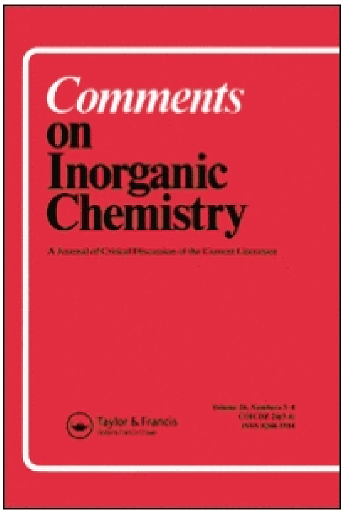

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Photo-Induced Generation of Dihydrogen and Reduction of Carbon Dioxide Using Transition Metal Complexes

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Photo-Induced Generation of Dihydrogen and Reduction of Carbon Dioxide Using Transition Metal Complexes

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Homogeneous and microheterogeneous transition-metal-based systems that generate dihydrogen and/or reduce carbon dioxide upon irradiation with visible light are considered. Most of the systems involve polypyridine complexes of the d^6 centers cobalt(III), rhodium(III), iridium(III), ruthenium(II) and rhenium(I). Complexes with diimine ligands serve as photosensitizers and/or catalyst precursors. The corresponding d^8 metal centers and d^6 hydrides are important intermediates: bimolecular reactions of the hydrides or their reactions with H_2O/H_3O^+ are responsible for formation of dihydrogen. When carbon dioxide is also present, it may insert into the metal-hydride bond to yield formate. Mechanistic schemes for some dual-acting photoconversion systems that generate both dihydrogen and carbon monoxide or formate are considered.

Key Words: *electron transfer, photoconversion, catalysis, metal complexes, metal hydrides, dihydrogen, carbon dioxide, carbon monoxide, formate, reduction*

INTRODUCTION

The photo-induced dissociation of water into dihydrogen and oxygen and the reduction of carbon dioxide to methanol or methane are of con-

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siderable interest as processes for photoconverting abundant materials to useful fuels. Both processes require photosensitizers capable of absorbing the incident light and catalysts for binding (and activating) the substrates. Transition metal complexes are well suited for use in photoconversion systems[1]—the complexes generally absorb strongly in the visible and their excited states are frequently long lived and capable of rapid electron transfer. In addition, transition metal complexes are able to undergo the multi-equivalent changes required for the formation of highly reduced or oxidized species and can be designed to have vacant (or readily accessible) coordination sites for the binding of intermediates. Further, they can effect the desired chemistry under homogeneous conditions. As a consequence, transition metal complexes have found widespread application in homogeneous and microheterogeneous systems that generate dihydrogen or reduce carbon dioxide upon irradiation with visible light. Systems that generate dihydrogen and oxygen from water when irradiated have recently been reviewed by Amouyal.[2] Some of these systems are also capable of reducing carbon dioxide to CO or formate and beyond. Such dual-acting systems raise intriguing mechanistic questions and are the primary focus of this review.

Thermodynamic Considerations. One- and two-electron potentials (vs. NHE) for H^+ and CO_2 reduction at pH 7 and 25°C are summarized below.[3] The standard state is 1 atmosphere for the gases H_2, CO_2 and CO, and 1 M for the other species.

$2H^+ + 2e^- = H_2$ -0.41 V
$H^+ + e^- = \cdot H$ -2.69 V
$\cdot H + e^- = :H^-$ $+0.03$ V
$H^+ + 2e^- = :H^-$ -1.33 V

$CO_2 + 2e^- = :CO_2^{2-}$ -1.55 V
$CO_2 + e^- = \cdot CO_2^-$ -1.9 V
$\cdot CO_2 + e^- = :CO_2^{2-}$ -1.2 V
$CO_2 + H^+ + 2e^- = HCO_2^-$ -0.49 V
$CO_2 + 2H^+ + 2e^- = CO + H_2O$ -0.53 V

The pH dependence of the two-electron reductions are shown in Fig. 1.[4–6] Both reductions are more favorable at low pH with the two-electron reduction of water being more favorable over the entire pH range.

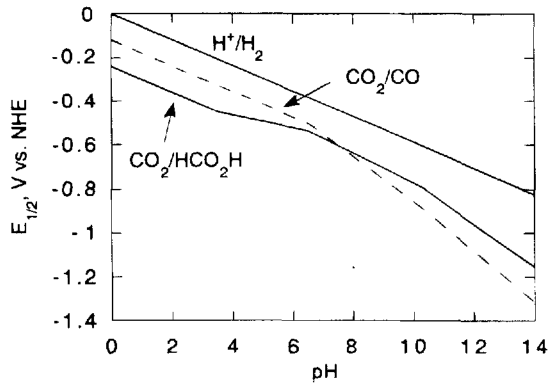


FIGURE 1 Two-electron reduction potentials for reduction of hydrogen ion/water to dihydrogen, carbon dioxide to carbon monoxide, and carbon dioxide to formic acid as a function of pH. Inflections occur at the pK_a's of the carbon dioxide oxidant (6.5 and 10.3) and at the pK_a of the formate product (3.5).

The pH dependence of the CO_2 reduction appears complex because of the CO_2-bicarbonate-carbonate and formic acid-formate equilibria. These result in the two-electron $CO_2(CO_3^{2-})$ reduction becoming appreciably less favorable than H_2O reduction above pH 6.5.

Mechanistic Considerations. In principle, all couples more reducing than the H_2O/H_2 and/or CO_2/CO couples are capable of generating dihydrogen and/or reducing carbon dioxide in an aqueous medium. However, in practice, these reactions generally proceed extremely slowly in the absence of a suitable catalyst. We consider the dihydrogen-generating reactions first. Both the one- and two-electron H^+ reduction steps are energetically very unfavorable, and the $\cdot H$ and H^- produced need to be stabilized in order for the reaction to proceed at a reasonable rate. Studies of homogeneous dihydrogen-formation reactions and their reverse, dihydrogen activation, mediated by a variety of metal complexes have shown that the d^6 hydrides[1,7-13] (and possibly H_2 complexes[12,14-16]) are important intermediates. The reaction scheme for d^6–d^8 (M^{III}–M^I) systems is illustrated in Eqs. (1)–(4).

$$M^{II}L + e^- \rightarrow M^IL \qquad (1)$$

$$M^IL + H^+ \rightleftharpoons M^{III}L(H^-) \qquad (2)$$

$$M^{III}L(H^-) + H^+ \rightleftharpoons ML(H_2) \rightleftharpoons M^{III}L + H_2 \tag{3a}$$

$$M^{III}L + e^- \rightarrow M^{II}L \tag{3b}$$

$$2M^{III}L(H^-) \rightleftharpoons ML(H_2) + M^{II}L \rightleftharpoons 2M^{II}L + H_2 \tag{4}$$

The parent d^7 (or d^6) metal complex is reduced to a coordinatively unsaturated d^8 complex which, depending on its basicity (metal hydride pK_a's range from <0 to >14) and the solution acidity, undergoes oxidative addition of H^+ to form a d^6 hydride (Eq. (2)). The hydride complex may either yield the d^6 complex and dihydrogen via a pathway first order in the hydride and in H_2O/H_3O^+ (Eq. (3a)), convert to the d^7 complex and dihydrogen in a second-order reaction (Eq. (4)), or generate dihydrogen by other even more complex pathways. One such pathway, implicated in the reactions of a macrocyclic cobalt(III) hydride, is second order in the hydride and *inverse* in acid, consistent with rate determining reaction of $M^{III}L(H^-)$ with M^IL.[17]

