

# Coordination ability of 1,10-phenanthroline-5,6-dione: syntheses and redox behavior of a Ru(II) complex with an *o*-quinoid moiety and of bridged Ru(II)–M(II) complexes (M = Pd, Pt)

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The synthesis and electrochemical properties of a Ru(II) complex having a redox active ligand, 1,10-phenanthroline-5,6-dione, [Ru(trpy)(PD-*N,N'*)Cl](PF<sub>6</sub>) (**[1]**(PF<sub>6</sub>)), and mixed-metal complexes [(PPh<sub>3</sub>)<sub>2</sub>Pd(*O,O'*-PD-*N,N'*)Ru(trpy)Cl](PF<sub>6</sub>) (**[2]**(PF<sub>6</sub>)) and [(PPh<sub>3</sub>)<sub>2</sub>Pt(*O,O'*-PD-*N,N'*)Ru(trpy)Cl](PF<sub>6</sub>) (**[3]**(PF<sub>6</sub>)) (trpy = 2,2':6',2''-terpyridine, PD = 1,10-phenanthroline-5,6-dione) are presented. The complex of **[1]**<sup>+</sup>, which was prepared by the reaction of Ru(trpy)(DMSO)Cl<sub>2</sub> with PD in hot ethanol, underwent two reversible reductions in the PD-based redox reactions. The quinoid moiety of **[1]**<sup>+</sup> was endowed with coordination ability to metals by one- and two-electron reduction of the complex. The mixed-metal complexes of **[2]**<sup>+</sup> and **[3]**<sup>+</sup> were synthesized by the reactions of **[1]**<sup>+</sup> with M(PPh<sub>3</sub>)<sub>4</sub> (M = Pd, Pt), and both complexes have the **[1]**<sup>+</sup> and M(II) frameworks.

## Introduction

Introduction of redox active ligands into transition metal ions often generates unique photochemical and electrochemical properties of the complexes. Especially, metal complexes with dioxolene ligands have been most intensively studied,<sup>1</sup> since dioxolene takes three oxidation states; quinone, semiquinone and catechol. A variety of metal–dioxolene complexes, particularly ruthenium complexes have been prepared by Pierpont *et al.*<sup>2</sup> and Lever *et al.*<sup>3</sup> Ruthenium–dioxolene complexes are featured by close energy levels between 3d orbitals of ruthenium and π\* orbitals of the ligand, resulting in delocalization of the electron between two orbitals, that is, charge distribution.<sup>2,3</sup> Recently, we have reported reversible conversion between a ruthenium–aqua complex with a dioxolene ligand,<sup>4</sup> and the analogous ruthenium–semiquinone oxyl radical complex, [Ru(trpy)(Bu<sub>2</sub>SQ)(O<sup>•−</sup>)] (Bu<sub>2</sub>SQ = 3,5-di-*tert*-butylbenzosemiquinone).<sup>5,6</sup> Such unusual conversion between aqua and oxyl radical groups is achieved by utilization of the low lying LUMO of ruthenium–dioxolene complexes.

Similarly to Ru–dioxolene complexes, the redox behavior of Ru(II) complexes with 1,10-phenanthroline-5,6-dione (PD) is also of interest since PD is linked to metals with not only a N–N chelate with a free *o*-quinoid group or an O–O chelate with two free diiminic nitrogen atoms but also a bridging mode with two different coordination sites.<sup>7–12</sup> Abruña and coworkers<sup>7</sup> and Steckhan and coworkers<sup>8</sup> showed participation of protons in the redox reactions of metal–PD complexes with the free *o*-quinoid group in protic media. Thus, the redox reactions of metal–PD complexes are regulated by proton concentrations in addition to the coordination modes of PD to metals.

In this paper, we report electrochemical properties of Ru(II) complexes with 1,10-phenanthroline-5,6-dione, [Ru(trpy)(PD-*N,N'*)Cl](PF<sub>6</sub>) (**[1]**(PF<sub>6</sub>)) and the mixed-metal complexes [(PPh<sub>3</sub>)<sub>2</sub>Pd(*O,O'*-PD-*N,N'*)Ru(trpy)Cl](PF<sub>6</sub>) (**[2]**(PF<sub>6</sub>)) and [(PPh<sub>3</sub>)<sub>2</sub>Pt(*O,O'*-PD-*N,N'*)Ru(trpy)Cl](PF<sub>6</sub>) (**[3]**(PF<sub>6</sub>)) (Fig. 1) in aprotic media.

