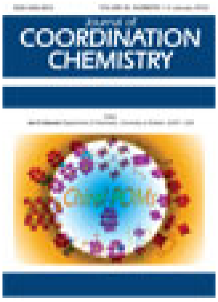


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

One-pot synthesis of cis-bis(2,2′-bipyridine)carbonylruthenium(II) complexes from a carbonato precursor: X-ray crystal structures and electron transfer processes of the series complexes

Dai Oyama [a], Koji Suzuki [a], Takashi Yamanaka [a] & Tsugiko Takase [b]

[a] Department of Industrial Systems Engineering, Cluster of Science and Technology, Fukushima University, 1 Kanayagawa, Fukushima 960-1296, Japan
[b] Center for Practical and Project-Based Learning, Cluster of Science and Technology, Fukushima University, 1 Kanayagawa, Fukushima 960-1296, Japan

To cite this article: Dai Oyama, Koji Suzuki, Takashi Yamanaka & Tsugiko Takase (2012) One-pot synthesis of cis-bis(2,2′-bipyridine)carbonylruthenium(II) complexes from a carbonato precursor: X-ray crystal structures and electron transfer processes of the series complexes, Journal of Coordination Chemistry, 65:1, 78-86, DOI: 10.1080/00958972.2011.641124

To link to this article: http://dx.doi.org/10.1080/00958972.2011.641124

Journal of Coordination Chemistry
Vol. 65, No. 1, 10 January 2012, 78–86

One-pot synthesis of *cis*-bis(2,2′-bipyridine) carbonylruthenium(II) complexes from a carbonato precursor: X-ray crystal structures and electron transfer processes of the series complexes

DAI OYAMA*†, KOJI SUZUKI†, TAKASHI YAMANAKA† and TSUGIKO TAKASE‡

†Department of Industrial Systems Engineering, Cluster of Science and Technology, Fukushima University, 1 Kanayagawa, Fukushima 960-1296, Japan
‡Center for Practical and Project-Based Learning, Cluster of Science and Technology, Fukushima University, 1 Kanayagawa, Fukushima 960-1296, Japan

(*Received 6 September 2011; in final form 2 November 2011*)

The reaction of Brønsted acids with *cis*-[Ru(bpy)$_2$(CO$_3$)] (bpy = 2,2′-bipyridine) under CO results in cleavage of the carbonato ligand and formation of cationic *cis*-[Ru(bpy)$_2$(CO)L]$^{n+}$ complexes [L = ONO$_2$ (**1**$^+$), OH$_2$ (**2**$^{2+}$), Cl (**3**$^+$), OCOH (**4**$^+$), and OCOCH$_3$ (**5**$^+$)]. The structures of **1**$^+$ and **2**$^{2+}$ were confirmed by single-crystal X-ray diffraction. Crystal data for **1**(PF$_6$): monoclinic, $P2_1/c$, $a = 10.5242(3)$, $b = 15.4727(3)$, $c = 14.6571(3)$ Å, $\beta = 92.3219(9)°$, $V = 2384.77(9)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.806$ g cm^{-3}, 5460 unique reflections ($R_{\text{int}} = 0.032$), $R_1 = 0.0540$ [$I > 2\sigma(I)$], $wR_2 = 0.1642$ (all reflections); crystal data for **2**(ClO$_4$)$_2 \cdot$H$_2$O: monoclinic, $C2/c$, $a = 20.4247(7)$, $b = 10.0777(3)$, $c = 15.6039(5)$ Å, $\beta = 127.7569(8)°$, $V = 2539.31(14)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.769$ g cm^{-3}, 2895 unique reflections ($R_{\text{int}} = 0.036$), $R_1 = 0.0343$ [$I > 2\sigma(I)$], $wR_2 = 0.0907$ (all reflections). Except for **2**(PF$_6$)$_2$ the complexes exhibit oxidation at 1.02–1.30 V *versus* Fc$^+$/Fc in acetonitrile. Bipyridine-centered reductions are also observed; these redox potentials depend on the nature of L. This convenient synthesis will be useful for producing *cis*-[Ru(bpy)$_2$(CO)L]$^{n+}$-type complexes in high yield.

