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An Integrated Re(I) Photocatalyst/Sensitizer that Activates the Formation of Formic Acid from Reduction of CO₂

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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

The complex *cis*-[Re(bpy)₂(CO)₂]⁺OTf (1⁺OTf) is an integrated photosensitizer/catalyst for the selective visible light promoted photocatalytic reduction of CO₂. The formation of formic acid is unique among this class of Re catalysts, which yield CO as the selective product. A supplemental photosensitizer, Ru(bpy)₃²⁺, considerably enhanced the performance of this catalyst.

The combination of addressing issues of sustainable energy with the environmental concerns regarding emission of greenhouse gases provides a forceful impetus to target the efficient chemical reduction of CO₂. This fundamentally challenging goal requires an input of energy to yield useful products. Photocatalysis is a particularly appealing approach to surmount the reaction barriers since it employs light, a clean and unlimited resource, for conversion of this waste by-product into a feedstock. Formic acid is an especially interesting twoelectron reduction product of CO₂ since it is an important commodity chemical and a potential carrier of H2.1,2 Identification of catalysts that can use light for this chemical transformation is critical for success.^{3–5} Generally. photocatalytic systems have three integrated core components: a photosensitizer (PS), for collecting the photon energy; an electron donor (ED), that provides electrons for the reduction; and a catalyst (CAT) that is a site for the conversion of CO_2 .

More than 30 years ago, the pioneering discovery that *fac*-Re(bpy)(CO)₃X (bipy = 2,2'-bipyridine, X = halide) complexes were photocatalysts for the selective reduction of CO₂ to CO using triethanolamine (TEOA) as an electron donor established the ongoing exploration of related *fac*-[Re(α - diimine)(CO)₃X] catalysts and these complexes remain as touchstones for this field.⁶⁻¹² The central role of group 7 complexes in this field continued with the report that the manganese analogue *fac*-[Mn(bpy)(CO)₃Br] was, with a Ru(bpy)₃²⁺ photosensitizer, competent for photocatalytic CO₂ reduction.^{13–16} The *fac*-Re(bpy)(CO)₃X catalysts are particularly unique in their ability to function as integrated **PS** and **CAT**, thus allowing light absorption and catalysis with one species.^{6,17–22} These features continue to drive the vigorous search for **PS** integrated catalysts

yet realization of this goal remains rather limited.^{17,23–25} The expansion of ligand scaffolds has recently revealed Re(I) complexes with N-heterocyclic carbene (NHC) ligands that display the amalgamation into a single species of **CAT** and **PS** for the reduction of CO₂ to CO.^{26,27} Ligand variation led to discovery of a new Ru complex that functions as both **PS** and **CAT**.¹⁷

With the objectives of discovering new environments for CO₂ catalysts, photoreduction revealing new integrated photosensitizer/catalyst species and potentially uncovering new reaction pathways for this transformation we targeted the preparation of the $bis(\alpha$ -diimine) Re carbonyl complexes. We were stimulated to pursue these targets based on the known catalytic abilities of the mono(α -diimine) species (e.g. [Re(bpy)(CO)₃X]) as well as the reported observation of the related proficiency of the mono- and $bis(\alpha$ -diimine) Ru species, $cis, trans-Ru(N^N)(CO)_2Cl_2^{28-30}$ and $cis-[Ru(N^N)_2(CO)_2]^{2+}$ in catalysis.^{31–34} We now provide the first documentation of this coordination environment as an entirely new photocatalyst with integrated photosensitizer ability for CO₂ reduction as well as revealing a notable change in a switch of product selectivity from CO to HCO₂H.

A literature survey revealed that a target complex, [Re(bpy)₂(CO)₂]⁺OTf (1⁺OTf) was reported.³⁵ The preparation involved the unusual conditions of using a melt of 2,2'bipyridine as the solvent at T \approx 275°C. This reflects the stability of the *fac*-[Re(bpy)(CO)₃X] and is consistent with the dominance of the mono-ligated compounds in Re(I) chemistry. Our success with the synthesis of 1⁺OTf⁻ in 83% yield was demonstrated through the spectroscopic features of our product and microanalysis (eqn 1). In particular, the ¹H and ¹³C NMR spectra displayed the expected signals for the C₂ symmetric structure. Although some fundamental physical characterization of 1⁺OTf⁻ was known, no reactivity is reported.