## Results and discussion

### Synthesis, characterization and structure of **[1]**(PF<sub>6</sub>)

We adapted Ru(trpy)(DMSO)Cl<sub>2</sub> as the precursor for the preparation of a Ru(II)–PD complex with a free *o*-quinoid

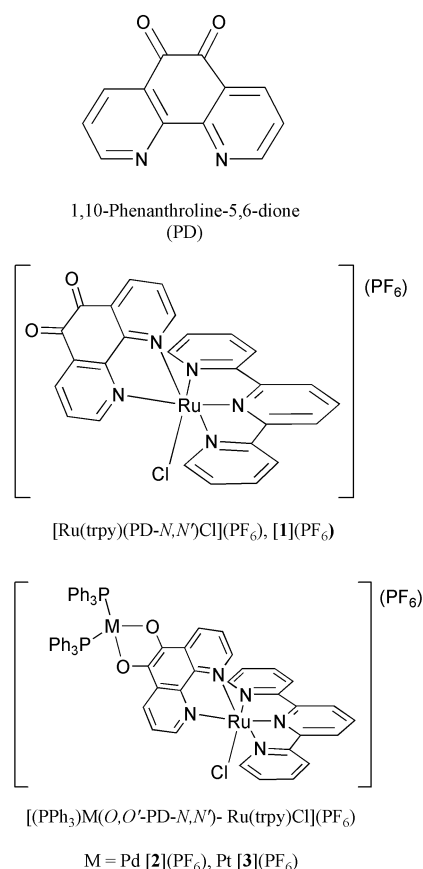


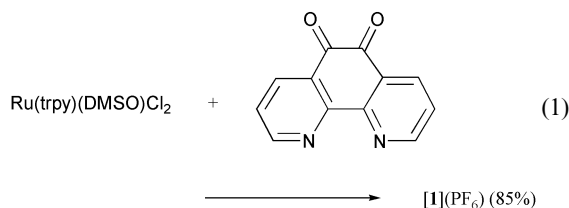
Fig. 1 1,10-Phenanthroline-5,6-dione and Ru(II) complexes in this study.

moiety. The reaction of Ru(trpy)(DMSO)Cl<sub>2</sub> with PD in hot ethanol and the subsequent exchange of counter anion from Cl<sup>−</sup> to PF<sub>6</sub><sup>−</sup> gave [Ru(trpy)(PD-*N,N'*)Cl](PF<sub>6</sub>) (**[1]**(PF<sub>6</sub>)) in a good yield (eqn. (1)).

The ESI MS spectrum of **[1]**(PF<sub>6</sub>) in CH<sub>3</sub>CN showed a main peak (*m/z* 580) with the isotope distribution pattern of ruthenium nuclei. The oxygen atoms of the PD ligand of **[1]**<sup>+</sup> were substituted with <sup>18</sup>O by treatment of **[1]**<sup>+</sup> with <sup>18</sup>OH<sub>2</sub>.<sup>13</sup> The IR spectra of **[1]**<sup>+</sup> and **[1\*]**<sup>+</sup> having <sup>18</sup>O substituted PD

**Table 1** Selected bond lengths (Å) and angles (°) for  $[1]^+$ 

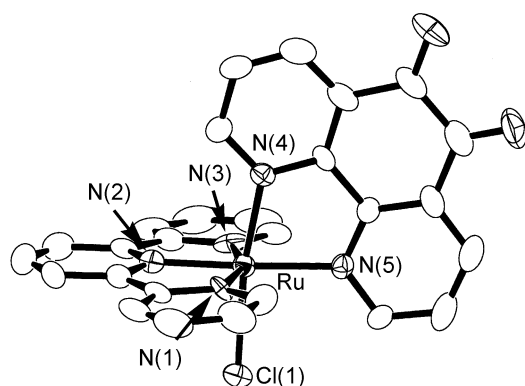
Ru(1)–N(1)	2.068(8)	Ru(1)–N(2)	1.963(8)
Ru(1)–N(3)	2.097(7)	Ru(1)–N(4)	2.035(7)
Ru(1)–N(5)	2.098(7)	Ru(1)–Cl(1)	2.395(2)
O(1)–C(26)	1.21(1)	O(1)–C(27)	1.20(1)
N(1)–Ru(1)–N(3)	159.1(3)	N(1)–Ru(1)–N(2)	79.6(4)
N(2)–Ru(1)–N(3)	79.5(3)	N(2)–Ru(1)–N(4)	99.2(3)
N(2)–Ru(1)–N(5)	177.5(3)	N(4)–Ru(1)–N(5)	78.3(3)
Cl(1)–Ru(1)–N(1)	89.2(2)	Cl(1)–Ru(1)–N(2)	88.9(2)
Cl(1)–Ru(1)–N(3)	89.6(2)	Cl(1)–Ru(1)–N(4)	171.9(2)
Cl(1)–Ru(1)–N(5)	93.6(2)		



