochemistry of $[Re(bipy)(CO)_3(PPh_3)]^+$ (bipy = 2,2′-bipyridine) in the presence of triethanolamine associated with photoreductive fixation of carbon dioxide: participation of a chain reaction mechanism

Hisao Hori,*[a] Frank P. A. Johnson,[a] Kazuhide Koike,[a] Koji Takeuchi,[a] Takashi Ibusuki[a] and Osamu Ishitani*[b]

[a] *National Institute for Resources and Environment, 16-3 Onogawa, Tsukuba, Ibaraki 305, Japan*
[b] *Graduate School of Science and Technology, Saitama University, 255 Shimo-Okubo, Urawa, Saitama 338, Japan*

The complex *fac*-$[Re(bipy)(CO)_3(PPh_3)]^+$ **1**$^+$ (bipy = 2,2′-bipyridine) was converted into a formate complex *fac*-$[Re(bipy)(CO)_3\{OC(O)H\}]$ **2** in a 52.2% yield by irradiation in the presence of triethanolamine (teoa) and CO_2. This photochemical fixation of CO_2 proceeds *via* a unique reaction mechanism: (*i*) irradiation of **1**$^+$ in teoa–dimethylformamide (dmf) resulted in the efficient formation of *fac*-$[Re(bipy)(CO)_3(teoa)]^+$ **3**$^+$ and *fac*-$[Re(bipy)(CO)_3(dmf)]^+$ **4**$^+$ in a quantum yield of 16.9; (*ii*) the ligand substitution was explained in terms of a chain mechanism involving an initial electron transfer from teoa to excited **1**$^+$, followed by substitution of the PPh_3 ligand of **1** with teoa and dmf to give **3** and **4**; subsequent electron exchange of **3** and **4** with **1**$^+$ leads to the formation of **3**$^+$ and **4**$^+$ accompanied by the regeneration of **1**; (*iii*) the formate complex **2** was formed in a quantum yield of 1.1×10^{-3} upon excitation of **3**$^+$ and **4**$^+$ in the presence of CO_2; (*iv*) further irradiation after the formation of **2** resulted in the photocatalytic reduction of CO_2 to CO in a quantum yield of 0.05.

Rhenium bipyridine carbonyl complexes have been receiving a great deal of attention from photophysical and photochemical viewpoints.[1–11] The photocatalytic abilities of these complexes have become of interest especially since Lehn and co-workers[2] reported the selective reduction of CO_2 to CO photocatalysed by $[ReX(bipy)(CO)_3]$ (X = Cl or Br). Very recently, we reported[3] that *fac*-$[Re(bipy)(CO)_3\{P(OEt)_3\}]^+$ has the highest photocatalytic ability in the reduction of CO_2 among related homogeneous photocatalysts reported so far. Although the electron transfer to excited-state complexes from an electron donor such as triethanolamine (2,2′,2″-nitrilotriethanol) (teoa) is generally accepted as the initiation process of the photocatalysis, the chemistry of the one-electron-reduced species *fac*-$[Re^I(bipy^{\bullet -})(CO)_3L]^{n-}$ [$n = 1$, L = Cl or Br; $n = 0$, L = $P(OEt)_3$] which may participate in the follow-up processes is still unexplored.[1–6] In other words, it is essential to determine the reactivities of the one-electron-reduced species involving labilization of a ligand or ligands followed by co-ordination of CO_2 to the metal centre. However, little is known on the chemical reactivities of such species except for only a few examples, *i.e.* exchange of a ligand or ligands[7,8] and alkylation of the bipy ligand.[9] In the present study we report the photochemical reaction of *fac*-$[Re(bipy)(CO)_3(PPh_3)]^+$ **1**$^+$ in the presence of teoa associated with the reductive fixation of CO_2. It has been found that the chemical behaviour of the reduced species *fac*-$[Re(bipy^{\bullet -})(CO)_3(PPh_3)]$ **1** is substantially different from that of other related species. A prominent observation is the efficient ligand exchange of **1** with teoa and dimethylformamide (dmf) through a chain reaction mechanism prior to formation of the formate complex *fac*-$[Re(bipy)(CO)_3\{OC(O)H\}]$ **2**, which eventually acts as a ‘real photocatalyst’ for the reduction of CO_2 in the present photoreaction system.