Keywords: Ruthenium; Bipyridine complex; Crystal structure; One-pot synthesis; Electron transfer

1. Introduction

For decades, ruthenium(II) complexes containing polypyridines have been used in a variety of areas such as catalysis and biochemistry because of their properties [1]. An important application of polypyridyl ruthenium compounds is transformation of various substrates coordinated to the metal center. For example, the monocarbonyl complexes containing two 2,2′-bipyridine (bpy), *cis*-[Ru(bpy)$_2$(CO)Cl]$^+$ and *cis*-[Ru(bpy)$_2$(CO)(OH$_2$)]$^{2+}$, are active species for the reduction of carbon dioxide [2]

---

*Corresponding author. Email: daio@sss.fukushima-u.ac.jp

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
http://dx.doi.org/10.1080/00958972.2011.641124

and in the water–gas shift reaction [3]. *Cis*-$[Ru(bpy)_2(CO)L]^{n+}$ complexes (L = monodentate ligand) are generally prepared by heating *cis*-$[Ru(bpy)_2(CO)Cl]^+$ under reflux in the presence of an excess of L, as shown in the following equation [4]:

$$\left[Ru(bpy)_2(CO)Cl\right]^+ + L \rightarrow \left[Ru(bpy)_2(CO)L\right]^{n+} + Cl^- \\ (L = \text{substituted pyridines, } CH_3CN,\ H_2O \text{ for } n = 2;\ L = NCS^-,\ H^- \text{ for } n = 1) \tag{1}$$

However, this synthetic route tends to offer low yields because *cis*-$[Ru(bpy)_2(CO)Cl]^+$ is essentially a side product in the synthesis of *cis*-$[Ru(bpy)_2Cl_2]$ [4]. A convenient "one-pot" synthesis of polypyridyl complexes of ruthenium(II) containing CO is the direct reaction of the corresponding precursors (*cis*-$[Ru(bpy)_2L_2]^{n+}$) with CO gas. The synthesis of compounds containing various monodentate ligands (L) (*cis*-$[Ru(bpy)_2L_2]^{n+}$), however, has been limited by the lack of a convenient synthetic methodology. Therefore, the development of a facile synthetic route to *cis*-$[Ru(bpy)_2(CO)L]^{n+}$ would provide access to a family of compounds that could lead to important applications.

Here, we report the convenient synthesis of *cis*-$[Ru(bpy)_2(CO)L]^{n+}$ [L = ONO_2 (**1**$^+$), OH_2 (**2**$^{2+}$), Cl (**3**$^+$), OCOH (**4**$^+$), and $OCOCH_3$ (**5**$^+$)] using various Brønsted acids (HNO_3, HPF_6, HBF_4, HCl, HCOOH, and CH_3COOH) under a CO atmosphere. We present the X-ray structures of nitrato [**1**(PF_6)] and aqua [**2**$(ClO_4)_2 \cdot H_2O$] complexes. We also examined the electrochemical properties of the series complexes. We used Lever's E_L parameters to confirm the electron transfer processes [5]. As expected, the aqua ligand of **2**$^{2+}$ is quickly replaced by an acetonitrile in CH_3CN solution. In addition, we newly evaluated the E_L parameter of the acetate ($OCOCH_3^-$) from the redox potentials of **5**$^+$.

2. Experimental

2.1. *Materials and methods*

All solvents were purchased as anhydrous solvents for organic synthesis and used without purification. The CH_3CN used in the electrochemical experiments was further distilled over CaH_2 under N_2 just before use. *Cis*-$[Ru(bpy)_2(CO_3)] \cdot 2H_2O$ was prepared according to a known procedure [6].

Elemental analysis was conducted at the Research Center for Molecular-Scale Nanoscience, Institute for Molecular Science. Infrared spectra were obtained using KBr pellets with a JASCO FT-IR 4100 spectrometer. Mass spectra were obtained with a Bruker Daltonics microTOF mass spectrometer. NMR spectra were recorded on a JEOL JMN-AL300 spectrometer. Electrochemical measurements were performed in CH_3CN containing tetra-*n*-butylammonium perchlorate (0.1 mol L^{-1}) as a supporting electrolyte in a one-compartment cell consisting of a Pt working electrode, a Pt wire counter electrode, and a $Ag/AgNO_3$ (0.01 mol L^{-1}) reference electrode. All potentials are reported in V *versus* the ferrocenium/ferrocene couple (Fc^+/Fc) at 25°C under Ar. These redox potentials were converted to the NHE according to the literature (+0.67 V in acetonitrile) [7].

