CO$_2$ Capture by a Rhenium(I) Complex with the Aid of Triethanolamine

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Ⓢ *Supporting Information*

ABSTRACT: A rhenium(I) tricarbonyl diimine complex with a *N,N*-dimethylformamide ligand captures one CO$_2$ molecule in the presence of triethanolamine (TEOA), giving *fac*-[Re^I(bpy)(CO)$_3$\{R$_2$N-CH$_2$CH$_2$O-COO\}] (bpy = 2,2′-bipyridine, R = CH$_2$CH$_2$OH). This could be a predominant complex in various photocatalytic CO$_2$ reduction reactions using [Re^I(N^N)(CO)$_3$X]$^{n+}$ (N^N = diimine ligand; X = monodentate ligand; n = 0, 1) type complexes in the presence of TEOA.

Reduction of CO$_2$ to produce energy-rich compounds has attracted much attention as an important part of artificial photosynthesis.[1−7] Among the photocatalysts for CO$_2$ reduction, such as metal complexes and semiconductors, Re(I) diimine complexes have been recognized as being very efficient and selective.[5−12] For example, *fac*-[Re^I(N^N)-(CO)$_3$(X)] (N^N = diimine ligand; X = Cl$^-$, Br$^-$) not only exhibits efficient CO$_2$ reduction as a photocatalyst[11,12] but also acts as a catalyst, selectively producing CO in a dimethylform-amide (DMF)/triethanolamine (TEOA) mixed solution.[13−15] Some plausible intermediates derived from reduced Re complexes and CO$_2$ for CO formation have been proposed, for example, the 17-electron species, i.e., [Re^0(N^N)(CO)$_3$] and/or [Re^I(N^N$^{•−}$)(CO)$_3$][14,16−18] and a Re dimer with CO$_2$ as a bridge ligand.[18,19] However, no clear evidence has been obtained to clarify the mechanism, especially a CO$_2$ addition step to the Re center.

According to reported reaction conditions, TEOA is known as a "magic" sacrificial electron donor, which can enhance the turnover number and the selectivity of CO formation, compared with other reductants such as triethylamine.[20] However, the reason for the "magic" has not yet been clarified.

In this study, the peculiar effect of TEOA was revisited. The results showed that a CO$_2$ molecule is captured by the [Re^I(N^N)(CO)$_3$]$^+$ species with the assistance of TEOA even when the Re complex is not reduced. Herein, we also report the importance of this CO$_2$ adduct in the photocatalytic reduction of CO$_2$ using *fac*-[Re^I(bpy)(CO)$_3$Br] (**1**, bpy = 2,2′-bipyridine).

Just after PF$_6$$^-$ salts of *fac*-[Re^I(bpy)(CO)$_3$(CH$_3$CN)]$^+$ (**2**) were dissolved in pure DMF, a sharp IR peak at 2037 cm^{-1} and a broad peak around 1935 cm^{-1} were observed (Figure 1a), which could be assigned to CO stretching peaks of **2**. In
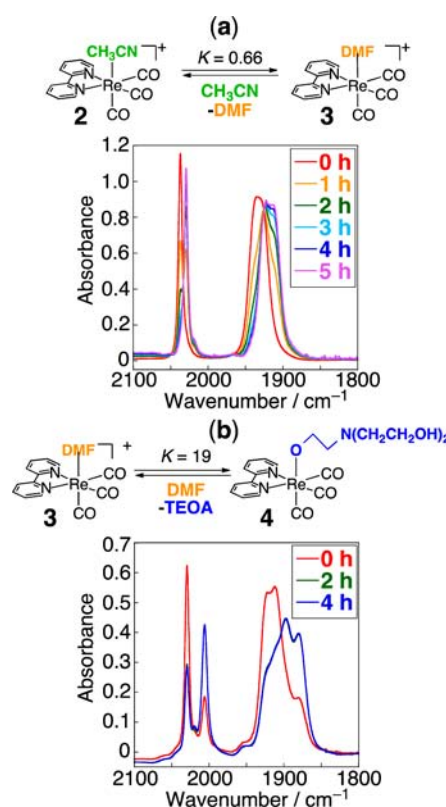

