Photoinduced Irreversible Insertion of CO_2 into a Metal–Hydride Bond

B. Patrick Sullivan* and Thomas J. Meyer

Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514, U.S.A.

The reactive organometallic trifluoromethanesulphonato ($CF_3SO_3^-$) complex *fac*-Re(bpy)$(CO)_3CF_3SO_3$ (bpy = 2,2′-bipyridine) has been used as a basis for the synthesis of the series of complexes *fac*-Re(bpy)$(CO)_3X$ (X = H, O_2CH, and O_2COH) all of which are involved in the reduction of CO_2; the hydrido complex has been found to undergo a slow thermal reaction with CO_2 to give the formato complex, a reaction which is greatly enhanced by visible light.

A new strategy for the reduction of carbon dioxide is based on the use of redox-active molecular excited states to both bind and reduce CO_2 to products such as carbon monoxide or the formate anion. Recently Hawecker, Lehn, and Ziessel[1] have observed the photoinduced reduction of CO_2 to CO based on *fac*-$Re^I(bpy)(CO)_3Cl$[2,3] (bpy = 2,2′-bipyridine) where a 'sacrificial' reductive quencher such as triethanolamine is the reducing agent. Possible intermediates[4—7] in this and related thermal or photochemical CO_2 reduction schemes are complexes like $M(S)^+$ (S = solvent), $M(\eta\text{-}CO_2)^+$, $M\text{–}O_2COH$, $M\text{–}O_2CH$, $M{\equiv}COH$, or $M(CO)^+$, or their reduced forms, where M is, for example, the *fac*-$Re^I(bpy)(CO)_3{}^+$ unit. Indeed, the formato complex $Re(bpy)(CO)_3O_2CH$ has been isolated by Hawecker *et al.* in the reduction of CO_2 and could be an intermediate in the production of free CO.[1]

We have developed synthetic routes to a variety of carbonyl and hydride containing polypyridyl complexes of Re^I,[8,9] Os^{II},[10,11,12] Ru^{II},[11,12] and Ir^{III},[13] and have described some of the thermal and photochemical properties of the series, Recently, we have extended our synthetic work to the preparation of the new trifluoromethanesulphonato complex *fac*-$Re(bpy)(CO)_3O_3SCF_3$ in which the lability of the CF_3SO_3-group is used for the preparation of the complexes *fac*-$Re(bpy)(CO)_3X$ (X = O_2COH, O_2CH, and H) in high yield. Especially notable is the hydrido complex since it provides the first reported example of a visible light induced reaction leading to the reduction of CO_2 to a thermally stable formato complex.[14]

The trifluoromethanesulphonato derivative[11,13,15,16] can be made conveniently and in high yield by the reaction between anhydrous CF_3SO_3H (6×10^{-3} mol, *ca.* 0.9 g) and the corresponding chloro complex (*ca.* 10^{-3} mol) in CH_2Cl_2 by stirring the reaction mixture at room temperature for 1 h [equation (1)]. Precipitation of the complex by the slow addition of Et_2O with continued stirring yields light yellow crystals in better than 90% yield.

$$fac\text{-}Re(bpy)(CO)_3Cl + CF_3SO_3H \xrightarrow[\text{Heat}]{CH_2Cl_2} fac\text{-}Re(bpy)(CO)_3\text{-}O_3SCF_3 + HCl \quad (1)$$

fac-$Re(bpy)(CO)_3SO_3CF_3$ is soluble in low-polarity solvents like CH_2Cl_2 but dissolves with ionization in polar solvents like MeCN or H_2O (with gentle heating) to give the solvato complex, *e.g.*, equation (2). The Re^I-aqua complex

$$fac\text{-}Re(bpy)(CO)_3O_3SCF_3 + H_2O \rightarrow fac\text{-}[Re(bpy)(CO)_3(H_2O)]^+ + {}^-O_3SCF_3 \quad (2)$$

provides an ideal intermediate for the preparation of the hydrido, formato, and hydrogen carbonato derivatives. In a typical reaction on a 1 mmol scale, a 10× or 20× molar excess of the sodium salts of BH_4^-, HCO_2^-, or $HOCO_2^-$ and the aqua complex were heated at reflux for 15—45 min in a 2 : 1 mixture of $EtOH\text{–}H_2O$. Slow removal of the solvent gave crystals of the desired complex which were then washed with H_2O and air dried.

Characterization of all of the complexes was achieved by elemental analyses,[†] cyclic voltammetry, and i.r., u.v.–visible, and ^1H n.m.r. spectroscopy (see Table 1). The products all have the *facial* geometry as shown by the appearance of three CO stretches in the 1500 to 2100 cm^{-1} region of the i.r. spectrum and two doublets and two triplets, in the first order, in the ^1H n.m.r. spectrum of the bpy region.

