Synthesis and Reactions of *fac*-Re(bpy)$(CO)_3(CH_2OR)$ (R = H, Acetyl; bpy = 2,2′-Bipyridyl)

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*Summary: Photoassisted reactions of fac-Re(bpy)$(CO)_3$$(CH_2OR)$ (**1**, R = H; **2**, R = OAc) and fac-Re(bpy)$(CO)_3$$CH_2Ph$ (**5**) in MeOH provide fac-Re(bpy)$(CO)_3(OCH_3)$ (**3**); **2** and **3** have been structurally characterized. Radical paths are indicated for **2** and **5**; a nonradical path, involving photoassisted β-hydride elimination from the hydroxymethyl group, is proposed for **1**.*

Ruthenium and rhenium polypyridyl complexes bearing C_1 ligands are of interest because of the possible intermediacy of such compounds in photochemically and electrochemically promoted reductions of carbon dioxide.[1] Some of the C_1 ligands are expected to be the same as those suggested in catalytic reductions of CO.[2] Furthermore, although many coordination complexes of ruthenium and rhenium with polypyridyl ligands are known, few organometallic compounds (those with carbon ligands other than CO) have been characterized and little is known of their chemical reactions.[3] We have begun to study compounds of these types, particularly those with metallocarboxylate and formyl ligands.[4]

Reaction of Re(bpy)$(CO)_4^+OTf^-$ (OTf = trifluoromethanesulfonate)[5] with $NaBH_4$ in MeOH afforded a red product which has been identified as *fac*-Re(bpy)$(CO)_3$$(CH_2OH)$ (**1**); the product, obtained in 69% yield, has been characterized by elemental analysis and spectral data.[6] The acetoxymethyl derivative of **1**, *fac*-Re(bpy)$(CO)_3(CH_2OAc)$ (**2**; Ac = acetyl), was prepared by treating **1** with acetic acid (or acetic anhydride). Compound **2** has been characterized by elemental analysis, spectral data[7], and an X-ray structure determination.[8,9]

In dry MeOH, under N_2, irradiation of **1** through Pyrex with a 450 W UV lamp (Ace-Hanovia) over 20 min afforded a yellow solution which yielded a red solid, *fac*-Re(bpy)$(CO)_3(OCH_3)$ (**3**), in 97% yield. The yield of **3** was not affected by the exposure of samples to O_2. Compound **3** has been characterized by elemental analysis, spectral data,[10] and X-ray crystallography[11] (see Figure 1). Photolyses of **1** in dry methanol-d_4, conducted in NMR tubes with and without O_2, showed that CH_2O (present as the hemiacetal[13,14] in 68% yield as established by an NMR internal standard) was the

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[6] To a solution of Re(bpy)$(CO)_4$OTf [5] (0.20 g, 0.35 mmol) in 25 mL of MeOH at 0 °C was added $NaBH_4$ (0.058 g, 1.5 mmol) in several portions. The reaction flask was wrapped in Al foil and stirred for 1 h at 0 °C. The solvent was evaporated, and the resultant red solid was collected and washed with water (100 mL). A red solid was obtained (**1**; 0.11 g, 69%) and dried under vacuum; mp 158−160 °C dec. Anal. Calcd for $C_{14}H_{11}N_2O_4Re$: C, 36.76; H, 2.42. Found: C, 36.86; H, 2.47. IR (DRIFTS, KCl): ν_{CO} 1987 (s), 1865 (vs) cm^{-1}. ^1H NMR (CD_3OD): δ 9.06 (2H, d, $J = 5.7$ Hz), 8.52 (2H, d, $J = 8.4$ Hz), 8.12 (2H, t, $J = 8.1$ Hz), 7.55 (2H, t, $J = 7.8$ Hz), 3.37 (2H, s). ^{13}C NMR (CD_3OD): δ 203.98, 194.44, 156.59, 153.74, 139.24, 127.80, 124.68, 70.05.