Figure 1. IR spectral changes of PF$_6$$^-$ salts of **2** dissolved in DMF for 5 h (a) and those of **3** in DMF after addition of TEOA for 4 h (b) to give a DMF/TEOA mixed solution (5:1 v/v).

addition to the peaks, other new peaks at 2029, 1922, and 1913 cm^{-1} appeared, and **2** was completely converted into a new species within 5 h, which was the DMF-coordinated complex *fac*-[Re^I(bpy)(CO)$_3$(DMF)]$^+$ (**3**). Addition of TEOA to the solution (DMF/TEOA = 5:1 v/v) gave a 1:2 thermodynami-cally equilibrated mixture of **3** and *fac*-[Re^I(bpy)-(CO)$_3$(OCH$_2$CH$_2$NR$_2$)] (**4**, R = CH$_2$CH$_2$OH), which could be characterized by the large shift to lower wavenumbers (2006, 1897, and 1881 cm^{-1}) in IR spectra (Figure 1b).[21] The higher-energy peaks of the three complexes were separated by curve

fitting (Figure S7). According to the peak areas of the separated peaks in the particular composition ratio of a mixed solvent CH_3CN/DMF, the equilibrium constant between **2** and **3** was estimated at 0.66 (Tables S1). Similar estimation in DMF/TEOA gave the value of the equilibrium constant between **3** and **4** as 19 (Figure S8, Table S2). Stepwise treatment by DMF and then TEOA was essential to the formation of the equilibrated mixture of **3** and **4**. When **2** was directly dissolved in a mixed solvent of DMF and TEOA, TEOA was found to attack the CH_3CN ligand and yielded the corresponding iminoester complex (Figure S9); that is, the Re(I) complex mediated the Pinner reaction partially.[22,23]

Bubbling CO_2 into the solution containing the equilibrated mixture of **3** and **4** exclusively afforded another *fac*-tricarbonyl complex (Figure 2), while treatment of only **3** with CO_2 did
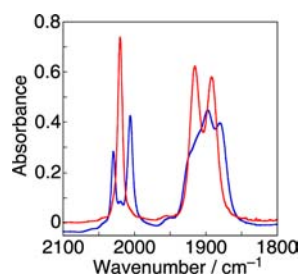
Figure 2. IR spectra of a DMF/TEOA (5:1 v/v) solution containing the equilibrated mixture of **3** and **4** before (blue) and after (red) CO_2 bubbling.

not yield any additional complexes. The IR spectrum of the complex displayed three distinct peaks at 2020, 1915, and 1892 cm^{-1}, which did not correspond to any of the three complexes mentioned above.[24] The peak positions indicated that the complex was composed of ligands that are more electron-donating than CH_3CN or DMF but less than alkoxido ligands. The ESI mass spectrum of the product showed an ion peak at $m/z = 642$, which could be assigned to the Re(I) tricarbonyl complex having both CO_2 and TEOA moieties with a sodium ion, $[Re(bpy)(CO)_3(CO_2)(TEOA) - H^+ + Na^+]^+$, in the presence of $NaNO_3$ (Figure 3). Furthermore, the exclusive formation of the new species was also confirmed by ^1H and ^{13}C NMR spectra (Figure S3).
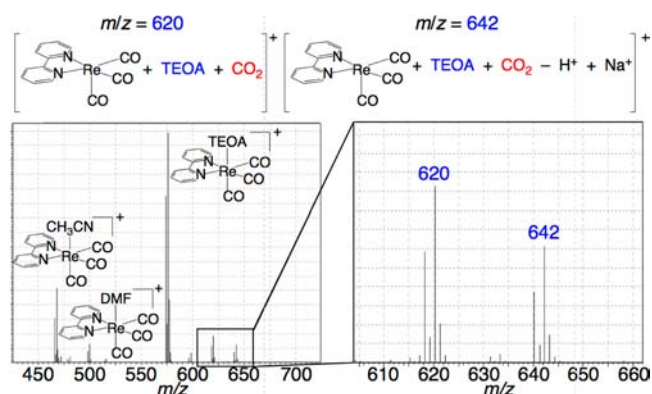
Figure 3. ESI-MS spectrum of the products (eluent: CH_3CN). The analyzed sample was prepared by diluting a DMF/TEOA (5:1 v/v) solution of **5** and $NaNO_3$ (1.3 equiv) with CH_3CN just before injection.