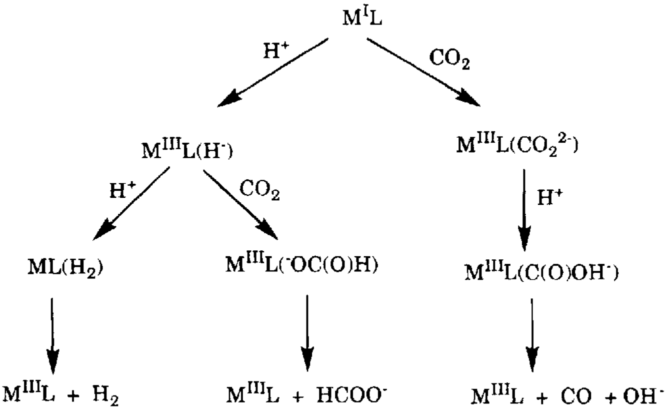
Similar considerations apply to the reduction of CO_2 to CO. Reduction of CO_2 to free CO_2^- or CO_2^{2-} is thermodynamically very unfavorable and, because of the large structural rearrangement, it is also kinetically unfavorable. In contrast, oxidative addition of CO_2 to M^IL to form a metallocarboxylate $M^{III}L(CO_2^{2-})$ (Eq. (5a)) stabilizes the reduced moiety which can then react with H^+ to form $M^{III}L$, CO and OH^- (Eq. (5b)).[5] Another pathway for CO_2 reduction is by insertion into a metal-hydride bond to form a formato complex (Eq. (5c)).[18,19]

$$M^IL + CO_2 \rightleftharpoons M^{II}L(CO_2^-) \rightleftharpoons M^{III}L(CO_2^{2-}) \tag{5a}$$

$$\begin{aligned} &M^{III}L(CO_2^{2-}) + H^+ \rightleftharpoons M^{III}L(C(O)OH^-) \\ &\rightleftharpoons M^{III}L + CO + OH^- \end{aligned} \tag{5b}$$

$$\begin{aligned} &M^{III}L(H^-) + CO_2 \rightleftharpoons M^{III}L(^-OC(O)H) \\ &\rightleftharpoons M^{III}L + HCOO^- \end{aligned} \tag{5c}$$

The relationships between the intermediates implicated in dihydrogen generation and carbon-dioxide reduction are illustrated in Scheme I. The H_2, CO and formate yields depend on the rates of the various competing reactions and accordingly on the various branching ratios.

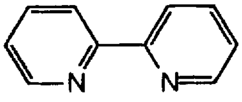


SCHEME I

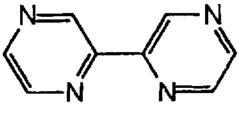
The water gas shift reaction (Eq. (6)) is also important in this context since it equilibrates CO, H_2 and CO_2, presumably via intermediates having much in common with those invoked above.

$$H_2O + CO \rightarrow H_2 + CO_2 \qquad (6)$$

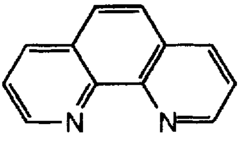
Excited-State Electron Transfer. Two types of excited-state electron-transfer reactions may be distinquished depending on whether the excited state donates (oxidative quenching) or accepts (reductive quenching) an electron from the substrate (quencher). The electron donor may be another metal complex or, in some of the systems to be discussed, an organic substrate which is consumed in the overall reaction (sacrificial donor). The most widely used photosensitizers are d^6 ruthenium(II) complexes RuL_3^{2+} where L = 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) or their substituted derivatives.



2,2'-bipyridine



2,2'-bipyrazine



1,10-phenanthroline

Oxidative quenching forms the very strong oxidant RuL_3^{3+} (Eq.(7a)), while reductive quenching yields the powerful reductant RuL_3^{+} (Eq. (7b)). Unless water oxidation (or some other oxidation reaction) is the goal, a sacrificial donor is generally added to reduce the RuL_3^{3+} produced (Eq. (7c)).

$$*RuL_3^{2+} + A \rightarrow RuL_3^{3+} + A^- \tag{7a}$$

$$*RuL_3^{2+} + D \rightarrow RuL_3^{+} + D^+ \tag{7b}$$

$$RuL_3^{3+} + D \rightarrow RuL_3^{2+} + D^+ \tag{7c}$$

Both quenching pathways find application in the systems to be considered. Commonly used sacrificial donors include triethylamine ($N(CH_2CH_3)_3$, TEA), triethanolamine ($N(CH_2CH_2OH)_3$, TEOA or NTE, nitrilotriethanol), ethylenediaminetetraacetate [$-CH_2N(CH_2COO^-)_2)]_2^{4-}$, EDTA) and ascorbic acid ($C_6H_8O_6$, H_2A). In the first three cases rearrangement of the initially formed radical to a highly reducing species introduces irreversibility, often doubling the quantum yield.

Ground- and excited-state reduction potentials for complexes used as light absorbers (sensitizers) and redox potentials for quenchers and other electron donors are presented in Table I.

SYSTEMS THAT PHOTOGENERATE DIHYDROGEN AND/OR REDUCE CARBON DIOXIDE

Homogeneous or microheterogeneous transition-metal based systems capable of photogenerating dihydrogen and/or reducing carbon dioxide are summarized in Table II. Several of the better characterized systems are discussed below.

RuL_3^{2+}/Co(II)/TEOA or TEA. A system consisting of $Ru(bpy)_3^{2+}$, Co^{2+} and a tertiary amine as electron donor has been reported to reduce CO_2 to CO and generate H_2 upon irradiation with visible light.[20] The amount of CO + H_2 produced and the CO/H_2 ratio depended markedly on the composition of the system. Added 2,9-$(CH_3)_2$phen is more effective than added bpy in promoting CO and H_2 formation in a DMF medium (quantum yields 0.012 and 0.065, respectively).[21]

TABLE I

Reduction potentials for ground- and excited-state couples at ~25°C.[a]