[7] Compound **1** (0.30 g, 0.65 mmol) was added to 5 mL of acetic acid. The mixture was stirred for 2 min; during this time, the solution became yellow as the starting material dissolved. The resulting solution was added to ca. 50 mL of water to effect precipitation of **2** (0.28 g; 86% yield); mp >210 °C. Anal. Calcd for $C_{16}H_{13}N_2O_5Re$: C, 38.47; H, 2.62. Found: C, 38.28; H, 2.63. IR (DRIFTS, KCl): ν_{CO} 2017, 1997 and 1885 cm^{-1}; $\nu_{ester\ CO}$ 1696 cm^{-1}. ^1H NMR (CD_3CN): δ 8.98 (2H, d, $J =$ 5.3 Hz), 8.37 (2H, d, $J = 8.0$ Hz), 8.11 (2H, t, $J = 7.8$ Hz), 7.53 (2H, t, $J = 6.2$ Hz), 3.94 (2H, s), 1.41 (3H, s). ^{13}C NMR (CD_3CN): δ 203.06, 194.37, 171.70, 156.29, 153.89, 139.52, 127.96, 124.40, 69.33, 20.98.

[8] Crystal data[9] for *fac*-Re(bpy)$(CO)_3(H_2COC(O)Me)$ (**2**): $C_{16}H_{13}N_2O_5$Re, $M_r = 499.48$; monoclinic, space group $P2_1/n$; $a = 9.7402(2)$ Å, $b =$ 15.8826(4) Å, $c = 11.2409(2)$ Å, $\alpha = 90°$, $\beta = 107.905(1)°$, $\gamma = 90°$. Final R indices ($I > 2\sigma(I)$): R1 = 0.0390, wR2 = 0.0768.

[9] Additional commentary about the structure and ORTEP packing diagrams are available in the Supporting Information.

[10] The crude product was recrystallized from CH_2Cl_2/hexane to give a red solid, mp >210 °C. Anal. Calcd for $C_{14}H_{11}N_2O_4Re$: C, 36.67; H, 2.42. Found: C, 36.51; H, 2.47. IR (DRIFTS, KCl): ν_{CO} 2003 and 1877 cm^{-1}. ^1H NMR (CD_3OD): δ 9.06 (2H, d, $J = 5.5$ Hz), 8.56 (2H, d, $J = 8.0$ Hz), 8.25 (2H, t, $J = 8.0$ Hz), 7.69 (2H, t, $J = 5.5$ Hz), 3.60 (3H, s). ^{13}C NMR (CD_3OD): δ 199.97, 194.26, 157.50, 154.07, 141.24, 128.60, 125.07, 61.60.

S0276-7333(98)00102-2 CCC: $15.00

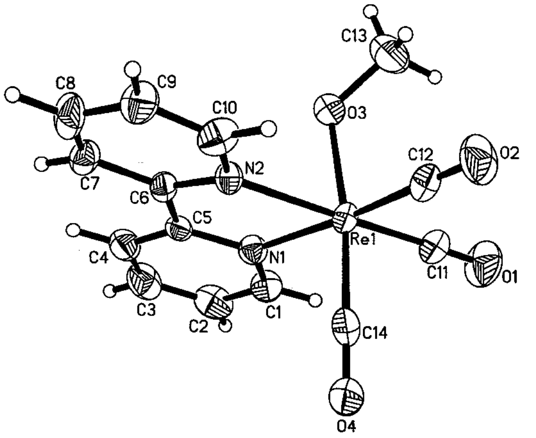

Figure 1. ORTEP drawing of **3** with thermal ellipsoids shown at the 30% probability level. Selected bond distances (Å) and bond angles (deg) are as follows: Re–O(3), 2.081(5); Re–C(14), 1.908(7); Re–C(11), 1.912(7); Re–C(12), 1.900(7); O(3)–C(13), 1.397(8); C(13)–O(3)–Re, 121.6(4); O(3)–Re–C(14), 172.7(2).

other major product in addition to **3**-OCD_3. As expected from previous work on related rhenium complexes,[15] samples of **3** are converted (within 5 min) to **3**-OCD_3 upon dissolution in methanol-d_4. Neither ethylene glycol nor formic acid was produced from **1** under either conditions. Solutions of **1** in MeOH, in the dark and without O_2, slowly converted to **3** over a period of several days. Photoinduced conversion of a hydroxymethyl complex to a metal hydride and CH_2O has been observed previously, but the reaction pathway was not detailed.[16]