2.2. *Synthesis of cis-[Ru(bpy)$_2$(CO)L]$^{n+}$*

In a typical preparation, *cis*-[Ru(bpy)$_2$(CO$_3$)] · 2H$_2$O (100 mg, 0.196 mmol) was added to a test tube containing 2-methoxyethanol (20 mL) and 2 equiv of nitric acid (0.1 mol L^{-1}). The mixture was heated to 80°C under a CO atmosphere (10 atm) for 15 h. The volume of the reaction mixture was reduced to 2 mL, and then a saturated solution of KPF$_6$ (5 mL) was added. The resulting yellow–orange solid was filtered and then washed with water followed by Et$_2$O. The crude products were purified by the diffusion of Et$_2$O into a solution of the compounds in acetone. The yield was 111 mg (87%) for **1**(PF$_6$). Analytical data for **1**(PF$_6$): Anal. Calcd for C$_{21}$H$_{16}$N$_5$O$_4$PF$_6$Ru (%): C, 38.90; H, 2.49; N, 10.80. Found (%): C, 38.88; H, 2.57; N, 11.05. ESI-MS (CH$_3$CN): $m/z = 504$ ([M]$^+$), 476 ([M–CO]$^+$). IR (KBr) (cm^{-1}): 1980 (νC≡O), 1475, 1272, and 991 (νNO$_3$). ^{1}H NMR (300 MHz, acetone-d$_6$): δ 9.69 (d, 1H), 9.02 (d, 1H), 8.88–8.70 (m, 4H), 8.57 (t, 1H), 8.42–8.30 (m, 2H), 8.24–8.11 (m, 2H), 8.01–7.92 (m, 2H), 7.77 (d, 1H), 7.64 (t, 1H), and 7.50 (t, 1H) ppm.

Analytical data for **2**(PF$_6$)$_2$: A similar reaction between *cis*-[Ru(bpy)$_2$(CO$_3$)] · 2H$_2$O and HPF$_6$ or HBF$_4$ under the same conditions described above gave **2**(PF$_6$)$_2$ with 96 mg (65%) yield. ESI-MS (CH$_3$CN): $m/z = 235$ ([M–H$_2$O + N$_2$]$^{2+}$). IR (KBr) (cm^{-1}): 1994 (νC≡O).

Analytical data for **3**(PF$_6$): A similar reaction between *cis*-[Ru(bpy)$_2$(CO$_3$)] · 2H$_2$O and HCl under the same conditions described above gave **3**(PF$_6$) with 106 mg (87%) yield. ESI-MS (CH$_3$CN): $m/z = 477$ ([M]$^+$), 449 ([M–CO]$^+$). IR (KBr) (cm^{-1}): 1965 (νC≡O).

Analytical data for **4**(PF$_6$): A similar reaction between *cis*-[Ru(bpy)$_2$(CO$_3$)] · 2H$_2$O and HCOOH under the same conditions described above gave **4**(PF$_6$) with 98 mg (79%) yield. ESI-MS (CH$_3$CN): $m/z = 487$ ([M]$^+$), 459 ([M–CO]$^+$). IR (KBr) (cm^{-1}): 1965 (νC≡O), 1626 and 1291 (νOCO).

Analytical data for **5**(PF$_6$): A similar reaction between *cis*-[Ru(bpy)$_2$(CO$_3$)] · 2H$_2$O and CH$_3$COOH under the same conditions described above gave **5**(PF$_6$) with 104 mg (82%) yield. ESI-MS (CH$_3$CN): $m/z = 501$ ([M]$^+$), 473 ([M–CO]$^+$). IR (KBr) (cm^{-1}): 1963 (νC≡O), 1621 and 1317 (νOCO).

Spectral data obtained for **2**(PF$_6$)$_2$–**5**(PF$_6$) were consistent with those reported previously [4a, 8].

2.3. *X-ray crystallographic analyses*

Single crystals of **1**(PF$_6$) were obtained by vapor diffusion of diethyl ether into an acetone solution of the complex. Single crystals of **2**(ClO$_4$)$_2$ · H$_2$O were obtained directly from the reaction mixture by using ClO$_4^-$ as an alternative counter ion. Data were collected at 20°C [**1**(PF$_6$)] or −100°C [**2**(ClO$_4$)$_2$ · H$_2$O] on a Rigaku RAXIS-RAPID diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71075$ Å). All data were collected and processed using the *PROCESS-AUTO* program [9]. All the calculations were conducted using the *CrystalStructure* crystallographic software package [10] except for refinement, which was performed using *SHELXL-97* [11]. The structures were solved either by direct methods [12] [**1**(PF$_6$)] or by the Patterson method [13] [**2**(ClO$_4$)$_2$ · H$_2$O]. Multi-scan absorption corrections were applied [14]. The fluorines of the anion of **1**(PF$_6$) were modeled as disordered over two sets of sites, set at

Table 1. Crystallographic data and details of diffraction experiments for **1**(PF_6) and **2**($(ClO_4)_2 \cdot H_2O$).