Couple	Medium	$E_{1/2}$, V	Ref.
$\mathrm{Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+}}$	aqueous	1.26	98
$\mathrm{Ru(bpy)_3^{2+}/Ru(bpy)_3^{+}}$	aqueous	–1.28	98
$\mathrm{Ru(bpy)_3^{3+}/{*}Ru(bpy)_3^{2+}}$	aqueous	–0.84	25
$\mathrm{{*}Ru(bpy)_3^{2+}/Ru(bpy)_3^{+}}$	aqueous	0.82	25
$\mathrm{Ru(4,7\text{-}(CH_3)_2phen)_3^{3+}/Ru(4,7\text{-}(CH_3)_2phen)_3^{2+}}$	aqueous	1.09	98
$\mathrm{Ru(4,7\text{-}(CH_3)_2phen)_3^{2+}/Ru(4,7\text{-}(CH_3)_2phen)_3^{+}}$	aqueous	–1.43	99
$\mathrm{Ru(4,7\text{-}(CH_3)_2phen)_3^{3+}/{*}Ru(4,7\text{-}(CH_3)_2phen)_3^{2+}}$	aqueous	–1.01	98
$\mathrm{{*}Ru(4,7\text{-}(CH_3)_2phen)_3^{2+}/Ru(4,7\text{-}(CH_3)_2phen)_3^{+}}$	aqueous	0.67	99
$\mathrm{Ru(bpz)_3^{3+}/Ru(bpz)_3^{2+}}$	CH_3CN	1.98	100
$\mathrm{Ru(bpz)_3^{2+}/Ru(bpz)_3^{+}}$	CH_3CN	–0.68	100
$\mathrm{Ru(bpz)_3^{3+}/{*}Ru(bpz)_3^{2+}}$	aqueous	–0.38	[b]
$\mathrm{{*}Ru(bpz)_3^{2+}/Ru(bpz)_3^{+}}$	aqueous	1.68	101
$\mathrm{Re(bpy)(CO)_3Cl^{+}/Re(bpy)(CO)_3Cl}$[c]	CH_3CN	1.32	102
$\mathrm{Re(bpy)(CO)_3Cl/Re(bpy)(CO)_3Cl^{-}}$	CH_3CN	–1.35	102
$\mathrm{Re(bpy)(CO)_3Cl^{+}/{*}Re(bpy)(CO)_3Cl}$	CH_3CN	–1.0	102
$\mathrm{{*}Re(bpy)(CO)_3Cl/Re(bpy)(CO)_3Cl^{-}}$	CH_3CN	1.0	102
$\mathrm{Co(bpy)_3^{3+}/Co(bpy)_3^{2+}}$	aqueous	0.30	23
$\mathrm{Co(bpy)_3^{2+}/Co(bpy)_3^{+}}$	aqueous	–0.95	23
$\mathrm{Co(4,4'\text{-}(CH_3)_2bpy)_3^{3+}/Co(4,4'\text{-}(CH_3)_2bpy)_3^{2+}}$	aqueous	0.16	23
$\mathrm{Co(4,4'\text{-}(CH_3)_2bpy)_3^{2+}/Co(4,4'\text{-}(CH_3)_2bpy)_3^{+}}$	aqueous	–1.03	23
$\mathrm{Co(2,9\text{-}(CH_3)_2phen)_3^{3+}/Co(2,9\text{-}(CH_3)_2phen)_3^{2+}}$	CH_3CN	0.6	23
$\mathrm{Co(2,9\text{-}(CH_3)_2phen)_3^{2+}/Co(2,9\text{-}(CH_3)_2phen)_3^{+}}$	CH_3CN	–1.16	23
$\mathrm{Co(dmgH)_2/Co(dmgH)_2^{-}}$	aqueous	–0.95	26
$\mathrm{MV^{2+}/MV^{+\cdot}}$	aqueous	–0.45	103
$\mathrm{\overset{+\cdot}{N}(CH_2CH_2OH)_3/N(CH_2CH_2OH)_3}$[d]	CH_3CN	0.60	24
		0.90	104
	aqueous	0.82	38
$\mathrm{\overset{+\cdot}{N}(CH_2CH_3)_3/N(CH_2CH_3)_3}$	CH_3CN	0.96	105
$\mathrm{(CH_3CH_2)_2\overset{+}{N}=CHCH_3/(CH_3CH_2)_2N\dot{C}HCH_3}$	CH_3CN	–1.12	106

[a] The potentials in CH_3CN are vs SCE.

[b] Estimated from the data in Refs. 101 and 100.

[c] The potentials for the bromo derivative are quite similar to those for the chloro complex.[54] The excited-state potentials were calculated from the corresponding ground-state values using an excitation energy of 2.3 eV.[107]

[d] The chemistry of the carbon-centered TEOA radicals is quite complex.[108]

The light-induced and thermal reactions obtaining in the $\mathrm{RuL_3^{2+}}$ (L = 4,7-$(CH_3)_2$phen)/$\mathrm{Co(bpy)_3^{2+}}$/TEOA system in 50% CH_3CN have been examined in some detail.[22,23] Upon irradiation with 450 nm light, dihydrogen is produced via an oxidative quenching pathway with a

TABLE II

Systems photogenerating hydrogen and/or reducing carbon dioxide.

Sensitizer	Quencher or Catalyst	Electron Donor	Medium	Products (ϕ)[a]	Ref.
$Ru(bpy)_3^{2+}$	Co^{2+}/bpy	TEA	$CH_3CN/TEA/H_2O$	CO, H_2	20
$Ru(bpy)_3^{2+}$	Co^{2+}/2,9-Me_2phen	TEA	$CH_3CN/TEA/H_2O$	CO (0.012), H_2 (0.065)	21
$Ru(bpy)_3^{2+}$	Co^{2+}/4,7-Me_2phen	TEOA	H_2O/CH_3CN	H_2 (0.29)	22,23
$Ru(bpy)_3^{2+}$	$Co^{II}(dmgH)_2$	TEOA	DMF/TEOA	H_2 (~0.13)	53
$Ru(bpy)_3^{2+}$	$Rh(bpy)_3^{3+}$, colloidal Pt	TEOA	H_2O	H_2 (0.11)	31
$Ru(bpy)_3^{2+}$	MV^{2+}, colloidal Pt	TEOA or EDTA	H_2O	H_2 (0.13)	37,38,109
$Ru(bpy)_3^{2+}$	MV^{2+}	TEOA	H_2O	$HCOO^-$ (0.01)	48
$Ru(bpy)_3^{2+}$		TEOA	$DMF/TEOA/H_2O$	$HCOO^-$	64
$ReCl(bpy)(CO)_3$		TEOA	DMF/TEOA	CO (0.14)	53,55
$ReBr(bpy)(CO)_3$		TEOA	DMF/TEOA	CO (0.15)	54
$Re(CO)_2bpy\{P(OEt)_3\}_2^+$		TEOA	DMF/TEOA	CO (0.38)	58a
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)_2^{2+}$	TEOA	DMF/TEOA	$HCOO^-$ (0.14)	65–67
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)_2^{2+}$	BNAH	H_2O/DMF	$HCOO^-$ (0.03), CO (0.15)	65–67
$Ru(bpy)_3^{2+}$	$CoHMD^{2+}$	H_2A	H_2O	CO, H_2	76
$Ru(bpy)_3^{2+}$	Ni(cyclam)	H_2A	H_2O	CO (0.001), H_2	77,78
$Ru(bpy)_3^{2+}$	NiPr-cyclam^{2+}	H_2A	H_2O	CO (~0.005), H_2	80
$Ru(bpz)_3^{2+}$	colloidal Ru	TEOA	H_2O	$CH_4(10^{-4})$	50,51
$Ru(bpy)_3^{2+}$	bipyridinium$^+$, colloidal Ru or Os	TEOA	H_2O	CH_4 (10^{-4}), H_2 (10^{-3})	50
p-Terphenyl	$Co(cyclam)^{3+}$	TEA or TEOA	$MeOH/CH_3CN/$ (TEA or TEOA)	[CO + $HCOO^-$] (0.25), H_2	90,91
p-Terphenyl	$CoHMD^{2+}$	TEA or TEOA	$MeOH/CH_3CN/$ (TEA or TEOA)	CO, HCOO , H_2	91,92
Phenazine	$Co(cyclam)^{3+}$	TEA	CH_3CN/CH_3OH	HCOO– (0.07)	97

[a] Quantum yield.

quantum yield of 0.29 under optimum conditions. The reactions leading to dihydrogen formation are shown below.

$$\mathrm{RuL_3^{2+}} \xrightarrow{h\nu} \mathrm{{}^*RuL_3^{2+}} \tag{8}$$

$$\mathrm{{}^*RuL_3^{2+} + Co(bpy)_3^{2+} \rightarrow RuL_3^{3+} + Co(bpy)_3^{+}} \tag{9}$$

$$\mathrm{RuL_3^{3+} + Co(bpy)_3^{2+} \rightarrow RuL_3^{2+} + Co(bpy)_3^{3+}} \tag{10}$$

$$\mathrm{RuL_3^{3+} + TEOA \rightarrow RuL_3^{2+} + TEOA^{+\cdot}} \tag{11}$$

$$\mathrm{Co(bpy)_3^{2+} + TEOA^{+\cdot} \rightarrow Co(bpy)_3^{3+} + TEOA} \tag{12}$$

$$\mathrm{TEOA^{+\cdot} + TEOA \rightarrow TEOA\cdot + TEOAH^{+}} \tag{13}$$

$$\mathrm{Co(bpy)_3^{+} + Co(bpy)_3^{3+} \rightarrow 2Co(bpy)_3^{2+}} \tag{14}$$

$$\mathrm{TEOA\cdot + Co(bpy)_3^{2+} \rightarrow TEOA_{ox} + Co(bpy)_3^{+}} \tag{15}$$

$$\mathrm{Co(bpy)_3^{+} + H_3O^{+} \rightarrow Co(bpy)_2(H_2O)H^{2+} + bpy} \tag{16}$$