In view of the recent observations of Schanze et al.[17] on the behavior of *fac*-Re(bpy)$(CO)_3$(R) (R = alkyl, benzyl) under photolysis and the related observations of Stufkens et al.[18] (on complexes with other α-diimine ligands) which appear to involve Re–R bond homolysis, we decided to probe the behavior of **1** and **2** further. It seemed possible that homolysis of the Re–CH_2OH bond in **1** might result in *fac*-Re(bpy)$(CO)_3$H (**4**)[19] and CH_2O being formed. However, the stability, and solubility, of **1** prevented the use of solvents other than methanol to examine this possibility. Since hydride **4** is known to insert CO_2 readily,[19] it seemed possible that insertion of CH_2O into the Re–H bond of **4** could account for some of **3** formed from **1**. Reaction of **4** with CH_2O (generated, *in situ*, by sonication of paraformaldehyde dispersed in acetone) occurs slowly in the dark and provides **3** as one of the products (the yield of **3** reaches a maximum of 25% after 1 h). This represents the first example of CH_2O insertion into a rhenium hydride bond; however, Berke et al.[20] have shown that some rhenium–hydrides are capable of inserting aromatic aldehydes to give phenoxy derivatives. Under photolysis conditions, multiple products were generated from the reaction of **4** with CH_2O in acetone and **3** was not present. The slow thermal reaction, and the complexity of the product mixture after a photolysis reaction, suggested that the formation of **3** from photolysis of **1** in MeOH does not occur by reaction of CH_2O with hydride **4**. Reaction of hydride **4** with MeOH occurs very slowly; however, the reaction is rapid (5 min) upon photolysis and provides **3** in 90% yield. Exact parallels with other hydrides are not known, although some hydrides have been reported[21] to react with more acidic hydroxylic reagents (e.g., phenol, hexafluoroisopropyl alcohol) to give phenoxide/alkoxide products. The observation that hydride **4** reacts rapidly with MeOH upon photolysis made the Re–CH_2OH bond homolysis pathway, followed by H-atom abstraction by the rhenium fragment, a viable possibility for the conversion of **1** to **3**. However, the absence of ethylene glycol as a product made it seem less likely.

The previous study of the photolysis of *fac*-Re(bpy)$(CO)_3(CH_2Ph)$ (**5**) in MeOH identified toluene as a reaction product but did not establish the fate of the rhenium fragment.[17] A sample of **5**[22] was prepared; its photolysis in MeOH provided **3** in 73% yield (isolated). Reactions in methanol-d_4 showed that the benzyl fragment from **5** is converted primarily to bibenzyl (identified by ^1H NMR spectral comparison with an authentic sample) together with other organic compounds, which were not identified; toluene was a very minor product, β-phenylethanol was absent, and most importantly, the formaldehyde hemiacetal was not present. Photolysis of **5** in methanol-d_4 which had been purged with O_2

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(11) Crystal data[9] for *fac*-Re(bpy)$(CO)_3(OCH_3)$ (**3**): $C_{14}H_{11}N_2O_4Re\cdot{}^1/_2H_2O$, M_r = 466.46; triclinic, space group $P\bar{1}$; a = 10.7936(2) Å, b = 11.2033(2) Å, c = 14.1032(10) Å, α = 113.0600(10)°, β = 106.4020(10)°, γ = 94.4960(10)°, V = 1470.37(4) Å^3, Z = 4, D_{calcd} = 2.107 Mg/m^3, T = 213(2) K, $F(000)$ = 884, λ = 0.710 73 Å (Mo Kα). Intensity data were collected on a crystal of dimensions 0.10 × 0.10 × 0.05 mm mounted on a Siemens SMART CCD area detector diffractometer. Of 7495 reflections measured (θ_{max} = 25.38°), 5146 were unique (R_{int} = 0.0282). Semiempirical absorption corrections were applied (transmission 0.43416–0.68708). The structure was solved by direct methods and refined by full-matrix least squares on F^2. Final R indices ($I > 2\sigma(I)$): R1 = 0.0298, wR2 = 0.0596. Programs used were standard control software and SHELXTL 5.03.[12]

(12) SHELXTL 5.03 (PC-version), Program Library for Structure Solution and Molecular Graphics; Siemens Analytical Instruments Division: Madison, WI, 1995.

