Acid-Promoted Metallacyclization and Partial Hydrogenation of the Pendant Pyridine Ring in a Terpyridine Ligand by a Ruthenium Formyl Complex

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*Summary: The reaction of cis,syn-N-[Ru(bpy)(η^2-tpy)(CO)(CHO)]PF_6 (**1**) with p-toluenesulfonic acid in MeOH/CH_2Cl_2 yields two major products and a minor product, **3**, formed by metallacyclization and partial hydrogenation of the pendant pyridine ring of the tpy ligand. The stereochemistry of **3** provides evidence for the accessibility of the linkage isomer of **1** in its chemical reactions; compound **1** and its linkage isomer are possible intermediates in catalytic CO_2 reductions leading to C_2 products.*

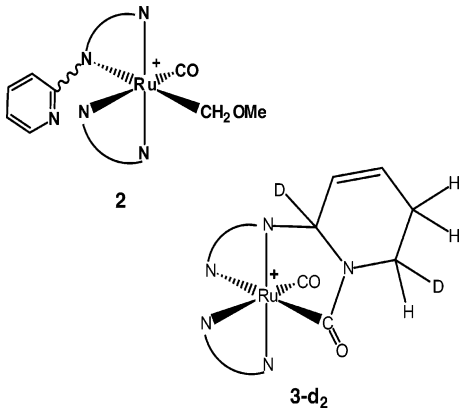
Ruthenium(II) complexes with polypyridine ligands have been studied for many years as electrocatalysts for the reduction of carbon dioxide.[1] While most reactions provide only CO or formate, one study reported that the use of [Ru(bpy)(tpy)(CO)]-$(PF_6)_2$ (bpy = 2,2′-bipyridine, tpy = 2,2′:6′,2″-terpyridine) as the electrocatalyst afforded C_2 products, glyoxylic acid and glycolic acid, in addition to formaldehyde, formic acid, and methanol.[2] Metal formyl complexes have been suggested as precursors to the C_2 products.[2−4] These suggestions followed the much earlier report by Kochi and co-workers[5] of the electrochemical synthesis of metal formyls from metal carbonyl cations and hydrogen atom donors. Thus, precedent existed for the suggestion[2] that a cationic complex such as [Ru(bpy)(tpy)-$(CO)](PF_6)_2$ might be converted to the corresponding formyl complex in the electrocatalytic reductions. Carbon dioxide insertion into the ruthenium−formyl carbon bond, without electrochemical promotion, was then suggested as the carbon−carbon bond forming step leading to glyoxylic acid. However, reactions of CO_2 with known ruthenium[6] and rhenium[7] formyl complexes bearing polypyridine ligands led only to formate. An alternate proposal by us[3,4] argues that the glyoxylic acid was derived differently. The initial [Ru(bpy)(tpy)(CO)]$(PF_6)_2$ was proposed to be converted to two isomeric, cationic [Ru-(bpy)(η^2-tpy)$(CO)_2](PF_6)_2$ complexes through reverse WGS chemistry. A formyl complex resulting from one of these could then lead to glyoxylic acid via CO insertion driven by the pendant pyridine group. To this time, we have not observed a product resulting from CO insertion.

Several years ago, we reported the synthesis of *cis,syn-N*-[Ru(bpy)(η^2-tpy)(CO)(CHO)]PF_6 (**1**),[3] a possible intermediate in the catalytic reactions according to our proposal, and more recently we reported the synthesis and reactions of the methoxymethyl complex derived from it, *cis,syn-N*-[Ru(bpy)(η^2-tpy)(CO)$(CH_2OMe)]PF_6$ (**2**).[4] The generalized sequence leading

$$\mathrm{M{-}CHO} + \mathrm{H^+} \xrightarrow[\mathrm{MeOH}]{} \mathrm{M{=}CHOMe^+} \xrightarrow[-\mathrm{M(CO)^+}]{+\mathrm{M{-}CHO}} \mathrm{M{-}CH_2OMe} \quad (1)$$

to **2** is shown in eq 1. The structure of **2** was established by X-ray crystallography and is shown in Chart 1.

