

## Molecular Approaches to the Photocatalytic Reduction of Carbon Dioxide for Solar Fuels

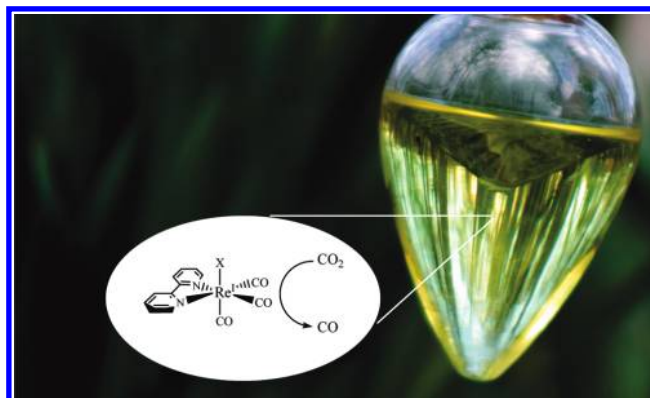
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### CON SPECTUS

The scientific community now agrees that the rise in atmospheric CO<sub>2</sub>, the most abundant green house gas, comes from anthropogenic sources such as the burning of fossil fuels. This atmospheric rise in CO<sub>2</sub> results in global climate change. Therefore methods for photochemically transforming CO<sub>2</sub> into a source of fuel could offer an attractive way to decrease atmospheric concentrations. One way to accomplish this conversion is through the light-driven reduction of carbon dioxide to methane (CH<sub>4(g)</sub>) or methanol (CH<sub>3</sub>OH<sub>(l)</sub>) with electrons and protons derived from water. Existing infrastructure already supports the delivery of natural gas and liquid fuels, which makes these possible CO<sub>2</sub> reduction products particularly appealing.



This Account focuses on molecular approaches to photochemical CO<sub>2</sub> reduction in homogeneous solution. The reduction of CO<sub>2</sub> by one electron to form CO<sub>2</sub><sup>•-</sup> is highly unfavorable, having a formal reduction potential of -2.14 V vs SCE. Rapid reduction requires an overpotential of up to 0.6 V, due at least in part to the kinetic restrictions imposed by the structural difference between linear CO<sub>2</sub> and bent CO<sub>2</sub><sup>•-</sup>. An alternative and more favorable pathway is to reduce CO<sub>2</sub> through proton-assisted multiple-electron transfer. The development of catalysts, redox mediators, or both that efficiently drive these reactions remains an important and active area of research.

We divide these reactions into two class types. In Type I photocatalysis, a molecular light absorber and a transition metal catalyst work in concert. We also consider a special case of Type 1 photocatalysis, where a saturated hydrocarbon links the catalyst and the light absorber in a supramolecular compound. In Type II photocatalysis, the light absorber and the catalyst are the same molecule. In these reactions, transition-metal coordination compounds often serve as catalysts because they can absorb a significant portion of the solar spectrum and can promote activation of small molecules. This Account discusses four classes of transition-metal catalysts: (A) metal tetraaza-macrocyclic compounds; (B) supramolecular complexes; (C) metalloporphyrins and related metallomacrocycles; (D) Re(CO)<sub>3</sub>(bpy)X-based compounds where bpy = 2,2'-bipyridine. Carbon monoxide and formate are the primary CO<sub>2</sub> reduction products, and we also propose bicarbonate/carbonate production. For comprehensiveness, we briefly discuss hydrogen formation, a common side reaction that occurs concurrently with CO<sub>2</sub> reduction, though the details of that process are beyond the scope of this Account. It is our hope that drawing attention both to current mechanistic hypotheses and to the areas that are poorly understood will stimulate research that could one day provide an efficient solution to this global problem.

## I. Introduction

The reduction of CO<sub>2</sub> by one electron to form CO<sub>2</sub><sup>•-</sup>, is highly unfavorable, having a formal reduction potential of -2.14 V vs SCE.<sup>1,2</sup> Rapid reduction requires an overpotential of 0.1–0.6 V, due at least in part to the kinetic restrictions imposed by the structural difference between linear CO<sub>2</sub> and bent CO<sub>2</sub><sup>•-</sup>.<sup>3</sup> An alternative and more favorable pathway is to reduce CO<sub>2</sub> through proton-assisted multiple-electron transfer (MET) (Table 1).<sup>1</sup> The development of catalysts, redox mediators, or both that efficiently drive the reactions in Table 1 remains an important and active area of research.

Transition-metal compounds are at the forefront of potential catalyst research. Such catalysts can have multiple and accessible redox states that have been shown to promote MET reactivity. Furthermore, the formal reduction potentials can be systematically tuned through ligand modification to better match the potential required for CO<sub>2</sub> reduction. Many transition-metal compounds have been studied for potential CO<sub>2</sub>-reduction applications; however, the focus here is on those that have garnered the most interest and, in some cases, are the most promising for development.

## II. Common Terms

There are three terms that are commonly used to quantify the efficiency of catalytic CO<sub>2</sub> reduction processes, eqs 1–3. Catalytic selectivity (CS) is defined as the molar ratio of the CO<sub>2</sub> reduction products to that of hydrogen, eq 1.

$$CS = \frac{[\text{CO}_2 \text{ reduction products}]}{[\text{H}_2]} \quad (1)$$

Any catalyst that reduces CO<sub>2</sub> to carbon monoxide or formate is also thermodynamically capable of proton reduction to hydrogen. The CS value provides quantitative data on the efficiency of CO<sub>2</sub> reduction relative to hydrogen formation at specific experimental conditions (i.e., pH, solvent). Synthetic modification of the transition-metal catalysts provides the opportunity to tune relative reactivity through inductive and steric effects. The ability to control reactivity at the molecular level represents a significant advantage of Type I and II approaches over heterogeneous materials.

The photochemical quantum yield,  $\phi$ , is a measure of the molar fraction of incident photons that result in CO<sub>2</sub> reduction products, eq 2.

$$\phi = \frac{[\text{CO}_2 \text{ reduction products}]}{[\text{incident photons}]} \quad (2)$$

**TABLE 1.** CO<sub>2</sub> Reduction Potentials

reaction	E° (V) vs SCE <sup>a</sup>
CO <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> → HCO <sub>2</sub> H	-0.85
CO <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> → CO + H <sub>2</sub> O	-0.77
CO <sub>2</sub> + 4H <sup>+</sup> + 4e <sup>-</sup> → C + 2H <sub>2</sub> O	-0.44
CO <sub>2</sub> + 4H <sup>+</sup> + 4e <sup>-</sup> → HCHO + H <sub>2</sub> O	-0.72
CO <sub>2</sub> + 6H <sup>+</sup> + 6e <sup>-</sup> → CH <sub>3</sub> OH + H <sub>2</sub> O	-0.62
CO <sub>2</sub> + 8H <sup>+</sup> + 8e <sup>-</sup> → CH <sub>4</sub> + 2H <sub>2</sub> O	-0.48

<sup>a</sup> E° potentials are reported at pH 7.

In the absence of current doubling reactivity that can occur when sacrificial donors are oxidized, the maximum  $\phi$  for a single-electron reduction is 1, while for  $n$  electron reductions, it is  $1/n$ .

Lastly, the turnover number (TN) is the number of reductions that occur per catalyst over the catalyst's lifetime. This is often calculated as the molar ratio of CO<sub>2</sub> reduction products to the catalyst initially present, eq 3.

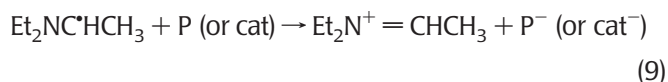
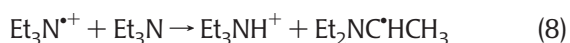
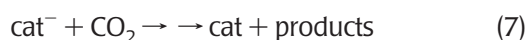
$$\text{Turnover Number (TN)} = \frac{[\text{CO}_2 \text{ reduction products}]}{[\text{catalyst}]} \quad (3)$$

Ideally a catalyst would have infinite TN, and in practical industrial applications, TNs of 1 million are common. For the molecules discussed herein, TNs range from 1 to 500.<sup>1,4</sup> It is important to note that TNs reported for photochemical reductions are not always measured by eq 3. A common alternative practice is to illuminate for a designated time interval rather than continuous illumination until catalysis ceases. As such, one needs to carefully examine the definition of TN used by different authors.