Fortunately, we obtained crystals of cis-[Re(bpy)₂(CO)₂]⁺OTf⁻ (**1**⁺**OTf**⁻) and single crystal X-ray analysis definitively confirmed the metrical parameters of this complex (eqn 1, Figure S1). As proposed, the cationic Re(I) species displayed a distorted octahedral geometry with the C₂ symmetry of the *cis* ligand

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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array and a distal triflate counter ion. The Re-C distances were identical (1.883(5) Å) and two slightly different Re-N distances of 2.121(3) Å (Re-N1, trans to N) and 2.165(3) Å (Re-N12, trans to CO) were observed. The largest distortion from orthogonality of the angles around the Re center arise from the restricted bite angle of the bpy with the observed N-Re-N angle of 75.15(13)°. We found only one reported analogue of this complex, the bis(1,10-phenanthroline) complex *cis*-[Re(phen)₂(CO)₂]⁺OTf⁻ and this species displayed very similar metrical features.³⁵



Before applying 1+OTf as a photoreduction catalyst, some fundamental physical chemistry characterizations using cyclic voltammetry, DFT optimization and UV-vis electronic spectral characterization were performed. Under reducing potentials we confirmed that, in acetonitrile, 1+OTf- exhibited reversible one electron reductions at $E_{1/2}$ = -1.67 V and -1.90 V vs Fc/Fc⁺ (Figures S2, S6-S8).³⁵ Both reduction peaks showed a linear dependence of peak current on the square root of the scan rate $(v^{1/2})$ indicating freely diffusing species (Figures S3—S5). An irreversible reduction at a more negative potential of -2.63 V was also observed. Furthermore, the two reduction potentials clearly shift to less negative potentials as the solvent is changed to dimethylacetamide (DMA) and DMF. Importantly, the two reduction potentials further shifted to $E_{1/2}$ values of -1.46 V and -1.70 V when TEOA is added to DMF solutions (Figure S8). This is significant since TEOA is a common ED species in photocatalysis. DFT optimization (B3LYP, def2TZVP) of the cationic complex 1+ yielded results consistent with the X-ray analysis (Figure S9, Table S1). A TD-DFT analysis using the integral equation formalism variant of the PCM model with CH_2Cl_2 as solvent confirmed MLCT ($d\pi$ - π *) absorptions at visible wavelengths of 419, 439, 501, 503, and 544nm. Consistent with these calculations is the appearance of the visible portion (350nm-800nm) of the electronic spectrum of 1+OTf in CH₂Cl₂ (Figure S10).

The first attempts at photocatalytic reduction of Q_{2le} were performed with no added photosensitize P_{1}^{1} 4 μ mdP 6P **1** OT 4 m DMA using TEOA as the electron donor. Irradiation of this reaction mixture was carried out under an atmosphere of CO₂ with visible LED light (405nm, 1050 mW at 700mA, 3.4 x 10⁻⁸ mol photons/sec) for 24 hr. GC analysis of the reaction headspace

photons/sec) for 24 hr. GC analysis of the reaction headspace revealed only substoichiometric (2-4µmol) amounts of CO, which we attribute as arising from loss of CO from 1^+ . The ¹H NMR spectrum of the reaction solution disclosed that the only product was formic acid, which was quantified by NMR analysis (Figure S12). These observations confirmed that the complex *cis*-Re(CO)₂(bipy)₂+OTf was a photocatalyst for reduction of CO₂ to formic acid. (Table 1, Table S2). Interestingly, 1^+OTf displayed similar catalytic activity in DMF but no products were observed when CH₃CN was used as solvent (Table S2). Table 1 also provides a comparison of selected benchmark Re-based catalysts along with our results for 1^+OTf . Notably, care is required when comparing the reaction parameters. For example, in Table 1, the turnover frequency (TOF) removes the time dependence of the TON, allowing a more direct comparison of catalyst activities.