Chart 1



In examining the crude product mixtures from these reactions, we determined that a small amount of a further product, **3**, was obtained in addition to the methoxymethyl complex and the carbonyl cation (**4**) that is the coproduct of the main reaction.

(1) (a) Hawecker, J.; Lehn, J. M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1983**, 536. (b) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, T. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1414. (c) Sullivan, B. P.; Conrad, D.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 3640. (d) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim Acta* **1986**, *69*, 1990. (e) Ishida, H.; Tanaka, K.; Tanaka, T. *Organometallics* **1987**, *6*, 181. (f) Bruce, M. R. M.; Megehee, E.; Sullivan, B. P.; Thorp, H.; O'Toole, T. R.; Downard, A.; Meyer, T. J. *Organometallics* **1988**, *7*, 238. (g) Sullivan, B. P.; Bruce, M. R. M.; O'Toole, T. R.; Bolinger, C. M.; Megehee, E.; Thorp, H.; Meyer, T. J. In *Catalytic Activation of Carbon Dioxide*; Ayers, W. M., Ed.; ACS Symp. Ser. 363; American Chemical Society: Washington, DC, 1988; Chapter 6. (h) Ziessel, R. In *Catalysis by Metal Complexes: Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*; Kalyanasundaram, K., Grätzel, M., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1993; p 217. (i) Christensen, P.; Hammett, A.; Muir, A. V. G.; Timney, J. H. *J. Chem. Soc., Dalton Trans.* **1992**, 1455. (j) Yoshida, T.; Tsutsumida, K.; Teratani, S.; Yasufuku, K.; Kaneko, M. *J. Chem. Soc., Chem. Commun.* **1993**, 631. (k) Stor, G. J.; Hartl, F.; van Outersterp, J. W. M.; Stufkens, D. J. *Organometallics* **1995**, *14*, 115. (l) Johnson, F. P. A.; George, M. W.; Hartl, F.; Turner, J. J. *Organometallics* **1996**, *15*, 3374. (m) Klein, A.; Vogler, C.; Kaim, W. *Organometallics* **1996**, 15, 236. (n) Sutin, N.; Creutz, C.; Fujita, E. *Comments Inorg. Chem.* **1997**, *19*, 67. (o) Scheiring, T.; Klein, A.; Kaim, W. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2569.

(2) Nagao, H.; Mizukawa, T.; Tanaka, K. *Inorg. Chem.* **1994**, *33*, 3415.

(3) Gibson, D. H.; Andino, J. G.; Bhamidi, S.; Sleadd, B. A.; Mashuta, M. S. *Organometallics* **2001**, *20*, 4956.

(4) Gibson, D. H.; Andino, J. G.; Mashuta, M. S. *Organometallics* **2005**, *24*, 5067.

(5) Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1986**, *5*, 926.

(6) Toyohara, K.; Nagao, H.; Mizukawa, T.; Tanaka, K. *Inorg. Chem.* **1995**, *34*, 5399.

(7) Gibson, D. H.; He, H. *Chem. Commun.* **2001**.

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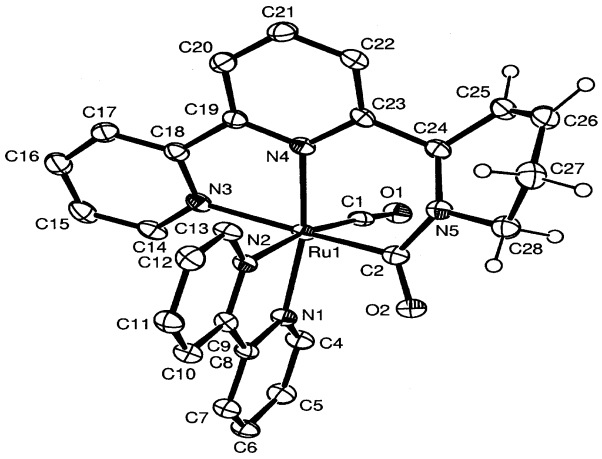
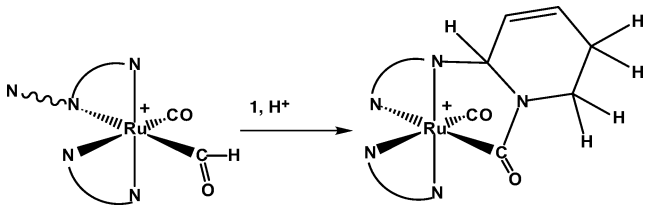