## III. Type I

Type I catalysis can be considered as a photosensitized CO<sub>2</sub> reduction process. Upon light excitation, a molecular light absorber, P, typically ruthenium(II) trisbipyridine, [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, is promoted to an excited state, P\* (eq 4). This excited state is then reductively quenched by a sacrificial amine donor, D, typically triethylamine (TEA) or triethanolamine (TEOA), to yield a reduced sensitizer, P<sup>-</sup>, and an oxidized amine donor, D<sup>•+</sup>, (i.e., Et<sub>3</sub>N<sup>•+</sup> or (HOC<sub>2</sub>H<sub>4</sub>)<sub>3</sub>N<sup>•+</sup>) as shown in eq 5. It is important to note that the oxidized amines are reactive and are known to undergo hydrogen atom abstraction and radical rearrangements that result in the

production of a highly reduced carbon-centered radical species, Et<sub>2</sub>NC<sup>•</sup>HCH<sub>3</sub> or (HO<sub>2</sub>C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>N(C<sup>•</sup>HCH<sub>2</sub>OH), that can under certain conditions reduce a second photosensitizer (eqs 8 and 9).<sup>5</sup> We denote this carbon-centered radical as D<sup>•</sup>. The reduced sensitizer, P<sup>-</sup>, is responsible for electron transfer to a molecular catalyst, which generates the reduced active state of the catalyst that then reduces CO<sub>2</sub> (eqs 6 and 7).<sup>6</sup>

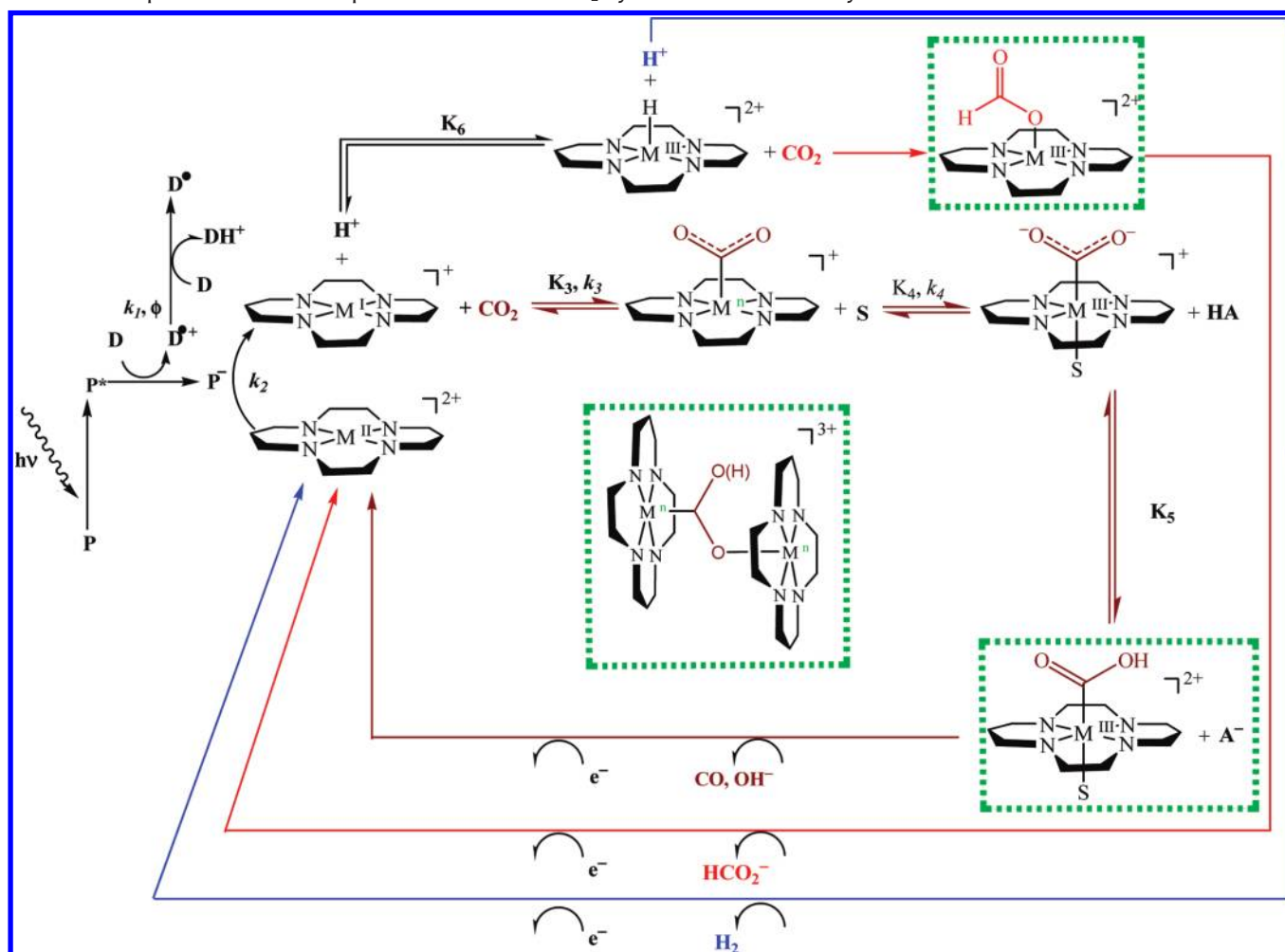


### Cobalt and Nickel Tetraaza-macrocylic Compounds.

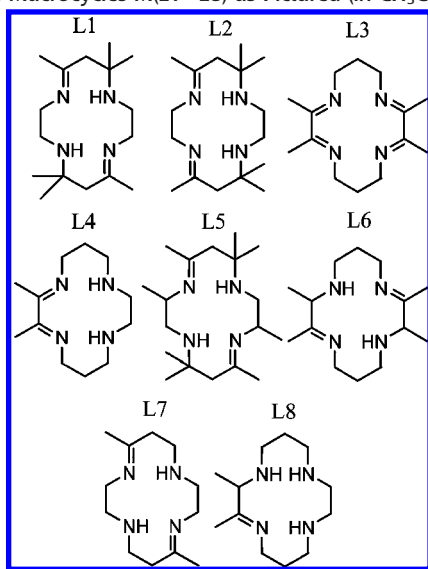
Tinnemans et al. were the first to investigate the Ru(bpy)<sub>3</sub><sup>2+</sup>-sensitized CO<sub>2</sub> reduction by transition-metal tetraaza-macrocylic compounds, [M<sup>II</sup>L].<sup>6</sup> The CO<sub>2</sub> reduction products were identified as carbon monoxide and formate. Scheme 1 displays the proposed formation pathways of each product using M<sup>II</sup>(cyclam) as a representative macrocycle. Since Tinneman's pioneering research, other photosensitizers have been employed including phenazine and *p*-terphenyl.<sup>6–8</sup> Both cobalt and nickel tetraaza-macrocylic compounds have been studied and will be discussed below.

Tinnemans originally proposed insertion of CO<sub>2</sub> into a metal–hydride bond to yield a metal–formato complex, [LM<sup>III</sup>–OC(H)O]<sup>2+</sup>, Scheme 1, red pathway.<sup>6</sup> The resultant M<sup>III</sup>L

**SCHEME 1.** Proposed Mechanistic Steps in the Reduction of CO<sub>2</sub> by Metal Tetraaza-macrocylics<sup>a</sup>



<sup>a</sup> Hydrogen production (blue), formate production (red), CO formation (brown), and putative intermediates (green) when M = Co or Ni. D<sup>•</sup> is a highly reduced carbon-centered radical species, such as Et<sub>2</sub>NC<sup>•</sup>HCH<sub>3</sub> or (HO<sub>2</sub>C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>N(C<sup>•</sup>HCH<sub>2</sub>OH).

