



# Novel [Ru(polypyridine)(CO)<sub>2</sub>Cl<sub>2</sub>] and [Ru(polypyridine)<sub>2</sub>(CO)Cl]<sup>+</sup>-type complexes: Characterizing the effects of introducing azopyridyl ligands by electrochemical, spectroscopic and crystallographic measurements

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## ABSTRACT

The reaction of ruthenium carbonyl polymer ([Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub>) with azopyridyl compounds (2,2'-azobispyridine; apy or 2-phenylazopyridine; pap) generated new complexes, [Ru(azo)(CO)<sub>2</sub>Cl<sub>2</sub>] (azo = apy, pap). [Ru(apy)(CO)<sub>2</sub>Cl<sub>2</sub>] underwent photodecarbonylation to give a chloro-bridged dimer complex, whereas the corresponding pap complex ([Ru(pap)(CO)<sub>2</sub>Cl<sub>2</sub>]) was not converted to a dimer. The reactions of the chloro-bridged dimer containing the bpy ligand (bpy = 2,2'-bipyridine) with either apy or pap resulted in the formation of mixed polypyridyl complexes, [Ru(azo)(bpy)(CO)Cl]<sup>+</sup>. The novel complexes containing azo ligands were characterized by various spectroscopic measurements including the determination of X-ray crystallographic structures. Both [Ru(azo)(CO)<sub>2</sub>Cl<sub>2</sub>] complexes have two CO groups in a *cis* position to each other and two chlorides in a *trans* position. The azo groups are situated *cis* to the CO ligand in [Ru(azo)(bpy)(CO)Cl]<sup>+</sup>. All complexes have azo N–N bond lengths of 1.26–1.29 Å. The complexes exhibited azo-based two-electron reduction processes in electrochemical measurements. The effects of introducing azopyridyl ligands to the ruthenium carbonyl complexes were examined by ligand-based redox potentials, stretching frequencies and force constants of CO groups and bond parameters around Ru–CO moieties.

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## 1. Introduction

Ruthenium(II) carbonyl complexes with bidentate pyridyl ligands are attractive catalysts for the water–gas shift reaction and for carbon dioxide reduction [1]. Additionally, ruthenium carbonyl complexes incorporating bidentate pyridyl ligands have been investigated as precursors to heteroleptic tris polypyridyl ruthenium complexes of the type [Ru(L<sub>1</sub>)(L<sub>2</sub>)(L<sub>3</sub>)]<sup>2+</sup> [2]. Currently, 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) and their derivatives have been predominantly used as polypyridyl ligands in this research field. While polypyridyl-based redox reactions play a significant role as electron reservoirs in photo- and electrochemical reductions of carbon dioxide [3,4], it should be possible to use other polypyridyl ligands which possess non-innocent properties. The characteristics of these new potential complexes should be explored. A candidate for the new complex is the azopyridyl derivatives. Azopyridyl compounds are photochemically active [5]. In addition, azopyridyl compounds can undergo one or two-electron transfer reactions because these compounds have

a low-lying azo-centered π\* MO [6]. Therefore, the construction of complex systems containing azopyridyl derivatives as ancillary ligands should be very interesting from the viewpoint of redox and structural chemistries. A variety of metal complexes including azopyridyl ligands have been reported [6,7]. We have recently reported specific properties of azopyridyl moieties in ruthenium carbonyl complexes [8,9]. In these reports, we have demonstrated that azopyridyl ligands can control the redox behavior or steric configurations of the complexes. Although metal complexes containing azopyridyl ligands demonstrate a variety of interesting properties compared with typical polypyridines such as bpy or phen, there have been no systematic reports on the effects of introduction of azopyridyl ligands to the ruthenium carbonyl complexes. In this paper, we report the preparation and characterization of mono-bidentate pyridyl complexes ([Ru(apy)(CO)<sub>2</sub>Cl<sub>2</sub>] and [Ru(pap)(CO)<sub>2</sub>Cl<sub>2</sub>]; apy = 2,2'-azobispyridine, pap = 2-phenylazopyridine) and bis-bidentate pyridyl complexes ([Ru(apy)(bpy)(CO)Cl]<sup>+</sup> and [Ru(pap)(bpy)(CO)Cl]<sup>+</sup>), both containing one azopyridyl ligand. Comparisons with other analogous polypyridyl-containing ruthenium complexes based on electrochemical, spectroscopic and crystallographic measurements are also described.