When the mixture of **3** and **4** in DMF/TEOA was exposed to $^{13}CO_2$, the ^{13}C NMR spectrum without ^1H decoupling displayed an intense triplet signal at 158.4 ppm with a coupling constant of 3.6 Hz (Figure 4). Because the chemical shift is
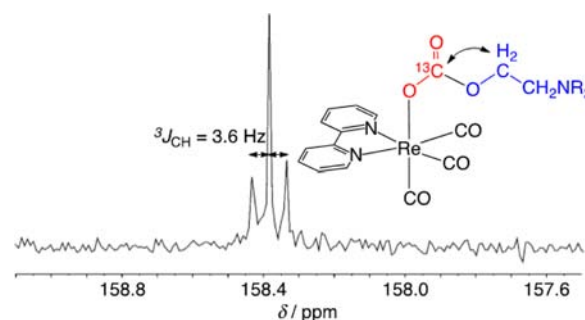
Figure 4. ^{13}C NMR spectrum of the product without ^1H decoupling under a $^{13}CO_2$ atmosphere.

typical of carbonate coordinated to a metal ion and the coupling constant is comparable to that for the three-bond coupling between ^{13}C and ^1H ($^{13}C-O-C^1H_2$),[25] this result strongly indicates that CO_2 was covalently bonded at the terminal oxygen atom of TEOA to form $R_2N-CH_2CH_2O-COO^-$ ($R = CH_2CH_2OH$) as a ligand.

On the basis of these results, we can conclude that the complex has the monoalkyl carbonate derivative composed of CO_2 and TEOA, $R_2N-CH_2CH_2O-COO^-$, as a monodentate ligand; that is, the complex is *fac*-$[Re^I(bpy)(CO)_3(R_2N-CH_2CH_2O-COO)]$ (**5**). A similar insertion of CO_2 to metal complexes coordinated by alkoxido ligands has also been reported. For example, a CO_2 molecule can be inserted into *fac*-$[Re^I(CO)_3(PMe_3)_2(OCH_3)]$ to form the corresponding Re(I) methoxide complex, *fac*-$[Re^I(CO)_3(PMe_3)_2(O(CO)OCH_3)]$.[25] Such CO_2 adducts did not form in either DMF/triethylamine or DMF/ethanol mixed solvent (Figures S5 and S6), probably because triethylamine has no hydroxyl group and the hydroxyl group of ethanol is less acidic ($pK_a = 16$) than those of TEOA ($pK_a = 9.5$). This should be the "magic" for CO_2 capture owing to the dual nature of TEOA as both an alcohol and a base.

Figure 5 shows IR spectral changes after bubbling Ar through a CO_2-saturated solution of **5** in DMF/TEOA, which clearly indicate the disappearance of **5** and concomitant reproduction of a mixture of **3** and **4**.[26] Therefore, both capture and release of CO_2 should proceed on the Re(I) center (eq 1). Measuring the composition ratios of **4** and **5** in solutions with various CO_2
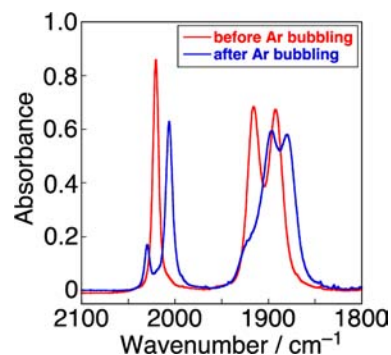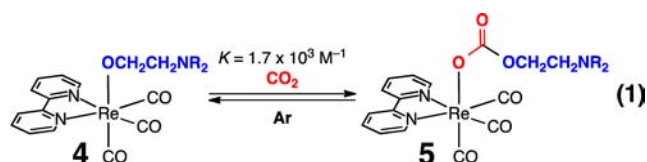
Figure 5. CO_2 release from tricarbonyl Re complex **5** in DMF/TEOA by Ar bubbling.