**TABLE 2.** Reduction Potentials and Association Constants in CH<sub>3</sub>CN for Cobalt(II) Macrocycles M(L1–L8) as Pictured (in CH<sub>3</sub>CN)

macrocyclic	$E_{1/2}^a$	$K_{CO_2}$
L3	-0.34	<0.5
L4	-0.89	<0.5
L5	-1.28	4 <sup>b</sup>
L2	-1.34	26 <sup>b</sup>
L1	-1.34	$1.2 \times 10^{4b}$
L6	-1.41	$9 \times 10^4$
L7	-1.51	$7 \times 10^5$
L8	-1.65	$3 \times 10^6$

<sup>a</sup> Potentials are vs SCE. <sup>b</sup> Spectroscopic determination of  $K_{CO_2}$ .

can be subsequently reduced by two electrons to regenerate the catalytically active state. The source of the reducing equivalents may be P<sup>-</sup>, D<sup>\*</sup>, or [M<sup>I</sup>L]<sup>+</sup> but is unknown for all mechanistic pathways independent of product formed, that is, H<sub>2</sub>, HCO<sub>2</sub><sup>-</sup>, or CO.

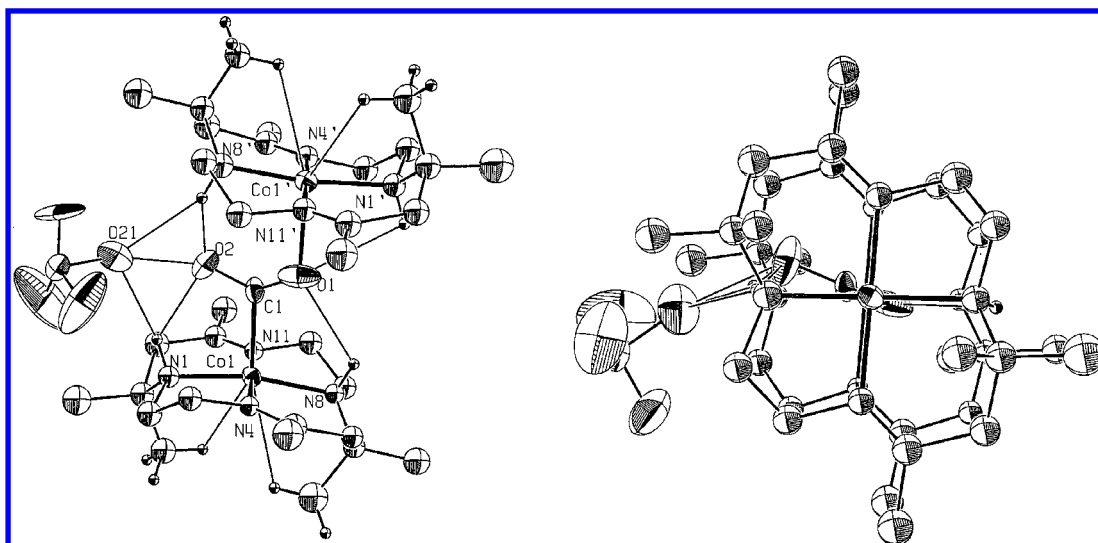
The insertion of CO<sub>2</sub> into a metal–hydride bond cannot easily account for the formation of carbon monoxide, which is proposed to proceed through a metal–CO<sub>2</sub> intermediate (brown pathway, Scheme 1). For example, CO<sub>2</sub> was found to coordinate to [Co<sup>I</sup>L]<sup>+</sup> (L1 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) forming a stable purple adduct that has been spectroscopically characterized in various solvents.<sup>9</sup> In a systematic study utilizing a series of cobalt tetraaza-macrocyclic compounds (Table 2), the association constants for the CO<sub>2</sub> adduct,  $K_3$  in Scheme 1, were found to increase with decreasing Co<sup>III</sup>/I reduction potential.<sup>10</sup> The equilibrium binding constant of CO<sub>2</sub> to [Co<sup>I</sup>L]<sup>+</sup> is much larger in water<sup>11</sup> than it is in CH<sub>3</sub>CN<sup>10</sup> ( $4.5 \times 10^8$  and  $1.2 \times 10^4$  M<sup>-1</sup>, respectively) possibly due to the stabilization of the bound CO<sub>2</sub> via the hydrogen-bonding network of water molecules. Such a trend in CO<sub>2</sub> binding constants for Ni<sup>I</sup>(cyclam)<sup>+</sup>

has been observed: 16 and 4 M<sup>-1</sup> in water and CH<sub>3</sub>CN, respectively.<sup>12,13</sup>

The [L1Co–CO<sub>2</sub>]<sup>+</sup> adduct exhibited thermochromic behavior and turned brownish-yellow in color when cooled.<sup>9</sup> This was attributed to the temperature-dependent solvent coordination to yield [S–L1Co–CO<sub>2</sub>]<sup>+</sup>, where S is solvent.<sup>14,15</sup> While in neat acetonitrile approximately 2% of [L1Co–CO<sub>2</sub>]<sup>+</sup> is six-coordinate and 98% is five-coordinate, in water the CO<sub>2</sub> adduct is entirely six-coordinate at room temperature. IR data supports the existence of such CO<sub>2</sub> adducts, and both five- and six-coordinate compounds were found to be stabilized by hydrogen bonds between the amine hydrogens of the tetraaza-macrocyclic and the bound CO<sub>2</sub>.<sup>14</sup> <sup>1</sup>H NMR studies of the CO<sub>2</sub> adducts showed the existence of only diamagnetic molecules. X-ray absorption near-edge spectroscopy (XANES) provided evidence for the existence of [S–L1Co<sup>III</sup>–(CO<sub>2</sub><sup>2-</sup>)]<sup>+</sup> and the first direct evidence that [Co<sup>I</sup>L]<sup>+</sup> promotes two-electron transfer to CO<sub>2</sub>.<sup>16</sup> On the other hand, the [(cyclam)Ni–CO<sub>2</sub>]<sup>+</sup> adduct exhibited no spectral features typical of Ni<sup>III</sup>, suggesting that the two-electron chemistry observed with [Co<sup>I</sup>L]<sup>+</sup> does not occur with [Ni(cyclam)]<sup>+</sup>.<sup>12</sup> Additionally, six-coordinate [S–(cyclam)Ni<sup>I</sup>–CO<sub>2</sub>]<sup>+</sup> compounds have not been observed or isolated.

Transient flash photolysis experiments with [Co<sup>II</sup>L1]<sup>2+</sup> provided the first conclusive evidence that P<sup>-</sup>, [Co<sup>I</sup>L]<sup>+</sup>, and [L1Co<sup>I</sup>–CO<sub>2</sub>]<sup>+</sup> were plausible intermediates in carbon monoxide production.<sup>15</sup> After laser excitation of P in the presence of [Co<sup>II</sup>L1]<sup>2+</sup> and TEA, spectral features consistent with electron transfer from P<sup>-</sup> to [Co<sup>II</sup>L1]<sup>2+</sup> to form a [Co<sup>I</sup>L]<sup>+</sup> species were observed with a rate constant of  $1.1 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup> ( $k_2$  in Scheme 1). When CO<sub>2</sub> was introduced, [Co<sup>I</sup>L]<sup>+</sup> was observed, but its lifetime decreased due to reaction with CO<sub>2</sub>. A bimolecular rate constant of  $1.7 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup> was extracted from the CO<sub>2</sub> concentration-dependence of the pseudo-first-order rate constant for [L1Co–CO<sub>2</sub>]<sup>+</sup> formation ( $k_3$  in Scheme 1). The product of the reaction of [Co<sup>I</sup>L]<sup>+</sup> and CO<sub>2</sub> displayed spectral features consistent with five- and six-coordinate CO<sub>2</sub> adducts.