	1(PF_6)	**2**($(ClO_4)_2 \cdot H_2O$)
Chemical formula	$C_{21}H_{16}N_5O_4PF_6Ru$	$C_{21}H_{20}N_4O_{11}Cl_2Ru$
Formula weight	648.42	676.39
Temperature (K)	293(1)	173(1)
Space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
Unit cell dimensions (Å, °)		
a	10.5242(3)	20.4247(7)
b	15.4727(3)	10.0777(3)
c	14.6571(3)	15.6039(5)
β	92.3219(9)	127.7569(8)
Volume (Å^3), Z	2384.77(9), 4	2539.31(14), 4
Calculated density (g cm^{-3})	1.806	1.769
Absorption coefficient (cm^{-1})	8.117	8.954
Number of measured reflections	22,715	11,995
Number of observed reflections	5460	2895
Refinement method	Full-matrix least-squares on F^2	
Parameters	338	196
R_1 [$I > 2\sigma(I)$][a]	0.0540	0.0343
wR_2 (all data)[b]	0.1642	0.0907
S	1.052	1.118

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = \{\Sigma_w(F_o^2 - F_c^2)^2/\Sigma_w(F_o^2)^2\}^{1/2}$.

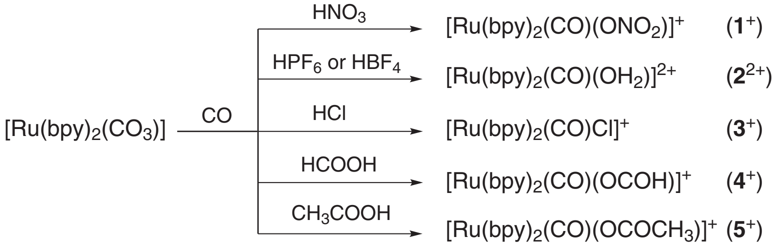
equal occupancy after trial refinement. The CO and OH_2 of **2**($(ClO_4)_2 \cdot H_2O$) were disordered over two sites with equal occupancy. The hydrogen atoms in both the aqua ligand and non-coordinated water were not included in the structure. The crystallographic parameters of **1**(PF_6) and **2**($(ClO_4)_2 \cdot H_2O$) are summarized in table 1.

3. Results and discussion

3.1. *Synthesis and structure*

Several methods are used for carbonylation of transition metal complexes. Gaseous carbon monoxide, formic acid, dimethylformamide, ethylene glycol, and terminal alkynes are employed as carbonylation reagents [3a, 15]. In this study, *cis*-$[Ru(bpy)_2(CO)L](PF_6)_n$ ($n = 1$ or 2) were prepared in high yield by reacting *cis*-$[Ru(bpy)_2(CO_3)]$ (the carbonato precursor, which was prepared from the corresponding dichlorido complex) [6] with CO in an excess of a suitable acid and 2-methoxyethanol mixture. The L varies with the acid used (scheme 1), acids with anions that possess coordination ability coordinate directly to ruthenium as an anionic ligand (NO_3^-, Cl^-, $OCOH^-$, and $OCOCH_3^-$), whereas water coordinates to the ruthenium in the case of HPF_6 or HBF_4.

Of the complexes produced, **1**(PF_6) was isolated as a new product. Its composition was confirmed by the elemental analysis and a single group of peaks in the electrospray ionization mass spectroscopy (ESI-MS) results matched the expected isotopic distribution pattern with intense peaks at m/z 504 (M^+) and 476 ($M–CO^+$). However, the coordination mode of the nitrato ligand in **1**(PF_6) was uncertain. The NO_3^- can non-coordinate, or coordinate in a monodentate (NO_3–O) or bidentate (NO_3–O,O')



Scheme 1. Synthesis of *cis*-$[Ru(bpy)_2(CO)L]^{n+}$.

