Photoassistance in Reactions of the *cis*-(Bis(2,2′-bipyridyl))(carbonyl)(formyl)ruthenium(II) Cation with Protic Reagents

Dorothy H. Gibson,* Yan Ding, Bradley A. Sleadd,
Jaime O. Franco, John F. Richardson, and Mark S. Mashuta

Department of Chemistry and
Center for Chemical Catalysis
University of Louisville, Louisville, Kentucky 40292

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Cationic ruthenium complexes with C_1 ligands have been implicated as important intermediates in photocatalytic or electrocatalytic reductions of CO_2 to formate and other products,[1] yet little is known about their chemistry. Prior to the recent report of the synthesis of *cis*-$Ru(bpy)_2(CO)(CHO)^+$ PF_6^- (**1**; bpy = 2,2′-bipyridyl) by Tanaka et al.,[1j] we had also synthesized the compound and begun a study of its reactions. We now describe our observations on the unusual reactions of **1** and suggest explanations for these reactions.

Characteristically, strong acids react with metal formyl complexes by initial protonation of the formyl oxygen center and follow the sequence shown in Scheme 1.[2] Compound **1** reacts with concentrated aqueous HCl at room temperature, affording approximately equal quantities of the new chloromethyl cation *cis*-$Ru(bpy)_2(CO)(CH_2Cl)^+$ (**2**)[3] and *cis*-$Ru(bpy)_2(CO)_2{}^{2+}$ (**3**)[4] as expected.[5] Formyl complexes do not characteristically transfer hydride directly to protic reagents;[2] if this were possible, only cation **3** should have been formed from the reaction of **1** with HCl. Thus, the report by Tanaka et al.[1j] that **1** reacted with methanol (MeOH), with liberation of H_2 and formation of the methyl ester *cis*-$Ru(bpy)_2(CO)(CO_2CH_3)^+$ PF_6^- (**4**)[4] was quite surprising. While we observed no reaction between **1** and MeOH at 0 °C, as reported previously,[1j] we found that **4** was formed in nearly quantitative yield after **1** was allowed to stand in dry MeOH for 7 h at room temperature under fluorescent lights (with or without O_2). Most importantly, when reaction was attempted in the dark, there was *no conversion* to **4** and little degradation of **1**. Furthermore, when a solution of **1** in MeOH was irradiated,[6] conversion of the formyl complex (mainly to **4**) was complete after 15 min.

Scheme 1

$$M(CHO)^+ \xrightarrow{H^+} M(CHOH)^{2+} \xrightarrow[-\ M(CO)^{2+}]{+\ MCHO^+} M(CH_2OH)^+ \xrightarrow[-\ H_2O]{+\ HCl} M(CH_2Cl)^+$$

Looking further, we conducted reactions of **1** with H_2O in dimethoxyethane (DME). In sharp contrast to reactions in MeOH, reactions in DME/H_2O required O_2. Furthermore, reactions conducted for 3 h in the dark afforded the same product as those done under fluorescent lights for the same time. The product, formed in approximately 75% yield in each case, has been identified as the $\mu_2-\eta^2$ CO_2-bridged compound *cis,cis*-$Ru(bpy)_2(CO)(CO_2)Ru(bpy)_2(CO)^{2+}(PF_6^-)_2$ (**5**).[7] Irradiation[6] of **1** in DME/water in the presence of O_2 results in its rapid conversion (5 min) to **5**. This is the first CO_2-bridged compound in the ruthenium bipyridyl series and only the second one with a CO_2 ligand,[8] despite many suggestions of the intermediacy of such compounds in reductions of CO_2 catalyzed by these complexes.[1] X-ray structural analysis of the compound shows disorder around the CO_2 bridge,[9] but the structural data and IR spectral properties of the compound clearly support the formulation.[10] Changing the anion to BPh_4 did not remove the disorder at the carboxyl group.