displayed a strong band at 1696 and 1666  $\text{cm}^{-1}$ , respectively. These bands were assigned to the  $\nu(\text{C}=\text{O})$  band of an *o*-quinoid group of the PD ligand, since the observed isotopic shift was consistent with the value calculated by assuming a harmonic oscillator. This  $\nu(\text{C}=\text{O})$  band of  $[1]^+$  was close to those of  $[\text{Ru}(\text{bpy})_2(\text{PD})]^{2+}$  (1690  $\text{cm}^{-1}$ ) and  $[\text{Ru}(\text{PD})_3]^{2+}$  (1650 and 1700  $\text{cm}^{-1}$ ),<sup>7</sup> and slightly shifted to higher wavenumber compared with metal-free PD (1675  $\text{cm}^{-1}$ ).<sup>7</sup>

The  $^1\text{H}$  NMR spectrum of  $[1]^+$  in  $\text{CD}_3\text{CN}$  showed six signals for the PD ligand and six signals (total 11 protons) for the trpy ligand in the region of aromatic rings. The assignments of all signals were performed with H–H COSY experiments. The pattern of the signals was consistent with the structure of  $[1]^+$  determined by the X-ray diffraction study (*vide infra*). Thus, the molecular structure of  $[1]^+$  in the solid state was stably retained in solution. The UV-vis spectrum of  $[1]^+$  in  $\text{CH}_3\text{CN}$  displayed a characteristic strong absorption band at 491 nm, which was attributed to the charge transfer from the  $d\pi$  orbital of Ru(II) to the LUMO of PD.

Single crystals of  $[\text{Ru}(\text{trpy})(\text{PD}-N,N')\text{Cl}](\text{PF}_6)\cdot 3/2(\text{CH}_3\text{CN})$  were obtained by slow diffusion of toluene into a  $\text{CH}_3\text{CN}$  solution of  $[1](\text{PF}_6)$ . Fig. 2 shows the molecular structure of  $[1]^+$  with selected bond lengths and angles listed in Table 1. The coordination environment around the ruthenium atom is distorted octahedral with one chloride atom, three nitrogen atoms of trpy, and two nitrogen atoms of PD. Thus, the structural determination of  $[1]^+$  demonstrated the selective formation of the Ru–(N–N) bonding mode despite the fact that PD has an ability to bind M–(O–O). The coordination feature observed in the structure is essentially comparable to those found for Ru(II)–terpyridine–chloride complexes with a bidentate N–N ligand.<sup>14</sup> The bond lengths of the three Ru–N(trpy) are

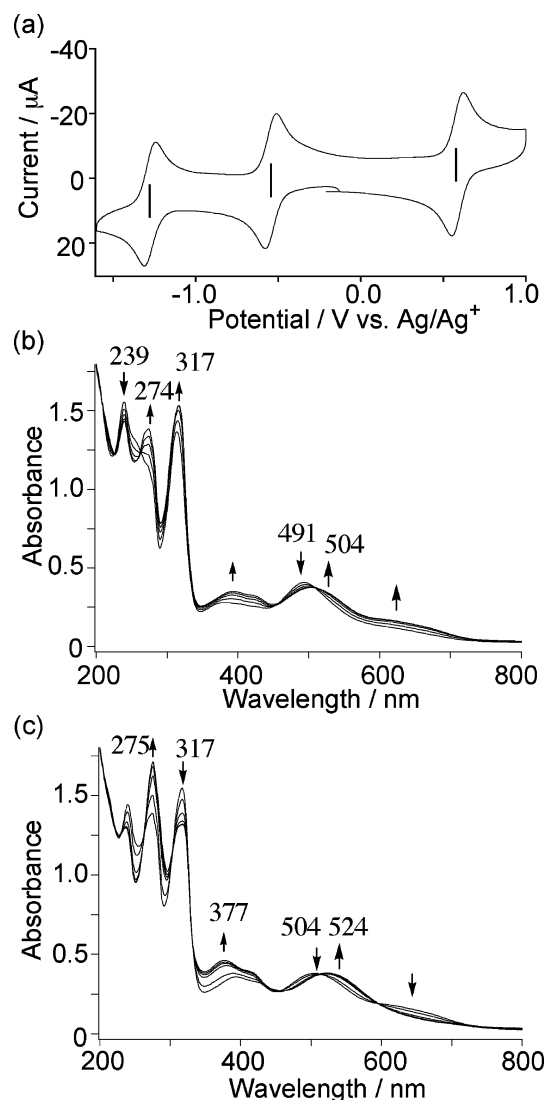
**Fig. 2** ORTEP drawing of  $[1]^+$ . Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