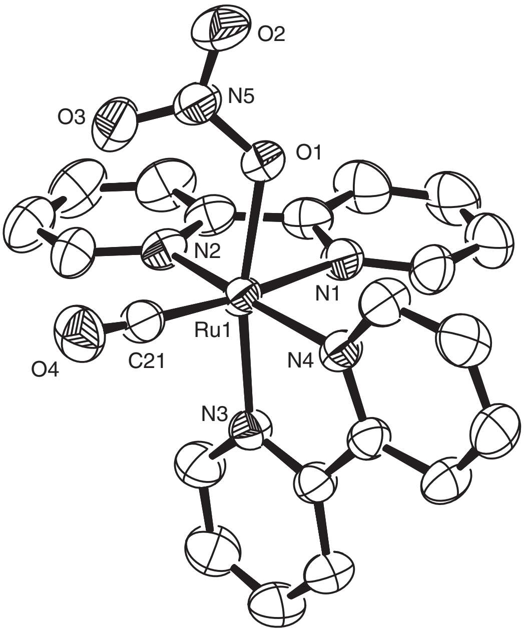


Figure 1. Molecular structure of $\mathbf{1}^+$, with atom labels and 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

fashion [16]. In the IR spectrum of $\mathbf{1}(PF_6)$, N–O stretching vibrations were observed at 1475, 1272, and 991 cm^{-1}. From these values, which agree with those in the literature [16, 17], it is difficult to distinguish between mono- and bidentate coordination of NO_3^-. However, the X-ray data clearly indicate monodentate coordination (see below). In addition, a single carbonyl vibration at 1980 cm^{-1} confirms the formation of the terminal carbonyl. Other compounds $[\mathbf{2}(PF_6)_2$–$\mathbf{5}(PF_6)]$ also possess a single ν(CO) band between 1963 and 1994 cm^{-1}. For $\mathbf{4}(PF_6)$ and $\mathbf{5}(PF_6)$, the agreement between the reported and observed frequencies assigned to carboxylate ions ($OCOH^-$ and $OCOCH_3^-$) indicate that both ions coordinate monodentate with Ru–O bonds [8].

The crystal structure of $\mathbf{1}(PF_6)$ is shown in figure 1 and the key bond parameters are listed in table 2. The cation has octahedral coordination geometry with a Ru–CO group [177.6(3)°] *cis* to nitrate. The crystal structure clearly shows monodentate coordination of nitrate [the Ru–O distance is 2.087(2) Å]. The sum of the three O–N–O bond angles in the nitrato ligand is 360.0°, indicating that nitrate has a planar structure. This agrees with the data reported for analogous nitrato complex *cis*-$[Ru(bpy)_2(NO)(ONO_2)](ClO_4)_2$ [18]. The carbonyl bond distances of Ru–C and C–O are comparable with those in ruthenium carbonyl analogs [8, 19]. X-ray analysis of a single crystal of $\mathbf{2}(ClO_4)_2$ revealed the molecular structure of the complex with a *cis* orientation of Ru–CO and Ru–OH_2 (figure 2). Although the Ru–O bond distance [2.112(10) Å] of $\mathbf{2}(ClO_4)_2$ is longer than that of $\mathbf{1}(PF_6)$ (table 2), it is typical for bis(bipyridine)ruthenium(II) complexes containing aqua ligand(s) (2.10–2.15 Å) [20]. The Ru–C–O angle [178.6(10)°] and the Ru–C and C–O distances [1.897(14) and 1.110(15) Å, respectively] are typical. In addition, the structural

Table 2. Selected bond distances (Å) and angles (°) for $\mathbf{1}(PF_6)$ and $\mathbf{2}(ClO_4)_2 \cdot H_2O$.

$\mathbf{1}(PF_6)$		$\mathbf{2}(ClO_4)_2 \cdot H_2O$	
Ru1–O1	2.087(2)	Ru1–N1	2.077(2)
Ru1–C21	1.874(3)	Ru1–N2	2.078(2)
Ru1–N1	2.126(3)	Ru1–O2	2.112(10)
Ru1–N2	2.074(3)	Ru1–C11	1.897(14)
Ru1–N3	2.054(3)	C11–O1	1.110(15)
Ru1–N4	2.070(3)		
O1–N5	1.297(4)		
O2–N5	1.219(4)		
O3–N5	1.220(5)		
C21–O4	1.128(4)		
O1–N5–O2	117.1(3)	Ru1–C11–O1	178.6(10)
O2–N5–O3	122.8(3)		
O1–N5–O3	120.1(3)		
Ru1–C21–O4	177.6(3)		

