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Synthesis and Reactions of *fac*-Re(dmbpy)$(CO)_3$X (dmbpy = 4,4′-dimethyl-2,2′-bipyridyl; X = COOH, COOMe, H, OH, and OCHO)

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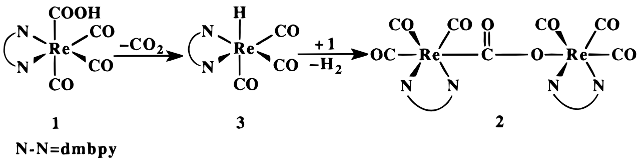
Metallocarboxylic acids (M-COOH) are proposed as intermediates in electrocatalytic and photocatalytic reductions of CO_2 by *fac*-Re(N−N)$(CO)_3$Cl (N−N = bidentate polypyridyl ligand), but have not been directly observed or isolated previously.[1,2] We report the synthesis and several reactions of *fac*-Re(dmbpy)$(CO)_3$COOH,[2] including its transformation to a CO_2-bridged complex by thermal or photoassisted processes. The preparations and reactions of several related compounds are also described.

Reaction of Re(dmbpy)$(CO)_4$OTf[3] (OTf = trifluoromethanesulfonate) with aqueous KOH afforded *fac*-Re(dmbpy)$(CO)_3$COOH (**1**) in 82% yield. The compound has been characterized by analytical and spectral data.[4] Dissolution of the acid in acetone, followed by standing (90 h) under laboratory fluorescent lights, afforded a 26% yield of a red solid identified as the μ_2-η^2-CO_2-bridged complex, *fac*, *fac*-Re(dmbpy)$(CO)_3(CO_2)$Re(dmbpy)$(CO)_3$ (**2**); the solution contained several unidentified compounds. Compound **2** has been characterized by analytical and spectral data;[5] DRIFTS data clearly indicate the type of bridging CO_2 ligand.[6] The formation of compound **2** can be attributed to the partial decarboxylation of **1** to *fac*-Re(dmbpy)$(CO)_3$H (**3**) followed by reaction of **3** with **1**, with liberation of H_2, as indicated in Scheme 1 (and expected from the reactions of other metallocarboxylic acids with active hydrides[6]). To our knowledge, this type of reaction is unique; previously, *trans*-Pt(Ph)$(PEt_3)_2$(COOH) was shown to convert to a CO_2-bridged complex with loss of CO and H_2O.[7] A sample of **3** was prepared[8] and allowed to stand in acetone with an equiv of **1** for 24 h. During this time, **2** precipitated, but the yield was only 31%; the solution contained several compounds, but no **1** or **3**. Further study showed that hydride **3** is unstable in acetone, generating a mixture of several unidentified products. Reaction of **1** with **3** in CH_2Cl_2 was conducted for 8 h at 0 °C (to reduce the degradation of **1**); the yield of **2** was still low (25%). Photolysis of a solution of acid **1** in acetone for 2 h beside a 450 W UV lamp (cooled in a Pyrex immersion well) afforded **2** in 67% yield.

Scheme 1



Since dimethylformamide (DMF) has been used as solvent in electrocatalytic reactions of *fac*-Re(N−N)$(CO)_3$Cl, we examined the behavior of **1** in DMF. Allowing a sample of **1** to stand in DMF for 5 min under laboratory fluorescent lights followed by removal of the DMF under vacuum afforded a mixture containing mainly **2** (63% yield). Photolysis of a second sample with the 450 W lamp for 5 min, followed by removal of DMF, afforded a slightly higher yield (74%) of **2**.

Compound **2** was obtained easily from reactions of **1** with the hydroxo complex, *fac*-Re(dmbpy)$(CO)_3$(OH) (**4**);[10] a 90% yield of **2** was obtained from the reaction of **1** with an equiv of **4** in CH_2Cl_2 during 1 h at 0 °C. Compound **4** was obtained as a hydrate; it is not yet known whether the compound is monomeric or dimeric as observed for a ruthenium complex.[11] Reactions of other hydroxo metal complexes have provided CO_2-bridged complexes previously.[6,12] The reaction may take place via nucleophilic addition of the hydroxo ligand in **4** to the carboxyl group of the acid followed by loss of water, or **2** could be