The [L1Co–CO<sub>2</sub>]<sup>+</sup> adduct gradually reacted consistent with a rate law second-order in [Co<sup>I</sup>L–CO<sub>2</sub>]<sup>+</sup> with an apparent rate constant of  $(1.0 \pm 0.1) \times 10^{-3}$  M<sup>-1</sup> s<sup>-1</sup> in CO<sub>2</sub>-saturated CH<sub>3</sub>CN, conditions where almost no free [Co<sup>I</sup>L]<sup>+</sup> exists ( $K_{CO_2} = 1.2 \times 10^4$  M<sup>-1</sup>). [Ni(cyclam)(CO<sub>2</sub>)]<sup>+</sup> also reacted with second-order kinetics,  $k = 1.08 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup> in CO<sub>2</sub>-saturated water at pH 5.2.<sup>17</sup> However, since these solutions contained Ni(cyclam)<sup>+</sup> as an equilibrium mixture ( $K_{CO_2} = 16$  M<sup>-1</sup>), a fast reaction of [Ni(cyclam)(CO<sub>2</sub>)]<sup>+</sup> with Ni<sup>I</sup>(cyclam)<sup>+</sup> as an electron donor was possible.



**FIGURE 1.** X-ray structure of  $[(\text{LCo}-\text{C}(\text{OH})\text{O})-\text{CoL}](\text{ClO}_4)_2^{2+}$ . The hydrogen atoms on the amine nitrogen atoms form hydrogen bonds to the bridging  $\text{CO}_2\text{H}^-$ , and one hydrogen on each of the axial methyl groups forms a hydrogen bond to the cobalt centers (left); top view, approximately perpendicular to the plane of the macrocycle (right).<sup>18</sup> This figure was reproduced from with permission of the copyright holders.

A second-order rate law suggests one of three mechanistic possibilities: (1) outer-sphere electron transfer that involves two  $\text{M}-\text{CO}_2$  complexes; (2) outer-sphere electron transfer that involves one  $\text{M}-\text{CO}_2$  complex and a metal complex, such as a  $\text{M}(\text{I})$  species, as an electron donor; (3) an inner-sphere electron transfer mechanism through a binuclear intermediate. In support of a binuclear intermediate,  $[\text{L1Co}-\text{C}(\text{OH})\text{O}-\text{CoL1}]^{3+}$  was isolated from the reaction mixture and crystallographically characterized in the solid state, Figure 1.<sup>9</sup> Because one cannot clearly distinguish among the three possible reaction pathways for  $[\text{Co}^{\text{I}}\text{L1}]^+$ , the binuclear complex was placed in a separate box in the Scheme 1 to highlight this inconsistency.

In nonaqueous solvents, the CS for  $\text{Co}^{\text{I}}\text{L}$  was on average 20.<sup>7</sup> However, the  $\text{pK}_a$  of the  $[\text{L1Co}-\text{H}]^{2+}$  was approximately 11, and therefore,  $[\text{Co}^{\text{I}}\text{L1}]^+$  showed poor selectivity (CS = 0.5–10) toward  $\text{CO}_2$  reduction, especially at low pH. When phenazine was employed as a photosensitizer for  $[\text{Co}(\text{cyclam})(\text{Cl})_2]^+$  in a TEA/ $\text{CH}_3\text{OH}/\text{CH}_3\text{CN}$  mixture ( $v/v/v = 1/1/2$ ), the  $[(\text{cyclam})\text{Co}^{\text{III}}-\text{H}]^{2+}$  formed reduced  $\text{CO}_2$  exclusively to form  $\text{HCO}_2^-$  with enhanced selectivity, CS = 140, and a quantum yield 0.07.<sup>8</sup> When *p*-terphenyl was used as a photosensitizer, the total quantum yield for CO and  $\text{HCO}_2^-$  reported is 0.13.<sup>7</sup>  $[\text{CoL1}]^{2+}$  also exhibited the highest TN of the compounds discussed in this Account, ~500 for 18 h of irradiation.<sup>6</sup> The  $[\text{Ni}^{\text{I}}(\text{cyclam})]^+$  compound was shown to electrochemically reduce  $\text{CO}_2$  to CO with 100% current efficiency and selectivity ratios over 100 indicating that it was an attractive option for photocatalysis.<sup>19</sup> However, this selectivity has

not been observed for  $\text{Ni}(\text{cyclam})^{2+}$  under illumination conditions, where the quantum yield for CO formation is only  $6.0 \times 10^{-4}$ .<sup>20</sup>

**Supramolecular Complexes.** Covalent attachment of a sensitizer to a coordination compound capable of  $\text{CO}_2$  catalysis, so-called supramolecular complexes, has been employed to increase the quantum efficiency of excited-state electron transfer from a photoactive donor to a catalytic acceptor moiety. Two classes of compounds have been investigated for  $\text{CO}_2$  reduction based on ruthenium polypyridyl sensitizers: (1) linkage to a nickel cyclam catalyst (Kimura)<sup>21–23</sup> and (2) linkage to  $\text{Re}(\text{bpy})(\text{CO})_3\text{X}$  catalysts (Ishitani).<sup>24,25</sup> Both classes of supramolecular catalysts have increased stability and higher turnover numbers than the corresponding bimolecular approach.

Kimura et al. synthesized the supramolecular complex  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{bpy}-6'-\text{cyclam})\text{Ni}^{\text{II}}]^{4+}$ , Figure 2. The 6' substitution on the bipyridine ligand induced severe steric hindrance about the  $\text{Ru}^{\text{II}}$  metal center. This structural change lowered the ligand field excited states and thus shortened the MLCT excited state lifetime significantly. Temperature-dependent emission studies indicated that the MLCT excited state was quenched via energy transfer and not the preferred electron transfer to the  $\text{Ni}^{\text{II}}^{2+}$  catalyst.<sup>26</sup> In efforts to prevent the distortion of the  $\text{Ru}-\text{N}$  core, Kimura et al. substituted 1,10-phenanthroline (phen) in the 5' position with the same Ni cyclam,  $[\text{Ru}(\text{phen})_2(\text{phen}-5'-\text{cyclam})\text{Ni}]^{4+}$ , Figure 2.<sup>22</sup> Although the overall efficiency was still comparable to a nontethered refer-

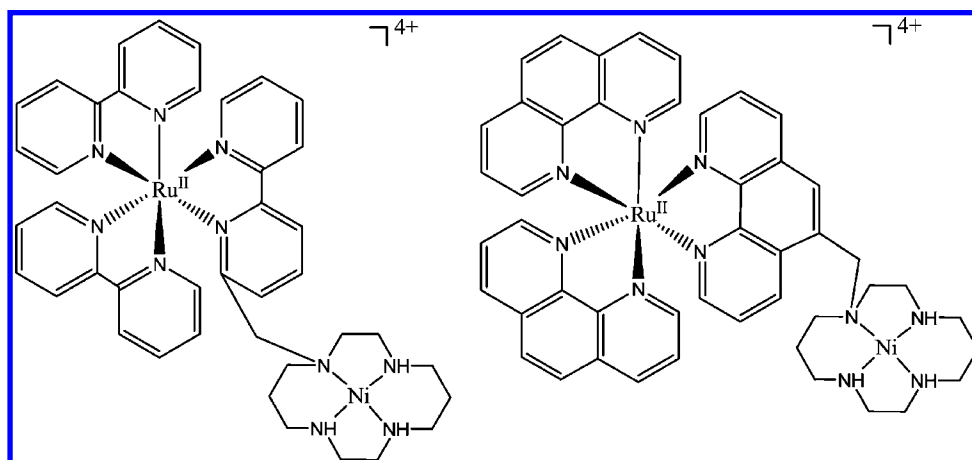


FIGURE 2. Chemical structure of (left) [Ru<sup>II</sup>(bpy)<sub>2</sub>(bpy-cyclam)Ni<sup>II</sup>]<sup>4+</sup> and (right) [Ru<sup>II</sup>(phen)<sub>2</sub>(phen-cyclam)Ni<sup>II</sup>]<sup>4+</sup>.