The $\mathrm{{}^*Ru(4,7\text{-}(CH_3)_2phen)_3^{2+}}$ is oxidized by $\mathrm{Co(bpy)_3^{2+}}$ to produce $\mathrm{Ru(4,7\text{-}(CH_3)_2phen)_3^{3+}}$ and $\mathrm{Co(bpy)_3^{+}}$. (There is no evidence for reduction of $\mathrm{{}^*Ru(4,7\text{-}(CH_3)_2phen)_3^{2+}}$ or $\mathrm{{}^*Ru(bpy)_3^{2+}}$ by TEOA in aqueous media or in acetonitrile, $k < 10^5$ $\mathrm{M^{-1}\ s^{-1}}$.)[23,24] The $\mathrm{Ru(4,7\text{-}(CH_3)_2phen)_3^{3+}}$ is reduced by TEOA, and the TEOA radical produced in this step, after undergoing rearrangement from a nitrogen-centered to a carbon-centered radical (Eq. (13)), reduces $\mathrm{Co(bpy)_3^{2+}}$ to $\mathrm{Co(bpy)_3^{+}}$. Reaction (16) does not proceed by direct reaction with $\mathrm{H_3O^+}$ but rather involves reduction of $\mathrm{bpyH^+}$ by $\mathrm{Co(bpy)_3^{+}}$ followed by H-atom transfer from the protonated bpy radical to a cobalt(II) bipyridine complex to form $\mathrm{Co(bpy)_2(H_2O)H^{2+}}$.

$$\mathrm{Co(bpy)_3^{+} + Hbpy^{+} \rightarrow Co(bpy)_3^{2+} + Hbpy\cdot} \tag{17a}$$

$$\mathrm{Co(bpy)_2^{2+} + Hbpy\cdot \rightarrow Co(bpy)_2(H_2O)H^{2+}} \tag{17b}$$

The $\mathrm{Co(bpy)_2(H_2O)H^{2+}}$ may then form $\mathrm{H_2}$ by reacting with $\mathrm{H_2O/H_3O^+}$ (Eq. (18a)), or in a bimolecular reaction (Eq. (18b)), but the actual pathway is not known.

$$\mathrm{Co(bpy)_2(H_2O)H^{2+} + H_3O^+ \rightarrow Co(bpy)_2(H_2O)_2^{3+} + H_2 + H_2O} \qquad (18a)$$

$$\mathrm{2Co(bpy)_2(H_2O)H^{2+} \rightarrow 2Co(bpy)_2(H_2O)_2^{2+} + H_2} \qquad (18b)$$

The optimal H_2 quantum yield (0.29) is close to the cage escape yield of the primary electron-transfer products (0.27, Eq. (9)). A similar system based on reductive quenching of $^*\mathrm{Ru(bpy)_3^{2+}}$ by ascorbate (Eq. (7 b–c), D = ascorbate) has also been described.[25]

The cobalt(I) species and the cobalt(III) hydrides formed from them are very reactive. In addition to mediating the generation of H_2 and the reduction of bpy to $\mathrm{bpyH_2}$ (Eq. (18c), cf. Eq(18a)) they also reduce CO_2 to CO (Eq. (18d)).[4,5,20,21]

$$\mathrm{bpy + 2H^+ + 2e^- \rightarrow bpyH_2} \qquad (18c)$$

$$\mathrm{CO_2(or\ HCO_3^-) + 2H^+ + 2e^- \rightarrow CO(or\ HCOO^-) + H_2O} \qquad (18d)$$

The rate law for the formation of H_2 and the reduction of CO_2 (as $\mathrm{HCO_3^-}$) to CO by $\mathrm{Co(bpy)_3^+}$ is first order in $[\mathrm{H^+}]$ and inverse in [bpy] consistent with the intermediate formation of $\mathrm{Co(bpy)_2(H_2O)H^{2+}}$ in both reduction pathways. Since formate is not an important reaction product it is unlikely that CO_2 insertion into the cobalt-hydride bond occurs to an appreciable extent.

Visible light irradiation of $\mathrm{Ru(bpy)_3^{2+}/Co^{II}(dmgH)_2}$ (dmgH = dimethylglyoxime) in a DMF/TEOA medium yields only H_2 (optimum quantum yield 0.13) in the presence of CO_2.[26] The authors propose that $\mathrm{Ru(bpy)_3^+}$ (formed in the reductive quenching of $^*\mathrm{Ru(bpy)_3^{2+}}$ by TEOA at the high levels of the latter present in the mixed medium) is the electron donor for the $\mathrm{Co^{II}(dmgH)_2}$ ($E_{1/2} = -0.95$ V), and that dihydrogen generation proceeds via a hydridocobaloxime intermediate. The reactions leading to dihydrogen evolution from hydridocobaloxime solutions had been characterized in an earlier study[27]—in methanol-water solutions the reaction proceeds by two parallel paths, one first order in hydridocobaloxime and first order in $[\mathrm{H^+}]$ and the other second order in hydridocobaloxime and independent of $[\mathrm{H^+}]$. These pathways are consistent with Eqs. (2) and (4).

As noted in the Introduction, the rate law for dihydrogen production can be quite complex. The reactions of a macrocyclic cobalt(III) hydride, formed by protonation of the corresponding cobalt(I) complex generated by reductive quenching in the $Ru(bpy)_3^{2+}/Co^{II}(Me_6[14]dieneN_4)^{2+}$/ascorbate system, are postulated to be responsible for the production of dihydrogen upon irradiation with visible light.[28] With the *meso* isomer of the macrocycle, the rate law for thermal dihydrogen production is of the form

$$d[H_2]/dt = k[meso\text{-}CoL(H_2O)(H)^{2+}]^2/[H^+] \tag{19}$$

with the rate of dihydrogen formation increasing with decreasing acidity.[17]

$Ru(bpy)_3^{2+}/Rh(bpy)_3^{3+}$/TEOA. The $Co(bpy)_3^{2+}$-based system discussed above exhibits both important similarities and differences with the analogous $Ru(bpy)_3^{2+}/Rh(bpy)_3^{3+}$/TEOA system.[29,30] Irradiation of the rhodium-based system at pH 7–8 in the absence of platinum yields rhodium(I) and free bpy but no H_2. In the presence of colloidal platinum, H_2 and very little free bpy are produced. Contrary to the original proposal that the H_2 was produced in platinum-catalyzed reactions of rhodium(I),[31] detailed mechanistic studies showed that the platinum-catalyzed reactions of rhodium(II) were responsible for the dihydrogen formation.[30] Analogous to Eq. (9), the $^*Ru(bpy)_3^{2+}$ is oxidized by $Rh(bpy)_3^{3+}$ to produce $Ru(bpy)_3^{3+}$ and $Rh(bpy)_3^{2+}$. As in the cobalt system, the $Ru(bpy)_3^{3+}$ is reduced by TEOA and the rearranged TEOA radical reduces $Rh(bpy)_3^{3+}$ to $Rh(bpy)_3^{2+}$. In the absence of platinum the rhodium(II) undergoes bpy loss and then disproportionates according to Eq. (20a).

$$Rh(bpy)_2^{2+} + Rh(bpy)_3^{2+} \rightarrow Rh(bpy)_2^{+} + Rh(bpy)_3^{3+} \tag{20a}$$

The dominant rhodium(I) species at low rhodium(I) concentration and at high and low pH are $Rh(bpy)_2^{+}$ and $Rh(bpy)_2(H_2O)H^{2+}$, respectively. Neither species is thermodynamically capable of producing dihydrogen under the conditions used. Based on pulse-radiolysis studies,[32,33] it has been proposed that under certain conditions H_2 could be generated by $Rh(bpy)_3^{2+}$ reduction of $Rh(bpy)_2(H_2O)H^{2+}$ to yield $Rh(bpy)_2H^+$ (Eq. (20b)) followed by $Rh(bpy)_2H^+$ reacting with H_2O/H_3O^+ (Eq. (20c)) or undergoing bimolecular reaction (Eq. (20d)).

