

***Photochemical CO₂ Reduction by Rhenuim and
Ruthenium Complexes***

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PHOTOCHEMICAL CO₂ REDUCTION BY RHENIUM AND RUTHENIUM COMPLEXES

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Introduction

Photochemical conversion of CO₂ to fuels or useful chemicals using renewable solar energy is an attractive solution to both the world's need for fuels and the reduction of greenhouse gases. Rhenium(I) and ruthenium (II) diimine complexes have been shown to act as photocatalysts and/or electrocatalysts for CO₂ reduction to CO. We have studied these photochemical systems focusing on the identification of intermediates and the bond formation/cleavage reactions between the metal center and CO₂.^{1,2} For example, we have produced the one-electron-reduced monomer (*i.e.* Re(dmb)(CO)₃S where dmb = 4,4'-dimethyl-2,2'-bipyridine and S = solvent) either by reductive quenching of the excited states of *fac*-[Re(dmb)(CO)₃(CH₃CN)]PF₆ or by photo-induced homolysis of [Re(dmb)(CO)₃]₂. We previously found that: (1) the remarkably slow dimerization of Re(dmb)(CO)₃S is due to the absence of a vacant coordination site for Re–Re bond formation, and the extra electron is located on the dmb ligand; (2) the reaction of Re(dmb)(CO)₃S with CO₂ forms a CO₂-bridged binuclear species (CO)₃(dmb)Re–CO(O)–Re(dmb)(CO)₃ as an intermediate in CO formation; and (3) the kinetics and mechanism of reactions are consistent with the interaction of the CO₂-bridged binuclear species with CO₂ to form CO and CO₃²⁻.

In photocatalytic systems with cobalt, nickel, ruthenium and rhenium complexes as CO₂ reduction catalysts to produce CO, the photoproduction of the reduced catalysts is fast (< 10 μs), the rate constants for CO₂ binding to the reduced metal centers depend on the catalysts and solvent, and range from 10⁻² to 10⁸ M⁻¹ s⁻¹.³ The detailed mechanism of CO formation from the CO₂ adducts remains unclear in most cases, and the production of CO is very slow with a turnover frequency typically less than 10 h⁻¹. Furthermore, despite substantial effort, to the best of our knowledge no one has succeeded in producing methanol from CO₂ using homogeneous systems with protons and electrons or H₂. Products in the homogeneous photochemical reduction of CO₂ reported so far have been limited to CO and/or HCOOH. In homogeneous electrochemical reduction of CO₂, a few additional C₂ species have been reported as minor products.¹

We believe that a very promising approach to homogeneous carbon dioxide reduction is a succession of hydride-ion and proton transfer reactions. As examples of these pathways, stoichiometric chemical conversion of a coordinated CO to methanol or methane using NaBH₄ has been reported for **Ru**⁰ → [Ru–CO₂] (*i.e.*, [Ru^{II}–(CO₂²⁻)]⁺) ⇌ [Ru–COOH]⁺ ⇌ [Ru–CO]²⁺ → [Ru–CHO]⁺ → [Ru–CH₂OH]⁺ (**Ru** = Ru(bpy)₂(CO))⁴ and for [Re–CO]⁺ → Re–CHO → Re–CH₂OH → Re–CH₃ (**Re** = Re(Cp)(NO)(CO)).⁵

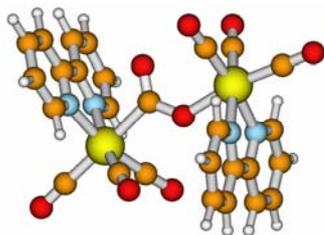
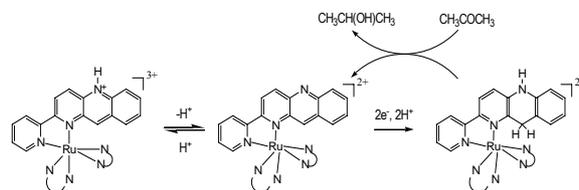


Figure 1 B3LYP calculated structure of the CO₂-bridged Re dinuclear species.

Then can we replace NaBH₄ by photochemically produced hydride donors?

While metal hydrides are good hydride donors to CO₂ and CO,⁶ the regeneration quite often requires H₂ or other hydride donors. In biological systems, nicotinamide adenine dinucleotide (NAD⁺) is one of the most important redox mediators and acts as a reservoir/source of two electrons and a proton (*i.e.*, hydride). We prepared a polypyridylruthenium complex with an NAD⁺/NADH model ligand, [Ru(bpy)₂(pbn)]²⁺ (bpy = 2,2'-bipyridine, pbn = 2-(2-pyridyl)-benzo[*b*]-1,5-naphthyridine), which acts as a catalyst in the electrochemical reduction of acetone to 2-propanol similar to the enzymatic NAD⁺/NADH.⁷ While the mechanism remains unclear, this is the first example that an NADH model complex such as [Ru(bpy)₂(pbnHH)]²⁺ (or other intermediates in this system) works as a catalytic hydride donor for the formation of 2-propanol. We have recently reported clear evidence of photochemical and radiolytic formation of [Ru(bpy)₂(pbnHH)]²⁺ with H⁺.⁸ These results open a new door for photocatalytic hydride (or proton-coupled-electron) transfer reactions originating from metal-to-ligand charge-transfer (MLCT) excited states of metal complexes with a bio-inspired NADH-like ligand, and for the utilization of photogenerated hydride donors for CO₂ reduction.