Irradiation with near u.v.–visible light[‡] of an orange solution of *fac*-$Re(bpy)(CO)_3H$ in freshly distilled tetrahydrofuran (THF), C_6H_6, or C_6D_6, which had been saturated with CO_2 (either Matheson 99.995% research grade or 'Bone Dry' Grade), resulted in a brownish-green solution which rapidly deposited the formato complex *fac*-$Re(bpy)(CO)_3O_2CH$. The identity of the product was demonstrated by its characteristic ^1H n.m.r. spectral and cyclic voltammetric properties. A small preparative scale reaction employing 50 mg of the hydride complex in 50 ml of CO_2-saturated THF formed the formato complex in 81% yield as determined by ^1H n.m.r. spectral analysis and by mass balance. The remaining Re product was present as two as yet uncharacterized complexes.

There is also a relatively slow thermal reaction between CO_2 and *fac*-$Re(bpy)(CO)_3H$. For example, 2.0×10^{-4} M solution of the complex in THF proceeds to completion in *ca.* 5 h as shown by spectral monitoring. Using the photolytic conditions described above the reaction is complete within 10 min.

Although both the thermal and photochemical reactions can be described in the net sense by the CO_2 insertion reaction shown in equation (3), the chemistry involved has some unusual features and it poses a series of tantalizing mechanistic questions.

$$fac\text{-}Re(bpy)(CO_3)H + CO_2 \xrightarrow{\text{Heat or } h\nu} fac\text{-}Re(bpy)(CO)_3O_2CH \quad (3)$$

Unlike most of the reported cases of CO_2 insertion into M–H bonds observed for group 8 metals, no dynamic thermal equilibrium exists in the Re system between the formato and hydrido complexes.[5—7] In our case addition of CO_2 occurs at a formal co-ordinatively saturated metal centre, and while a mechanism involving CO dissociation[17] may be operative, the thermal stability of the *fac*-$Re^I(bpy)(CO)_3{}^+$ unit toward CO loss is known to be high. The photoinduced reaction is clearly

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[†] Elemental analyses of the new complexes supported the assigned structures.

[‡] A 275 W sunlamp with a 360 nm cut off filter was used in conjunction with a water cooled sample holder. For the spectral studies a 1000 W xenon lamp was used with a monochromator which isolated 436 nm light.

Table 1. Characteristics of the Re^I complexes.

	δ_H[a]	ν_{CO}/cm^{-1}	$E_{\frac{1}{2}}/V$[b]	λ/nm[c]
fac-$Re(bpy)(CO)_3OSO_2CF_3$	7.64(t),8.20(t),8.26(d),9.08(d)[d]	2030,1941,1921[d]	—[d]	360[d]
fac-$Re(bpy)(CO)_3O_2CH$	7.61(t),7.81(s),8.19(t),8.39(d),9.04(d)[e]	2008,1917,1895[d]	+1.37,−1.29,−1.71[e]	382[d]
fac-$Re(bpy)(CO)_3O_2COH$	7.78(t),8.36(t),7.77(d),9.06(d)[f]	[g]	−1.31[f]	362[f]
fac-$Re(bpy)(CO)_3H$	1.54(s),7.49(t),8.05(t),8.36(d),9.14(d)[e]	1993,1905,1888 (2018)[i]	+0.90,[h] −1.46[d]	415[d]

[a] Shifts downfield from tetramethylsilane. [b] Measured *vs.* standard calomel electrode with 0.1 M tetraethylammonium perchlorate for MeCN solution, or 0.2 M for CH_2Cl_2 solution. Determined at a scan rate of 100 mV/s at a Pt working electrode. [c] Refers to the maximum of the longest wavelength metal to ligand charge transfer transition. [d] Recorded in CD_2Cl_2 or CH_2Cl_2 solution. [e] Recorded in CD_3CN or MeCN solution. [f] Recorded in $(CD_3)_2SO$ or Me_2SO solution. [g] Low solubility results in inaccurate values. [h] E_p value at 100 mV/s scan rate. [i] Value in parentheses refers to assigned Re–H stretch.

initiated by irradiation into the MLCT (metal to ligand charge transfer) [$\pi^*(bpy) \leftarrow Re^I$] transitions,[3,8] but it is not clear whether the photoreactivity is inherent to the MLCT states or whether these states act as intramolecular sensitizers of another reactive excited state or states.

As a last point, both the thermal and photochemical properties of *fac*-$Re(bpy)(CO)_3H$ may be capable of providing a basis for a photoelectrochemical cell[18] which would function to reduce CO_2 to soluble formate salts while producing current.

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