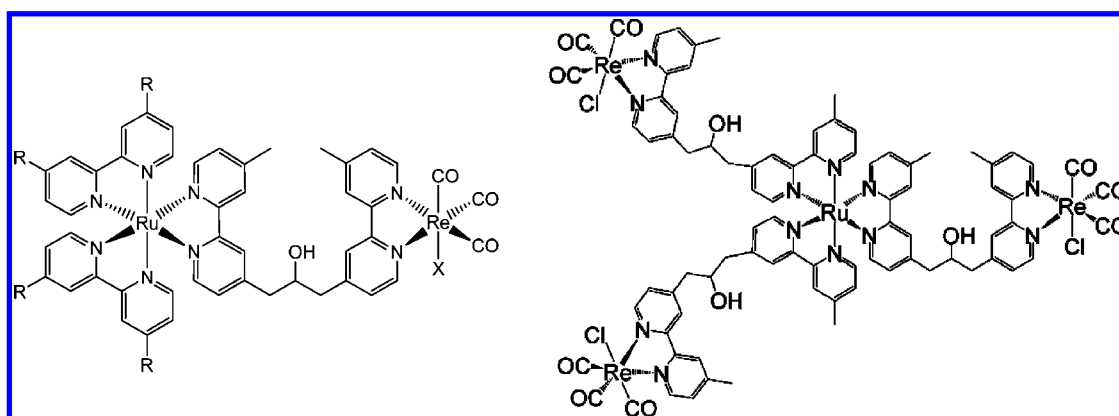


FIGURE 3. Supramolecular complexes utilized by Ishitani et al.: (left) ReRu; (right) Re<sub>3</sub>Ru.

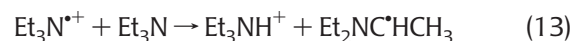
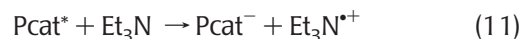
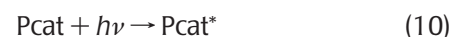
ence system, the photochemical stability increased, resulting in higher TNs.<sup>22</sup>

Ishitani, et al. synthesized supramolecular molecules based on [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and [Re(4,4'-R<sub>2</sub>-2,2'-bpy)(CO)<sub>3</sub>(X)]<sup>n+</sup>, where R = H, CH<sub>3</sub>, and CF<sub>3</sub>; X = Cl<sup>-</sup> (*n* = 0) or X = P(OEt)<sub>3</sub> and pyridine (*n* = 1) (Figure 3).<sup>24,25</sup> The molecules had one, two, or three pendent Re moieties covalently bonded to a Ru<sup>II</sup> sensitizer, RuRe, RuRe<sub>2</sub>, and RuRe<sub>3</sub>, respectively. The use of a central Ru–polypyridyl sensitizer increased the light-harvesting efficiency over Re(4,4'-R<sub>2</sub>-2,2'-bpy)(CO)<sub>3</sub>(X) alone, thereby addressing a significant drawback to near-UV-absorbing Re-based catalysts. The RuRe(P(OEt)<sub>3</sub>) compound exhibited the highest quantum efficiency,  $\phi = 0.21$ , and a TN of 232.<sup>25</sup>

## IV. Type II

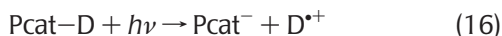
Type II catalysis occurs when one single compound acts as both the light absorber and the catalyst. The photocatalyst, Pcat, is reduced by excited-state reductive quenching as described for Type I catalysis (eqs 10 and 11). Similar to the reactivity discussed with Type I complexes, oxidized amine donors undergo subsequent reactivity to produce, D\*, which

can reduce a second Type II compound (eqs 13 and 14). The reduced compound, Pcat<sup>-</sup>, is an active state of the catalyst and directly interacts with CO<sub>2</sub> (eq 12).



The compounds that have been investigated for Type II catalysis are the MLCT excited states of Re(bpy)(CO)<sub>3</sub>X and the  $\pi$ - $\pi^*$  excited states of metallo-macrocycles. The latter excited states are efficiently quenched by the d-orbitals of the transition metal such that efficient reductive quenching requires the formation of a ground-state inner-sphere complex with the sacrificial amine donor, Pcat–D (eq 15). Upon light excitation, the Pcat–D bond is heterolytically cleaved resulting in a reduced compound, Pcat<sup>-</sup>, and an oxidized amine donor, D<sup>+</sup> (eq 16). It should be noted that all Type II complexes could

also be used as catalysts for Type I approaches with an appropriate photosensitizer.



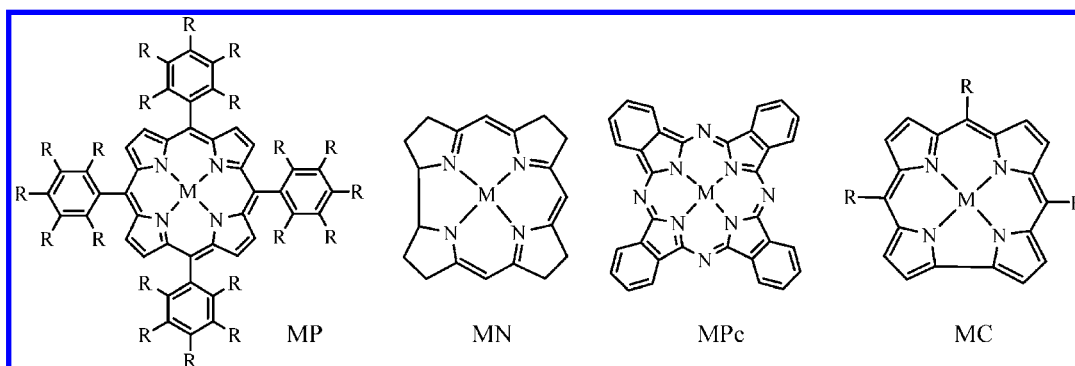
### Metalloporphyrins and Related Metallomacrocycles.

The metalloporphyrins and related metallo-macrocycles studied for CO<sub>2</sub> reduction reactivity include metalloporphyrins (MP), metallocorrins (MN), metallophthalocyanines (MPc), and metallocorroles (MC), Figure 4, where M = Fe or Co.<sup>27–31</sup>

Scheme 2 illustrates a Type II reaction mechanism with a metalloporphyrin, MP, as a representative macrocycle. The active