$$Rh(bpy)_2(H_2O)H^{2+} + Rh(bpy)_3^{2+} \rightarrow Rh(bpy)_2H^+ + Rh(bpy)_3^{3+} \tag{20b}$$

$$Rh(bpy)_2H^+ + H_3O^+ \rightarrow Rh(bpy)_2^{2+} + H_2 + H_2O \tag{20c}$$

$$2Rh(bpy)_2H^+ \rightarrow 2Rh(bpy)_2^{+} + H_2 \tag{20d}$$

By contrast, in the presence of platinum, the $Rh(bpy)_3^{2+}$ reduces H_2O/H_3O^+ to dihydrogen with a quantum yield of 0.11, close to the cage escape yield of the primary products (0.15). Evidently the reactions that convert the reduced complex to dihydrogen are remarkably efficient in both the cobalt- and rhodium-based systems. The efficiencies of both systems decline on prolonged photolysis due to the formation of reduced bipyridine.

The effect of CO_2 on the course of the photolysis has not been reported. The rhodium(III) hydride $Rh(bpy)_2(CO)H^{2+}$ does, however, exhibit relatively high water gas shift activity.[34] Electrochemical reduction of CO_2 to CO or formate can be effected at a platinum or carbon cloth electrode in acetonitrile with *cis*-$Rh(bpy)_2(O_3SCF_3)_2^+$ as the catalyst precursor (the highly reduced $Rh(bpy)_2^-$ is believed to be the active catalyst).[35] The formation of CO/formate is accompanied by the evolution of dihydrogen resulting from the degradation of the tetra-*n*-butylammonium salt used as the supporting electrolyte.[36]

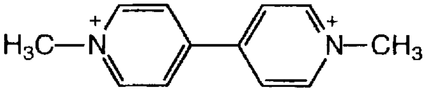
$Ru(bpy)_3^{2+}$/Bipyridinium Derivatives/TEOA, TEA or EDTA/ Colloidal Metals. The mechanism for dihydrogen production in the rhodium-based system strongly resembles that in the well-studied microheterogeneous $Ru(bpy)_3^{2+}$/methylviologen (MV^{2+}, 1,1′-dimethyl-4,4′-bipyridinium dication)/TEOA (or EDTA)/colloidal Pt systems with $Rh(bpy)_3^{2+}$ fulfilling the role of the MV^+ radical.[37,38]

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} {}^*Ru(bpy)_3^{2+} \tag{21}$$

$$^*Ru(bpy)_3^{2+} + MV^{2+} \rightarrow Ru(bpy)_3^{3+} + MV^{+\cdot} \tag{22}$$

$$Ru(bpy)_3^{3+} + TEOA \rightarrow Ru(bpy)_3^{2+} + TEOA^{+\cdot} \tag{11}$$

Like the rhodium system, the methylviologen-based systems are subject to efficiency-lowering side reactions, mainly hydrogenation of MV^{2+} via the protonated viologen radical (Eqs. (23)–(24)).[39] Interestingly, the protonated radical has been postulated to be the precursor for H_2 formation



1,1′-dimethyl-4,4′-bipyridinium dication, MV^{2+}

at low pH both in the presence of platinum (Eq. (24a)) and, in low yield, in its absence (Eq. (24c), cf. Eq. (4)).[40–42]

$$MV^{+\cdot} + H^{+} \rightarrow MVH^{2+\cdot} \qquad (23a)$$

$$2\,MVH^{2+\cdot} \rightarrow MV^{2+} + MVH_2^{2+\cdot} \qquad (23b)$$

$$MVH^{2+\cdot} + Pt \rightarrow MV^{2+} + PtH\cdot_{ads} \qquad (24a)$$

$$MVH^{2+\cdot} + PtH\cdot_{ads} \rightarrow MVH_2^{2+} + Pt \qquad (24b)$$

$$2\,MVH^{2+\cdot} \rightarrow 2\,MV^{2+} + H_2 \qquad (24c)$$

At higher pH, electron transfer from $MV^{+\cdot}$ to platinum provides the pathway for dihydrogen formation. Considerable improvement in the efficiency of the system is obtained by using tetramethyl- or hexamethylviologen or other structurally modified viologens as quenchers[43,44] and/or by using the triplet state of 9-anthracenecarboxylate, formed either by direct photo-excitation[45] or by energy transfer from $*Ru(bpy)_3^{2+}$,[46] as the primary electron donor. Interestingly, MV^{2+} is not necessarily required for the production of dihydrogen in the above type of systems since dihydrogen is also generated upon irradiation of $Ru(bpy)_3^{2+}/TEA/PtO_2$ in an acetonitrile-water mixture.[47] The authors propose that the active species is $Ru(bpy)_3^{+}$, produced in the reductive quenching of $*Ru(bpy)_3^{2+}$ by TEA.

An aqueous solution containing $Ru(bpy)_3^{2+}$, MV^{2+} and TEOA photoreduces CO_2 to formate with a quantum yield of 0.01.[48] Since direct electron transfer from $MV^{+\cdot}$ (produced in reactions (21) and (22)) to CO_2 is energetically very unfavorable, the authors suggest a mechanism involving CO_2 reduction with proton participation. No mechanistic details were given. Moreover, the difficulty of ruling out formation of formic acid in degradative reactions has been noted.[49]

The photoreduction of CO_2 to methane and hydrocarbons occurs in a pH 7.8 aqueous solution containing $Ru(bpy)_3^{2+}$, a bipyridinium derivative, TEOA and a Ru or Os colloid.[50] Oxidative quenching by the bipyridinium derivative is proposed (Eqs. (21) and (22)) with the quantum yields for H_2 evolution ($\sim 10^{-3}$) and hydrocarbon formation ($\sim 10^{-4}$ for CH_4, $\sim 10^{-5}$ for C_2H_4) depending on the bipyridinium derivative used. It is further proposed that the CO_2 reduction proceeds via electron transfer from the reduced bipyridinium to the metal-activated CO_2 followed by protonation rather than through the reaction of the metal-activated CO_2 with in situ generated H atoms. In other words, carbon dioxide reduction proceeds independently of dihydrogen generation. A similar system consisting of $Ru(bpz)_3^{2+}$ (bpz = 2,2′-bipyrazine) and colloidal ruthenium but without the bipyridinium derivative leads to the formation of methane, ethylene and ethane but no H_2.[50,51] The authors propose reductive quenching by TEOA to yield $Ru(bpz)_3^+$ followed by electron transfer to the metal-activated CO_2. $^*Ru(bpz)_3^{2+}$ is a much more powerful oxidant than $^*Ru(bpy)_3^{2+}$ (Table I), and its ready reductive quenching by TEOA is reasonable.[52]

$Re(bpy)(CO)_3X$/TEOA/DMF. The reduction of CO_2 to CO without significant amounts of H_2 being produced occurs upon irradiation of the $Re(bpy)(CO)_3Br$/TEOA or TEA/DMF system at 436 nm with the rhenium(I) complex acting as both the photosensitizer and the homogeneous catalyst.[53–55] The quantum yield for CO formation is 0.13 with TEOA and somewhat lower with TEA. The rate constants for quenching by the two amines are quite similar, and the difference in the CO quantum yields is ascribed to the subsequent amine radical chemistry. Addition of water or ethanol lowers the quantum yield. The photoreduction is believed to proceed via reductive quenching of the Re^I-to-bpy charge-transfer excited state to yield $[Re^I(bpy^-)(CO)_3Br]^-$, possibly followed by CO_2 reduction by the latter complex (or by a reduced product) or by CO_2 insertion into a hydride intermediate. $Re(bpy)(CO)_3H$ is known to undergo a slow thermal reaction with CO_2 in tetrahydrofuran (THF) to give the formato complex, a reaction that is greatly enhanced by visible light.[19]