Figure 1. ORTEP drawing of **3** (cation only) with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and bond angles (deg): Ru−C(2) = 2.033(3); Ru−N(1) = 2.077(3); Ru−N(2) = 2.137(2); Ru−N(3) = 2.165(3); Ru−N(4) = 2.055(3); C(2)−N(5) = 1.387(4); C(24)−N(5) = 1.474(5); C(1)−Ru−N(2) = 169.65(13); C(2)−Ru−N(3) = 165.23(1); N(1)−Ru−N(4) = 167.94(10); Ru−C(2)−N(5) = 118.3(3). See the Supporting Information for details.

We report the characterization of this new compound, studies of the reactions leading up to it, and the implications of the structure of the compound to possible steps in the catalytic cycle leading to C_2 products from CO_2.

The new compound was isolated by careful separation of the components of the crude reaction product from a slightly modified version of the synthesis of **2** using less methanol and conducted at room temperature.[8] The orange product has been characterized by IR and ^{1}H and ^{13}C NMR spectroscopy and by X-ray crystallography.[9] The ORTEP[10] diagram for **3** (cation only) is shown in Figure 1 together with selected bond distances and bond angles. The cation shows distorted-octahedral geometry around the ruthenium center as a result of the demands of the bidentate and terdentate ligands. The bond angles around the ruthenium that should be linear are distorted well below 180°. The ruthenacycle ring containing the amide nitrogen and the partially reduced pyridyl ring are also distorted. The methylene protons in **3** that are on carbon α to nitrogen in the partially reduced ring appear as multiplets at δ 3.88 (1H) and 2.84 (1H) in the ^{1}H NMR spectrum. The methine proton on the other α-carbon atom appears as a singlet at δ 5.36. The allylic methylene protons on this ring appear as a broadened singlet at δ 2.10. The assignments were confirmed by examination of the proton−proton COSY spectrum of **3**.

Scheme 1[a]



[a] Abbreviations: N-N = 2,2′-bipyridine; N-N-N = 2,2′:6′,2″-terpyridine.

Clearly, compound **3** formed as the result of the transfer of three hydrogens to the pendant pyridyl ring of the tpy ligand, as illustrated in Scheme 1. To obtain a better understanding of the sequence of hydride and proton transfers and their destinations in the reduced product, we prepared the deuterated analogue of the formyl complex **1-d** by using $NaBD_4$ (98% deuterium) and subjected it to the same conditions used previously to create **3**.[8] Analysis of the ^{1}H NMR spectrum of the product, **3-d$_2$**, showed that the intensity of the resonance at δ 3.88 was diminished by about 95% relative to the one-proton resonances. The methine resonance at δ 5.36 was diminished by about the same amount, indicating that deuteride transfers had taken place on both carbons α to the amide nitrogen in the partially reduced ring and that protonation took place on the carbon β to the amide nitrogen in that ring, as illustrated for **3-d$_2$** in Chart 1. Furthermore, deuteride transfer occurred preferentially on one face of the pyridyl ring, since the resonance for the other methylene proton α to nitrogen, at δ 2.84, showed very little reduction in intensity relative to other one-proton resonances. Although we have tried to promote a reaction involving a single hydride transfer from the formyl group to the pendant pyridyl ring by carrying out reactions with a catalytic amount of acid, these led only to incomplete conversions of **1** to **3** and not to a new product. Also, no conversion to ring-closed product occurs in the absence of acid; solutions of **1** that are allowed to stand show degradation of the formyl complex but do not lead to a precursor to **3**. Therefore, we have not established the exact sequence of events that results in compound **3**.