Three key points are notable. First, complex **1*OTf** contributes a wholly new geometry to photocatalysis with Re. Second, this compound displayed activity in the absence of an added photosensitizer which was similar to reported mononuclear α diimine Re(I) catalysts under visible light. Finally, in contrast to reported Re catalysts, which produce CO as the reduction product, CO₂ reduction with complex **1*OTf** led selectively to formic acid.^{11,36}

By adding the photosensitizer $[Ru(bpy)_3]^{2+}$ to this active catalyst system the plan was to improve the catalytic behaviour of **1+OTf** by taking advantage of the longer lived excited state (1100 ns³⁷) for $[Ru(bpy)_3]^{2+}$ and increasing the light absorption of the catalyst system in the visible region (see Figure S10). A similar strategy was employed to increase the activity of $[Re(dmb)(CO)_3CI]$ by adding an equimolar amount of $[Ru(dmb)_3]^{2+}$ as a supporting photosensitizer (dmb = 4,4'dimethyl-2,2'-bipyridine) (Table 1).³⁸ As anticipated, this resulted in a significant increase in production of HCO₂H as measured by TON, TOF and ϕ , and improvement of catalytic ability was expanded across all of the three solvents, DMA, DMF and CH₃CN that were used in this investigation (Tables 1 and S2).

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CAT [conc.]	Solvent/ED	PS [conc.]	λ (nm)	Product	TON (time)	Φ%	TOF (hr-1)
[Re(bpy) ₂ (CO) ₂] ⁺ [1mM]	DMA/TEOA	-	405	HCO ₂ H	10 (24h)	1.4	0.43
[Re(bpy) ₂ (CO) ₂] ⁺ [0.1mM]	DMA/TEOA	Ru(bpy) ₃ ²⁺ [1mM]	405	HCO₂H	428 (24h)	5.8	17.8
Re(bpy)(CO) ₃ Cl [0.87mM] ^{6,18}	DMF/TEOA	-	365	со	27 (4h)	8.7	6.75
[0.5mM] ¹⁹		-		со	15 (25h)	16	0.60
Re(dmb)(CO) ₃ Cl ^{38,(a)} [0.05mM]	DMF/TEOA/BNAH	-	365	со	15 (25h)	-	0.60
		Ru(dmb) ₃ ²⁺ [0.05mM]	480	со	101 (16h)	6.2	6.3
Re(Py-NHC-PhCF ₃) ^{26,(b)} [0.1mM]	MeCN/TEA/BIH	-	>300	со	32 (4h)		8.0
		lr(ppy)₃			51 (4h)		12.8
Re(<i>N,S</i> -NHC) ^{27,(b)} [0.5mM]	DMF/TEOA/BIH	-	≥400	со	102 (15h)		6.8
		-	≥ 480	со	153 (15h)		10.2
[Re(κ ² -PN)(CO) ₃ Br] ³⁹ , ^(c) [0.1mM]	DMF/TEOA	Ru(bpy) ₃ ²⁺ [1mM]	405	HCO₂H	343 (24h)	4.7	14.3
(a) dmb = $4,4'$ -dimethyl- $2,2'$ -bipyridine. (b) structures shown in Fig. S11, (c) PN = (Ph ₂ P)NH(NC ₅ H ₄)							

Table 1. Comparison of the performance parameters for selected Re photocatalysts.

Adding either water or phenol to the reaction mixture led to an increase of H₂ production and decrease in formic acid (Table S4). Under these conditions, with added PS, it was determined that the ED from TEOA to N-benzylchanging 1.4dihydridonicotinamide (BNAH), ascorbic acid, sodium ascorbate triethylamine gave little or no product.Definitive or confirmation that the formic acid originated photocatalytic CO₂ reduction was given through a ¹³C tracer experiment that was carried out for the photoreaction with 1^{+} OTf⁻, Ru(bpy)₃²⁺, and TEOA in DMA under a ¹³CO₂ atmosphere. HRMS analysis of the reaction headspace clearly documented selective formation of H13CO2H with less than 3% H12CO2H (Figure S11). Furthermore, the NMR data shown in Figure 1 (Figures S12, S13) provided conclusive evidence that the formic acid observed in these experiments arose from ¹³CO₂, further highlighting the remarkable switch in product selectivity with the reported production of CO from all other Re α - diimine species. 11,36



Figure 1. ¹H NMR spectra for the formyl proton of formic acid obtained from photocatalytic reduction of CO_2 using *cis*-Re(CO)₂(bipy)₂⁺OTf as the catalyst. The bottom spectrum is reaction with unlabeled CO₂ and the top spectrum is with ¹³CO₂.



