Transformations of *fac*-Re(dmbpy)$(CO)_3(CO_2H)$ in the presence of carbon dioxide (dmbpy = 4,4′-dimethyl-2,2′-bipyridine)

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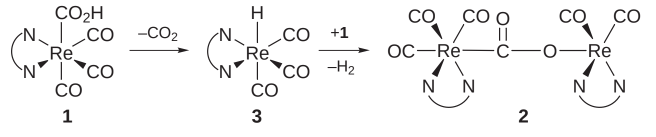
Reactions of *fac*-Re(dmbpy)$(CO)_3(CO_2H)$ 1 or *fac*, *fac*-Re(dmbpy)$(CO)_3(CO_2)$Re(dmbpy)$(CO)_3$ 2 with CO_2, in DMSO or DMF containing small amounts of water, lead to the bicarbonato complex, *fac*-Re(dmbpy)$(CO)_3$[OC(O)OH] 4; the formato complex, *fac*-Re(dmbpy)$(CO)_3$(OCHO) 5, is not a major product in any of these reactions.

The proposed intermediacy of metallocarboxylic acids in reductions of CO_2 catalyzed by ruthenium and rhenium polypyridyl complexes[1] has prompted our interest in the synthesis and chemistry of compounds of this type. Previously, the production of formate in the catalytic reactions has been attributed to CO_2 insertion into metal hydrides generated from decarboxylations of metallocarboxylic acids.[1] We recently described the first synthesis of a rhenium acid of this type, *fac*-Re(dmbpy)$(CO)_3(CO_2H)$ **1**[2] which had been proposed to be an intermediate in electrocatalytic reductions of CO_2 by *fac*-Re(dmbpy)$(CO)_3$Cl.[1] Thermolysis of **1** in dimethyl formamide (DMF) gave the new CO_2-bridged compound, *fac*, *fac*-Re(dmbpy)$(CO)_3(CO_2)$Re(dmbpy)$(CO)_3$ **2**; the reactions could be photoassisted. We suggested that **2** was formed *via* β-hydride elimination from **1**, followed by CO_2 loss, to give *fac*-Re(dmbpy)$(CO)_3$H **3** as an intermediate.[2] Subsequent reaction of **3** with additional **1** was proposed to yield **2** (and hydrogen) as shown in Scheme 1. Since formate was absent from the thermolysis products of **1**, additional reactions of **1** and **2**, with and without CO_2, have been explored because of their relevance to proposed steps in the catalytic processes.[1]

Although the ^{1}H NMR spectrum of **1** can be obtained in DMF-d_7 at 0 °C, **1** is labile in this solvent at room temperature and readily converts to **2**.[2] We attempted to follow this transformation by ^{1}H NMR in order to probe for the intermediacy of hydride **3**. A solution of **1** in DMF-d_7 was prepared and the spectrum quickly recorded. The spectrum showed none of **3**, but did not correspond exactly to that of **2**[2] either; resonances appeared at the same chemical shift positions as those observed for **2**, but some were broadened (suggesting dynamic behavior) while others were sharp. After 1 h, all resonances had sharpened to those of **2** together with a small amount of a second compound, identified as the bicarbonato complex *fac*-Re(dmbpy)$(CO)_3$[OC(O)OH] **4**.† Importantly, the major features of the spectrum obtained from a sample of **1** after a few minutes in DMF-d_7 were reproduced by mixing equimolar quantities of hydride **3** and **1** in this solvent and quickly obtaining the spectrum. The hydride resonance at δ 1.8 had already disappeared by the time the spectrum could be observed, although the spectrum of **3**, alone, can easily be obtained under these conditions. Eventually, the mixture of **3** and **1** afforded **2**, a small amount of formate, *fac*-Re(dmbpy)$(CO)_3$(OCHO) **5**,[2,3] and a small amount of **4**.