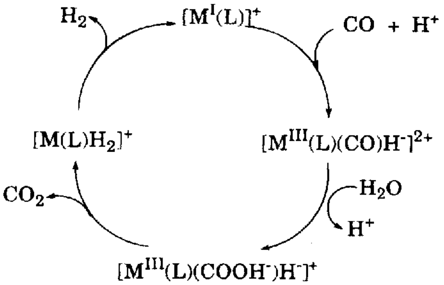
In parallel studies, the formato complex was isolated as a minor product of the photolysis of $Re(bpy)(CO)_3Cl$ in 5:1 mixtures of DMF/TEOA in the absence of added chloride.[55] Substitution by added chloride yields free formate and regenerates the starting complex. Irradiation of the formato complex yields CO_2 and the rhenium hydride—a nonproductive pathway as far as further formate reduction is concerned. The reduction of CO_2 to CO is proposed to proceed via the five-coordinate species formed by CO loss or pyridine detachment (to form monodentate bpy) from $[Re^I(bpy^-)(CO)_3Cl]^-$, with chloride loss being inhibited by the presence of excess chloride in the solution.[55] The results of an IR spectroelectrochemical study of the electrocatalytic reduction of CO_2 with a variety of $[Re(bpy)(CO)_3L]^n$ complexes (n = 0, L = Cl^-, $CF_3SO_3^-$; n = +1, L = CH_3CN, $P(OEt)_3$) as catalyst precursors provide strong evidence that the active catalysts are the reduced five-coordinate complexes $[Re(bpy)(CO)_3]\cdot$ (one-electron pathway) and $[Re(bpy)(CO)_3]^-$ (two-electron pathway).[56] The effect of added chloride ion was not studied. A mechanism of this type involving parallel $[Re(bpy)(CO)_3]\cdot$ and $[Re(bpy)(CO)_3]^-$ pathways had been proposed earlier on the basis of cyclic voltammetry and bulk electrolysis studies of $Re(bpy)(CO)_3Cl$ in acetonitrile.[57]

$Re(bpy)(CO)_2\{P(OEt)_3\}_2^+$ also photoreduces CO_2 to CO with a quantum yield up to 0.38. Both the quantum yield and turnover number of the photocatalytic reaction depend strongly on the irradiation light intensity and wavelength.[58a] The photophysical behavior has been studied by time-resolved UV-vis and IR spectroscopies.[58b] The reduced photogenerated catalyst, $Re(bpy)(CO)_2(\{P(OEt)_3\}_2$, is believed to be involved in the CO_2 activation, but mechanistic details are lacking.

The Water Gas Shift Reaction. The water gas shift reaction (WGSR) affords a route to dihydrogen formation by using CO to reduce water. It also effectively equilibrates CO, H_2 and CO_2.

$$H_2O + CO \rightarrow H_2 + CO_2 \qquad (6)$$

The reaction is thermodynamically favorable ($\Delta G^\circ = -4.75$ kcal/mol) and is catalyzed by a variety of metal complexes.[59] Scheme II has been proposed for the $Rh(bpy)_2^+$-catalyzed WGSR.[34] The CO adds to $Rh(bpy)_2^+$ to yield $Rh(bpy)_2CO^+$ which is then protonated to give $Rh(bpy)_2(CO)H^{2+}$ (however, this pathway cannot be distinguished kinetically from proton addition followed by CO addition). $Rh(bpy)_2(CO)H^{2+}$ then adds hydroxide to form the hydroxycarbonyl. The latter eliminates CO_2 to form the dihydride which decomposes to yield H_2 and $Rh(bpy)_2^+$.



SCHEME II

The use of light permits the WGSR to be run under extremely mild conditions. For example, the reaction can be carried out at room temperature, ambient pressure, and neutral pH by using the iridium(III) complex $[(\eta^5\text{-}Me_5C_5)Ir^{III}(bpyRR' \text{ or } phen)X]^+$ ($X = H, Cl$) and visible light.[60] Key steps in the photocatalyzed reaction are the elimination of CO_2 and H^+ from a hydroxycarbonyl iridium(III) intermediate to form an iridium(I) complex (Eq. (27)) which undergoes protonation to yield the iridium(III) hydride. The reaction of the *excited* iridium(III) hydride with protons reforms the starting iridium(III) complex and dihydrogen. The electrocatalytic properties of the iridium(III) complexes in dihydrogen generation have recently been described.[61]

$$[Cp^*Ir^{III}(L)Cl]^+ + CO \rightarrow [Cp^*Ir^{III}(L)CO]^{2+} + Cl \qquad (25)$$

$$[Cp^*Ir^{III}(L)CO]^{2+} + H_2O \rightarrow [Cp^*Ir^{III}(L)COOH]^+ + H^+ \qquad (26)$$

$$[Cp^*Ir^{III}(L)COOH]^+ \rightarrow Cp^*Ir^{I}(L) + CO_2 + H^+ \qquad (27)$$

$$Cp^*Ir^{I}(L) + H^+ \rightarrow [Cp^*Ir^{III}(L)H]^+ \qquad (28)$$

$$[Cp^*Ir^{III}(L)H]^+ + HCl \xrightarrow{h\nu} [Cp^*Ir^{III}(L)Cl]^+ + H_2 \qquad (29)$$

Analogous intermediates have been identified in the $[Ru^{II}(bpy)_2(CO)Cl]^+$- and $[Ru(bpy)_2(CO)_2]^{2+}$-catalyzed WGSR.[62] These systems are discussed further below.

The WGSR has much in common with the dihydrogen generating and CO_2-reducing systems discussed earlier. Indeed, the dihydrogen formed in some CO_2-reducing systems could derive from the CO produced undergoing a WGSR.

$Ru(bpy)_3^{2+}$/$Ru(bpy)_2(CO)_2^{2+}$ and TEOA or BNAH. The reduction of CO_2 to formate without significant amounts of H_2 being produced can be accomplished by using $Ru(bpy)_3^{2+}$ as both the photosensitizer and catalyst precursor in a DMF/TEOA/H_2O medium.[63,64] It is proposed that the reaction involves formation of $Ru(bpy)_3^+$ and carbon dioxide insertion into a hydride intermediate.

Reduction of CO_2 to formate also occurs upon irradiating a solution containing $Ru(bpy)_3^{2+}$ and $Ru(bpy)_2(CO)_2^{2+}$ and either TEOA in DMF[64–66] or 1-benzyl-1,4-dihydronicotinamide (BNAH)[65,66] in H_2O/ DMF as the electron donor. The TEOA system produces formate with a quantum yield of 0.14, whereas the BNAH system yields formate and CO with quantum yields of 0.03 and 0.15, respectively. (BNAH, with $E_{1/2} = 0.57$ V vs SCE, is much superior to TEOA as a reductive quencher.) The reduction potential of $Ru(bpy)_3^{2+}$ (−1.33 V vs SCE in DMF) is more negative than the reduction potential of $Ru(bpy)_2(CO)_2^{2+}$ (−0.98 V) and nearly the same as that of $Ru(bpy)_2(CO)(CO_2)$ (−1.30 V). Therefore, photochemically produced $Ru(bpy)_3^+$ could serve as the reductant of $Ru(bpy)_2(CO)_2^{2+}$.[64–66] The proposed mechanism in CO_2-saturated TEOA/DMF involves the reduction of $Ru(bpy)_2(CO)_2^{2+}$ by two molecules of $Ru(bpy)_3^+$ to yield $Ru(bpy)_2(CO)$ and CO. The doubly reduced $Ru(bpy)_2(CO)$ then adds CO_2 to form $Ru(bpy)_2(CO)(CO_2)$ (Eqs. (30) and (31)).

