

Reductive Carbonylation of Ruthenium(III) by Ethylene Glycol in the Synthesis of Ruthenium(II) α,α' -Diimine Complexes

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Introduction

The potential use of ruthenium complexes as catalysts¹ and in solar energy conversion^{2,3} has created interest in their chemistry,⁴ electrochemistry,⁵ and photochemistry.² Research in this laboratory has focused on the use of ruthenium complexes as oxidation catalysts. *cis*-[Ru(α,α' -diimine)₂(O)₂]²⁺ complexes are more powerful oxidants than the *trans* complexes, but with unsubstituted α,α' -diimine ligands, isomerization to the poorer oxidant^{6,7} *trans*-[Ru(α,α' -diimine)₂(O)₂]²⁺ occurs. The first successful applications of ruthenium complexes as catalyst for the oxidation of alkenes and alkanes were reported from this laboratory¹ when the sterically encumbered α,α' -diimine ligand 2,9-dimethyl-1,10-phenanthroline (DMP) was used. This complex also is a selective catalyst for the oxidation¹ of CH₄ by H₂O₂ at mild conditions, producing CO₂ and low conversion to methanol. The bulky ligand not only prevents isomerization to the *trans* complex but also prevents formation of the μ -oxo dimer and the tris diimine complex. These successes motivated the synthesis of other bulky ligands.⁸

The 5,6-benzo derivatives of α,α' -bipyridine (bpy), for instance, in 2-(2'-pyridyl)quinoline (pq) or 2,2'-biquinoline (biq), have steric properties that may afford the DMP advantages. However, their metal chelating properties are reported to change markedly compared to those of bpy.^{9,10} In the present work, we describe complexes with biq as the sterically encumbered diimine ligand. The synthesis and spectroscopic and X-ray crystallographic characterization of the compound formed led to the discovery of a novel reaction. The product [Ru(biq)₂(CO)Cl]PF₆ obtained from ethylene glycol solvent showed, for the first time, that this solvent can function as the source of the CO ligand. In contrast to the reductive nitrosylation reactions of transition metal ions, which are frequently accomplished by a variety of reagents¹¹ other than the gaseous nitric oxide,

carbonylation reactions invariably are carried out using carbon monoxide. The rare known exceptions include the synthesis of ruthenium¹² and iridium^{13a} halogen carbonyls using formic acid, the synthesis of Vaska's compound in 2-methoxyethanol,^{13b} and the isolation of [Ru(bpy)₂(CO)Cl]ClO₄^{14,15} in the reaction of RuCl₃ and bpy in dimethylformamide (DMF).¹⁶ Carbonylation by HCOOH and DMF is not surprising, for it is well known that both of these compounds undergo thermal decomposition, producing CO.

The complex [Ru(bpy)₂(CO)Cl]PF₆ found in this work was previously¹⁷ synthesized in ethylene glycol using a heterobimetallic oxidation catalyst. We suggest carbonylation by ethylene glycol for the synthesis of analogous compounds of other diimines (L-L) besides the L-L = biq and bpy complexes reported.

Experimental Section

Materials and Methods. 2,2'-Biquinoline, ruthenium(III) chloride hydrate, sodium hexafluorophosphate, lithium chloride, and tetraethylammonium perchlorate were purchased from Aldrich and used as received. Ethylene glycol, hydrogen peroxide, 2,2'-bipyridine, copper(II) sulfate pentahydrate, dichloromethane, benzene, and pentane were obtained from Fisher Scientific (ACS grade). Diethyl ether (AR; anhydrous) was obtained from Mallinckrodt and dimethyl sulfoxide-*d*₆ (DMSO-*d*₆ 99.8 atom %) from Aldrich.

Physical Measurements. Infrared spectra (4000–400 cm⁻¹) were recorded as KBr disks using a Nicolet Model 5 DS FT-IR spectrophotometer, and NMR spectra were recorded on a Varian VXR 300 spectrometer, using TMS as a calibrant. Electronic spectra were obtained with a Hitachi U-3400 UV/vis-near IR spectrophotometer. Magnetic susceptibilities were measured by the Guoy method using CuSO₄·5H₂O as the calibrant. FAB mass spectral data in a *m*-nitrobenzyl alcohol matrix were obtained with a Finnigan MAT 95Q spectrometer by the University of Florida (UF) mass spectral facility. Elemental analyses were performed by UF Analytical Services using a Carlo-Erba 1106 instrument. Voltammetric measurements were done with a PAR Model 370-4 electrochemistry system: Model 174 A polarographic analyzer, Model 175 universal programmer, Model RE 0074 XY recorder, Model 173 potentiostat, Model 179 digital coulometer, and Model 377A cell. All experiments were made at 25 °C under a dinitrogen atmosphere in a three-electrode configuration using a platinum button working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE). The potentials reported are uncorrected for the junction contribution.