Scheme 1 Protonation and acetone reduction by [Ru(bpy)₂(pbn)]²⁺

We have prepared rhenium and ruthenium complexes with a pbn ligand, and herein we report the acid-base properties, electrochemical properties, and reactivity toward CO₂ reduction using C–H hydride transfer reactions.

Experimental Section.

The ligand pbn was prepared from 3-aminoquinoline by a seven-step synthesis using previously published methods. [Ru(bpy)₂(pbn)](PF₆)₂ was prepared as previously described and characterized by NMR, UV-vis, IR, ES-MS spectroscopy. Re(pbn)(CO)₃Cl and [Re(pbn)(CO)₃(PCy₃)]PF₆ (Cy = cyclohexyl) were prepared using previously published methods with slight modifications.

UV-vis spectra were measured on a Hewlett-Packard 8452A diode array spectrophotometer. FTIR spectra were measured on a Thermo Nicolet NEXUS 670 FT-IR spectrometer or a Bruker IFS 66/s spectrometer. NMR spectra were measured on a Bruker UltraShield 400 MHz spectrometer. Transient absorption spectra were measured with home-built TA setup. The second or third harmonic of a Continuum Surelite I YAG:Nd³⁺ laser was used as an excitation source. The laser was operated in pulsed mode with a repetition rate of 10 Hz and energy 2 mJ per pulse. Flash photolysis experiments were performed using a sample prepared by a vacuum distillation of a solvent (CH₃CN, THF, etc.) to a container equipped with an optical cell at 25 °C under vacuum or with a known pressure of CO₂ and/or Ar. Transient FTIR spectra of Re complexes were measured using a Bruker IFS 66/s spectrometer with a Kolmar HgCdTe detector and a flow cell (1.0 – 2.8 mm pathlength) for step-scan (time resolution: 10 ns) or with a Graseby Infrared photoconductive HgCdTe detector and a 0.1 – 0.5 mm pathlength vacuum tight cell for rapid scan. Acetonitrile solutions containing

1–2 mM Re complex with or without 1 M TEA were pressurized by ~2 atmospheric pressure of Ar or CO₂. The sample was excited with the third harmonic (355 nm, 6 ns) of a Continuum Surelite-1 Nd:YAG laser. The excitation energy was typically 20 mJ cm⁻² per pulse. Photochemical reduction of rhenium and ruthenium species was conducted in either CH₃CN/Et₃N (4:1 v/v) under vacuum or N₂-bubbled DMF/TEOA (4:1 v/v). The solution was irradiated either with monochromated light or light through a cut-off filter using a 75 W lamp at 25 °C.

Electrochemical measurements were conducted with BAS 100b electrochemical analyser from Bioanalytical Systems using solutions (1 mM) in acetonitrile. A glassy carbon electrode, SCE, and Pt wire were used with a standard H-shape cell.

Gas and solution phase DFT calculations were carried out using the hybrid B3LYP method and the Hay-Wadt VDZ (n+1) ECP (LANL2DZ ECP) 5d basis set. Geometry optimizations and frequency analyses were performed using the Gaussian 03 package of programs.

Results and Discussion

Thermodynamic hydricity, the ability to donate a hydride ion (H⁻), for metal hydrides and dihydrobenzonicotinamides in acetonitrile has been determined through systematic studies of electrochemistry and acidity by DuBois and his coworkers.⁹ Hydricity is defined as the free-energy change for dissociation of H⁻, in contrast with acidity and homolytic cleavage. Experimental estimates of hydricity of substrate DH are obtained from cycles based on combinations of the processes from the free-energy changes as $\Delta G_{\text{H}^-}^{\circ} = \Delta G_{\text{H}^+}^{\circ}(\text{D}-\text{H}) - 2 E^{\circ}(\text{D}^{\cdot+}/\text{D}^{\cdot-}) + \Delta G_{\text{H}^+}^{\circ}(\text{H}_2) + E^{\circ}(\text{NHE})$, where $\Delta G_{\text{H}^-}^{\circ}$, $\Delta G_{\text{H}^+}^{\circ}(\text{D}-\text{H})$, $E^{\circ}(\text{D}^{\cdot+}/\text{D}^{\cdot-})$, $\Delta G_{\text{H}^+}^{\circ}(\text{H}_2)$, and $E^{\circ}(\text{NHE})$ are hydricity of DH, acidity of DH, reduction potential of DH, H₂ acidity, and reduction potential of H⁺, respectively. Hydricities obtained in our preliminary calculations in acetonitrile solution are compared to experimental values in Table 1. The computed electronic energy hydricity differs somewhat from the hydricity free energy (comparable to that derived from experimental data) in that it does not include the contribution of zero-point and thermal energy or entropic effects, but these effects are generally small and trends can be compared. The strongest hydride donor, CHO⁻, will transfer a hydride to any acceptor listed below it. Several metal complexes seem capable of hydride transfer to CO₂ in acetonitrile: Cp(bpy)Mo(CO)(H) from the metal and Re(bpy)(CO)₃(CHO) and Re(CO)₃(dcb)(CHO) from the C–H of the formyl ligand.