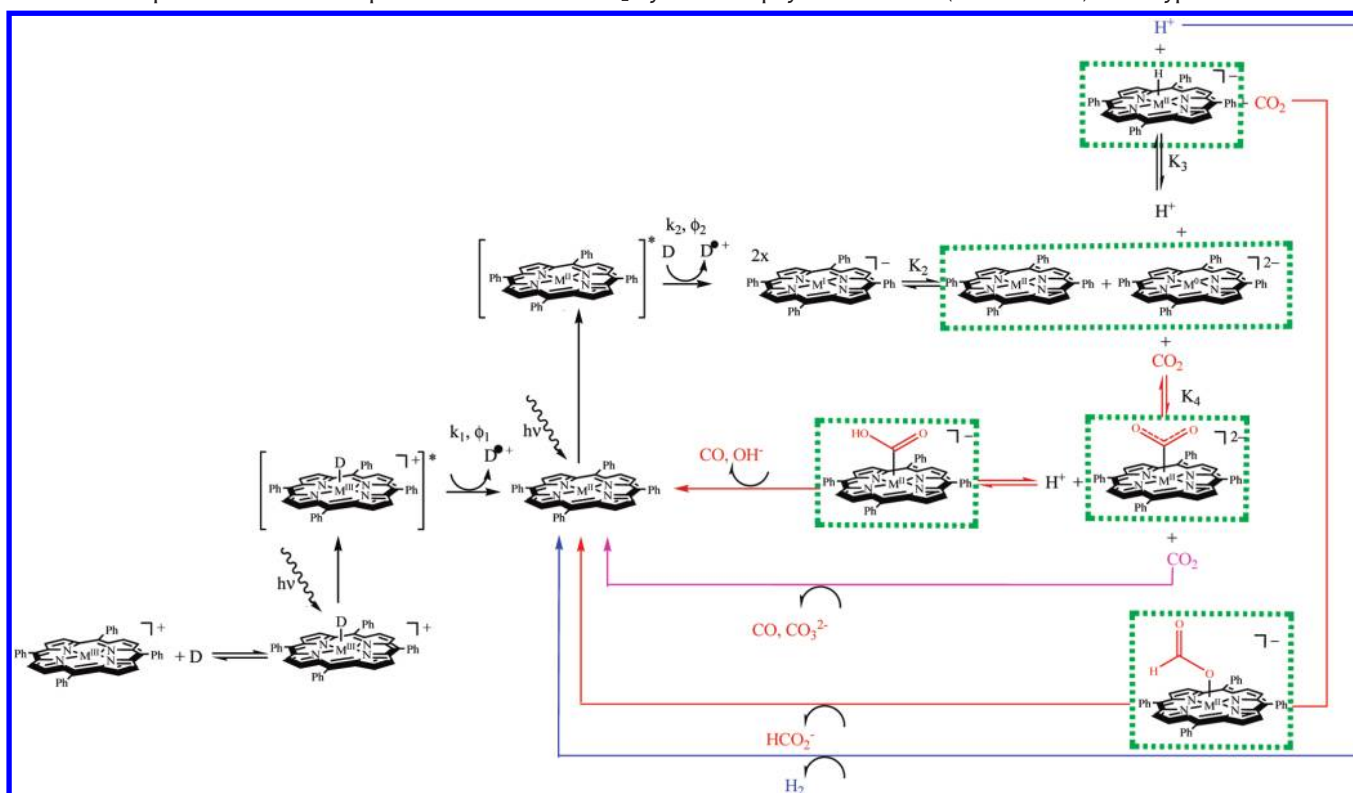
catalytic states as identified by cyclic voltametry have the metal in the formal oxidation state of zero for porphyrins [M<sup>0</sup>P]<sup>2-</sup> and corrins [M<sup>0</sup>N]<sup>2-</sup>, +1 for corroles [M<sup>I</sup>C]<sup>2-</sup>, and +1 with a reduced phthalocyanine ring [M<sup>I</sup>Pc<sup>-</sup>]<sup>2-</sup>. Some MPs previously investigated bear functional groups with negative or positive charges at the meso substituents. Because the effects of these charges on the redox reaction is secondary, these peripheral charges are ignored in the following discussions.

Prolonged photolysis of metallo-macrocycles in the presence of TEA resulted in the formation of [M<sup>I</sup>P]<sup>-</sup>, [M<sup>I</sup>N]<sup>-</sup>, [M<sup>I</sup>Pc]<sup>-</sup>, and [M<sup>I</sup>C]<sup>-</sup> through stepwise reductive quenching with quan-



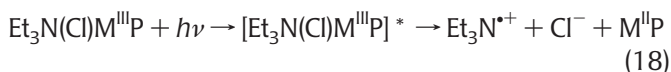
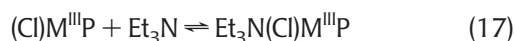
**FIGURE 4.** Metal porphyrin derivatives investigated for CO<sub>2</sub> reduction: (left to right) metalloporphyrin (MP), metallocorrin (MN), metallophthalocyanine (MPc), and metallocorrole (MC, where R = C<sub>6</sub>F<sub>5</sub> or 2,6-C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>).

**SCHEME 2.** Proposed Mechanistic Steps in the Reduction of CO<sub>2</sub> by Metal Porphyrin Derivatives (M = Fe or Co) via a Type II Mechanism<sup>a</sup>



<sup>a</sup> Hydrogen production (blue), formate production (red), CO formation (brown and pink), and putative intermediates (green); as a representative compound, metalloporphyrin is illustrated.

tum yields for the sequential steps,  $\phi_1$  and  $\phi_2$  (Scheme 2). More specifically, a TEA donor binds axially to  $[M^{III}P]^+$ , eq 17.<sup>27,28</sup> Light excitation of this adduct is proposed to result in intramolecular reductive quenching to yield  $[M^{II}P]$ , eq 16. While TEA binds to  $[M^{III}P]^+$ , the UV–vis spectrum of the resultant  $[M^{II}P]$  was not dependent upon the TEA concentration, suggesting that TEA does not bind to  $[M^{II}P]$ . However, given the extremely short lifetime of metalloporphyrins, like hemes, a weak TEA adduct must form prior to absorption of the second photon to account for the observed formation of  $[M^IP]^-$ , not shown schematically.<sup>32</sup> The quantum yield for the second quenching step is typically an order of magnitude smaller than that of the first quenching step due to the weaker ground state adduct formed.<sup>32</sup>



Note that for each of these catalysts, further reduction is needed to generate the catalytically active state.

Formation of the catalytically active state,  $[M^0P]^{2-}$ , by direct light excitation has not been observed. Alternatively, it is proposed that this state is formed via disproportionation, eq 19.<sup>27</sup>



Kinetic evidence for a disproportionation reaction of  $[Fe^IP]^{-}$ , where P = tetrakis(*N*-methyl-2-pyridyl)porphyrin, was found.<sup>27</sup> While the kinetic data was complicated by the presence of different porphyrin isomers, the rate law was clearly second-order in  $[Fe^IP]^{-}$ , consistent with eq 19.

Disproportionation is highly unfavorable for all the metalloporphyrins discussed, and therefore the concentration of the active state,  $[M^0P]^{2-}$ , must be small. The observed reactivity has been rationalized by a favorable interaction between the active state and H<sup>+</sup> or CO<sub>2</sub> ( $K_3$  and  $K_4$  in Scheme 2). Recall that increased electron density on the cobalt(II) in tetraaza-macrocycles favored CO<sub>2</sub> binding; therefore it is likely that the active  $[M^0P]^{2-}$  favors adduct formation relative to more oxidized forms.<sup>10</sup> Protonation of the putative  $[M^0P-CO_2]^{2-}$  to form a metal carboxylic acid compound that subsequently decomposes to M<sup>II</sup>P, CO, and OH<sup>-</sup> has been proposed. Alternatively, under high CO<sub>2</sub> concentrations,  $[M^0P-CO_2]^{2-}$  may react with CO<sub>2</sub> to yield M<sup>II</sup>P, CO, and CO<sub>3</sub><sup>2-</sup> (cyan in Scheme 2). Experimental proof of  $[M^0P-CO_2]^{2-}$  species is lacking due to the reactive nature of these highly reduced compounds; indeed,  $[M^0P-CO_2]^{2-}$  has neither been observed nor isolated. However, electrochemical reduction of CO<sub>2</sub> reported by Ham-mouche et al.<sup>33</sup> indicate that  $[Fe^0P]^{2-}$  is the catalytically active

species, consistent with photochemical data. Therefore the reaction mechanisms proposed for formate and carbon monoxide production are based on presumed similarities to other catalysts discussed (i.e., metal tetraaza-macrocycles).