Synthesis of Compounds. Monochlorobis(2,2'-biquinoline)carbonylruthenium(II) Hexafluorophosphate Hydrate ([Ru(biq)₂(CO)Cl]PF₆·1.5H₂O, 1). RuCl₃·3H₂O (1.0 g, 3.8 mmol), biq (2.1 g, 8.0 mmol), and LiCl (2.5 g, 59 mmol) were stirred in 25 mL of ethylene glycol under dinitrogen or argon in a three-neck round-bottom flask equipped with a reflux condenser. The dark brown-red solution was allowed to reflux rather vigorously while being stirred rapidly. Refluxing was continued for 6 h, by which time the solution had become purple-red. The heating source was removed, acetone (50 mL) was very slowly added to the hot solution, which was then allowed to cool to 25 °C with stirring, and then 15 mL of water was added. The resulting mixture was allowed to stand for 15 h. The solution was

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- (1) (a) Bailey, C. L.; Drago, R. S. *J. Chem. Soc., Chem. Commun.* **1987**, 179. (b) Cundari, T. R.; Drago, R. S. *Inorg. Chem.* **1990**, *29*, 487. (c) Goldstein, A. S.; Beer, R. H.; Drago, R. S. *J. Chem. Soc., Chem. Commun.* **1991**, 21. (d) Goldstein, A. S.; Beer, R. H.; Drago, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 2424.
- (2) Lehn, J. M.; Sauvage, J.-P.; Ziessel, R. *Nouv. J. Chim.* **1979**, *3*, 423.
- (3) Connolly, J. S. *Photochemical Conversion and Storage of Solar Energy* Academic: New York, 1981; Chapter 6.
- (4) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium* Elsevier, Amsterdam, 1984 (see also references cited therein).
- (5) (a) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271. (b) Dobson, J. C.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 3283. (c) Robbins, M. H.; Drago, R. S. *J. Chem. Soc., Dalton Trans.* **1996**, 105.
- (6) Durham, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 600.
- (7) Nijs, H.; Cruz, M. I.; Fripat, J. J.; Van Damme, H. *Nouv. J. Chim.* **1982**, *6*, 551.
- (8) Beer, R. H.; Jimenez, J.; Drago, R. S. *J. Org. Chem.* **1993**, *58*, 1746.
- (9) Charlton, R. J.; Harris, C. M.; Patil, H. R. H.; Stephenson, N. C. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 409.
- (10) Harris, C. M.; Patil, H. R. H.; Sinn, E. *Inorg. Chem.* **1967**, *6*, 1102.
- (11) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *xx*, xxxx.

- (12) Colton, R.; Farthing, R. H. *Aust. J. Chem.* **1971**, *24*, 903.
- (13) (a) Grinsborg, A. P.; Koepke, J. W.; Hauser, J. J.; West, K. W.; DiSalvo, F. J.; Sprinkle, C. R.; Cohen, R. L. *Inorg. Chem.* **1976**, *15*, 514. (b) Vaska, L.; Luzio, D. J. *Am. Chem. Soc.* **1961**, *83*, 2784.
- (14) Clear, J. M.; Kelly, J. M.; O'Connell, C. M.; Vos, J. G.; Cardin, C. J.; Costa, S. R.; Edwards, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 750.
- (15) Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1213.
- (16) RuCl₃·3H₂O, bpy, and LiCl in refluxing DMF are reported to form [Ru(bpy)₂Cl₂·2H₂O] first. See: Sprintschnick, G.; Sprintschnick, H. W.; Kirsch, P. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 4967. Sullivan, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.
- (17) Ishida, H.; Tanaka, K.; Morimoto, M.; Tanaka, T. *Organometallics* **1986**, *5*, 724.

then filtered (Whatman filter paper), leaving behind a small amount of green-brown solid. The filtrate was added to 75 mL of an aqueous solution of NH_4PF_6 (7.0 g) under dinitrogen with stirring. A burnt amber solid separated, was filtered off, and was washed with 1% aqueous NH_4PF_6 , water, benzene, and diethyl ether. After recrystallization from CH_2Cl_2 and drying in vacuum, a 64% yield of **1** resulted. Anal. Calcd for $\text{C}_{37}\text{H}_{24}\text{N}_4\text{ClO}_{2.5}\text{PF}_6\text{Ru}$: C, 52.5; H, 2.84; N, 6.82. Found: C, 53.81; H, 3.14; N, 6.77.

