

CO₂ Capture by a Rhenium(I) Complex with the Aid of TriethanolamineTatsuki Morimoto,^{*,†,‡} Takuya Nakajima,[†] Shuhei Sawa,[†] Ryoichi Nakanishi,[†] Daisuke Imori,[†] and Osamu Ishitani^{*,†}[†]Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-NE1, O-okayama, Meguro-ku, Tokyo 152-8550, Japan[‡]PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi-shi, Saitama 332-0012, Japan

Supporting Information

ABSTRACT: A rhenium(I) tricarbonyl diimine complex with a *N,N*-dimethylformamide ligand captures one CO₂ molecule in the presence of triethanolamine (TEOA), giving *fac*-[Re^I(bpy)(CO)₃{R₂N-CH₂CH₂O-COO}] (bpy = 2,2'-bipyridine, R = CH₂CH₂OH). This could be a predominant complex in various photocatalytic CO₂ reduction reactions using [Re^I(N[^]N)(CO)₃X]ⁿ⁺ (N[^]N = diimine ligand; X = monodentate ligand; n = 0, 1) type complexes in the presence of TEOA.

Reduction of CO₂ to produce energy-rich compounds has attracted much attention as an important part of artificial photosynthesis.^{1–7} Among the photocatalysts for CO₂ 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 CO₂ reduction as a photocatalyst^{11,12} but also acts as a catalyst, selectively producing CO in a dimethylformamide (DMF)/triethanolamine (TEOA) mixed solution.^{13–15} Some plausible intermediates derived from reduced Re complexes and CO₂ for CO formation have been proposed, for example, the 17-electron species, i.e., [Re⁰(N[^]N)(CO)₃] and/or [Re^I(N[^]N^{•−})(CO)₃]^{14,16–18} and a Re dimer with CO₂ as a bridge ligand.^{18,19} However, no clear evidence has been obtained to clarify the mechanism, especially a CO₂ 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 CO₂ 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 CO₂ adduct in the photocatalytic reduction of CO₂ using *fac*-[Re^I(bpy)(CO)₃Br] (1, bpy = 2,2'-bipyridine).

Just after PF₆[−] salts of *fac*-[Re^I(bpy)(CO)₃(CH₃CN)]⁺ (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

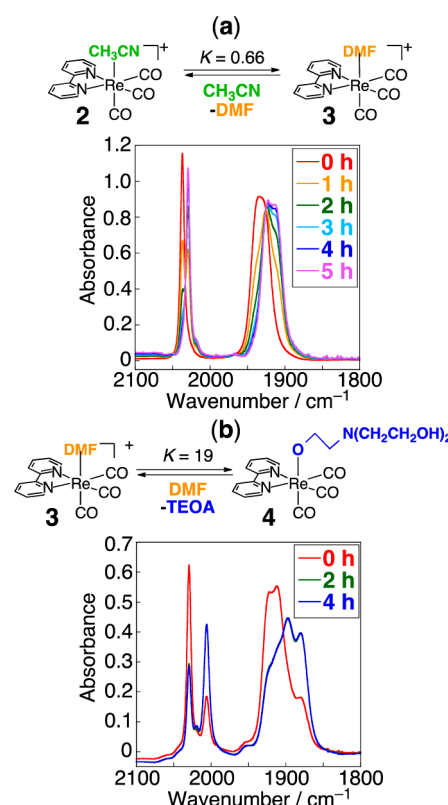


Figure 1. IR spectral changes of PF₆[−] salts of 2 dissolved in DMF for 5 h (a) and those of 3 in DMF after addition of TEOA for 4 h (b) to give a DMF/TEOA mixed solution (5:1 v/v).

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 thermodynamically equilibrated mixture of 3 and *fac*-[Re^I(bpy)(CO)₃(OCH₂CH₂NR₂)] (4, R = CH₂CH₂OH), 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

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fitting (Figure S7). According to the peak areas of the separated peaks in the particular composition ratio of a mixed solvent CH₃CN/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 CH₃CN ligand and yielded the corresponding iminoester complex (Figure S9); that is, the Re(I) complex mediated the Pinner reaction partially.^{22,23}

Bubbling CO₂ 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 CO₂ did

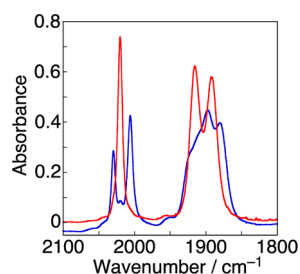


Figure 2. IR spectra of a DMF/TEOA (5:1 v/v) solution containing the equilibrated mixture of 3 and 4 before (blue) and after (red) CO₂ bubbling.