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(4) To Re(dmbpy)$(CO)_4$OTf (0.15 g, 0.25 mmol) in water (30 mL) was added KOH (0.014 g, 0.25 mmol); the mixture became yellow immediately. After the mixture stirred for 1 h, the precipitated yellow solid was collected by filtration, washed with water (200 mL), and dried under high vacuum to give **1** (0.10 g, 82% yield); mp 162−165 °C dec. Anal. Calcd for $C_{16}H_{13}N_2O_5$-Re: C, 38.47; H, 2.62. Found: C, 38.39; H, 2.59. DRIFTS (KCl) ν_{CO}: 2012 (s), 1916 (sh), and 1892 (vs) cm^{-1}; ν_{OCO}: 1572 (m) and 1194 (w) cm^{-1} . ^1H NMR (DMF-d_7, 0 °C): δ 9.49 (1H, s), 8.91 (2H, d, $J = 6$ Hz), 8.65 (2H, s), 7.54 (2H, d, $J = 6$ Hz), and 2.54 (6H, s). ^{13}C NMR (DMF-d_7, 0 °C): δ 211.62, 201.12, 195.50, 156.53, 153.02−152.69 (two broad peaks), 151.90, 128.38, 125.72−124.45 (three peaks), and 21.09.

(5) Compound **1** (0.10 g, 0.20 mmol) in 60 mL of acetone was allowed to stand for 90 h. The resulting red solid was collected and washed with acetone (10 mL) then $CHCl_3$ (3 × 10 mL) affording **2**, *fac, fac*- [Re(dmbpy)$(CO)_3]_2$-(CO_2), (0.025 g, 26% yield) after drying under vacuum, mp 243−245 °C dec. Anal. Calcd for $C_{31}H_{24}N_4O_8Re_2$: C, 39.07; H, 2.54. Found: C, 38.88; H, 2.84. DRIFTS (KCl) ν_{CO}: 1992 (s), 1888 (s), and 1866 (sh) cm^{-1}; ν_{OCO}: 1485 (m) and 1155 (m) cm^{-1}. ^1H NMR (DMF-d_7): δ 8.60 (2H, d, $J = 6$ Hz), 8.48 (2H, d, $J = 6$ Hz), 8.44 (2H, s), 8.25 (2H, s), 7.40 (2H, d, $J = 6$ Hz), 7.24 (2H, d, $J = 6$ Hz), 2.64 (6H, s), and 2.57 (6H, s). ^{13}C NMR (DMF-d_7): δ 211.59, 203.24, 201.83, 199.44, 196.07, 155.59, 155.56, 152.98, 152.08, 151.75, 150.15, 127.77, 127.53, 124.83, 124.03, 21.33, and 21.15.

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(8) Synthesis and characterization data were not provided previously (Sullivan, B. P.; Meyer, T. J. *Organometallics* **1986**, *5*, 1500), for **3**: $NaBH_4$ (0.37 g, 9.8 mmol) and *fac*-Re(dmbpy)$(CO)_3$OTf[9] (0.27 g, 0.48 mmol) were added to MeOH (40 mL, 0 °C) under N_2, then stirred for 2 h. Cold water (50 mL) was added, and the resulting yellow solid was collected, washed with water, and then dried to give **3**: (0.19 g, 87% yield), mp 180−182 °C dec. DRIFTS (KCl) ν_{CO}: 1992 (m), 1887 (s), and 1865 (s) cm^{-1}. ν_{ReH}: 2036 (w) and 2019 (w) cm^{-1}. ^1H NMR (DMF-d_7): δ 9.04 (2H, d, $J = 6$ Hz), 8.64 (2H, s), 7.55 (2H, d, $J = 6$ Hz), 2.58 (6H, s), and 1.86(1H, s). ^{13}C NMR(DMF-d_7): δ 203.54, 194.32, 155.91, 153.82−152.23(m), 151.14, 129.18−127.69(m), 125.92−124.42(m), and 21.02. Satisfactory analytical data were obtained.

(9) This triflate complex was prepared, but not isolated, previously: Koike, K.; Hori, H.; Ishizuka, M.; Westwell, J. R.; Takeuchi, K.; Ibusuki, T.; Enjouji, K.; Konno, H.; Sakamoto, K.; Ishitani, O. *Organometallics* **1997**, *16*, 5724. Acceptable analytical and spectral data have been obtained for the compound.