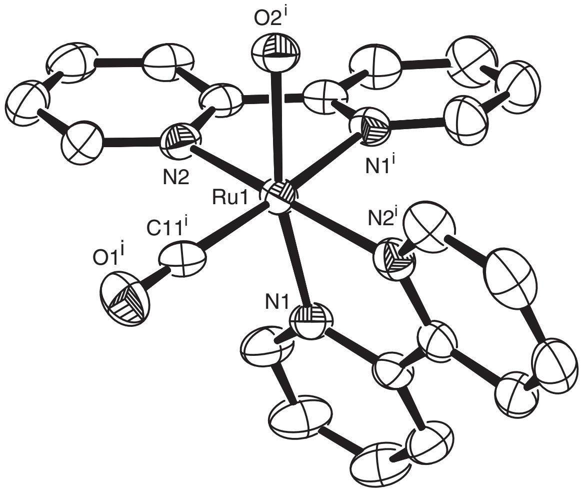


Figure 2. Molecular structure of $\mathbf{2}^{2+}$, with atom labels and 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. Only one component of the disordered CO and OH_2 groups is shown.

parameters of $\{Ru(bpy)_2\}^{2+}$ of $\mathbf{2}(ClO_4)_2$ are essentially the same as those of *cis*-$[Ru(bpy)_2(CO)L]^{n+}$ [8, 19].

3.2. *Electron transfer properties*

The results of electrochemical studies of the complexes in CH_3CN are summarized in table 3. The complexes exhibit typical behavior of a bis(bipyridine)ruthenium(II) complex with a pair of one-electron reduction peaks from −1.55 to −1.75 V and −1.73 to −1.96 V *versus* Fc^+/Fc. In the anodic scan, a one-electron oxidation wave was observed between 1.02 and 1.30 V, except for $\mathbf{2}(PF_6)_2$, which did not show any anodic waves within the potential window. The reduction potentials and pattern of waves in $\mathbf{2}(PF_6)_2$ agree with those of the corresponding acetonitrile complex ($[Ru(bpy)_2(CO)(CH_3CN)]^{2+}$) [21]. The aqua ligand is highly labile and seems to be replaced quickly by a solvent molecule (CH_3CN). On the other hand, it is surprising that weakly coordinating anion such as NO_3^- is not replaced by CH_3CN. In fact, NMR measurements suggest that anions bound to ruthenium remain bound in acetonitrile.

It is important to understand electron transfer processes of a metal complex. Lever's electrochemical parameters (E_L) have been widely used for predicting the redox potentials and sites of metal complexes. For $\{Ru(bpy)_2\}^{2+}$, the redox potential is given by equations (2) and (3), respectively [5, 22].

$$E_{ox}\ (V) = 0.97[\Sigma E_L] + 0.04 \tag{2}$$

$$E_{red}\ (V) = 0.25[\Sigma E_L] - 1.40 \tag{3}$$

Line (a) in figure 3 is a plot of the $Ru^{III/II}$ potential, which corresponds to equation (2); line (b) represents the $Ru^{II}(bpy)/Ru^{II}(bpy^-)$ couple, which corresponds to equation (3). As shown in figure 3, $\mathbf{1}(PF_6)$, $\mathbf{3}(PF_6)$, and $\mathbf{4}(PF_6)$ show good correlations for both equations, suggesting that the oxidation and reduction sites of the complexes can be assigned to ruthenium and bipyridine moieties, respectively. The plot of $\mathbf{2}(PF_6)_2$ using the E_L value of acetonitrile also fits line (b), which is defined by equation (3) [23]. Therefore, $\mathbf{2}(PF_6)_2$ can also be assigned to acetonitrile complex in CH_3CN on the basis of the sum of the complex's E_L values.

Although E_L parameters have been defined for more than 200 ligands, these do not include acetate. We evaluated the E_L parameter of acetate using the experimental data, estimated from equation (2), as −0.36, which is the lowest value among the

Table 3. Electrochemical data for the complexes.

Complex	$Ru^{III/II}$, $V^{a,b}$	$bpy^{0/-}$, $V^{a,b}$	$bpy^{-/2-}$, $V^{a,c}$
$\mathbf{1}(PF_6)$	1.26	−1.57	−1.80
$\mathbf{2}(PF_6)_2$		-1.55^c	−1.73
$\mathbf{3}(PF_6)$	1.12	−1.69	−1.91
$\mathbf{4}(PF_6)$	1.08	−1.70	−1.91
$\mathbf{5}(PF_6)$	0.99	−1.72	−1.96

[a] V *vs*. Fc^+/Fc in CH_3CN.
[b] $E_{1/2}$ values.
[c] E_{pc} values.