Probe reactions were conducted to gain further insight. Reaction of **1** in DME/H_2O containing 2 equiv of Et_4NOH (and under O_2) gave the CO_2 complex *cis*-$Ru(bpy)_2(CO)(CO_2)$ (**6**)[7] in 65% yield, suggesting that the acid, *cis*-$Ru(bpy)_2(CO)(COOH)^+$ PF_6^- (**7**),[4] can be formed in reactions of **1** which yield **5**. Attempted reactions of acid **7** with O_2 in DME/H_2O showed little conversion of the acid even with irradiation; thus, secondary reactions of **7** cannot account for the formation of **5** from **1.** However, direct reaction of equimolar quantities of **1** and **7** in DME/H_2O in the presence of O_2 was complete after 15 min and afforded **5** in 74% yield, suggesting that acid **7** is consumed by reaction with an intermediate formed from **1**. Irradiation[6] of **1** in dry DME under N_2 afforded a small amount of the hydride *cis*-$Ru(bpy)_2(CO)H^+$ PF_6^- (**8**)[11] after 1 h, but the reaction mixture contained mainly unreacted **1**. Also, there was no reaction between acid **7** and hydride **8** under any conditions.

Proposed mechanisms must accommodate differences in the requirements for reactions of **1** in MeOH and those in H_2O. In

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[3] Compound **1** (0.15 g, 0.24 mmol) was dissolved in 20 mL of CH_2Cl_2; 0.5 mL of concentrated HCl was added, and the mixture was stirred for 30 min. The mixture was evaporated to dryness and then triturated with 10 mL of CH_2Cl_2. A pale yellow solid separated and was collected and then treated with NH_4PF_6; spectral properties of the product were identical to those of **3**,[4] $Ru(bpy)_2(CO)^{2+}$ $2PF_6^-$ (0.08 g, 84% yield). The filtrate was concentrated, and ether was added to precipitate a yellow solid. After anion exchange, 0.06 g (78% yield) of **2**, PF_6^- was obtained. Anal. Calcd for $C_{22}H_{18}F_6ClN_4OPRu$: C, 41.55; H, 2.85. Found: C, 41.47; H, 2.93. IR (CH_2Cl_2): ν_{CO} 1950 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 9.15 (d, J = 5.0 Hz), 9.08 (d, J = 5.0 Hz), 8.45−7.27 (m), 4.23 and 4.16 (pair of doublets, J = 9.0 Hz, CH_2). ^{13}C NMR (CD_2Cl_2): δ 201.86 (CO), 158.10−123.09 (20 resonances, bpy ligands), 44.74 (CH_2).

[4] Ishida, H.; Tanaka, K.; Morimoto, M.; Tanaka, T. *Organometallics* **1986**, *5*, 724.

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[6] Irradiation was done with a 450 W Hg arc lamp placed in a water-cooled pyrex immersion well. A solution of **1** was placed in a pyrex flask beside the assembly; the reaction temperature did not exceed 23 °C.

[7] Compound **1** (0.10 g, 0.016 mmol) was added to 20 mL of DME and 1 mL of H_2O, and the resulting solution was allowed to stand for 3 h under fluorescent lighting. The mixture was then concentrated, and the yellow-orange solid which separated was collected and dried to give **5** (0.07 g, 75% yield). Anal. Calcd for $C_{43}H_{32}F_{12}N_8O_4P_2Ru_2$: C, 42.44; H, 2.65. Found: C, 42.36; H, 2.67. IR (DRIFTS, KCl): ν_{CO} 1954 cm^{-1}; ν_{OCO} 1507 and 1176 cm^{-1}. ^{1}H NMR (CD_3CN): δ 9.90 (d, J = 5.0 Hz), 9.34 (d, J = 5.0 Hz), 9.07 (d, J = 5.0 Hz), 8.40−6.80 (m). ^{13}C NMR (CD_3CN): δ 203.85, 203.78, 202.62, 158.36−122.54 (35 resonances due to 40 carbons).