Results and Discussion

Photochemical fixation of CO_2

Fig. 1 shows the *in situ* UV/VIS absorption for a CO_2-saturated dmf solution of complex **1**$^+$ and teoa during 365 nm irradiation. The spectrum taken after 70 s of irradiation was similar to that of the reduced species **1**, as measured by a flow-electrolysis technique (Fig. 2). However, **1** was relatively unstable under this condition and its maximum yield is less than 34% in the photoreaction,† in contrast to the quantitative formation of *fac*-$[Re(bipy^{\bullet -})(CO)_3\{P(OEt)_3\}]$ under similar photoreaction conditions.[3] Irradiation for 230 s gave a new absorption maximum at ≈380 nm, which was relatively stable under irradiation. This final product was isolated by extraction

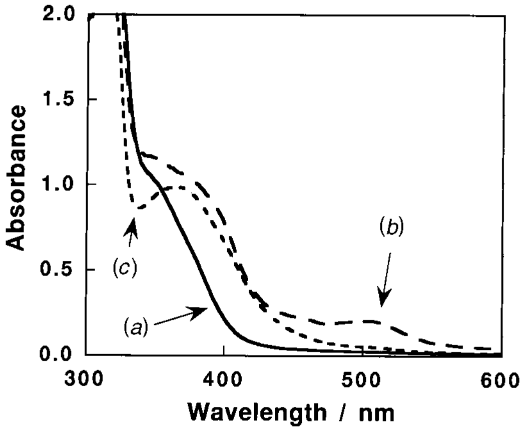

Fig. 1 *In situ* UV/VIS absorption spectra of a teoa–dmf (1:5, v/v) solution containing complex **1**$^+$ (0.25 mmol dm^{-3}) under an atmosphere of CO_2 during irradiation (365 nm) for (*a*) 0, (*b*) 70 and (*c*) 230 s. Path length 1.0 cm

---

† The solution probably contains not only complex **1** but also the reduced species of the complexes having a solvent molecule as a ligand because of the instability of **1** in teoa–dmf solution (see following section). The yield of **1** was calculated by assuming its exclusive contribution to the absorption around 500 nm in Fig. 1(*b*), thus giving a maximum value of 34%.

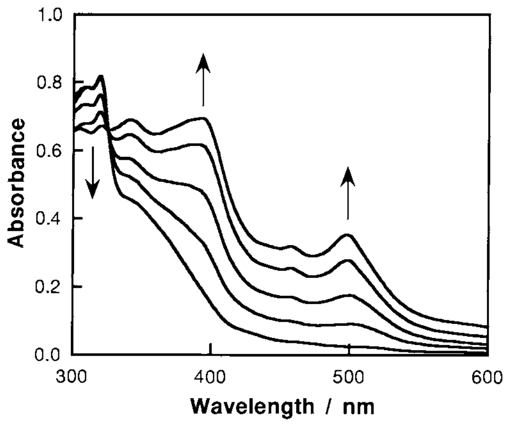

Fig. 2 The UV/VIS absorption spectra recorded following flow electrolysis of complex $\mathbf{1}^+$ (0.5 mmol dm^{-3}) in an Ar-saturated MeCN solution containing 0.1 mol dm^{-3} NBu_4ClO_4. The solution of $\mathbf{1}^+$ was reduced from 0 to −3.0 V *vs.* Ag–$AgNO_3$ at a constant flow rate of 0.3 cm^3 min^{-1}. An ohmic potential drop of several hundred mV was observed between the reference and working electrodes. Path length 3 mm. The arrows indicate the generation of the one-electron reduced species **1**

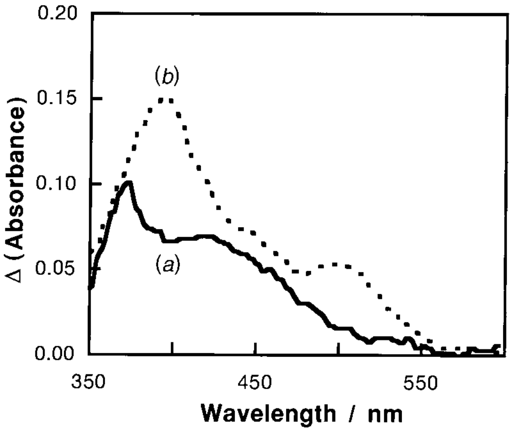

Fig. 3 Difference UV/VIS transient spectra of an Ar-saturated MeCN solution of complex $\mathbf{1}^+$ (0.15 mmol dm^{-3}) recorded (*a*) 20 ns after the laser flash (355 nm) in the absence of teoa, (*b*) 100 ns after the laser flash in the presence of teoa (0.32 mol dm^{-3})

with CH_2Cl_2–water, and identified as the formate complex **2** on the basis of its NMR, IR and UV/VIS spectra which are almost identical with those reported.[2a,10] The yield of **2** was dependent upon irradiation time, and the maximum was 52.2% based on **1** used (see **Mechanistic studies using HPLC and electrospray mass spectrometry**). Under an argon atmosphere, **1** was formed but **2** did not appear at all. These observations can be summarized as in equation (1).