$$Ru(bpy)_2(CO)_2^{2+} + 2e^- \rightarrow Ru(bpy)_2(CO) + CO \qquad (30)$$

$$Ru(bpy)_2(CO) + CO_2 \rightarrow Ru(bpy)_2(CO)(CO_2) \qquad (31)$$

$$Ru(bpy)_2(CO)(CO_2) + H^+ + 2e^- \rightarrow Ru(bpy)_2(CO) + HCOO^- \qquad (32)$$

The formate is then generated from $Ru(bpy)_2(CO)(CO_2)$ by a two-electron reduction involving participation of a proton (Eq. (32)). There is independent electrochemical evidence for this last step.[67] In addition, the $Ru(bpy)_2(CO)$ formed in Eq. (30) may react with H^+ to form $Ru(bpy)_2(CO)H^+$. Carbon dioxide can then insert into the carbonyl hydride to form the formato complex, or the carbonyl hydride may react with a proton source to generate H_2. In support of this, $Re(bpy)(CO)_3H$ reacts with CO_2 to afford $Re(bpy)(CO)_3OC(O)H$ quantitatively,[68] and $Ru(bpy)_2(CO)H^+$ reacts with CO_2 to form a formato complex, $Ru(bpy)_2(CO)(O(O)CH)$, which produces $HCOO^-$ upon further one-electron reduction.[69] The formate complex resulting from CO_2 insertion into $Ru(bpy)_2(CO)H^+$ has not been isolated. Finally, the change from $HCOO^-$ to CO as the main product with BNAH in H_2O/DMF is postulated to involve competition between Eqs. (30) and (32) together with acid-base equilibria between $Ru(bpy)_2(CO)_2{}^{2+}$, $Ru(bpy)_2(CO)(COOH)^+$ and $Ru(bpy)_2(CO)(CO_2)$.[66]

In their earlier papers Ishida *et al.*[62,65,66] formulate $Ru(bpy)_2(CO)(CO_2)$ as a "Ru(II)-(CO_2^-)" complex. However, their recent structural data suggest that $Ru(bpy)_2(CO)(CO_2)$ is more reasonably described as a Ru(II)-(CO_2^{2-}) complex.[70] The molecular structures of several complexes, postulated as intermediates in the CO_2 reduction and in the WGS reaction catalyzed by

$Ru(bpy)_2(CO)Cl^+$ and $Ru(bpy)_2(CO)_2^{2+}$, have been determined: $[Ru(bpy)_2(CO)_2](PF_6)_2$, $[Ru(bpy)_2(CO)(CO(O)OCH_3)](B(C_6H_5)_4 \cdot CH_3CN$, $Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)$, $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2H)](CF_3SO_3)(H_2O)$ and $Ru(bpy)_2(CO)(CH_2OH)^+$.[70–74] Ru–C bond distances to the bound carboxylate moiety decrease and the O–C–O angles become smaller in the order $CO_2 > CO(OCH_3) > COOH$: $[Ru(bpy)_2(CO)(CO_2)]$, 2.064 (13) Å and 120.9 (12)°; $[Ru(bpy)_2(CO)(CO(O)OCH_3)]^+$, 2.042 (6) Å and 119.2(6)°; and $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2H)]^+$, 2.003 (7) Å and 114.9 (6)°. However, an unusual dependence of ν(Ru–C) upon the Ru–C bond distance is observed: $[Ru(bpy)_2(CO)(CO_2)]$, 520.2 cm^{-1}; $[Ru(bpy)_2(CO)(CO(O)OCH_3)]^+$, 518.1 cm^{-1}; and $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2H)]^+$ 511.3 cm^{-1}.[75]

$Ru(bpy)_3^{2+}$/Nickel or Cobalt Macrocycles/Ascorbate. Carbon monoxide (and, in some cases, formate) and dihydrogen are produced upon irradiation of a solution containing $Ru(bpy)_3^{2+}$, a nickel(II) or cobalt(II) macrocycle (shown in Fig. 2), CO_2, and ascorbate as the reductive quencher.[76–80] The following scheme, in which M^IL^+ and/or $ML(H)^{2+}$ are common to both the CO_2 reduction and H_2 formation pathways, has been proposed.

$$^*Ru(bpy)_3^{2+} + HA^- \rightarrow Ru(bpy)_3^+ + HA\cdot$$

$$HA\cdot \rightleftharpoons H^+ + A^-\cdot$$

$$Ru(bpy)_3^+ + M^{II}L^{2+} \rightarrow Ru(bpy)_3^{2+} + M^IL^+$$

$$M^IL^+ + CO_2 \rightarrow ML(CO_2)^+$$

$$M^IL^+ + H^+ \rightarrow ML(H)^{2+}$$

$$ML(H)^{2+} + H^+ + \text{“}e^-\text{”} \rightarrow ML^{2+} + H_2$$

$$ML(H)^{2+} + CO_2 \rightarrow ML(OOCH)^{2+}$$

$$ML(CO_2)^+ + H^+ + \text{“}e^-\text{”} \rightarrow ML^{2+} + CO + OH^-$$

$$ML(OOCH)^{2+} + \text{“}e^-\text{”} \rightarrow ML^{2+} + HCOO^-$$

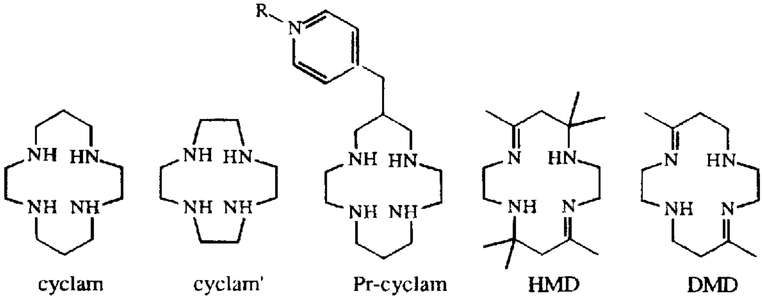
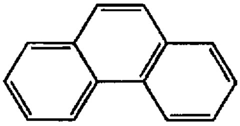


FIGURE 2 Abbreviations and structures of the macrocycles.

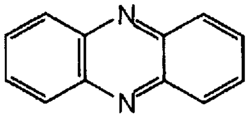
The "e⁻" in the above scheme is presumably $Ru(bpy)_3^+$, M^IL^+ or the ascorbate radical. When $CoHMD^{2+}$ is used as the catalyst at pH 4, the system produces a mixture of CO and H_2 with low selectivity ($CO/H_2 = 0.06–0.3$, depending on the conditions).[76] $Ni(cyclam)^{2+}$ is reported to be an extremely efficient and selective catalyst for the electrochemical reduction of CO_2 to CO, even in an aqueous medium.[81,82] With $Ni(cyclam)^{2+}$ as the catalyst,[77,78] the quantum yield for CO production is 5×10^{-4} at pH 5. (There is some confusion regarding the H_2 yield in the $Ni(cyclam)^{2+}$ system. The CO and H_2 yields are reported to be comparable in the earlier work.[77] On the other hand, the H_2 yield is reported to be negligible in the later study,[78] while Kimura *et al.*[80] report very high H_2 yields.) $Ni(cyclam')^{2+}$, a high-spin, six-coordinate complex with two *cis* water molecules, produces both CO and formate, while $Ni(cyclam)^{2+}$, which is mainly low-spin, square-planar in H_2O, yields only CO.

Ni(cyclam) complexes containing pendant pyridinium groups mediate the photochemical dihydrogen generation at a Pt colloid.[50,83] The catalytic behavior of these systems toward photochemical CO_2 reduction with $Ru(bpy)_3^{2+}$ has also been examined.[80] The system containing $Ni(Pr\text{-}cyclam)^{2+}$ (Pr = *p*-methoxybenzyl and benzyl) at pH 5 evolves about 5 times more CO than obtained with underivatized $Ni(cyclam)^{2+}$.