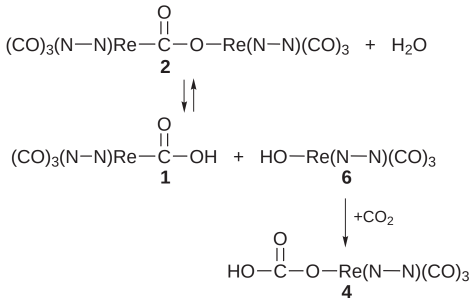
Scheme 1 N–N = 4,4′-dimethyl-2,2′-bipyridine

Compound **1** is more stable in DMSO-d_6 and its ^{1}H NMR spectrum can be obtained easily at room temperature. After about 40 min, however, all low field resonances of **1** (dmbpy ring and carboxyl H atoms) became broadened and new resonances that are analogous to those of **2** in this solvent appeared; no resonances for hydride **3** were observed. Compound **2** shows doublets at δ 8.44, 8.34, 7.31 and 7.15 and singlets at δ 8.28 and 8.10 in DMSO-d_6; the new species showed resonances at all of these positions, but those at δ 8.28 and 7.31 were broadened while the others were sharp. After about 2.5 h, all resonances of **1** had disappeared, but the two broadened resonances of the new species were still broadened. Such spectra have been reproduced several times with different samples of **1**; any disturbance (shaking, purging with N_2, *etc.*) of samples which have been allowed to stand for 2 h results in immediate transformation of this species to products, primarily **2**. In a separate experiment, a 73% yield of **2** together with 10% of **4** was obtained from a solution of **1** after 2 h standing in DMSO-d_6 under laboratory fluorescent lights followed by purging the solution with N_2; formate **5** was absent. However, a sample of **1**, dissolved in DMSO-d_6 and allowed to stand under laboratory fluorescent lights after purging with CO_2, generated bicarbonato complex **4** in 97% yield after 3 h.

The thermolysis, at ambient temperature, of an equimolar mixture of acid **1** and hydride **3** was followed by ^{1}H NMR spectroscopy in DMSO-d_6 in the same manner as for **1** alone. The spectrum was recorded 10 min after dissolving both compounds in the solvent; all resonances of the two substrates were broadened. After 40 min, the carboxyl proton of **1** and the hydride resonance of **3** had disappeared and broadened resonances characteristic of the species formed from **1** alone had appeared. Conversion to **2** occurred slowly, as before; again, formate **5** was not observed.

Other changes in thermolysis samples of **1** in DMSO-d_6 accompany changes in the ^{1}H NMR spectra; the initially yellow solutions darken and gas evolution becomes evident after 1.5 h (CO_2 is soluble at these concentrations). As the spectra change to more closely resemble **2**, the solutions become dark orange; with prolonged standing, the solutions become pale yellow and a precipitate of the sparingly soluble bicarbonato complex **4** appears. Thus, it is clear that CO_2 was liberated and available for the eventual production of **4.** Formate **5** was not observed as a product in the reactions conducted in DMSO, although it can be readily formed from hydride **3** and CO_2 in this solvent.[3]

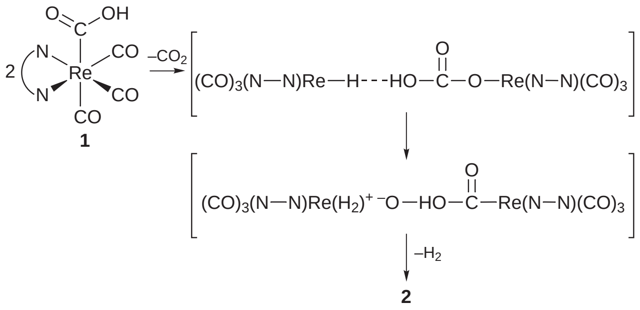
Reactions of **2** were then conducted in DMF-d_7 or DMSO-d_6 together with 'bone-dry' CO_2[4] in order to provide further clarification. A solution of **2** in DMF-d_7 was purged with the CO_2 for a few minutes; during this time, the initially red solution became yellow and a yellow precipitate formed. Further analysis of the solution, and the precipitate, showed that **2** had converted completely to bicarbonate **4**. A similar experiment conducted with **2** in DMSO-d_6 showed approximately equal quantities of acid **1** together with **4** after 10 min; formate **5** was formed in only trace quantities in the experiment. Independently, we showed that the hydroxo complex, *fac*-Re(dmbpy)$(CO)_3(OH)\cdot H_2O$ **6**,[2] was rapidly converted to **4** in quantitative yield upon exposure to CO_2. These results suggest