$$\mathbf{1}^+ \xrightarrow[\text{teoa}]{h\nu} \mathbf{1} \xrightarrow[\text{CO}_2]{} \mathbf{2} \qquad (1)$$

Laser flash photolysis

The excited state of complex $\mathbf{1}^+$ emits at $\lambda_{max} = 517$ nm with a lifetime of 416 ns under anaerobic conditions. Fig. 3(*a*) shows a difference transient UV/VIS absorption spectrum of $\mathbf{1}^+$ taken 20 ns after the laser flash, which is attributed to the excited state. The emissive state of $\mathbf{1}^+$ was assigned to a triplet metal-to-ligand charge transfer (^{3}m.l.c.t.) state by comparison with reported transient spectra of other rhenium–bipy complexes.[3–6] While the ^{3}m.l.c.t. state of $\mathbf{1}^+$ was not quenched by CO_2 at all, efficient quenching by teoa occurred at a rate constant of 1.7×10^9 dm^3 mol^{-1} s^{-1}. Fig. 4 shows the Stern–Volmer plots for the quenching of the luminescence of $\mathbf{1}^+$ by teoa. The quenching gives a new species which has broad absorption bands at ≈400 and ≈500 nm [Fig. 3(*b*)]. The spectrum of this new species is similar to that of the one-electron reduced species **1** obtained by the flow-electrolysis method (Fig. 2), strongly suggesting that teoa reductively quenches the ^{3}m.l.c.t. state of $\mathbf{1}^+$ to give **1**.

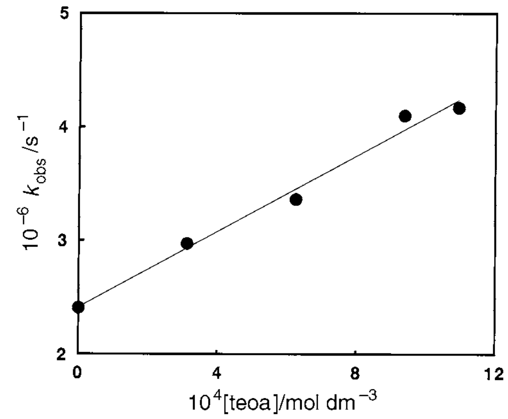

Fig. 4 Stern–Volmer plots for the quenching of the luminescence of complex $\mathbf{1}^+$ by teoa under an argon atmosphere: k_{obs} = observed rate constant of luminescence decay of $\mathbf{1}^+$

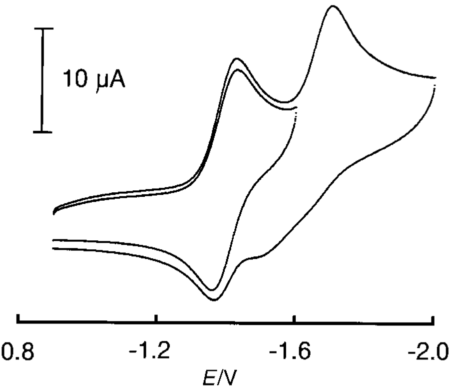

Fig. 5 Cyclic voltammogram of complex $\mathbf{1}^+$ (0.5 mmol dm^{-3}) in an Ar-saturated MeCN solution containing 0.1 mol dm^{-3} NBu_4ClO_4 with a scan rate of 100 mV s^{-1}

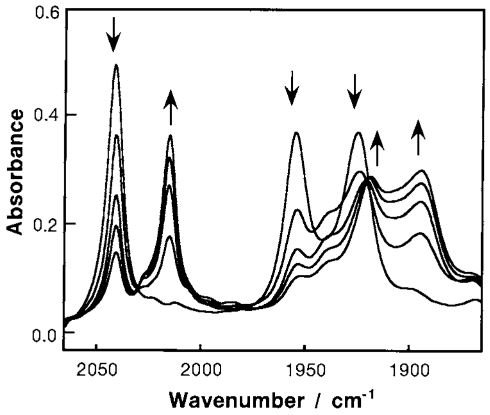

Fig. 6 The ν(CO) IR spectra following flow electrolysis of complex $\mathbf{1}^+$ (0.5 mmol dm^{-3}) in an Ar-saturated MeCN solution containing 0.1 mol dm^{-3} NBu_4ClO_4. The solution of $\mathbf{1}^+$ was reduced from 0 to −1.8 V *vs.* Ag–$AgNO_3$ at a constant flow rate of 0.4 cm^3 min^{-1}. An ohmic potential drop of several hundred mV was observed between the reference and working electrodes. Path length 3 mm. Downward arrows indicate a loss of $\mathbf{1}^+$, upward arrows the generation of the one-electron-reduced species **1**