$$K = 1.7 \times 10^3 \ M^{-1} \qquad (1)$$

concentrations gave the equilibrium constant between **4** and **5** under a CO_2 atmosphere as $1.7 \times 10^3 \ M^{-1}$. The value can also explain the exclusive formation of **5** in the CO_2-saturated mixed solution of DMF and TEOA, which also suggests that even a very low concentration of CO_2 is enough to produce the CO_2–TEOA adduct. A significant amount of complex **5** (14% yield) was formed in the equilibrated mixture of **3** and **4**, even when the solution was exposed to air (<0.1% of CO_2 concentration, Figure S11).

Cyclic voltammetry of **5** (Figure 6a) showed the first irreversible reduction wave, attributed to the bpy-based (bpy$^{\bullet-}$/
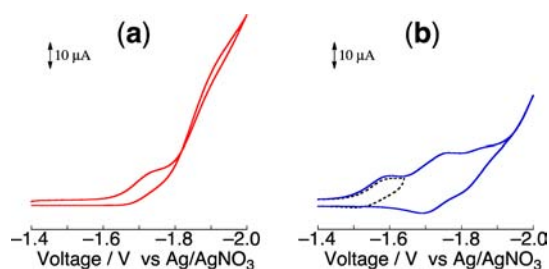

Figure 6. Cyclic voltammograms of (a) **5** in DMF/TEOA under a CO_2 atmosphere using 0.1 M TEABF$_4$ as an electrolyte and (b) **3** in DMF under a CO_2 atmosphere using 0.1 M TEABF$_4$ as an electrolyte.

bpy) reduction,[27] around -1.7 V vs Ag/AgNO$_3$, which is more negative than the quasi-reversible wave of **3** (ca. -1.6 V, Figure 6b) measured under a CO_2 atmosphere. This is understandable because the carbonato ligand is a stronger electron donor than DMF, as discussed above with regard to IR spectra. A large catalytic wave for CO_2 reduction was observed from -1.8 V in the case of **5**, which was in sharp contrast to **3**, which did not give a large current even at -1.9 V. The significant difference implies that capturing CO_2 with the aid of TEOA in the Re(I) complex could promote more rapid CO_2 reduction compared to the intermolecular reaction of the one-electron-reduced Re(I) species and CO_2.

The CO_2/TEOA adduct **5** had the characteristic $\pi-\pi^*$ and metal-to-ligand charge transfer (MLCT) absorption around 320 and 360 nm, respectively, in DMF/TEOA under a CO_2 atmosphere (Figure S12). No emission from **5** was observed.

Various Re(I) tricarbonyl complexes fac-[Re^I(N^N)-(CO)$_3$L]$^{n+}$ (L = Cl$^-$, Br$^-$, SCN$^-$, $n = 0$; L = phosphine derivatives, pyridine derivatives, $n = 1$) have been well known to act as photocatalysts and/or catalysts for CO_2 reduction. In many cases, the ligand L is dissociated from the one-electron-reduced species of the Re(I) complex, which is produced photochemically or electrochemically,[14,16−18] to give the "17-electron species", i.e., [Re^0(N^N)(CO)$_3$] $\leftrightarrow$ [Re^I(N^N$^{\bullet-}$)-(CO)$_3$]. Although it has been conjectured that the species reacts with CO_2 during the reduction of CO_2, Fujita et al. reported that the reaction of the species with CO_2 is very slow ($k_{obs} = 0.003 \ s^{-1}$, N^N = 4,4'-dimethyl-2,2'-bipyridine (dmb)),[18] even though the turnover frequency (TOF$_{CO}$) of some photocatalytic systems containing the Re(I) complex as a catalyst unit is high, e.g., TOF$_{CO} = 0.053 \ s^{-1}$ with

[(dmb)$_2$Ru^{II}(BL)Re^I(CO)$_3$Cl]$^{2+}$ (BL = 1,2-bis(4'-methyl-[2,2'-bipyridin]-4-yl)ethane).[15] We believe that **5** would form in many reported photocatalytic reaction systems because TEOA was used as an electron donor or a base in most of those cases.