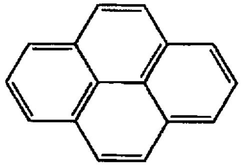
$[Ni_3(\mu_3\text{-}I)_2(dppm)_3]$. The trinuclear cluster $[Ni_3(\mu_3\text{-}I)_2(dppm)_3]$ {dppm = bis(diphenylphosphino)methane} is reported to reduce CO_2 to $\cdot CO_2^-$ in THF when irradiated at wavelengths > 300 nm.[84] Photolysis of $[Ni_3(\mu_3\text{-}I)_2(dppm)_3]$ in a 4:1 v/v THF/cyclohexene solution under 1 atm CO_2 leads to oxidation of $[Ni_3(\mu_3\text{-}I)_2(dppm)_3]$ and the formation of *cis*- and *trans*-1,2-cyclohexanedicarboxylates. Although the system is not photocatalytic, it is a rare case of purported involvement of $\cdot CO_2^-$.



phenanthrene



phenazine

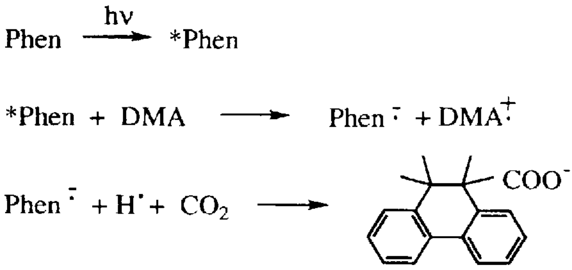


pyrene

Organic Photosensitizers/Cobalt Macrocycles/TEA. Irradiation of aromatic hydrocarbons such as phenanthrene (Phen), anthracene or pyrene in the presence of an amine and CO_2 in aprotic solvents results in reductive carboxylation of the hydrocarbons.[85-87]

The reactions are considered to proceed via the anion radical of the hydrocarbon reacting with CO_2 and then abstracting a hydrogen atom, possibly from the solvent (dimethylaniline), to yield the corresponding product.

Unlike these hydrocarbons, oligo(*p*-phenylene)s ranging from *p*-terphenyl to *p*-sexiphenyl catalyze the photoreduction of CO_2 to $HCOO^-$ with TEA in dry aprotic solvents such as DMF and CH_3CN.[88,89] Although the apparent quantum yield is 0.072 with *p*-terphenyl, the latter undergoes photo-Birch reduction to dihydroterphenyl derivatives so that the stability of the system is limited. Addition of a cobalt macrocyclic complex suppresses the degradative photo-Birch reduction, and leads to efficient formation of both carbon monoxide and formate.[90,91]



The *p*-terphenyl/Co^{II}HMD/TEA system has been investigated in some detail.[92] Transient spectra provide clear evidence for the sequential formation of the *p*-terphenyl radical anion, Co^{I}HMD^{+}, Co^{I}HMD-CO_2^{+} and [S-Co^{III}HMD-(CO_2^{2-})]$^{+}$, where S = solvent, in the catalytic system. These species, together with Co^{I}HMD-CO^{+}, have previously been identified by various spectroscopic techniques including UV-vis, IR, NMR, XANES and EXAFS.[93–96] The XANES study indicates that six-coordinate [S-CoHMD-(CO_2^{2-})]$^+$, in which a significant amount of charge is transferred from the metal to the bound CO_2, can be regarded as a Co(III) carboxylate.[96] The authors propose the following reactions for the production of CO from [S-Co^{III}HMD-(CO_2^{2-})]$^+$.[92]

$$[\text{S-Co}^{III}\text{HMD-}(\text{CO}_2^{2-})] + \text{HA} \rightleftharpoons [\text{S-Co}^{III}\text{HMD-}(\text{COOH}^-)]^{2+} + \text{A}^-$$
$$\text{HA} = \text{TEAH}^+(\text{TEA, MeOH}) \qquad (33)$$

$$[\text{S-Co}^{III}\text{HMD-}(\text{COOH}^-)]^{2+} + \text{“e}^-\text{”} \rightarrow \text{Co}^{II}\text{HMD}^{2+} + \text{CO} + \text{OH}^-$$
$$\text{“e}^-\text{”} = \text{Co}^{I}\text{HMD}^+,\ \text{Et}_2\text{NC}\cdot\text{HCH}_3, \qquad (34)$$

$$\text{OH}^- + \text{CO}_2 \rightleftharpoons \text{HCO}_3^- \qquad (35)$$

The slow step is likely to be the C–O bond breakage in the bound carboxylic acid with either $Et_2NC{\cdot}HCH_3$, or Co^{I}HMD$^+$ acting as the electron donor. Studies with other cobalt macrocycles[92] provide evidence for the importance of steric hindrance and reduction potentials in determining the CO_2 reduction yields.

Photoreduction of CO_2 to $HCOO^-$, together with a small amount of CO and H_2, has been achieved by UV-irradiation of a system consisting of phenazine as photosensitizer, Co(cyclam)$^{3+}$ as electron mediator and TEA as electron donor.[97] The quantum yield for the formation of $HCOO^-$ is 0.07. Electron transfer from the photoproduced phenazine anion radical to Co(cyclam)$^{3+}$ results in the formation of Co(cyclam)$^{2+}$. Since the reduction potential of the Co(cyclam)$^{2+/+}$ couple is ~–1.9 V vs SCE in CH_3CN, the phenazine anion radical is not able to reduce Co(II) to Co(I). The authors propose that the anion radical undergoes protonation and that the resulting neutral radical transfers a hydrogen atom to Co(cyclam)$^{2+}$ to form Co(cyclam)H^{2+}. Carbon dioxide insertion into the hydride then produces $HCOO^-$ via the Co^{III}-formate complex.

CONCLUSIONS

A number of transition-metal based systems that photogenerate dihydrogen and/or reduce carbon dioxide to carbon monoxide or formate have been described. Most of the systems considered are based on complexes of the d^6 metal centers cobalt(III), rhodium(III), iridium(III), ruthenium(II) and rhenium(I), and all require a sacrificial donor or acceptor. $Ru(bpy)_3^{2+}$ remains the sensitizer of choice in the visible, and most of the reaction schemes involve the intermediate formation of reduced d^8 complexes and/or d^6 hydrides, either of the sensitizer or of an added catalyst. The d^6 hydrides may also be formed by H-atom transfer to the corresponding d^7 complex from a protonated nitrogen-containing organic radical, for example, a protonated bipyridine, methyl viologen or phenanthrene radical. Although the quantum yields for H_2 and CO formation are quite high in individual systems, none are presently capable of sustained synthesis gas or methanol production. The design of economically viable, homogeneous or microheterogeneous transition-metal-based systems that generate dihydrogen and/or reduce carbon dioxide upon visible light irradiation remains a challenging problem.

APPENDIX: LIST OF ABBREVIATIONS

bpy	2,2′-bipyridine
bpz	2,2′-bipyrazine
BNAH	1-benzyl-1,4-dihydronicotinamide
cyclam	1,4,8,11-tetraazacyclotetradecane
DMA	N,N-dimethylaniline
DMF	N,N-dimethylformamide
dmgH	dimethylglyoxime
EDTA	ethylenediaminetetraacetate
HMD	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene
H_2A	ascorbic acid
MV^{2+}	methylviologen, 1,1′-dimethyl-4,4′-bipyridinium dication
phen	1,10-phenanthroline
Phen	phenanthrene
Pr-cyclam	6-((N-R)pyridin-4-yl)methyl-1,4,8,11-tetraazacyclotetradecane where R = p-methoxybenzyl and benzyl
TEA	triethylamine
TEOA	triethanolamine, nitrilotriethanol
THF	tetrahydrofuran
WGSR	water gas shift reaction

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