Metal formyl complexes are well-known to be hydride donors in acid-catalyzed reactions that lead to derivatives of the formyl complexes, such as alkoxymethyl complexes.[11,12] However, Ishitani and co-workers reported several years ago that *cis*-[Ru(bpy)$_2$(CO)(CHO)]PF$_6$ would transfer hydride to nicotine adenine dinucleotide coenzyme (NAD^+) model compounds.[13] Reduction took place exclusively at the 4-position of the ring system in the model compounds and did not require acid catalysis. The conversion of **1** to **3** represents, to our knowledge, the first report of multiple hydrogen transfer reactions involving

(8) Synthesis of **3**: compound **1** (1.00 g, 1.40 mmol) was dissolved in 150 mL of dry CH_2Cl_2. To this solution was added dropwise *p*-toluenesulfonic acid monohydrate (0.28 g, 1.40 mmol) dissolved in 5 mL of dry MeOH. The mixture was stirred for 1 h. A white precipitate of **4** was separated by filtration, and the filtrate was extracted with 10 mL of saturated $NaHCO_3$ solution. The organic layer was dried over $MgSO_4$, and then the solvent was evaporated to dryness. The residue was dissolved in 25 mL of acetone and treated with 5 mL of a saturated solution of NH_4PF_6, and the mixture was concentrated on a rotary evaporator until a red solid precipitated. The solid was collected by filtration and dried. Proton NMR analysis of the crude product showed that it was a mixture of **2** (67%) and **3** (33%). A pure sample of **3** was obtained by crystallization from 2:1 acetone:hexane (**3** crystallizes first). Mp: 219 °C. Anal. Calcd for $C_{27}H_{22}F_6N_5O_2PRu$: C, 46.69; H, 3.19. Found: C, 46.29; H, 3.25. IR (DRIFTS, KCl): ν_{CO} 1926 cm^{-1}; $\nu_{C=O}$ 1550 cm^{-1}. ^{1}H NMR (CD_3CN): δ 9.29 (1H, d), 8.44 (1H, d), 8.39 (2H, t), 8.29 (2H, m), 8.12 (1H, t), 8.00 (1H, t), 7.91 (2H, m), 7.80 (1H, d), 7.61 (1H, t), 7.34 (1H, t), 7.14 (1H, t), 6.54 (1H, d), 6.42 (1H, m), 6.12 (1H, dd), 5.37 (1H, t), 3.88 (1H, m), 2.84 (1H, m), 2.10 (2H, m). ^{13}C NMR (CD_3CN): δ 204.35 (CO), 204.15 (CHO), 165.26, 158.62, 157.24, 156.06, 154.80, 154.53, 151.79, 147.35, 140.55, 140.38, 140.28, 138.47, 132.20, 127.97, 127.76, 127.18, 125.23, 125.00, 124.98, 124.39, 124.32, 123.64, 60.70, 38.04, 26.36.

(9) Crystal data for **3**: $C_{30.5}H_{30}F_6N_5O_2PRu$, M_r = 744.63, size 0.221 × 0.176 × 0.030 mm, monoclinic, space group *C*2/*c*, a = 28.431(5) Å, b = 17.262(3) Å, c = 12.000(2) Å, β = 98.784(3)°, F(000) = 3016, V = 5820.5(17) Å^3, T = 100(2) K, Z = 4, D_c = 1.568 Mg/m^3, μ = 0.672 mm^{-1}, Refinement method: full-matrix least-squares on F^2, R1 = 0.0451, wR2 = 0.1076 (observed data with $I > 2\sigma(I)$).