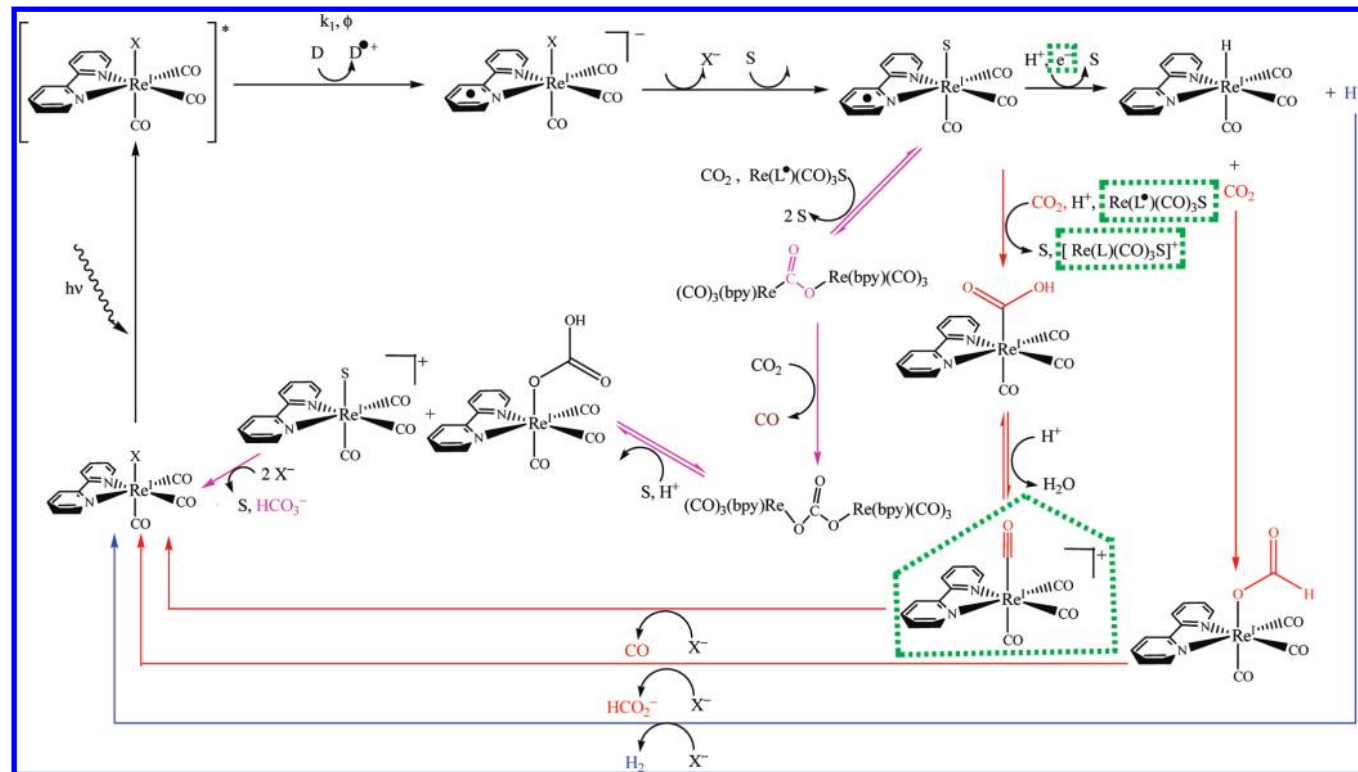
Metalloporphyrins and related metallo-macrocycles are strong light absorbers with extremely large extinction coefficients in the visible spectral region. However, yields of active catalyst formed after light absorption are very low, behavior reasonably attributed to the short picosecond lifetimes of the excited states that are formed. In addition, metalloporphyrins and related metallo-macrocycles undergo unwanted hydrogenation of the macrocycle ring, and these degradation products seem to catalyze the reduction of protons over CO<sub>2</sub>. The TNs reported range from 40 to 300, and the best reported are as follows: metalloporphyrins, 300 (8 h); metallocorrins, 100 (30 h); metallophthalocyanines, 50 (6 h); metallocorroles, 300 (8 h).<sup>29–31</sup>

**Re(CO)<sub>3</sub>(bpy)X-Based Complexes.** Hawecker et al. were the first to investigate Re<sup>I</sup>(L)(CO)<sub>3</sub>X, where X = Cl<sup>-</sup> or Br<sup>-</sup> and L = 4,4'-R<sub>2</sub>-2,2'-bipyridine (R = H or CH<sub>3</sub>) or 1,10-phenanthroline, for photochemical CO<sub>2</sub> reduction.<sup>34</sup> Upon light excitation, Re<sup>I</sup>(L)(CO)<sub>3</sub>X is promoted to an MLCT excited state with a Re<sup>II</sup> metal center and an electron located on the L ligand. In the presence of sacrificial amine donors, the excited state is reductively quenched to yield  $[Re^I(L^*)(CO)_3X]^{-}$  (where L\* is an anion radical),  $k_1$  and  $\phi_1$  in Scheme 3. Solvent (S) is proposed to replace the halide ligand to yield the putative catalytically active state,  $[Re^I(L^*)(CO)_3S]$ .<sup>35</sup> Halide ligand exchange, Cl<sup>-</sup> for Br<sup>-</sup>, was observed for  $[Re^I(L^*)(CO)_3X]^{-}$ .<sup>34</sup>

Reactions of  $[Re^I(L^*)(CO)_3S]$  with a proton are proposed to result in the formation of a rhenium–hydride bond. Formate production is thought to occur by CO<sub>2</sub> insertion into the Re–hydride bond (red in Scheme 3), behavior consistent with other catalysts discussed. Sullivan prepared  $[Re^I(bpy)(CO)_3H]$  and reacted it with CO<sub>2</sub>.<sup>36</sup> The rate constant of this dark reaction indicated a remarkable solvent dependency that increased with the dielectric constant of the medium.<sup>36,37</sup>  $[Re^I(bpy)(CO)_3(OC(H)O)]$  was formed in 81% yield in CO<sub>2</sub>-saturated THF. Addition of excess halide to the solvent prevented  $[Re^I(bpy)(CO)_3(OC(H)O)]$  formation and increased the yield of CO production.<sup>34</sup>

While formate production is reasonably understood, the mechanism of CO formation is still an area of active investigation and debate. Upon protonation of a putative Re–CO<sub>2</sub> adduct, a metal carboxylate intermediate was observed that undergoes acid-promoted hydrolysis to yield H<sub>2</sub>O and CO. Gibson et al. characterized Re(L)(CO)<sub>3</sub>(COOH) and proposed that proton-promoted dehydroxylation of Re(L)(CO)<sub>3</sub>(COOH)



SCHEME 3. Proposed Mechanistic Steps in the Reduction of CO<sub>2</sub> by Re(CO)<sub>3</sub>(X<sub>2</sub>-bpy)X<sup>a</sup>

<sup>a</sup> Hydrogen generation (blue), formate production (red), CO formation (pink and brown), bicarbonate formation (pink), and putative intermediates and electron sources (green).

could yield  $\text{Re}(\text{L})(\text{CO})_4^+$ , which would release CO under irradiation (or when it reacts with  $\text{X}^-$ ) and regenerate the initial compound.<sup>38,39</sup> As all CO in  $\text{Re}(\text{L})(\text{CO})_4^+$  may exchange with  $\text{X}^-$ , this pathway explains prior results that demonstrated that the use of  $^{13}\text{CO}_2$  resulted in the formation of the fully labeled *fac*- $\text{Re}(\text{L})(^{13}\text{CO})_3\text{X}$ .<sup>34</sup>

The source of the second electron necessary to form the carboxylic acid intermediate is unknown. Ishitani's recently conducted systematic study of  $\text{Re}(\text{bpy})(\text{CO})_3\text{X}$  with  $\text{X} = \text{SCN}^-$ ,  $\text{Cl}^-$ , or  $\text{CN}^-$  provided insight into this unknown.<sup>4</sup> A mixed solution of  $\text{Re}(\text{bpy})(\text{CO})_3\text{CN}$  and  $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$  displayed photocatalytic activity 1.2 times greater than that of  $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$  alone. It was proposed that  $[\text{Re}^+(\text{bpy}^*)(\text{CO})_3\text{CN}]^-$  provides the second electron and reduces the CO<sub>2</sub> adduct  $[\text{Re}^+(\text{bpy}^*)(\text{CO})_3(\text{CO}_2)]$ . Based on the presumed additive effect between certain Re complexes, they studied a mixed solution of 1:25  $[\text{Re}^+(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})]^+$  and  $[\text{Re}^+(4,4'-(\text{MeO})_2\text{bpy})(\text{CO})_3(\text{P}(\text{OEt})_3)]^+$ . The acetonitrile compound,  $[\text{Re}^+(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})]^+$ , is expected to have a high efficiency for solvent ligand loss, and  $[\text{Re}^+(4,4'-(\text{MeO})_2\text{bpy})(\text{CO})_3(\text{P}(\text{OEt})_3)]^+$  has both a high efficiency for  $\text{Re}(4,4'-(\text{MeO})_2\text{bpy})(\text{CO})_3(\text{P}(\text{OEt})_3)$  formation ( $\phi = 1.6$ ) and high reducing power ( $E_{1/2} = -1.67$  V vs  $\text{Ag}/\text{AgNO}_3$ ). To date, this combination of Re compounds displays the highest efficiency of all molecular CO<sub>2</sub> photocatalysts ( $\phi = 0.59$ ) and