(10) *fac*-Re(dmbpy)$(CO)_3$OTf[9] (0.50 g, 0.88 mmol) and KOH (6 mL of 4 M solution) in acetone (30 mL)/water (70 mL) were refluxed for 21 h. After the mixture was cooled to ambient temperature and concentrated, a yellow solid precipitated which was collected, washed with water (2 × 20 mL), and dried under high vacuum to give **4** (now orange; 0.31 g, 72% yield); mp 135−136 °C dec. Anal. Calcd for $C_{15}H_{13}N_2O_4Re{\cdot}H_2O$: C: 36.81; H, 3.09. Found: C, 36.92; H, 3.20. DRIFTS (KCl) ν_{CO}: 2001 (s), 1887 (s), and 1867 (vs) cm^{-1}; ν_{OH}: 3636 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.82 (2H, d, $J = 6$ Hz), 8.01 (2H, s), 7.33 (2H, d, $J = 6$ Hz), 2.54 (6H, s), and 1.22 (broad singlet, 3H; hydroxyl hydrogens). ^{13}C NMR (CD_2Cl_2): δ 200.38, 194.58, 155.72, 152.24, 151.84, 127.92, 124.17, and 21.76. Redissolving the orange solid in acetone/H_2O gave a yellow solution from which the yellow solid could be obtained as before; structural differences between the two forms are being examined.

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generated as the result of addition of **4** to Re(dmbpy)(CO)$^{4+}$, formed by ionization of **1**. Although ionization was not evident, low concentrations of cation could go undetected. We also prepared the corresponding ester, *fac*-Re(dmbpy)(CO)$_3$COOMe[13] (**5**); reaction of equimolar amounts of **5** and **4**, in CH_2Cl_2 as described above, also provided **2** (87% yield). There was no evidence for dissociation of **5** either; thus, these two reaction paths cannot be distinguished. However, deprotonation of **1** by **4**, followed by displacement of H_2O by the carboxylate, seems unlikely since ester **5** reacts with **4** to give **2** also.

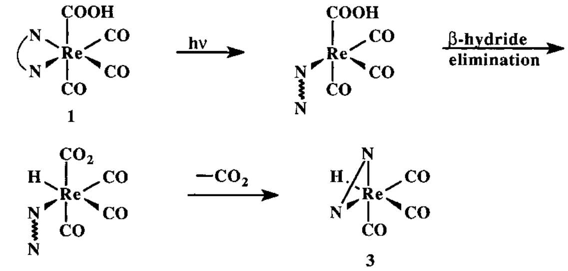
Since reactions of **1** did not provide direct evidence for hydride **3**, we sought further support for its intermediacy. A sample of acid **1** was allowed to stand in the dark, in dry $CDCl_3$, for 25 h; after this time, NMR analysis showed that **1** was unchanged. Photolysis of a similar solution of **1**, in an NMR tube beside the 450 W UV lamp, as described above, afforded complete conversion to the known compound,[14] *fac*-Re(dmbpy)(CO)$_3$Cl (**6**), after 1 h. For comparison, a sample of **3** allowed to stand in the dark, in dry $CDCl_3$, for 24 h showed 90% conversion to **6**; photolysis of **3** in $CDCl_3$, as described for **1**, converted it to **6** after only 10 min.

Recent work on complexes of the general type *fac*-Re(N−N)(CO)$_3$CH$_2$R, has shown that some of them are susceptible to metal−carbon bond cleavage at the methylene group upon photolysis.[15,16] Therefore, we looked for evidence of other products from the reaction of **1** with $CDCl_3$; however, only **6** was present. A sample of **5** allowed to stand in dry $CDCl_3$ for 24 h was unchanged. A second sample was irradiated beside the 450 W lamp, as described for **1**, but for 6 h; during this time about 25% of **5** was converted to **6**; an equiv MeOH was also generated, suggesting that the small conversion of **5** occurred via hydrolysis of **5** to **1** by adventitious water. Compound **6** was the only other product; dimethyl oxalate, a possible radical coupling product, was absent.

Recently, we determined that the reaction of *fac*-Re(bpy)(CO)$_3$(CH$_2$OH) (or the related hydride complex) with MeOH occurs with photoassistance and yields *fac*-Re(bpy)(CO)$_3$(OMe).[16] The reaction pathway was suggested to involve β-hydrogen elimination from the hydroxymethyl group to a vacant site on rhenium generated by photodechelation of the bipyridyl to a monodentate ligand. Intermediates with monodentate bipyridyl ligands have been suggested previously to rationalize photochemically promoted ligand substitution reactions in Ru(bpy)$_3^{+2}$ and spectral evidence for one such compound was described.[17] Also, thermally induced dynamic behavior of bipyridyl-type ligands in square-planar complexes has been demonstrated and rationalized in terms of monodentate intermediates.[18]