Electrochemistry

The cyclic voltammogram of complex $\mathbf{1}^+$ in an MeCN solution is shown in Fig. 5. The first reduction is reversible with a half-wave potential of −1.40 V, and the second one chemically irreversible with a peak potential of −1.70 V. Fig. 6 shows the

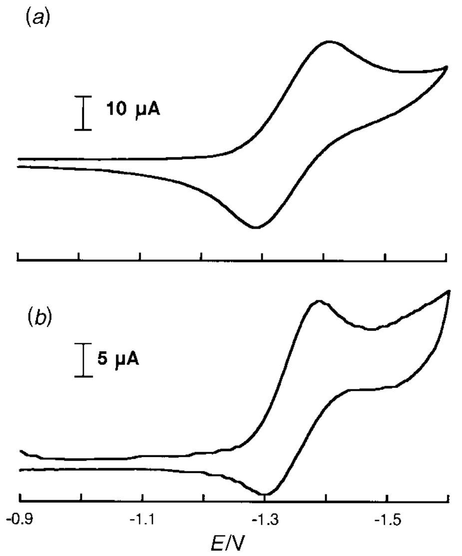

Fig. 7 Cyclic voltammogram of complex **1**$^+$ (5.0 mmol dm^{-3}) in an Ar-saturated dmf solution containing 0.1 mol dm^{-3} NBu_4ClO_4 with scan rates of (*a*) 30 and (*b*) 5 mV s^{-1}

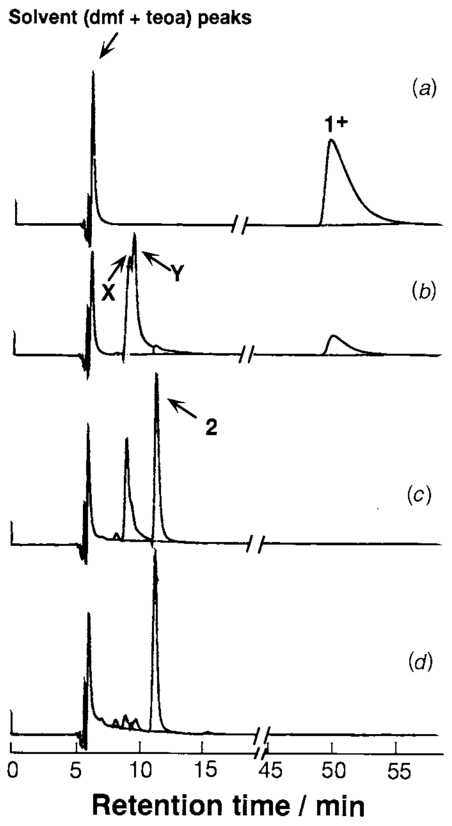

Fig. 8 Changes in HPLC chromatograms upon irradiation for (*a*) 0, (*b*) 5, (*c*) 600 and (*d*) 1200 s. A teoa–dmf solution (1:5, v/v) containing complex **1**$^+$ (1.28 mmol dm^{-3}) was irradiated (>330 nm) under an atmosphere of CO_2 and then introduced into the HPLC apparatus

ν(CO) IR absorption spectra recorded following the flow electrolysis of **1**$^+$ with reduction potentials of 0 to −1.8 V. The IR data indicate that the reduced species generated has the C_s symmetry, the same as **1**$^+$. The three ν(CO) bands of the reduced species are shifted down in frequency from **1**$^+$ by 26, 38 and 31cm^{-1}. In previous reports,[3,6] we have shown that similar low-frequency shifts occur upon one-electron reduction of *fac*-$[Re^I(bipy)(CO)_2\{P(OEt)_3\}_2]^+$ and *fac*-$[Re^I(bipy)(CO)_3\{P(OEt)_3\}]^+$ to the corresponding 19-e$^-$ species *fac*-$[Re^I(bipy^{\bullet-})(CO)_2\{P(OEt)_3\}_2]$ and *fac*-$[Re^I(bipy^{\bullet-})(CO)_3\{P(OEt)_3\}]$. Consequently, the first cathodic wave of the cyclic voltammogram is