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 CH₃CN 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 CO₂ and TEOA moieties with a sodium ion, [Re(bpy)(CO)₃(CO₂)(TEOA) - H⁺ + Na⁺]⁺, in the presence of NaNO₃ (Figure 3). Furthermore, the exclusive formation of the new species was also confirmed by ¹H and ¹³C NMR spectra (Figure S3).

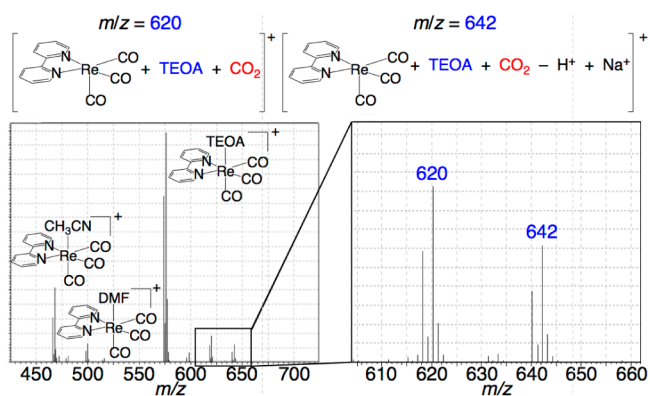


Figure 3. ESI-MS spectrum of the products (eluent: CH₃CN). The analyzed sample was prepared by diluting a DMF/TEOA (5:1 v/v) solution of 5 and NaNO₃ (1.3 equiv) with CH₃CN just before injection.

When the mixture of 3 and 4 in DMF/TEOA was exposed to ¹³CO₂, the ¹³C 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

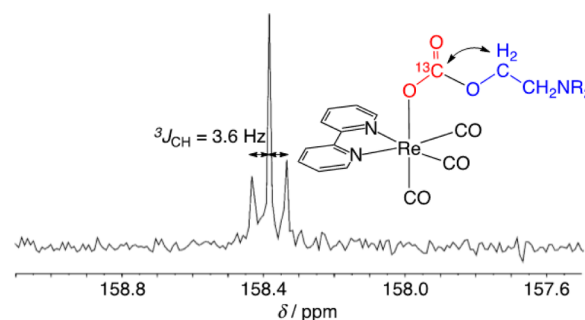


Figure 4. ¹³C NMR spectrum of the product without ¹H decoupling under a ¹³CO₂ atmosphere.

typical of carbonate coordinated to a metal ion and the coupling constant is comparable to that for the three-bond coupling between ¹³C and ¹H (¹³C-O-C¹H₂),²⁵ this result strongly indicates that CO₂ was covalently bonded at the terminal oxygen atom of TEOA to form R₂N-CH₂CH₂O-COO⁻ (R = CH₂CH₂OH) as a ligand.

On the basis of these results, we can conclude that the complex has the monoalkyl carbonate derivative composed of CO₂ and TEOA, R₂N-CH₂CH₂O-COO⁻, as a monodentate ligand; that is, the complex is *fac*-[Re^I(bpy)(CO)₃(R₂N-CH₂CH₂O-COO)] (5). A similar insertion of CO₂ to metal complexes coordinated by alkoxido ligands has also been reported. For example, a CO₂ molecule can be inserted into *fac*-[Re^I(CO)₃(PMe₃)₂(OCH₃)] to form the corresponding Re(I) methoxide complex, *fac*-[Re^I(CO)₃(PMe₃)₂(O(CO)OCH₃)]²⁵. Such CO₂ 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 CO₂ 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 CO₂-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 CO₂ should proceed on the Re(I) center (eq 1). Measuring the composition ratios of 4 and 5 in solutions with various CO₂

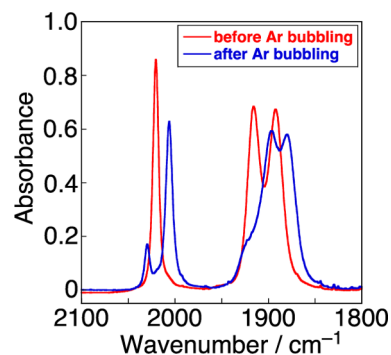
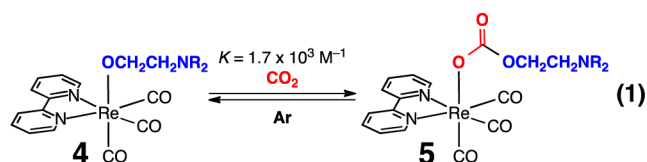


Figure 5. CO₂ release from tricarbonyl Re complex 5 in DMF/TEOA by Ar bubbling.



concentrations gave the equilibrium constant between **4** and **5** under a CO₂ atmosphere as $1.7 \times 10^3 \text{ M}^{-1}$. The value can also explain the exclusive formation of **5** in the CO₂-saturated mixed solution of DMF and TEOA, which also suggests that even a very low concentration of CO₂ is enough to produce the CO₂-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 CO₂ concentration, Figure S11).