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## 2. Experimental

### 2.1. Physical measurements

Elemental analyses were carried out at the Research Center for Molecular-Scale Nanoscience, Institute for Molecular Science. IR spectra were obtained on KBr pellets with a JASCO FT-IR 4100 spectrometer. Mass spectra were obtained with a Bruker Daltonics microTOF mass spectrometer equipped with an electrospray ionization (ESI) interface. UV–Vis spectra were obtained with a JASCO V-570 UV/Vis/NIR spectrophotometer. NMR spectra were recorded on a JEOL JMN-AL300 spectrometer operating at  $^1\text{H}$  and  $^{13}\text{C}$  frequencies of 300 and 75.5 MHz, respectively. Chemical shifts were calibrated against tetramethylsilane (TMS). Cyclic voltammograms were obtained in a one-compartment cell consisting of a platinum working electrode, a platinum counterelectrode and an Ag/AgNO<sub>3</sub> (0.01 M) reference electrode in CH<sub>3</sub>CN containing tetra-*n*-butylammonium perchlorate (0.1 M) as a supporting electrolyte and the complex (1 mM). The data were collected with an ALS/Chi model 620A electrochemical analyzer. All potentials are reported in volts versus ferrocene/ferrocenium couple (Fc<sup>+</sup>/Fc) at 25 °C under N<sub>2</sub>.

### 2.2. Preparation of compounds

All solvents were dehydrated solvents for organic synthesis and used without further purification. CH<sub>3</sub>CN for electrochemical experiments was distilled over CaH<sub>2</sub> under N<sub>2</sub> just prior to use. 2-phenylazopyridine (pap), 2,2'-azobispyridine (apy), [Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>*n*</sub>, and [Ru(bpy)(CO)<sub>2</sub>Cl<sub>2</sub>] were prepared according to procedures outlined elsewhere [10,11].

#### 2.2.1. [Ru(apy)(CO)<sub>2</sub>Cl<sub>2</sub>]

A methanolic solution (10 mL) containing [Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>*n*</sub> (200 mg, 0.88 mmol) and apy (200 mg, 0.92 mmol) was refluxed for 1 h. The black precipitate was collected by filtration and washed with methanol and diethyl ether, and then dried in vacuo. The yield was 200 mg (55%). *Anal. Calc.* for C<sub>12</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub>Cl<sub>2</sub>Ru: C, 34.96; H, 1.96; N, 13.60. Found: C, 34.83; H, 2.00; N, 13.58%. IR (KBr): 2074, 2004 cm<sup>-1</sup> (νC≡O).  $^1\text{H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 9.23 (d, 1H), 8.92 (d, 1H), 8.72 (t, 1H), 8.38–8.28 (m, 2H) and 8.05–7.71 (m, 3H) ppm.  $^{13}\text{C}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 196.53, 194.53 (each CO), 163.43, 152.09, 149.27, 141.96, 139.51, 131.27, 130.29, 129.56, 116.89 and 114.90 ppm.

#### 2.2.2. [Ru(pap)(CO)<sub>2</sub>Cl<sub>2</sub>]

A similar reaction between [Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>*n*</sub> and pap under the same conditions described above gave rise to [Ru(pap)(CO)<sub>2</sub>Cl<sub>2</sub>] with a 39% (140 mg) yield. *Anal. Calc.* for C<sub>13</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub>Ru: C, 37.97; H, 2.21; N, 10.22. Found: C, 37.82; H, 2.25; N, 10.23%. IR (KBr): 2074, 2010 cm<sup>-1</sup> (νC≡O).  $^1\text{H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 9.13 (d, 1H), 8.65 (d, 1H), 8.35 (t, 1H), 8.11–8.08 (m, 2H) and 7.83–7.60 (m, 4H) ppm.  $^{13}\text{C}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 195.54, 194.57 (each CO), 163.32, 155.47, 151.50, 142.32, 134.14, 130.33, 130.01, 129.88, 123.97 and 123.66 ppm.

#### 2.2.3. [Ru(apy)(CO)Cl<sub>2</sub>]<sub>2</sub>

The dimer complex was prepared according to the method in the literature [12]. [Ru(apy)(CO)<sub>2</sub>Cl<sub>2</sub>] (60 mg, 0.14 mmol) was dissolved in dichloromethane (60 mL) and filtered. The filtrate was placed in a quartz flask with a stopper and irradiated with a 100 W mercury lamp for 15 h, after which time a dark green precipitate had formed. The precipitate was collected by filtration, washed with diethyl ether and dried in vacuo. The yield was 50 mg (45%). *Anal. Calc.* for C<sub>22</sub>H<sub>16</sub>N<sub>8</sub>O<sub>2</sub>Cl<sub>4</sub>Ru<sub>2</sub> · 3CH<sub>2</sub>Cl<sub>2</sub>: C, 29.35; H, 2.17; N, 10.95. Found: C, 29.42; H, 2.15; N, 10.75%. IR (KBr): 1991 cm<sup>-1</sup> (νC≡O).