 $Ph_2P)NH(NC_5H_4)$ The time profile for the photocatalytic reduction of CO₂ with **1+OTf** is presented in Figure 2 and display behaviour typical of related photocatalytic systems.^{29,30,38} There is a decrease in selectivity over the time (Table S3) and this may be associated

with a change in pH during the experiment. Figure 2. Time profile for the catalytic production of HCO₂H (red) and H₂ (blue) using 1µmol *cis*-Re(CO)₂(bipy)₂*OTf, 1µmol **PS**, TEOA in DMF under a CO₂ atmosphere.

Based on literature precedent and the experimental observations, a proposed catalytic mechanism for HCO₂H production from the CO_2 photoreduction using complexes 1^+ is presented in Figure 3. Photoreduction catalysis couples an electron production cycle with a catalysis cycle.^{28,30,40} The electron production cycle provides the electrons to the catalyst. In the case of an integrated catalyst/photosensitizer, electrons for the catalytic cycle can come directly from the ED through electron transfer to photoexcited 1+ (i.e. reductive quenching) (Figure S20). When photosensitizer is added to the reaction, the electrons for the catalytic cycle are likely produced from a reduced photosensitizer (PS-). In addition to the two electron reduction of CO₂ this mechanism relies on a source of protons that is provided by the decay reactions of oxidized TEOA (Figure S20). The catalytic cycle represents the steps where the Re complex, 1⁺, catalytically reduces CO₂ using these supplied electrons/protons. Generally, successful transformation of CO2 to formate is envisioned to proceed through a metal hydride intermediate (ReH) that can insert CO₂ leading to a formato complex.^{41,42} To help guide the proposed reactions, all of the Re compounds in the mechanism were computationally optimized using DFT with the B3LYP functional and def2TZVP basis set (Figures S6 and S15-S19). A likely entry into the catalysis cycle comes from the reduction of 1⁺ and the two photoreduction routes to complex A are presented in Figure S20 and summarized in Figure 3.

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Figure 3. Proposed mechanism for the photocatalytic reduction of CO_2 using 1⁺. The initial reduction step for 1⁺ to A is presented in more detail in Figure S20.

The hydride intermediate [Re(bpy)₂(CO)H] (ReH) (Figure S16-18) may be generated by addition of a proton and a second electron to A. The protonation of the hydride intermediate (ReH), provides an alternate catalytic cycle, bypasses formic acid production and rationalizes the experimental observation of H₂ formation. This proposed mechanism is reminiscent of the current mechanism invoked for conversion of CO₂ using the isoelectronic ruthenium (II) complex [Ru(bpy)₂(CO)₂]^{2+.30}The insertion of CO₂ into the Re-H complex would yield the formate complex **Re(form).** Closing the cycle with a proton transfer to liberate formic acid and trapping of the Re complex by CO (or solvent) regenerates a 1⁺ equivalent.

This report has revealed a functionally integrated photosensitizer/catalyst, cis-[Re(bpy)2(CO)2]+OTf- (1+OTf-), for the visible light photocatalytic reduction of CO_2 . Not only does this complex possess a structure that is unprecedented among Re(I) photoreduction catalysts, the selective formation of formic acid is unique among this class of catalysts, which uniformly yield CO as the reduction product. We further established substantial improvements in performance parameters and more broad application of the photocatalyst when a PS is added. Our active goals are to expand on this class of catalysts and interrogate the mechanism of this transformation.

Conflicts of interest

"There are no conflicts to declare".

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