2.068(8), 1.963(8) and 2.097(7) Å. The shortening of the Ru–N(2) distance is a general feature observed in the structures of other Ru(II)–terpyridine complexes.<sup>14</sup> The bond distance of Ru–Cl (2.395(2) Å) is also in the range of those of Ru(II)–terpyridine–chloride complexes.<sup>14</sup> The bond lengths of Ru–N(PD) are 2.035(7) and 2.098(7) Å. The Ru–N bond length *trans* to the nitrogen atom of the central pyridyl ring is slightly longer than that *trans* to chloride atom. The average C=O bond length of the PD ligand (1.21 Å) is nearly the same as that of metal-free PD (1.209(3) Å),<sup>9</sup> and those of other metal–PD complexes.<sup>15</sup>

### Redox behavior of $[1]^+$ in $\text{CH}_3\text{CN}$

The redox behavior of  $[1](\text{PF}_6)$  was investigated by cyclic voltammetry and spectroelectrochemical measurements. Fig. 3 shows the cyclic voltammogram of  $[1](\text{PF}_6)$  in  $\text{CH}_3\text{CN}$  containing 0.1  $\text{mol dm}^{-3}$   $n\text{-Bu}_4\text{NPF}_6$ , together with the UV-vis spectral changes caused by the redox reactions of  $[1]^+$ . The redox potentials of  $[1](\text{PF}_6)$  as well as related compounds are listed in Table 2.

The CV of  $[1](\text{PF}_6)$  showed three reversible redox reactions of the  $[1]^+/[1]^{2+}$ ,  $[1]^+/[1]^0$  and  $[1]^0/[1]^-$  couples at  $E_{1/2} = +0.59$ ,  $-0.53$  and  $-1.27$  V vs.  $\text{Ag}/\text{Ag}^+$ , respectively (Fig. 3(a)). The  $[1]^+/[1]^0$  and  $[1]^0/[1]^-$  redox couples are associated with the

**Fig. 3** Cyclic voltammogram of  $[1](\text{PF}_6)$  (a) and UV-vis spectral changes during the electrochemical reduction of  $[1]^+$  in 0.1  $\text{mol dm}^{-3}$   $n\text{-Bu}_4\text{NPF}_6\text{-CH}_3\text{CN}$ . The first and the second reductions were conducted at  $-0.75$  V (b) and  $-1.4$  V (vs.  $\text{Ag}/\text{Ag}^+$ ) (c), respectively. The arrows in the figures indicate the direction of the changes of the spectra during the reduction of  $[1]^+$ .