Monochlorobis(2,2'-bipyridine)carbonylruthenium(II) Hexafluorophosphate ($[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]\text{PF}_6$, **2**). The same experimental procedure as followed for the biquinoline complex was used, except that the solution was heated to 170–175 °C. The compound was obtained in 70% yield. The crude product was vacuum dried and then crystallized from dichloromethane–pentane, giving a yield of 60%. Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{N}_4\text{OCIPF}_6\text{Ru}$: C, 40.54; H, 2.57; N, 9.01. Found: C, 40.21; H, 2.59; N, 8.99.

Crystallographic Structure Determination. $\text{C}_{40}\text{H}_{30}\text{N}_4\text{O}_1\text{PF}_6\text{Cl}_7\text{Ru}$, $M_r = 1076.87$, monoclinic, $P2(1)/c$, $a = 14.146(4)$ Å, $\beta = 97.36(2)^\circ$, $V = 4332(2)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.651$ g cm⁻³, Mo K α ($\lambda = 0.71073$ Å), $T = 298$ K. A small crystal was loaded into a thin-walled glass capillary and immersed in the mother solution during data collection. In anticipation of crystal instability (44% decay), data were collected at a high scan speed. The structure was solved by direct methods and refined in *SHELXTL plus*¹⁸ using full-matrix least-squares. The Ru, Cl, N, and P atoms were treated anisotropically, whereas the carbon and fluorine atoms were refined with isotropic thermal parameters. The positions of the hydrogen atoms were calculated in ideal positions, and their isotropic thermal parameters are fixed. The asymmetric unit of the crystal structure consists of the Ru complex, a hexafluorophosphate ion, and three dichloromethane molecules of crystallization. In the final cycle of refinement, 307 parameters and 2545 reflections [with $I > 3\sigma(I)$] gave R and wR of 0.0869 and 0.0842, respectively.

Results and Discussions

Spectroscopic Characterization. Compound **1** contains an absorption band in the infrared at 1964 cm⁻¹, and **2** absorbs at 1968 cm⁻¹. These bands are assigned to $\nu\text{C}\equiv\text{O}$ stretching vibrations. The free biq ligand in CDCl_3 exhibits a complex ¹H NMR spectrum, with signals ranging from 7.5 to 8.9 ppm vs TMS. Compound **1** in $\text{DMSO}-d_6$ shows an approximate doubling of the signals. The peaks occur in the δ range of 6.4–10.0 ppm, indicating that the complex is diamagnetic, as confirmed by susceptibility measurements. The ¹³C resonances for pure biq in CDCl_3 occur between δ 100 and 200 ppm, while **1** shows an approximate doubling of peaks in the same spectral region. This doubling indicates that the biq ligands in **1** are in the *cis* positions with respect to each other and the ligand binding is intact in solution. The bpy complex **2** in $\text{DMSO}-d_6$ also shows a similar doubling of the resonances in the ¹H and ¹³C NMR spectra.

The electronic spectrum of **1** contains bands at 465 (Gaussian analyzed $\epsilon_M = 300$ mol⁻¹ cm⁻¹) and 555 nm ($\epsilon_M = 925$ mol⁻¹ cm⁻¹) which can be assigned to a $d\pi \rightarrow \pi^*$ metal-to-ligand charge transfer (MLCT) transition.⁴ In **2**, bands are observed at 445, 425, and 390 nm.

The formation of $[\text{Ru}(\text{biq})_2(\text{CO})(\text{Cl})]\text{PF}_6$ is confirmed by FAB mass spectroscopic analyses in the positive mode. Positive molecular ion peaks at $m/z = 677$ amu, corresponding to $\text{Ru}(\text{biq})_2(\text{CO})\text{Cl}^+$, and at $m/z = 649$ amu, for $\text{Ru}(\text{biq})_2\text{Cl}^+$, are observed. A peak at $m/z = 613$, corresponding to $\text{Ru}(\text{biq})_2^+$, is found, indicating a stable Ru(I) in the FAB mass spectrum.