(13) The ^1H NMR spectrum showed a singlet at δ 4.64 assigned to the methylene protons of the hemiacetal. This resonance also results after sonication of paraformaldehyde in methanol-d_4 for several hours (a small resonance at δ 9.50, for the CH_2O monomer, is also present). Addition of a drop of commercial formalin (which contains mainly formaldehyde hydrate) to methanol-d_4 generates the same single resonance at δ 4.64 after several hours of equilibration. Under our conditions, the hemiacetal is expected to be the predominant species present (see: Hurd, C. D. *J. Chem. Educ.* **1966**, *43*, 527). After removal of solvent from the product mixture resulting from photolysis of **1** in MeOH and dissolution in methanol-d_4, the formaldehyde hemiacetal is present in low yield (diminished by partial removal with solvent).

(14) Addition of dimedone to the mixture results in slow disappearance of the resonance at δ 4.64 and formation of the dimedone–formaldehyde derivative (compared with an authentic sample: Kemp, W. *Qualitative Organic Analysis*; McGraw-Hill: Maidenhead, England, 1986; p 89).

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(20) Nietlispach, D.; Yeghini, D.; Berke, H. *Helv. Chim. Acta* **1994**, *77*, 2197.

(21) Ayllón, J. A.; Gervaux, C.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1997**, *16*, 2000.

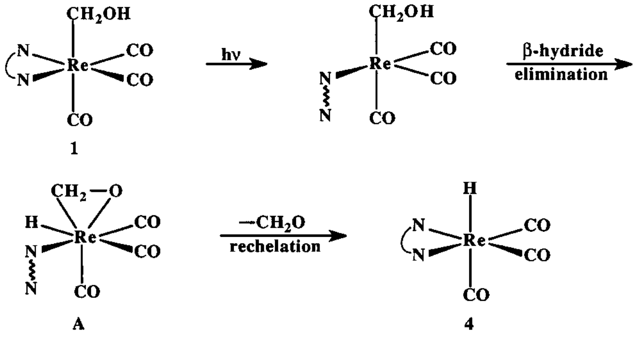
(22) Compound **5** has been prepared previously,[17] utilizing THF as solvent. We obtained better results as follows: 0.40 g (0.79 mmol) of Re(bpy)$(CO)_3$Br was added to a Schlenk flask under N_2; 50 mL of anhydrous ether was then added, followed by 4 mL of $PhCH_2MgCl$ (2.2 M in ether), and the mixture was stirred for 2.5 h. Water was then added to destroy the remaining Grignard reagent, and solvent was removed under vacuum. The residue was extracted with 3 × 20 mL of CH_2Cl_2. These extracts were combined and dried over $MgSO_4$; after filtration, the filtrate was concentrated to 20 mL. Hexane was then added to effect precipitation of 0.34 g (83% yield) of **5**.

afforded benzaldehyde (18%) and benzyl alcohol (51%) at the expense of bibenzyl; the yield of **3**-OCD_3 was 85−90% (NMR internal standard) and was not affected by O_2. Benzylic radicals, photogenerated in MeOH/O_2, are known to yield aromatic aldehydes as final products.[23]

We investigated reactions of complex **2** to determine whether Re−CH_2OR bond homolysis would occur in a compound more closely related to **1**. Photolysis of **2** in MeOH, without O_2, results in a 70% yield of the methoxy complex **3** together with ethylene glycol diacetate ($AcOCH_2CH_2OAc$, the product expected from radical coupling; identified by ^1H NMR spectral comparison with an authentic sample). After photolysis of **2** in methanol-d_4, the reaction mixture showed, in addition to **3**-OCD_3, the same diacetate together with a small amount of formaldehyde hemiacetal; these two products account for most of the methylene groups which were lost from **2**. Interestingly, when the reaction was conducted in the presence of O_2, compound **3** was not in the product mixture; the major rhenium product (80%) was *fac*-Re(bpy)$(CO)_3$(OAc) (**6**)[24] together with 7% of *fac*-Re(bpy)$(CO)_3(O_2CH)$[19] (**7**; identified by comparison with an authentic sample). Solvolysis of **2** by MeOH does not occur, and there is no direct source of acetic acid which could react with the initially formed **3** to give **6**. However, if the acetoxymethylene radical ($^\bullet CH_2OAc$) follows the path of the benzyl radical in MeOH/O_2, a possible rationale is available. Acetic formic anhydride could be formed by oxidation of the radical. Solvolysis of this anhydride by methanol-d_4 could give both methyl formate and methyl acetate (both deuterated at the methoxy group) and the corresponding acids (deuterated only at the carboxyl carbon atom). The acids could react with initially formed **3** to give **6** and **7**. Alternatively, reaction of the mixed anhydride with **3** is possible; acetic anhydride cleaves **3** rapidly to give acetate **6** as the final product. Thus, both **6** and **7** could result from the mixed anhydride. We have not investigated these possibilities further.