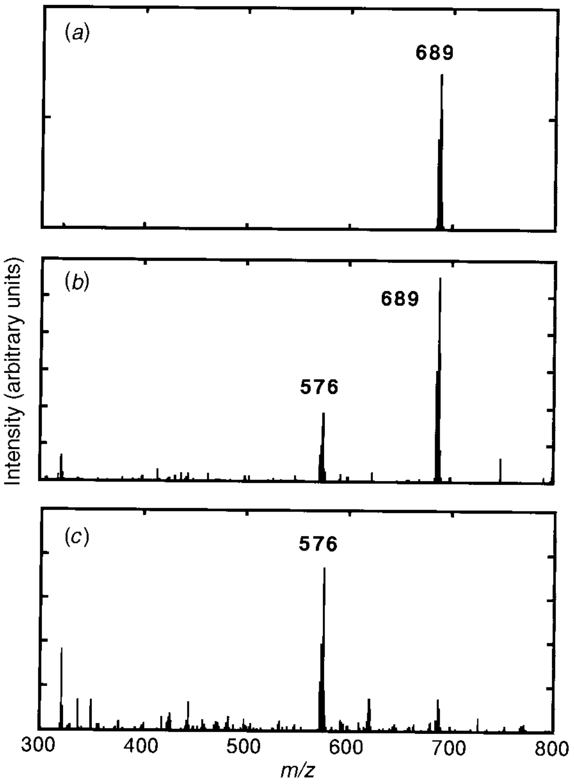

Fig. 9 Changes in electrospray mass spectra upon irradiation for (*a*) 0, (*b*) 5 and (*c*) 600 s. A teoa–dmf solution (1:5, v/v) containing complex **1**$^+$ (1.28 mmol dm^{-3}) was irradiated (>330 nm) under an atmosphere of CO_2 and then introduced into the mass spectrometer

attributable to the one-electron reduction of **1**$^+$ to **1**, and the additional electron of **1** should be located on the bipy ligand. This identification is also supported by the UV/VIS absorption spectrum (Fig. 2), which is similar to those of the one-electron reduced species of other rhenium–bipy complexes.[3,6,11] The cyclic voltammogram in an MeCN solution suggests that **1** is stable in such a solution at least for several seconds. However, **1** is less stable in a dmf solution, as shown by the cyclic voltammogram of **1**$^+$ in dmf at different scanning rates (Fig. 7). The anodic peak at ≈−1.3 V became smaller compared to the corresponding cathodic peak at slower scan rate, accompanied by the appearance of a new anodic peak at ≈−1.5 V. These results suggest that **1** reacts in a dmf solution to give new species that have more negative oxidation potentials than does **1**.

Mechanistic studies using HPLC and electrospray mass spectrometry

The photoreaction of complex **1**$^+$ in teoa–dmf (1:5, v/v) was analysed by HPLC and electrospray (ES) mass spectral measurements on the reaction solutions at different irradiation times (Figs. 8 and 9). Before irradiation **1**$^+$ was stable and no other complexes were detected [Figs. 8(*a*) and 9(*a*)]. When irradiation started HPLC showed a 81.6% loss of **1**$^+$ even after 5 s of irradiation accompanied by the appearance of two new peaks, X and Y. Further irradiation caused decreases in X and Y, which resulted in the formation of the formate complex **2**. Notably, the formation of **2** still proceeded even after the complete consumption of **1**$^+$, but was not increased in the dark after irradiation had been stopped at the maximum formation of X and Y. It is, therefore, strongly suggested that **2** should be photochemically, but not thermally, formed from X and/or Y. When an excess of NBu_4Cl was added and then warmed at 40 °C after the solution had been irradiated until the peaks X and Y attained maxima, $[ReCl(bipy)(CO)_3]$ formed in 78.3% yield based on the initial **1**$^+$ concentration. Therefore, these two species have an easily removable ligand, such as a solvent molecule. As shown in Fig. 9(*b*) and 9(*c*), the ES mass spectra of the irradiated solutions revealed a peak of $m/z = 576$ for a single positively-charged species, which is clearly attributable to *fac*-[Re(bipy)(CO)$_3$(teoa)]$^+$ **3**$^+$. In order to identify another photoproduct we carried out a reaction of [ReCl(bipy)(CO)$_3$] with Ag$^+$ in a dmf solution, which should yield the dmf complex *fac*-[Re(bipy)(CO)$_3$(dmf)]$^+$ **4**$^+$. This reaction product showed the same retention time as that of X in HPLC. Unfortunately, no corresponding peak was detected in the ES mass spectra. Presumably, **4**$^+$ should be labile enough to undergo substitution of the dmf ligand with such anions as OMe$^-$ or OH$^-$, present in the mobile phase. Although ES mass spectrometry is potentially useful for *in situ* analysis of charged metal complexes in solution,[12–14] neutral complexes are hard to detect by this method, unless ionized by addition of some ionizing agents.[14] Consistently, the neutral species [ReCl(bipy)(CO)$_3$] and **2** gave no peaks in the ES mass spectra. Therefore, Y was identified as the teoa complex **3**$^+$, whereas X is supposed to be derived from the dmf complex **4**$^+$.