Scheme 2 N–N = 4,4′-dimethyl-2,2′-bipyridine

that the CO_2-bridged compound **2** exists in these solutions in equilibrium with a small amount of its hydrolysis products, acid **1** and hydroxo complex **6** (generated by adventitious water), and that subsequent conversion of **6** to **4** occurs quickly, and irreversibly, in the presence of CO_2. In DMF-d_7, the conversion of **2** proceeds to **4** rapidly; in DMSO-d_6, a mixture containing **4** and **1** can be observed because **1** is more stable in this solvent. These reactions are shown in Scheme 2. Although not typical of CO_2-bridged complexes of this type,[5] similar hydrolysis of one has been suggested previously;[6] the reverse reaction is facile and well known.[5]

In recent years, both intra- and inter-moleclar interactions between basic transition metal hydrides and H-donor reagents containing N–H or O–H groups have been well documented.[7] These have been described in terms of initial hydrogen bonding between the two species followed by formation of a dihydrogen ligand. A linear H···HO hydrogen bond has been suggested previously;[7d] thus, we suggest the pathway outlined in Scheme 3 for the transformation of **1** to **2**. The precise nature of the intermediate species leading to **2** is not known at present. However, the suggested partial conversion of **1** to **3**, followed by the reaction of **3** with additional **1** and loss of H_2 leading to **2**, is directly analogous to the reactions of other rhenium hydrides with weakly acidic, and protic, substrates. The poor solubility of **1** ensures that free H_2 cannot be spectroscopically observed in our reactions, although gas evolution is evident after the intermediate species develops. Also, the limited solubilities of **1** and **2** prevent low temperature NMR experiments or probes of H-bonding *via* IR spectra of the solutions for further information about the nature of the intermediate species; the existence of the intermediate is clear, however.



Scheme 3 N–N = 4,4′-dimethyl-2,2′-bipyridine

Previous spectral studies of the interactions of hydrides with hydroxylic species have been done in non-polar solvents to avoid competition for the hydroxyl hydrogen.[7] However, the very polar solvents (DMF and DMSO) used with **1** (or **1** and **3**) do not appear to disrupt the association of **1** with **3**. We conclude that it is this strong association with **1** that prevents hydride **3** from being accessible for reaction with CO_2 to form formate **5**.

The behavior of **1** in the presence of CO_2, in solvents and under the not rigorously dry conditions that are typically used in electrocatalytic reactions involving CO_2,[1] casts doubt on the intermediacy of **1** as a precursor to formate in the reactions. We have suggested[2,8] that metal formyl complexes, through the hydrides formed by their degradation, are more likely precursors to formates generated in the reactions. Rapidly in DMF solution, and more slowly in DMSO, acid **1** is transformed to products not identified in the catalytic reactions. Catalytic reactions conducted in acidic media, however, could yield CO as the result of carboxyl cleavage of either **1** or **2**.[1] Efforts are in progress to define the chemical behavior of these reactive compounds further.

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Notes and references

† An authentic sample of **4** was obtained as follows: a flask containing a red solution of *fac*-Re(dmbpy)$(CO)_3OH\bullet H_2O$ **6**[2] (0.031 g, 6.6×10^{-2} mmol) in 10 mL of acetone was flushed with dry CO_2. The solution immediately changed to yellow and a yellow solid precipitated. The solid was collected by filtration and washed with acetone (2 × 5 mL). After drying under high vacuum, 0.025 g (75% yield) of **4** was obtained, mp 199–201 °C. Anal. Calc. for $C_{16}H_{13}N_2O_6Re\bullet H_2O$: C, 36.02; H, 2.83. Found: C, 36.13; H, 2.65%. IR ν_{CO} (KCl, DRIFTS): 2026s, 1906s, 1872s; ν_{OCOO} 1630m, 1422m, 1350m cm^{-1}. ^1H NMR (DMF-d_7): δ 9.21 (1H, br), 8.97 (2H, d, *J* 6 Hz), 8.68 (2H, s), 7.65 (2H, d, *J* 6 Hz) and 2.59 (6H, s). ^{13}C NMR (DMSO-d_6): δ 198.33, 194.62, 158.64, 154.96, 152.67, 152.49, 128.10, 124.72 and 20.96.

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