The lack of sensitivity of solutions of **1** in MeOH toward O_2, the absence of ethylene glycol in product mixtures, and absence of either formic acid or formate **7** as products when O_2 was present, support a nonradical pathway for conversion of **1** to **3** in MeOH. Also, CH_2O is liberated only in conversions of compound **1** to **3**. Hydride **4** could be generated from **1**, as suggested in Scheme 1. Photolysis of **4** in MeOH, as discussed above, will provide **3**. The proposed dynamic behavior of the bipyridyl ligand, with formation of monodentate bpy intermediates, has been demonstrated for bipyridyl-like ligands in other metal complexes.[25] Alternatively, intermediate hydride **A** might react with methanol directly and provide **3** after loss of CH_2O. Base-promoted conversion of hydroxymethyl complexes to hydrides, with loss of CH_2O, has been observed previously.[26] Thus, a pendant pyridyl ligand might assist the conversion of **1** to **4**; however, added pyridine does not promote the conversion thermally. Thus, we favor a β-elimination pathway for the conversion of **1** to a hydride (**A** or **4**).

Scheme 1. Possible Pathway for the Conversion of 1 to 4



Reactions of **1** in MeOH differ from those of **2** and **5**. The presence of the hydroxyl group in **1** allows an alternate pathway to be dominant which does not involve Re−CH_2R bond homolysis. As with our results on photoassisted reactions of a ruthenium formyl complex with bipyridyl ligands,[4a] the determinative factors are believed to be (a) photoassisted dechelation of one bipyridyl nitrogen ligand and (b) the availability of a group (from a cis location) which can quickly occupy the newly created coordination vacancy. Further work is required to support these proposals and to define their implications in catalytic chemistry.

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Supporting Information Available: Tables of data collection and refinement parameters, anisotropic thermal parameters, atomic positional parameters, bond distances, and bond angles, ORTEP and packing diagrams, and text giving additional commentary about the structures of **2** and **3** (18 pages). Ordering information is given on any current masthead page.

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[24] (a) Photolysis of **2** in methanol-d_4/O_2 for 10 min resulted in two major products, **6** and another compound believed to be an isomer (the ^1H NMR showed an acetoxy methyl resonance at δ 1.91 and resonances for bipyridyl protons which are distinct from **6**; the ratio of the two compounds was 2:1 of the unknown to **6**). Continued photolysis, or evaporation of solvent and redissolution, resulted in conversion of the second compound to **6**. Samples were too dilute to provide meaningful IR spectral data. (b) Alternate preparation of **6**: hydride **4** (0.050 g, 0.12 mmol) was added to AcOH (7 mL) at room temperature. The mixture was stirred for 5 min. Solvent was removed, and the residue was washed with 3 × 10 mL of ether. The resultant yellow solid was dried to give **6** (0.056 g, 98%), mp >210 °C. Anal. Calcd for $C_{15}H_{11}N_2O_5$-Re: C, 37.11; H, 2.28. Found: C, 36.96; H, 2.37. IR (DRIFTS, KCl): ν_{CO} 2018, 1904, and 1888 cm^{-1}; ν_{COO} 1624 and 1316 cm^{-1}. ^1H NMR (CD_3CN): δ 9.04 (2H, d, J = 4.9 Hz), 8.38 (2H, d, J = 8.2 Hz), 8.18 (2H, t, J = 7.9 Hz), 7.60 (2H, t, J = 11.5 Hz), 1.45 (3H, s). ^{13}C NMR (CD_3CN): δ 207.86, 198.11, 175.89, 156.70, 154.57, 140.52, 128.01, 124.65, 23.13. The product obtained from photolysis of **2** in MeOH/O_2 had identical spectral properties.

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