Photochemical formation of complexes **3**$^+$ and **4**$^+$ from **1**$^+$ should be a chain reaction because the quantum yield of the decrease in **1**$^+$ was 16.9 upon irradiation at 365 nm with intensity 8.30×10^{-10} einstein s^{-1} (1 einstein ≈ 6.022×10^{23} photons). Wrighton and co-workers[8] reported the chain ligand substitution of *fac*-[Re(phen)(CO)$_3$(MeCN)]$^+$ (phen = 1,10-phenanthroline) by pyridine or PPh$_3$ in the presence of an electron donor with quantum yields of $\gg 1$. Based on these results, the mechanism in the present case can be expressed by equations (2)–(5).

$$\mathbf{1}^+ + h\nu \longrightarrow (\mathbf{1}^+)^* \ (^3\text{m.l.c.t.}) \qquad (2)$$

$$(\mathbf{1}^+)^* + \text{teoa} \longrightarrow \mathbf{1} + \text{teoa}^{\cdot +} \qquad (3)$$

$$\mathbf{1} + \text{teoa or dmf} \longrightarrow \mathbf{3} \text{ or } \mathbf{4} + \text{PPh}_3 \qquad (4)$$

$$\mathbf{1}^+ + \mathbf{3} \text{ or } \mathbf{4} \longrightarrow \mathbf{1} + \mathbf{3}^+ \text{ or } \mathbf{4}^+ \qquad (5)$$

The ^{3}m.l.c.t. excited species (**1**$^+$)* generated by irradiation [equation (2)] undergoes an electron transfer with teoa to give the reduced species **1** [equation (3)], which then undergoes the substitution of the PPh$_3$ ligand with teoa or dmf to give **3** or **4** [equation (4)]. Evidence in support of this substitution is provided by the cyclic voltammetric behaviour of **1**$^+$, which reveals the instability of **1** in dmf solution, as described above (Fig. 7). Subsequent electron exchange of **3** and **4** with another **1**$^+$ leads to the formation of **3**$^+$ and **4**$^+$ accompanied by the regeneration of **1** [equation (5)].

The formate complex **2** was formed in 52.2% yield based on **1**$^+$ used and in a quantum yield of 1.1×10^{-3} at 365 nm. It was reported that insertion of CO$_2$ into the hydride complex *fac*-[Re(bipy)(CO)$_3$H] occurs slowly in the dark, but much faster upon irradiation, to give **2**.[10] For the formation of **2** from **3**$^+$ and/or **4**$^+$, therefore, it is reasonable to assume the intervention of a hydride complex. This might be formed by a photochemical intramolecular redox reaction of **3**$^+$, a presumption based on our previous work that [Ru(terpy)(bipy)(NEt$_3$)]$^{2+}$ (terpy = 2,2′:6′,2″-terpyridine) photochemically gives the ruthenium hydride complex [Ru(terpy)(bipy)H]$^+$.[15] The mechanistic details of the formation of **2** in the present photoreaction are now under investigation in our laboratory.