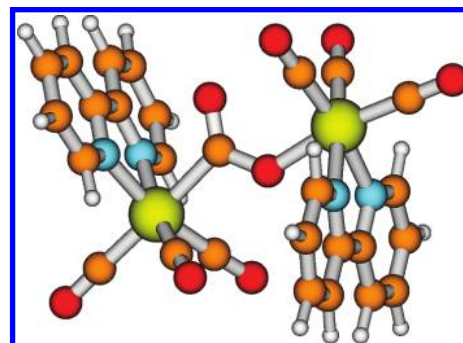


FIGURE 5. Calculated structure of a rhenium dimer,  $(\text{bpy})(\text{CO})_3\text{Re}-\text{CO}_2-\text{Re}(\text{CO})_3(\text{bpy})$ , that is a proposed intermediate in the reduction of CO<sub>2</sub> by  $\text{Re}(\text{CO})_3(\text{bpy})\text{X}$ , where  $\text{X} = \text{Cl}^-$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$ ,  $\text{Br}^-$ ,  $\text{S}$ , or  $\text{PR}_3$  [J. T. Muckerman, unpublished].

provides compelling evidence that the second reducing equivalent comes from another Re compound.<sup>4</sup>

Ishitani's data suggests the possibility of a binuclear intermediate. A Re dimer is an attractive intermediate since a similar product has been isolated from the reaction of CO<sub>2</sub> with a cobalt(I) tetraaza-macrocyclic. In support of a bimetallic intermediate, a CO<sub>2</sub>-bridged Re dimer,  $[\text{Re}(\text{Me}_2\text{bpy})(\text{CO})_3]_2(\text{CO}_2)$ , has been isolated (Figure 5).<sup>38</sup> Clear evidence for the involvement of the CO<sub>2</sub>-bridged dimer as an intermediate in CO formation in photochemical CO<sub>2</sub> reduction was obtained. Photoinduced homolysis of  $[\text{Re}(\text{Me}_2\text{bpy})(\text{CO})_3]_2$  in dry CO<sub>2</sub>-

saturated CH<sub>3</sub>CN resulted in the formation of CO providing evidence that this dimer occurs along the reaction pathway.<sup>35</sup> While the CO<sub>2</sub>-bridged dimer is stable in the absence of CO<sub>2</sub>, it reacts slowly with CO<sub>2</sub> and liberates CO with a 30–50% yield based on Re(Me<sub>2</sub>-bpy)(CO)<sub>3</sub>S. The rate constants are  $9.7 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  in the dark and  $5.1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  under illumination.<sup>35</sup> This stoichiometric reaction resulted in the formation of [Re(Me<sub>2</sub>-bpy)(CO)<sub>3</sub>]<sub>2</sub>(OCO<sub>2</sub>) and Re(Me<sub>2</sub>-bpy)(CO)<sub>3</sub>-(OC(O)OH), which can in principle be recycled before the precipitation as photocatalysts with adequate quencher and added X (e.g., X = Cl<sup>-</sup>) (cyan, Scheme 3).

Because rigorously dry solvents are rarely employed and the usage of amine donors, TEA and TEOA, can eventually introduce proton-rich conditions, it is very possible that both proposed reaction pathways of [Re(L\*)(CO)<sub>3</sub>S] are operative during prolonged photolysis. Under the initial photolysis conditions of low proton concentration inner-sphere two-electron transfer involving a binuclear intermediate may be favored. Over time as the proton concentration increases with TEA decomposition, outer-sphere second electron transfer to Re(L)(CO)<sub>3</sub>(COOH) may become the predominate pathway.

Re(L)(CO)<sub>3</sub>X complexes exhibit the highest selectivity and quantum efficiencies of the catalysts discussed. Little-to-no hydrogen gas is detected resulting in a CS that approaches infinity. [Re(bpy)(CO)<sub>3</sub>(P(OEt)<sub>3</sub>)<sup>+</sup> exhibited the highest single-molecule quantum efficiency of 0.38 and, as previously mentioned, Ishitani's two-molecule approach exhibited a quantum yield of 0.59.<sup>4,40</sup> Turnover numbers were generally low due to complex degradation, and the best reported value was 48.<sup>34</sup> Hori et al.<sup>41</sup> investigated the effects of pressure in liquid CO<sub>2</sub> on the TN using CO<sub>2</sub>-soluble cationic rhenium complexes incorporating a fluorinated counterion and found slight increases in the TN. While a fluorinated counterion impacts the CO<sub>2</sub> solubility of the corresponding rhenium cationic species, it does not help to dissolve the neutral species, which is involved as an intermediate in CO<sub>2</sub> reduction.<sup>42</sup> Recently, neutral CO<sub>2</sub>-soluble rhenium bipyridine complexes bearing fluorinated alkyl substituents were prepared, and their photophysical and photochemical properties were investigated. The photocatalysis investigation with these scCO<sub>2</sub> soluble complexes is an area of current research. In addition to exhibiting low TNs, Re(L)(CO)<sub>3</sub>X only absorbs light at wavelengths shorter than 400 nm in the UV–vis spectral region. These shortcomings are addressed by the supramolecular complexes previously discussed.<sup>24,42</sup>

## V. Summary and Future Outlook

In this Account, we focused on mechanistic and kinetic discussions of photochemical CO<sub>2</sub> reduction to CO and formate using several types of molecular assemblies including metal macrocycles with or without a photosensitizer, Re(bpy)(CO)<sub>3</sub>X and related species, and supramolecular complexes. We gave particular attention to mechanistic steps including the formation of the reduced metal species, the interaction with CO<sub>2</sub>, the reaction kinetics of the CO<sub>2</sub> adduct, and the source of the second electron to produce CO or formate. Moreover, we discussed intermediates that are unknown or controversial.

Clearly, researchers in this field have achieved the efficient coupling of light absorption and charge separation with dark catalytic reactions to produce CO and formate. The quantum yield for CO formation has reached 59% using Re(bpy)(CO)<sub>3</sub>X-type catalysts. Carbon dioxide, a stable end-product of combustion, was activated by proton-assisted, multielectron transfer reactions using metal catalysts, and in some cases, a CO<sub>2</sub>- or C(OH)O-bridged dinuclear species was observed or isolated during the catalytic reactions. Metal catalysts such as monomeric cobalt(II) macrocycles can donate two electrons to the bound CO<sub>2</sub>, thereby facilitating a low-energy pathway to produce two-electron-reduced CO from CO<sub>2</sub> via the Co(III) carboxylate, L–Co(III)(CO<sub>2</sub><sup>2-</sup>). However, a typical turnover frequency and a turnover number for CO formation are less than 10 h<sup>-1</sup> and 200, respectively, owing to the nature of the extremely stable CO<sub>2</sub> molecule and low stability of catalysts and photosensitizers. There exist many formidable challenges for CO<sub>2</sub> utilization. Can we produce a liquid fuel, for example, methanol, from CO<sub>2</sub> by molecular photochemical methods? Can we couple reductive (i.e., CO<sub>2</sub> reduction) and oxidative (i.e., water oxidation) half-reactions to remove the need for a sacrificial electron donor? Can we develop robust inexpensive catalysts or photosensitizers? Innovative explorations that strive to improve catalysts or photosensitizers to produce renewable fuels (CO and methanol) via low-energy pathways using earth-abundant materials are essential for creating carbon-neutral energy sources and for avoiding catastrophic global warming.

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