In fact, our study found that **5** was produced during the photocatalytic reaction using fac-[Re^I(bpy)(CO)$_3$Br] (**1**) in DMF/TEOA (5:1 v/v) under a CO_2 atmosphere, which is one of the most investigated CO_2 reduction systems.[12] During the constant formation of CO, the quick consumption of **1** was confirmed by changes in the IR spectra and HPLC (Figures S13 and S14). At the same time, **5** was a main product, with the formation of a small amount of the formate complex, fac-[Re^I(bpy)(CO)$_3$(OCOH)].[12,28] The HPLC data revealed that 45% of **1** was consumed in 5 min and the yield of **5** was 92% based on **1** consumed. After 12 min irradiation, **5** was the predominant species during the photocatalytic reaction (Figure 7).
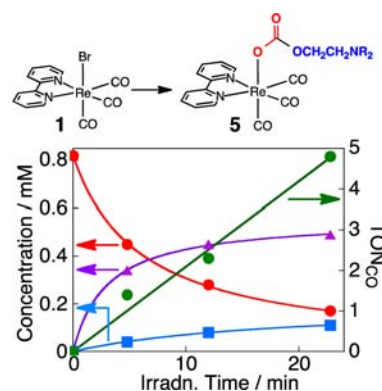

Figure 7. Time courses of concentrations of the starting complex **1** (red), **5** (purple), and Re(bpy)(CO)$_3$(OCOH) (blue), and the turnover number of CO formation (green) during the photocatalytic reaction in DMF/TEOA (5:1 v/v) under a CO_2 atmosphere ($\lambda > 400$ nm).

The second example is the most efficient photocatalytic system for CO_2 reduction using fac-[Re^I{4,4'-(MeO)$_2$bpy}-(CO)$_3${P(OEt)$_3$}]$^+$ as a photosensitizer and **2** as a catalyst in the reported photocatalysts ($\Phi_{CO} = 0.59$).[14] We carefully checked the IR spectra and HPLC charts of the reaction solution before and after irradiation and found that **2** was completely converted to **5** via the corresponding iminoester complex during the photocatalytic reaction and **5** was continuously present as a veritable catalyst in the reaction solution (Figure S15).

In summary, the equilibrated mixture of **3** and **4** could capture a CO_2 molecule and was completely converted into another Re(I) complex with an alkyl carbonato ligand composed of both CO_2 and TEOA molecules (**5**) in a CO_2-saturated DMF/TEOA solution. A CO_2 molecule could be captured to form **5** even in the air. The CO_2-capturing complex **5** should be the real catalyst in many of the photocatalytic systems for CO_2 reduction using Re(I) complexes in DMF/TEOA mixed solutions. This concept of capturing CO_2 is potentially important in order to reduce CO_2 in low concentration conditions, such as in the air, and thus studies on the other metal complex systems are in progress to explore this concept in detail. Since the systems with the Re(I) complexes for fixing CO_2 into the photocatalyst or catalyst have

functions of both condensation and reduction of CO_2, which have been separately investigated, this might open up new methods for utilization of CO_2, especially at dilute CO_2 sources.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, crystallographic data, photophysical data, and photocatalytic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(21) TEOA coordinated to the Re(I) center as the deprotonated form, namely as the ligand $R_2NCH_2CH_2O^-$, where the proton should be trapped by another TEOA molecule. Similar species were obtained in the presence of both triethylamine and ethanol, but not in the presence of only triethylamine or only ethanol (see Figures S4–S6).

(22) A similar reaction of **2** with ethanol also proceeded to give *fac*-$[Re(bpy)(CO)_3(N=CH(CH_3)OCH_2CH_2)]^+$, whose structure was roughly determined by X-ray diffraction analysis (see Figure S10).

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(26) The differences in the IR spectrum of the Ar-bubbled mixed solution in Figure 5 and that in Figure 2 arose from the kinetic product distribution owing to the different coordination abilities of DMF and TEOA. In fact, the profiles were comparable to each other after the solution was kept at room temperature for 2 h.

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