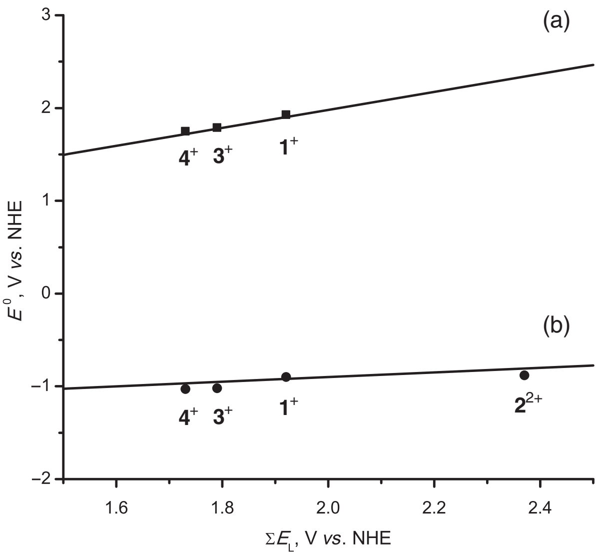


Figure 3. Redox potential *vs.* sum of the E_L values for the series complexes.

present ligands. The reduction potential calculated by equation (3) (–0.98 V) was similar to the experimental data for **5**(PF_6) (–1.05 V).

4. Conclusion

We developed a convenient synthetic method for producing *cis*-$[Ru(bpy)_2(CO)L]^{n+}$using various acids. In particular, a novel nitrato complex was prepared and characterized by X-ray structural analysis together with the corresponding aqua complex, which is a useful precursor. All the complexes were redox active and the redox properties of the complexes varied according to the σ- and π-donor abilities of the ligand L. This approach to the synthesis of *cis*-$[Ru(bpy)_2(CO)L]^{n+}$ complexes is broadly applicable and can increase the range of complexes that can be obtained in much higher yields than the conventional process provides.

Supplementary material

Further details on the crystal structure investigations of **1**(PF_6) and **2**$(ClO_4)_2 \cdot H_2O$ may be obtained from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Telephone: +44-1223-762-910, Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk/deposit], by quoting the depository number [CCDC-822117 for **1**(PF_6) and 822118 for **2**$(ClO_4)_2 \cdot H_2O$].

Acknowledgments

We thank Mr Hiroki Hoshi of Fukushima University for his technical assistance.

References

[1] (a) M. Dakkach, M.I. López, I. Romero, M. Rodríguez, A. Atlamsano, T. Parella, X. Fontrodona, A. Llobet. *Inorg. Chem.*, **49**, 7072 (2010); (b) Y. Matsubara, K. Koga, A. Kobayashi, H. Konno, K. Sakamoto, T. Morimoto, O. Ishitani. *J. Am. Chem. Soc.*, **132**, 10547 (2010); (c) T. Koizumi, K. Tanaka. *Angew. Chem., Int. Ed.*, **44**, 5891 (2005); (d) S.C. Weatherly, I.V. Yang, H.H. Thorp. *J. Am. Chem. Soc.*, **123**, 1236 (2001).

[2] (a) E. Fujita. *Coord. Chem. Rev.*, **185–186**, 373 (1999); (b) J.-M. Lehn, R. Ziessel. *J. Organomet. Chem.*, **382**, 157 (1990); (c) H. Ishida, K. Tanaka, T. Tanaka. *Organometallics*, **6**, 181 (1987).

[3] (a) H. Ishida, K. Tanaka, M. Morimoto, T. Tanaka. *Organometallics*, **5**, 724 (1986); (b) K. Tanaka, M. Morimoto, T. Tanaka. *Chem. Lett.*, **12**, 901 (1983); (c) D. Choudhury, D.J. Cole-Hamilton. *J. Chem. Soc., Dalton Trans.*, 1885 (1982); (d) D.J. Cole-Hamilton. *J. Chem. Soc., Chem. Commun.*, 1213 (1980).

[4] (a) J.M. Kelly, C.M. O'Connell, J.G. Vos. *J. Chem. Soc., Dalton Trans.*, 253 (1986); (b) J.M. Kelly, J.G. Vos. *Angew. Chem., Int. Ed. Engl.*, **21**, 628 (1982).

[5] (a) E.S. Dodsworth, A.A. Vlcek, A.B.P. Lever. *Inorg. Chem.*, **33**, 1045 (1994); (b) A.B.P. Lever. *Inorg. Chem.*, **29**, 1271 (1990).

[6] E.C. Johnson, B.P. Sullivan, D.J. Salmon, S.A. Adeyemi, T.J. Meyer. *Inorg. Chem.*, **17**, 2211 (1978).