Photocatalytic reduction of CO$_2$

Irradiation of a solution containing complex **1**$^+$ and teoa under an atmosphere of CO$_2$ produced CO. An induction period for the formation of CO was observed, as shown in Fig. 10, and the quantum yield of formation of CO measured after the induction period was 0.05. The formation of CO occurred continuously to reach a turnover number of ≈12 based on **1**$^+$, but was not observed at all in the dark nor in the absence of **1**$^+$. Although CO was photochemically formed in the absence of teoa, the turnover was less than unity even after a long period of irradiation.‡ These results clearly indicate that **1**$^+$, teoa and irradiation are essential for the catalytic formation of CO. It should be noted that the molar quantity of the CO formed was only 1.03 times as much as that of **1**$^+$ used when the peak height of **2** attained its maximum and all the species except **2** disappeared upon HPLC. Lehn and co-workers[2b] reported that **2** in teoa–dmf works as a photocatalyst for the reduction of CO$_2$ to CO and the quantum yield for formation of CO is 0.05, the same as in the present photocatalytic system. These results indicate that the 'real' photocatalyst is **2**.

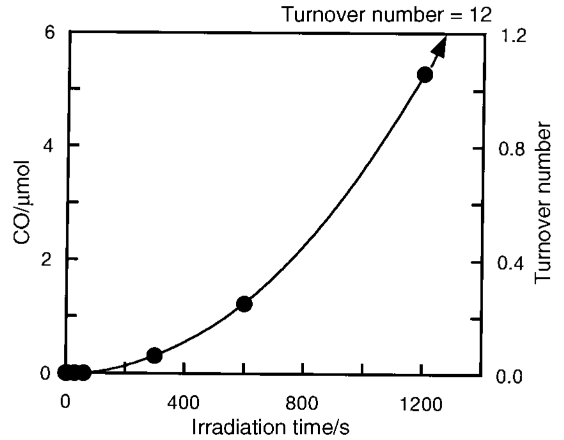

Fig. 10 Catalytic formation of CO by complex **1**$^+$. A teoa–dmf solution (1:5, v/v) containing **1**$^+$ (1.28 mmol dm^{-3}) was irradiated (>330 nm) under an atmosphere of CO$_2$

Conclusion

The complex *fac*-[Re(bipy)(CO)$_3$(PPh$_3$)]$^+$ **1**$^+$ is photochemically reduced by teoa to produce **1**, which undergoes facile substitution of the PPh$_3$ ligand with teoa or dmf. This substitution proceeds through a chain reaction mechanism which is a rare example of chain ligand substitution for rhenium complexes and the first report on the photoreductive fixation of CO$_2$ *via* chain ligand substitution. In a previous paper[3] we described that *fac*-[Re(bipy)(CO)$_3${P(OEt)$_3$}]$^+$ works as a reduction photocatalyst for CO$_2$ strongly dependent on both the irradiation wavelength and light intensity. However, in the case of **1**$^+$, irradiation at 365 or at >330 nm resulted in little difference in the photocatalysis. The reduced species **1** is unstable to substitution of the PPh$_3$ ligand by teoa and/or dmf upon irradiation. The one-electron-reduced species *fac*-[Re(bipy$^{\cdot -}$)(CO)$_3$-{P(OEt)$_3$}], which has a similar structure to that of **1**, is much more stable than **1**. No removal of the P(OEt)$_3$ ligand was observed. These differences indicate that the nature of the phosphorus ligands (steric bulk, electron-acceptor strength, *etc.*) is very important for the design of CO$_2$-reduction photocatalysts.

Experimental

Materials

All reagents and solvents were of high purity commercially available from Kanto Chemical Co. Inc. and Aldrich Chemical Company. The teoa and dmf were distilled and kept under an argon atmosphere. The salt **1**$^+$SbF$_6^-$ was prepared from *fac*-[Re(bipy)(CO)$_3$(MeCN)]SbF$_6$ and PPh$_3$ according to a previous method.[16]

---

‡ Photochemical ligand loss from complex **1**$^+$ resulting in the formation of CO in the absence of teoa. Details of this reaction will be reported elsewhere.

Photochemical procedures

A teoa–dmf (1:5, v/v) solution containing $\mathbf{1}^{+}SbF_6^{-}$ was placed in a glass cell and purged with CO_2 for 20 min. Degassed samples were prepared by five freeze–pump–thaw cycles using a turbo pump. A monochromator and an Uranil glass filter with a high-pressure mercury lamp (500 W) were used to obtain light at 365 and >330 nm, respectively. The incident light intensity (365 nm) was determined by a $K_3[Fe(C_2O_4)_3]$ actinometer.