On the basis of our observations on **1**, we propose a pathway involving β-hydrogen elimination, followed by CO_2 loss, for its conversion to **3** as shown in Scheme 2; where both **1** and **3** are present in the same solvent (nonhalogenated), conversion to **2** can take place. Reactions of both **1** and **3** (and its 2,2′-bipyridyl analog[16]) can be photoassisted; thus, formation of **2** from **1** and **3** can be photochemically promoted. Photoassistance in CO_2 insertion reactions of *fac*-Re(bpy)(CO)$_3$H has been documented previously.[19] Additionally, rates of thermal reactions of the hydride with CO_2 were enhanced with increasing solvent polarity, consistent with a highly polar, charge-separated transition state for the reaction.[20] Reactions of **1** in DMF are much faster than those in less polar solvents, suggesting that the rate of CO_2 loss from **1** may be enhanced by increased solvent polarity also.

Scheme 2



Our observations on *fac*-Re(bpy)(CO)(CH$_2$OH)[16] and on acid **1** in the present work complement our observations on some photoassisted reactions of the formyl complex, *cis*-Ru(bpy)$_2$(CO)(CHO)(PF$_6$), which were rationalized through hydride migration from the formyl group to a vacant site on ruthenium created as the result of photodechelation of one bipyridyl nitrogen ligand.[21] Thus, dechelation, followed by intramolecular migration of an active hydrogen and then ligand loss (CO, CH_2O, or CO_2), can be expected to play a major role in determining the outcome of photocatalytic processes involving ruthenium and rhenium polypyridyl complexes bearing C_1 ligands.

Interestingly, although hydride **3** reacts readily with excess CO_2 to provide formate complex **7**,[7,22] this compound was not observed as a major product in decompositions of acid **1**. Compound **7** was identified (12% yield) in reactions involving equivalent amounts of **1** with **3** conducted in CH_2Cl_2 (described above); the yield of **2** from this reaction was only 25%, and there were several unidentified products. Thus, when substantial amounts of **3** are available, the rate of its thermal reaction with CO_2 appears to be competitive with the rate of its reaction with **1**; when **1** is in excess and the amount of CO_2 is limited, little **7** is generated. Reactions of **1**, including the lack of facile conversion of **1** (via hydride **3** and CO_2) to **7**, suggest that the pathways which have been proposed[1] for the generation of formate in catalytic reactions of *fac*-Re(N−N)(CO)$_3$Cl may not be correct. Further work on the reactions of **1** in the presence of CO_2 is in progress.[23] We have suggested[24] that formates observed in the catalytic reactions may result from CO_2 insertion into M−H bonds formed as the result of transformations of metal formyl complexes. Additional work is in progress to address these points.

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(13) Addition of acid **1** to MeOH followed by brief stirring and then evaporation to dryness afforded **5** in quantitative yield, mp 205−210 °C. dec. DRIFTS (KCL) ν_{CO}: 2004 (s), 1905 (sh), and 1876 (s) cm^{-1}; ν_{OCO}: 1609 (m) and 1025 (m) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 8.82 (2H, d, $J = 6$ Hz), 8.02 (2H, s), 7.25 (2H, d, $J = 6$ Hz), 3.13 (3H, s), and 2.55 (6H, s). ^{13}C NMR (CD$_2$Cl$_2$): δ 210.89, 200.42, 194.57, 156.22, 152.63, 150.87, 127.51, 123.81, 47.48, and 21.68. Satisfactory analytical data were also obtained.

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(22) Synthesis and characterization data were not reported previously[8] for **7**: **3** (0.050 g, 0.11 mmol) was added to 20 mL of CO_2-saturated MeOH, giving a yellow solution. After stirring under a CO_2 atmosphere for 2 h, the solution was evaporated to dryness to give pure **7** (0.052 g, 95% yield); mp 223−226 °C dec. DRIFTS (KCl) ν_{CO}: 2022 (m), 1906 (s), and 1864 (s) cm^{-1}; ν_{OCO}: 1634 (m) and 1287 (m) cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 8.84 (2H, d, $J =$ 6 Hz), 8.25 (2H, s), 7.82 (1H, s), 7.43 (2H, d, $J = 6$ Hz) and 2.54 (6H, s). ^{13}C NMR(CD$_3$CN): δ 199.24, 195.30, 167.12, 156.30, 153.72, 153.60, 128.78, 125.25, and 21.49. Satisfactory analytical data were also obtained.

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