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

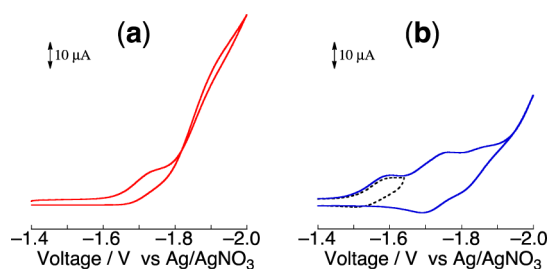


Figure 6. Cyclic voltammograms of (a) **5** in DMF/TEOA under a CO₂ atmosphere using 0.1 M TEABF₄ as an electrolyte and (b) **3** in DMF under a CO₂ atmosphere using 0.1 M TEABF₄ as an electrolyte.

bpy) reduction,²⁷ around -1.7 V vs Ag/AgNO₃, which is more negative than the quasi-reversible wave of **3** (ca. -1.6 V , Figure 6b) measured under a CO₂ 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 CO₂ 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 CO₂ with the aid of TEOA in the Re(I) complex could promote more rapid CO₂ reduction compared to the intermolecular reaction of the one-electron-reduced Re(I) species and CO₂.

The CO₂/TEOA adduct **5** had the characteristic π - π^* and metal-to-ligand charge transfer (MLCT) absorption around 320 and 360 nm, respectively, in DMF/TEOA under a CO₂ atmosphere (Figure S12). No emission from **5** was observed.

Various Re(I) tricarbonyl complexes $\text{fac}[\text{Re}^{\text{I}}(\text{N}^{\wedge}\text{N})-(\text{CO})_3\text{L}]^{n+}$ (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 CO₂ 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., $[\text{Re}^0(\text{N}^{\wedge}\text{N})(\text{CO})_3] \leftrightarrow [\text{Re}^{\text{I}}(\text{N}^{\wedge}\text{N}^{\bullet-})(\text{CO})_3]$. Although it has been conjectured that the species reacts with CO₂ during the reduction of CO₂, Fujita et al. reported that the reaction of the species with CO₂ is very slow ($k_{\text{obs}} = 0.003 \text{ s}^{-1}$, 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

$[(\text{dmb})_2\text{Ru}^{\text{II}}(\text{BL})\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}]^{2+}$ (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 $\text{fac}[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3\text{Br}]$ (**1**) in DMF/TEOA (5:1 v/v) under a CO₂ atmosphere, which is one of the most investigated CO₂ 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, $\text{fac}[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{OCOH})]$.^{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).

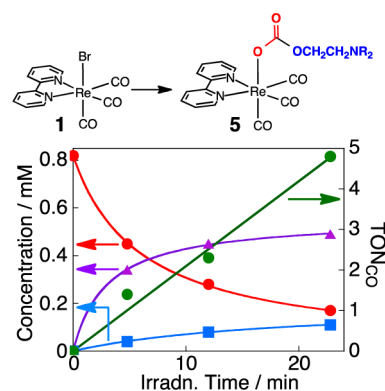


Figure 7. Time courses of concentrations of the starting complex **1** (red), **5** (purple), and $\text{Re}(\text{bpy})(\text{CO})_3(\text{OCOH})$ (blue), and the turnover number of CO formation (green) during the photocatalytic reaction in DMF/TEOA (5:1 v/v) under a CO₂ atmosphere ($\lambda > 400 \text{ nm}$).

The second example is the most efficient photocatalytic system for CO₂ reduction using $\text{fac}[\text{Re}^{\text{I}}\{4,4'-(\text{MeO})_2\text{bpy}\}-(\text{CO})_3\{\text{P}(\text{OEt})_3\}]^+$ as a photosensitizer and **2** as a catalyst in the reported photocatalysts ($\Phi_{\text{CO}} = 0.59$).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 CO₂ molecule and was completely converted into another Re(I) complex with an alkyl carbonato ligand composed of both CO₂ and TEOA molecules (**5**) in a CO₂-saturated DMF/TEOA solution. A CO₂ molecule could be captured to form **5** even in the air. The CO₂-capturing complex **5** should be the real catalyst in many of the photocatalytic systems for CO₂ reduction using Re(I) complexes in DMF/TEOA mixed solutions. This concept of capturing CO₂ is potentially important in order to reduce CO₂ 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 CO₂ into the photocatalyst or catalyst have

functions of both condensation and reduction of CO₂, which have been separately investigated, this might open up new methods for utilization of CO₂, especially at dilute CO₂ 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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The authors declare no competing financial interest.

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- (21) TEOA coordinated to the Re(I) center as the deprotonated form, namely as the ligand R₂NCH₂CH₂O⁻, 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(CH₃)OCH₂CH₃)]⁺, 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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