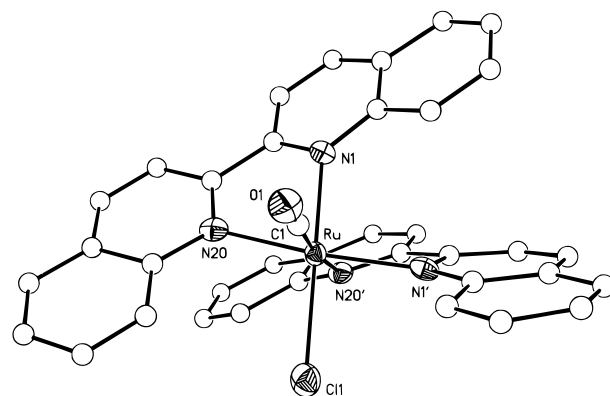


Figure 1. Structure of the biq complex with 50% probability ellipsoids. Carbon atoms are not labeled for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[\text{Ru}(\text{biq})_2(\text{CO})\text{Cl}]\text{PF}_6 \cdot 3\text{CH}_2\text{Cl}_2$

atom			bond 1–2	angle 1–2–3
1	2	3		
C11	Ru	N1	2.406(6)	171.4(4)
C11	Ru	N20		100.7(4)
C11	Ru	C1		95.6(5)
C11	Ru	N1'		86.7(4)
N1	Ru	N20	2.099(14)	77.1(5)
N1	Ru	C1		92.7(6)
N1	Ru	N1'		93.8(6)
N1	Ru	N20'		81.7(5)
N20	Ru	C1	2.101(15)	90.8(6)
N20	Ru	N1'		166.0(5)
N20	Ru	N20'		91.9(5)
C1	Ru	N1'	1.91(2)	100.4(6)
C1	Ru	N20'		173.1(6)
N1'	Ru	N20'	2.104(14)	76.1(5)
N20'	Ru	C11	2.181(14)	90.1(4)

In the negative mode, only PF_6^- is detected, at $m/z = 145$ amu. Similar species with corresponding masses are obtained in the FAB mass spectrum of **2**.

Molecular Structure of $[\text{Ru}(\text{biq})_2(\text{CO})\text{Cl}]\text{PF}_6 \cdot 3\text{CH}_2\text{Cl}_2$.

The asymmetric unit of the crystal structure consists of the discrete Ru cation, a hexafluorophosphate ion, and three dichloromethane molecules of crystallization. A thermal ellipsoid drawing of the complex cation with the atom labeling scheme is shown in Figure 1. Selected bond distances and angles are shown in Table 1. The ruthenium atom has an octahedral geometry, with the four nitrogens of the bidentate ligands *cis*, a carbonyl carbon, and a chlorine completing the first coordination sphere. (N1 and N20 are from biq1, while N1' and N20' are from biq2). The N20–Ru distance is slightly greater than the average of the other Ru–N distances, being *trans* to the π acceptor CO ligand. In general, the metal–ligand distances are comparable to those in the corresponding bpy complexes.¹⁴

Electrochemistry. Redox properties of a wide variety of ruthenium complexes have been compiled.^{4,5} It is evident that the formal potential (E_{298}^0) of the II to III couple is very dependent on the coordinated ligands. Complex **1** shows a metal-centered oxidative cyclic voltammetric (CV) response at $E_{298}^0 = 1.58$ V ($E_{\text{pc}} = 1.54$ V, $E_{\text{pa}} = 1.62$ V, and hence $\Delta E_p = 80$ mV) vs SCE (Figure 2), while **2** exhibits a similar response at 1.50 V ($E_{\text{pc}} = 1.47$ V and $E_{\text{pa}} = 1.54$ V; $\Delta E_p = 70$ mV) vs SCE in $\text{CH}_3\text{CN}/\text{TEAP}$. This indicates that the biq complex is a slightly stronger oxidant than the bpy complex. Isomerization of **2** (but not of **1**) is detected in the cyclic voltammetric analysis. A low-current cyclic response (Figure 2) obtained at $E_{298}^0 = 1.27$ V ($E_{\text{pc}} = 1.25$ V, $E_{\text{pa}} = 1.30$ V) vs SCE is attributed to

(18) Sheldrick, G. M. *SHELXTL plus*; Nicolet XRD Corp.: Madison, WI, 1990.