Our preliminary calculations predict that the reduction of acetone to 2-propanol can take place in acetonitrile by the sequential transfer of a proton from solution followed by a hydride from [Ru(bpy)₂(pbnHH)]²⁺ in two slightly exoergic steps in disagreement with the previously published proposed mechanism.⁷ The calculations also predict that neither [Ru(bpy)₂(pbnHH)]²⁺ nor [Ru(bpy)₂(pbn)]²⁺ can reduce CO₂. We are therefore exploring the development of a stronger hydride donor than [Ru(bpy)₂(pbnHH)]²⁺ with the guidance of calculations of hydricities to screen the possibilities.

In order to test if this type of scenario will work, we have prepared several new complexes including [Ru(bpy)₂(pbnHH)]²⁺, Re(pbn)(CO)₃Cl and [Re(pbn)(CO)₃(PCy₃)]⁺. We examined the acid-base and electrochemical properties of the ground and excited states of Re(pbn)(CO)₃Cl and [Re(pbn)(CO)₃(PCy₃)]⁺. The titration of a solution containing Re(pbn)(CO)₃Cl or [Re(pbn)(CO)₃(PCy₃)]⁺ by acid shows the disappearance of the lowest MLCT absorption band and the appearance of the red-shifted band indicating the formation of the protonated species as found in [Ru(bpy)₂(pbn)]²⁺ to form

Table 1. Computed Electronic Energy Hydricities in Acetonitrile (B3LYP/LANL2DZ level of theory)

Hydride Donor	Product	El. Energy Hydricity (kcal/mol)
CHO ⁻	CO	-61
CH ₃ CHN ⁻	CH ₃ CN	0
isopropoxide ⁻	acetone	24
Cp(bpy)(CO)MoH (+ CH ₃ CN)	Cp(bpy)(CO)Mo(NCCH ₃) ⁺	39 ^a
[Re(bpy)(CO) ₃ (CHO)] ⁰	[Re(bpy)(CO) ₃] ⁺	45
[Re(CO) ₃ (dcb)(CHO)] ⁰	[Re(CO) ₃ (dcb)] ⁺	49 ^b
HCOO ⁻	CO ₂	51 (43)
N-Me-nicH	N-Me-nic ⁺	60
N-Bz-nicH	N-Bz-nic ⁺	61 (59)
Cp(bpy)(CO)MoH	Cp(bpy)(CO)Mo ⁺	65 ^a
para-monohydroquinone ⁻	para-benzoquinone	69
[CpRe(NO)(CO)(CHO)] ⁰	[CpRe(NO)(CO) ₂] ⁺	70 (55) ^c
H ₂ (+ CH ₃ CN)	CH ₃ CN ⁺	80 (76)
[Ru ^{II} (bpy) ₂ (pbnHH)] ²⁺	[Ru ^{II} (bpy) ₂ (pbnH ⁺)] ³⁺	92
isopropanol	CH ₃ C(OH)CH ₃ ⁺	94
[Ir ^{III} (bpy) ₂ (pbnHH)] ³⁺	[Ir ^{III} (bpy) ₂ (pbnH ⁺)] ⁴⁺	104
para-hydroquinone	para-monohydroquinone ⁺	128

^a LANL2DZ/6-31G(d,p) 6D basis; ^b dcb=(4,4'-dichloro-(2,2')-bipyridine);

^c Experimental value corresponds to Cp⁺, not Cp as calculated;

N-Me-nicH =N-methylnicotinamide, N-Bz-nicH=N-benzylnicotinamide;

calculations compared to DuBois ΔG° values (in parentheses) are in blue.

[Ru(bpy)₂(pbnH)]³⁺. The excited-state properties under presence and absence of acid, and the reactivity of the ground and excited-state species toward CO₂ activation are currently investigated using [Ru(bpy)₂(pbnHH)]²⁺, Re(pbn)(CO)₃Cl and [Re(pbn)(CO)₃(PCy₃)]⁺. The results will be presented at the ACS National Meeting in New Orleans, LA.

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