#### 2.2.4. [Ru(apy)(bpy)(CO)Cl]PF<sub>6</sub>

The complex was prepared by modification of a previously reported method [13]. A mixture of [Ru(bpy)(CO)Cl<sub>2</sub>]<sub>2</sub> (140 mg, 0.39 mmol) and apy (108 mg, 0.58 mmol) was heated under reflux in 2-methoxyethanol (10 mL) for 2 h. The mixture was evaporated to dryness under reduced pressure and the remaining solid was dissolved in water (24 mL). The solution was filtered and added to an excess of KPF<sub>6</sub>. The precipitate was collected by filtration and washed with water and diethyl ether. The product was then dried in vacuo. The crude product was purified by column chromatography using Al<sub>2</sub>O<sub>3</sub> (eluent: CH<sub>3</sub>CN). The volume of the solution was reduced to ca. 5 mL using a rotary evaporator. The black crystals were precipitated by the addition of diethyl ether, collected, washed with diethyl ether and finally dried in vacuo. The yield was 80 mg (31%). *Anal. Calc.* for C<sub>21</sub>H<sub>16</sub>N<sub>6</sub>OCIPF<sub>6</sub>Ru: C, 38.86; H, 2.68; N, 12.78. Found: C, 38.81; H, 2.48; N, 12.93%. ESI-MS (CH<sub>3</sub>CN): *m/z* = 505 (M<sup>+</sup>), 477 (M–CO<sup>+</sup>). IR (KBr): 2002 cm<sup>-1</sup> (νC≡O).  $^1\text{H}$  NMR (CD<sub>3</sub>CN): δ 9.50 (d, 1H), 8.83 (bs, 1H), 8.57 (d, 1H), 8.42–8.20 (m, 6H), 8.07–7.89 (m, 5H), 7.52 (bs, 1H) and 7.29 (t, 1H) ppm.  $^{13}\text{C}$  NMR (CD<sub>3</sub>CN): δ 196.48 (CO), 156.81–156.43 (multiple signals), 155.10, 152.78, 141.51, 140.70, 129.61, 128.91, 128.62 and 125.43–125.28 (multiple signals) ppm.

#### 2.2.5. [Ru(pap)(bpy)(CO)Cl]PF<sub>6</sub>

The complex was prepared in a similar manner as outlined in Section 2.2.4 [9]. Recrystallization of the crude product from acetonitrile/diethyl ether gave single crystals of [Ru(pap)(bpy)(CO)Cl]PF<sub>6</sub>. The yield was 54 mg (21%). *Anal. Calc.* for C<sub>22</sub>H<sub>17</sub>N<sub>5</sub>OCIPF<sub>6</sub>Ru: C, 40.72; H, 2.64; N, 10.79. Found: C, 40.71; H, 2.83; N, 10.89%. ESI-MS (CH<sub>3</sub>CN): *m/z* = 504 (M<sup>+</sup>), 476 (M–CO<sup>+</sup>). IR (KBr): 2001 cm<sup>-1</sup> (νC≡O).  $^1\text{H}$  NMR (CD<sub>3</sub>CN): δ 9.53 (d, 1H), 8.54 (d, 1H), 8.41–8.29 (m, 5H), 8.09–7.60 (m, 8H), 7.50 (bs, 1H) and 7.40 (t, 1H) ppm.  $^{13}\text{C}$  NMR (CD<sub>3</sub>CN): δ 194.96 (CO), 156.62–156.25 (multiple signals), 154.00, 152.64, 141.50, 140.80, 129.01, 128.85 and 125.33–125.26 (multiple signals) ppm.

### 2.3. X-ray crystallography

#### 2.3.1. [Ru(apy)(CO)<sub>2</sub>Cl<sub>2</sub>] · CH<sub>2</sub>Cl<sub>2</sub> and [Ru(pap)(CO)<sub>2</sub>Cl<sub>2</sub>]

The single crystals of the complexes were obtained from dichloromethane/methanol mixtures. A black crystal of [Ru(apy)(CO)<sub>2</sub>Cl<sub>2</sub>] · CH<sub>2</sub>Cl<sub>2</sub> with the dimensions 0.2 × 0.2 × 0.2 mm was mounted on a glass fiber. A dark red crystal of [Ru(pap)(CO)<sub>2</sub>Cl<sub>2</sub>] with the dimensions 0.2 × 0.2 × 0.2 mm was mounted on a glass fiber. All data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71070 Å) at –100(1) °C. Data were collected to a maximum 2θ value of 55.0°. All calculations were carried out using the TEXSAN crystallographic software package [14]. The structures were solved either by the heavy-atom Patterson method [15] for [Ru(apy)(CO)<sub>2</sub>Cl<sub>2</sub>] · CH<sub>2</sub>Cl<sub>2</sub> or by a direct method [16] for [Ru(pap)(CO)<sub>2</sub>Cl<sub>2</sub>], and were expanded using Fourier techniques. Empirical absorption corrections were applied using Lorentz polarization (Lp) and absorption. Structures were refined using full-matrix least-square techniques. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were built in using standard geometry. The final cycle of full-matrix least-squares refinements was based on 3860 observations (all data) and 217 variable parameters for [Ru(apy)(CO)<sub>2</sub>Cl<sub>2</sub>] · CH<sub>2</sub>Cl<sub>2</sub>, whereas 3109 observations (all data) and 190 variable parameters were used for [Ru(pap)(CO)<sub>2</sub>Cl<sub>2</sub>]. Crystallographic parameters are summarized in Table 1 and selected bond lengths and angles are listed in Table 3.

#### 2.3.2. [Ru(apy)(bpy)(CO)Cl]PF<sub>6</sub>

Crystals suitable for X-ray crystallography were prepared by a week-long diffusion of diethyl ether into an acetonitrile solution

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