[8] Tanaka, H.; Nagao, H.; Peng, S.-M.; Tanaka, K. *Organometallics* **1992**, *11*, 1450.

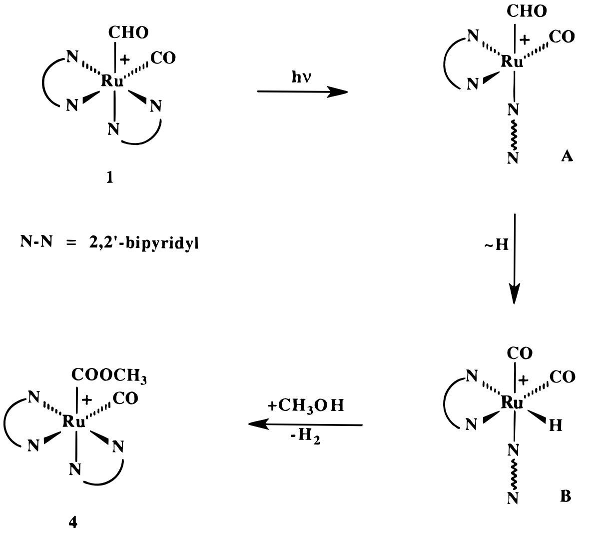
[9] Compound **5** crystallizes in the tetragonal space group $P4_32_12$ having cell parameters $a = 13.690(6)$ Å, $c = 24.464(9)$ Å, $V = 4583(2)°$, and $Z = 4$ with $R = 0.062$ and $R_w = 0.062$ (refinement of the enantiomer in $P4_12_12$ gave identical R factors); the GOF was 2.70. The cation sits on a crystallographically imposed 2-fold axis resulting in a disordered CO_2 bridge in which the C atom and one O atom are each bound to a Ru atom 50% of the time. The mixed C/O atom is represented by C2 in the disorder model. The second, unbound, O atom of the CO_2 is represented by an atom (O2) having 50% occupancy at two equivalent positions. One carbonyl and two bidentate bpy ligands occupy the remaining coordination sites on each metal. The carboxyl bridging ligand and a terminal CO occupy cis positions on each Ru atom. Refinement was further hindered by a disordered PF_6 anion.

[10] For discussions of the relationship between IR spectral properties of CO_2-bridged complexes and their bonding modes, see: Gibson, D. H. *Chem. Rev.* **1996**, *96*, 2063.

[11] Kelly, J. M.; Vos, J. G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 628.