[7] T. Gennett, D.F. Milner, M.J. Weaver. *J. Phys. Chem.*, **89**, 2787 (1985).

[8] D.H. Gibson, Y. Ding, R.L. Miller, B.A. Sleadd, M.S. Mashuta. *Polyhedron*, **18**, 1189 (1999).

[9] Rigaku. *PROCESS-AUTO*, Rigaku Corporation, Tokyo, Japan (1998).

[10] Rigaku. *CrystalStructure (Version 3.8), Crystal Structure Analysis Package*, Rigaku and Rigaku Americas, The Woodlands, Texas, USA (2007).

[11] G.M. Sheldrick. *SHELXL-97*, University of Göttingen, Göttingen, Germany (1997).

[12] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori, M. Camalli. *J. Appl. Cryst.*, **27**, 435 (1994).

[13] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla. *PATTY, The DIRDIF Program System, Technical Report of the Crystallography Laboratory*, University of Nijmegen, The Netherlands (1992).

[14] T. Higashi. *ABSCOR*, Rigaku Corporation, Tokyo, Japan (1995).

[15] (a) D. Ooyama, T. Tomon, K. Tsuge, K. Tanaka. *J. Organomet. Chem.*, **619**, 299 (2001); (b) R. Bhattacharyya, R.S. Drago, K.A. Abboud. *Inorg. Chem.*, **36**, 2913 (1997); (c) B.P. Sullivan, J.V. Caspar, S.R. Johnson, T.J. Meyer. *Organometallics*, **3**, 1241 (1984); (d) B.P. Sullivan, R.S. Smythe, E.M. Kober, T.J. Meyer. *J. Am. Chem. Soc.*, **104**, 4701 (1982); (e) B.P. Sullivan, D.J. Salmon, T.J. Meyer. *Inorg. Chem.*, **17**, 3334 (1978); (f) G. Sprintschnik, H.W. Sprintschnik, P.P. Kirsch, D.G. Whitten. *J. Am. Chem. Soc.*, **99**, 4967 (1977); (g) R. Colton, R.H. Farthing. *Aust. J. Chem.*, **24**, 903 (1971).

[16] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn, p. 254, Wiley-Interscience, New York (1986).

[17] A.C.G. Hotze, A.H. Velders, F. Ugozzoli, M. Biagini-Cingi, A.M. Manotti-Lanfredi, J.G. Haasnoot, J. Reedijk. *Inorg. Chem.*, **39**, 3838 (2000).

[18] M. Mukaida, Y. Sato, H. Kato, M. Mori, D. Ooyama, H. Nagao, F.S. Howell. *Bull. Chem. Soc. Jpn.*, **73**, 85 (2000).

[19] (a) K. Tanaka, D. Ooyama. *Coord. Chem. Rev.*, **226**, 211 (2002); (b) H. Tanaka, H. Nagao, K. Tanaka. *Inorg. Chem.*, **31**, 1971 (1992); (c) J.G. Haasnoot, W. Hinrichs, O. Weir, J.G. Vos. *Inorg. Chem.*, **25**, 4140 (1986); (d) J.M. Clear, J.M. Kelly, C.M. O'Connell, J.G. Vos, C.J. Cardin, S.R. Costa, A.J. Edwards. *J. Chem. Soc., Chem. Commun.*, 750 (1980).

[20] (a) H. Jude, P.S. White, D.M. Dattelbaum, R.C. Rocha. *Acta Crystallogr.*, **E64**, m1388 (2008); (b) M. Gama Sauaia, E. Tfouni, R.H. de Almeida Santos, M.T. do Prado Gambardella, M.P.F.M. Dal Lama, L. Fernando Guimarães, R. Santana da Silva. *Inorg. Chem. Commun.*, **6**, 864 (2003); (c) N.R. Weathers, R.C. Sadoski, B. Durham, A.W. Cordes. *Acta Crystallogr.*, **C53**, 1047 (1997).

[21] (a) D. Ooyama. *Inorg. Chem. Commun.*, **7**, 903 (2004); (b) J.R. Pugh, M.R.M. Bruce, B.P. Sullivan, T.J. Meyer. *Inorg. Chem.*, **30**, 86 (1991).

[22] For consistency with the literatures used for the ligand parameter E_L, data are shown here *versus* NHE.

[23] The E_L parameters of the aqua and the acetonitrile ligand are 0.04 and 0.34, respectively [5b].