Measurements

Flash photolysis was performed in the manner reported previously.[3,6] *In situ* UV/VIS spectra were measured by a Photal MCPD-1000 spectrophotometer connected to the photochemical cell through optical fibres. Cyclic voltammetry was performed on a BAS 100B electrochemical analyser using a glassy carbon working electrode and a Ag–$AgNO_3$ reference electrode. The method of flow electrolysis has been described in detail elsewhere.[6] A reversed-phase HPLC system consisting of a Hitachi 638–80 pump, Nakalai $5C_{18}$-ODS column, JASCO UV-970 detector (wavelength 360 nm) and a Rheodyne 7125 injector was used, and the mobile phase was a mixture (3:2, v/v) of MeOH and KH_2PO_4–NaOH buffer (0.05 mol dm^{-3}, pH 5.9). Positive-ion ES mass spectra were recorded on a Hitachi M-1200 spectrometer with an M-1206 electrospray probe operating at a needle voltage of 3 kV. The drift voltage was set at 10 V at which fragment-ion formation can be prevented. A Hitachi L-6200 pump and mobile phase of MeOH–water (3:2, v/v) were used to deliver the sample solutions to the electrospray probe. The irradiated sample solutions were directly introduced into the electrospray probe through a Rheodyne 7125 injector. The CO gas produced was analysed by a Yanako G-3800 gas chromatograph system using an active carbon column (2 m) and a thermal conductivity detector.

Acknowledgements

This work was partially supported by a Grant-in-Aid for the Development of Global Environment Technology from the Agency of Industrial Science and Technology. F. P. A. J. thanks Research Institute of Innovative Technology for the Earth for a postdoctoral fellowship. We also thank Dr. C. Pac of Kawamura Institute of Chemical Research for useful discussions.

References

1 D. J. Stufkens, *Comments Inorg. Chem.*, 1992, **13**, 359; K. K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, London, 1992; C. Pac, S. Kaseda, K. Ishii, S. Yanagida and O. Ishitani, in *Photochemical Processes in Organized Molecular Systems*, ed. K. Honda, Elsevier, Amsterdam, 1991, pp. 177.

2 (*a*) J. Hawecker, J.-M. Lehn and R. Ziessel, *J. Chem. Soc., Chem. Commun.*, 1983, 536; (*b*) *Helv. Chim. Acta*, 1986, **69**, 1990.

3 H. Hori, F. P. A. Johnson, K. Koike, O. Ishitani and T. Ibusuki, *J. Photochem. Photobiol. A: Chem.*, 1996, **96**, 171.

4 C. Kutal, M. A. Weber, G. Ferraudi and D. Geiger, *Organometallics*, 1985, **4**, 2161; C. Kutal, A. J. Corbin and G. Ferraudi, *Organometallics*, 1987, **6**, 553.

5 K. Kalyanasundaram, *J. Chem. Soc., Faraday Trans. 2*, 1986, 2401.

6 O. Ishitani, M. W. George, T. Ibusuki, F. P. A. Johnson, K. Koike, K. Nozaki, C. Pac, J. J. Turner and J. R. Westwell, *Inorg. Chem.*, 1994, **33**, 4712.

7 C. Pac, S. Kaseda, K. Ishii and S. Yanagida, *J. Chem. Soc., Chem Commun.*, 1991, 787.

8 D. P. Summers, L. C. Luong and M. S. Wrighton, *J. Am. Chem. Soc.*, 1981, **103**, 5238.

9 O. Ishitani, H. Namura, S. Yanagida and C. Pac, *J. Chem. Soc., Chem. Commun.*, 1987, 1153.

10 B. P. Sullivan and T. J. Meyer, *J. Chem. Soc., Chem. Commun.*, 1984, 1244.

11 G. J. Stor, F. Hartl, J. W. M. van Outersterp and D. J. Stufkens, *Organometallics*, 1995, **14**, 1115.

12 R. Colton, A. D'Agostino and J. C. Traeger, *Mass Spectrom. Rev.*, 1995, **14**, 79.

13 R. Arakawa, S. Tachiyashiki and T. Matsuo, *Anal. Chem.*, 1995, **67**, 4133; R. Arakawa, L. Jian, A. Yoshimura, K. Nozaki, T. Ohno, H. Doe and T. Matsuo, *Inorg. Chem.*, 1995, **34**, 3874.

14 W. Henderson and B. K. Nicholson, *J. Chem. Soc., Chem. Commun.*, 1995, 2531.

15 O. Ishitani, N. Inoue, K. Koike and T. Ibusuki, *J. Chem. Soc., Chem. Commun.*, 1994, 367.

16 H. Hori, K. Koike, M. Ishizuka, K. Takeuchi, T. Ibusuki and O. Ishitani, *J. Organomet. Chem.*, in the press.

Received 16*th October* 1996; *Paper* 6/07058B