S0002-7863(96)02168-3 CCC: $12.00

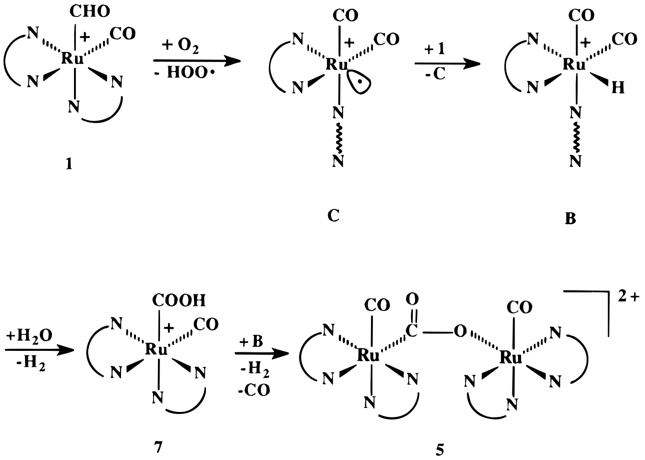
Scheme 2



MeOH, light is required but not O_2; we suggest that the initial step is photolabilization of a single bipyridyl nitrogen from ruthenium (presumably cis to the formyl ligand) to allow migration of the formyl hydrogen to the metal in the manner shown in Scheme 2. Reaction of intermediate hydride **B** with MeOH would be followed by rechelation of the bpy ligand then addition of methoxide ion to the resulting cation to give **4**. The first steps in Scheme 2, involving $\eta^2-\eta^1-\eta^2$ changes for a bidentate bpy ligand, are similar to ones suggested by Cole-Hamilton[12] to rationalize results from thermolysis reactions of *trans*-Ru(dppe)$_2$(CO)(CHO)$^+$ SbF$_6^-$ which yield *cis*-Ru(dppe)$_2$(CO)(H)$^+$ SbF$_6^-$; an intermediate similar to **B** was proposed.

Even with light, reactions of **1** with H_2O do not proceed without O_2. This lack of reactivity may be due to the ability of H_2O, unlike MeOH, to quench the migratory rearrangement of the formyl hydrogen (conversion of **A** to **B**, Scheme 2) by ligating the photochemically-generated vacant site on ruthenium. Indeed, a stable aquo complex, *cis*-Ru(bpy)$_2$(CO)(H$_2$O)$^{2+}$(PF$_6^-$)$_2$ (**9**),[4,13] in this series has been characterized.[14] However, in the presence of O_2, hydride **B** could be formed from **1** by H-atom abstraction**,** followed by dechelation of a bpy nitrogen and formation of a 17e radical (**C**) which could then abstract hydrogen from **1** as outlined in Scheme 3. Such radical chain decompositions of formyl complexes to metal hydrides are well-known and occur through the conversion of 18e acyl radicals to 19e metal-centered radicals followed by ligand dissociation and formation of a 17e radical,[15] as suggested for the conversion of **1** to **5**. Reaction of **B** with H_2O would give **7** in the same manner that **B** gives **4** in reaction with MeOH; **7** could intercept additional **B**, generating a bridging CO_2 ligand in the manner of other metallocarboxylic acids in combination with active metal hydrides.[16] Rechelation and loss of CO would produce **5**. Unlike some formyl complexes, room temperature reactions of **1** are not accelerated by azobisisobutyronitrile (AIBN) nor inhibited by H-atom donors such as HSn(n-Bu)$_3$.[15] However, the extreme air-sensitivity of solutions of formyl complexes toward ligand loss and metal hydride formation is well-known.[2,17] Direct evidence for intermediate **B** in MeOH or DME/H_2O reactions is not available; the speed of the reaction of **1** with **7** suggests that the intermediate is short-lived in the presence of protic reagents.

Scheme 3



The hydroxylic solvents play a further role in transformations of **1** since irradiation of **1** in dry DME did not promote its decomposition. This additional role could be one of hydrogen bonding to the dechelated bipyridyl nitrogen, (e.g., in **A** in Scheme 2) thus maintaining the vacant site for subsequent reactions.

Photolabilization of a bipyridyl ligand in Ru(bpy)$_3^{2+}$ is well-known[1g,h] and is thought to be a crucial step in catalytic processes but has been evidenced only by loss of a bpy ligand. The intermediacy of η^1-coordinated species in these reactions seems likely, but is more difficult to establish. Such η^1 intermediates have been suggested in reactions of other bpy complexes.[18] Our results with **1** suggest that the photoactivity of C_1 complexes in this series may have a profound impact on catalytic reactions. Complex **1** is unique in being able to place a highly reactive ligand in a photochemically-generated vacant site (or radical site) and then, later, rechelating the bpy ligand. Also, complex **1** appears to be unique among mononuclear formyl complexes in being photolabile. Our results suggest that reactive hydride complexes (such as **B** in Schemes 2 and 3) could be formed from ruthenium formyl complexes and give rise to formate via CO_2 insertion.[1f,19]

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Supporting Information Available: Tables of data collection and refinement parameters, anisotropic thermal parameters, atomic positional parameters, bond distances, bond angles, and ORTEP diagrams for **5** (14 pages). See any current masthead page for ordering and Internet access instructions.

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