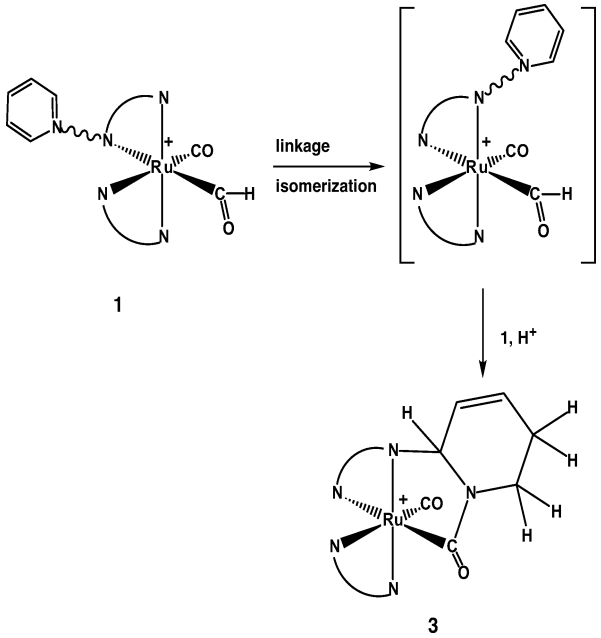
(10) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(11) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.

(12) (a) Gibson, D. H.; Mandal, S. K.; Owens, K.; Richardson, J. F. *Organometallics* **1987**, *6*, 2624. (b) Gibson, D. H.; Owens, K.; Mandal, S. K.; Sattich, W. E.; Franco, J. F. *Organometallics* **1991**, *10*, 1203. (c) Ellis, W. E.; Miedaner, A.; Curtis, C. J.; Gibson, D. H.; DuBois, D. L. *J. Am. Chem. Soc.* **2002**, *124*, 1926.

(13) Konno, H.; Sakamoto, K.; Ishitani, O. *Angew. Chem., Int. Ed.* **2000**, *39*, 4061.

Scheme 2[a]



[a] Abbreviations: N-N = 2,2′-bipyridine; N-N-N = 2,2′:6′,2″-terpyridine.

a metal formyl complex. Tanaka and co-workers[14] recently reported the electrochemical hydrogenation of the pendant ring in $[Ru(bpy)_2(\eta^1\text{-napy})(CO)](BF_4)_2$ (napy = 1,8-naphthyridine), which led to a metallacycle. The reductions were formulated in terms of electron transfers followed by proton transfers; a formyl complex was not suggested as a possible intermediate in the reductions. The final product resulted from the addition of three hydrogens to the previously pendant napy ring, similar to the conversion of **1** to **3** in the present work.

(14) Tomon, T.; Koizumi, T.; Tanaka, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 2229.

The stereochemistry of compound **2** has been established by X-ray crystallography[4] and suggests that the stereochemistry of the formyl precursor to **2** should be that shown in Scheme 1. However, the stereochemistry of **3** indicates that it has been derived from the linkage isomer of **1**, as indicated in Scheme 2 (for convenience, an abbreviated form of the tpy ligand is used). Since we have observed equilibria involving linkage isomerization with two structural isomers of **2**,[4] it is reasonable to expect that **1** and its linkage isomer may be in equilibrium, although we have not been able to observe the linkage isomer in ^{1}H NMR spectra of samples containing **1**. We have proposed previously[3,4] that the linkage isomer of **1** is necessary for the carbon−carbon bond forming step in the electrocatalytic reductions of CO_2 reported by Tanaka and co-workers.[2] The conversion of **1** to **3** represents the first concrete evidence that the linkage isomer is accessible in chemical reactions of **1**. This linkage isomer would be the necessary precursor to a migratory insertion reaction leading to the C_2 product glyoxylic acid in the catalytic reaction, as we suggested previously.[3,4]

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Supporting Information Available: Tables giving full details of the crystallographic data and data collection parameters, atomic coordinates, anisotropic displacement parameters, bond distances, bond angles, and hydrogen atom coordinates for **3**. This material is available free of charge via the Internet at http://pubs.acs.org. Alternatively, the file CCDC 285725 contains the supplementary crystallographic data for compound **3**. This can be downloaded free of charge via www.ccdc.cam.ac.uk/conts/retrieving.hmtl (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB21EZ, U.K.; fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

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