(19) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1994; Vol. IV, p 55 (present distributor, D. Reidel, Dordrecht, the Netherlands).

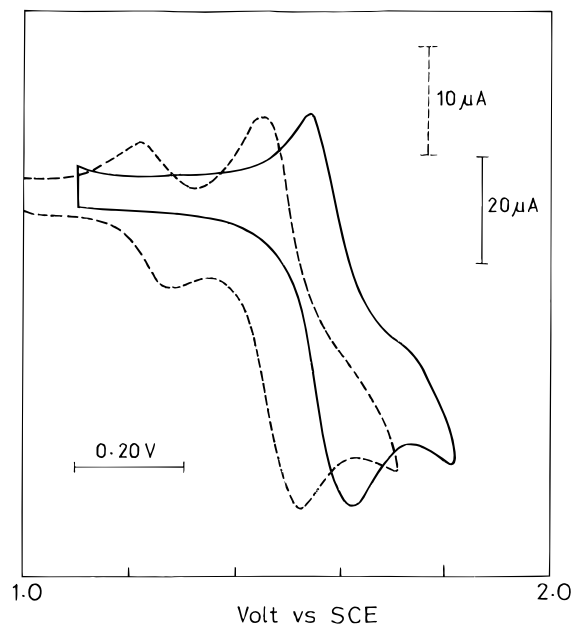
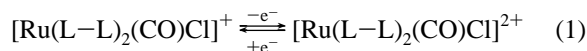


Figure 2. Cyclic voltammograms of $[\text{Ru}(\text{CO})\text{Cl}(\text{biq})_2]\text{PF}_6$ (—) and $[\text{Ru}(\text{CO})\text{Cl}(\text{bpy})_2]\text{PF}_6$ (- - -) in $\text{CH}_3\text{CN}/\text{Pt}/\text{TEAP}$ (scan rate, 50 mV s^{-1}).

the *trans* form of **2**. The cyclic voltammogram of **1** shows that such isomerization does not occur in solution with the sterically encumbered ligand, biq. The CV responses can be assigned to the redox reaction shown in eq 1. The Ru(II)–Ru(III) redox



potential is in the range expected for a ruthenium(II)/(III) complex containing π -acceptor ligands.⁵ π Backbonding lowers electron density on the metal, making it more difficult to oxidize.

The single-electron process shown in eq 1 was confirmed by constant potential coulometry at 1.65 V vs SCE for both **1** and **2**.

Synthetic Aspects. Vigorous refluxing of hydrated RuCl_3 , LiCl , and 2,2'-biquinoline in ethylene glycol produces, upon addition of acetone and water, the burnt amber **1**. The same product is obtained with the same yield even when the acetone addition step is omitted, indicating that ethylene glycol is the source of the CO ligand. A similar experimental procedure using bpy instead of biq produces the orange bpy complex **2**. The structure of **2** has been reported previously.¹⁴

Shiny, amber crystals of $[\text{Ru}(\text{biq})_2(\text{CO})\text{Cl}]\text{PF}_6$ as a methylene chloride solvate are obtained by crystallizing it from a dichloromethane–pentane solvent mixture. In contact with the mother solution, the crystals exist as solvates containing three CH_2Cl_2 molecules per ruthenium. When solvent is removed, CH_2Cl_2 escapes, and the crystals are not suited for X-ray diffraction.

Reductive carbonylation by ethylene glycol is proposed to involve two steps: (1) reduction of Ru(III), accompanied by oxidation of ethylene glycol to form 2 mol of formaldehyde, and (2) reaction of formaldehyde with $\{\text{Ru}(\text{L}-\text{L})_2\}^{2+}$ ($\text{L}-\text{L} = \text{biq}, \text{bpy}$) to generate $\{\text{Ru}(\text{L}-\text{L})_2\text{CO}\}^{2+}$. Formaldehyde is known¹⁷ to react with Ru(II), generating carbonylruthenium(II) complexes.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates and thermal parameters, and bond distances and angles (11 pages). Ordering information is given on any current masthead page.

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