**Table 2** Electrochemical data for the PD complexes

Complex	Solvent	Potential/V			Ref.
		Ligand	Ru(III/II)		
[Ru(trpy)(PD- <i>N,N'</i> )Cl](PF <sub>6</sub> ), [1](PF <sub>6</sub> ) <sup>a</sup>	CH <sub>3</sub> CN	-0.53, -1.27	+0.59	<sup>d</sup>	
[(PPh <sub>3</sub> ) <sub>2</sub> Pd( <i>O,O'</i> -PD- <i>N,N'</i> )Ru(trpy)Cl](PF <sub>6</sub> ), [2](PF <sub>6</sub> ) <sup>a</sup>	CH <sub>2</sub> Cl <sub>2</sub>	+0.09, +0.52 ( <i>E</i> <sub>pa</sub> )	+0.69	<sup>d</sup>	
[(PPh <sub>3</sub> ) <sub>2</sub> Pt( <i>O,O'</i> -PD- <i>N,N'</i> )Ru(trpy)Cl](PF <sub>6</sub> ), [3](PF <sub>6</sub> ) <sup>a</sup>	CH <sub>2</sub> Cl <sub>2</sub>	+0.25, +0.73 ( <i>E</i> <sub>pa</sub> )	–	<sup>d</sup>	
PD <sup>b</sup>	CH <sub>3</sub> CN	-0.45, -1.25	–	7	
[Ru(bpy) <sub>2</sub> (PD- <i>N,N'</i> )](PF <sub>6</sub> ) <sup>b</sup>	CH <sub>3</sub> CN	-0.16, -0.89	+1.35	7	
(PPh <sub>3</sub> ) <sub>2</sub> Pt( <i>O,O'</i> -PD) <sup>c</sup>	CH <sub>2</sub> Cl <sub>2</sub>	-0.207, +0.416 ( <i>E</i> <sub>pa</sub> )	–	10	
(PPh <sub>3</sub> ) <sub>2</sub> Pt( <i>O,O'</i> -PD- <i>N,N'</i> )PdCl <sub>2</sub> <sup>c</sup>	CH <sub>2</sub> Cl <sub>2</sub>	+0.170, +0.747 ( <i>E</i> <sub>pa</sub> )	–	10	
(PPh <sub>3</sub> ) <sub>2</sub> Pt( <i>O,O'</i> -PD- <i>N,N'</i> )Ru(PPh <sub>3</sub> )Cl <sub>2</sub> <sup>c</sup>	CH <sub>2</sub> Cl <sub>2</sub>	+0.199, +0.682 ( <i>E</i> <sub>pa</sub> )	-0.228	10	
(PPh <sub>3</sub> ) <sub>2</sub> Pt( <i>O,O'</i> -PD- <i>N,N'</i> )Ru(PPh <sub>3</sub> )Cl <sub>2</sub> <sup>c</sup>	CH <sub>2</sub> Cl <sub>2</sub>	+0.15, +0.63 ( <i>E</i> <sub>pa</sub> )	-0.24	11	
[(PPh <sub>3</sub> ) <sub>2</sub> Pt( <i>O,O'</i> -PD- <i>N,N'</i> )Ru(PPh <sub>3</sub> ) <sub>2</sub> (CO)Cl](PF <sub>6</sub> ) <sup>c</sup>	CH <sub>2</sub> Cl <sub>2</sub>	+0.15, +0.74	–	11	
[(PPh <sub>3</sub> ) <sub>2</sub> Pt( <i>O,O'</i> -PD- <i>N,N'</i> )Ru(PPh <sub>3</sub> ) <sub>2</sub> (CH <sub>3</sub> CN)Cl](PF <sub>6</sub> ) <sup>c</sup>	CH <sub>2</sub> Cl <sub>2</sub>	+0.05, +0.73	+0.91	11	
[(PPh <sub>3</sub> ) <sub>2</sub> Pt( <i>O,O'</i> -PD- <i>N,N'</i> )Ru(PPh <sub>3</sub> ) <sub>2</sub> Cl](PF <sub>6</sub> ) <sup>c</sup>	CH <sub>2</sub> Cl <sub>2</sub>	+0.09, +0.75	+0.56	11	

<sup>a</sup> Supporting electrolyte: 0.1 mol dm<sup>-3</sup> *n*-Bu<sub>4</sub>NPF<sub>6</sub>, potential referenced to Ag/Ag<sup>+</sup>. <sup>b</sup> Supporting electrolyte: 0.1 mol dm<sup>-3</sup> *n*-Bu<sub>4</sub>NClO<sub>4</sub>, potential referenced to SSCE. <sup>c</sup> Supporting electrolyte: 0.1 mol dm<sup>-3</sup> *n*-Bu<sub>4</sub>NClO<sub>4</sub>, potential referenced to Fc/Fc<sup>+</sup>. <sup>d</sup> This work.

ligand-based redox reactions of PD on the basis of the redox potentials of [Ru(trpy)<sub>2</sub>]<sup>2+</sup> and other Ru(II)–PD complexes.<sup>7,8</sup> The fact that the LUMO of [1]<sup>+</sup> is a π\* orbital of PD indicates the appearance of the MLCT band from Ru(II) to PD at longer wavelength compared with that of Ru(II) to trpy. The lowest energy MLCT band of [1]<sup>+</sup>, therefore, would be largely influenced by the PD-based redox reactions. Indeed, the controlled potential electrolysis of [1](PF<sub>6</sub>) at -0.75 V (vs. Ag/Ag<sup>+</sup>) resulted in a decrease of the MLCT band at 491 nm in intensity with time and an appearance of a new absorption band at 504 nm (Fig. 3(b)). The 504 nm MLCT band further moved to 524 nm under the controlled potential electrolysis of [1]<sup>+</sup> at -1.4 V (Fig. 3(c)). One- and two-electron reduction of [1]<sup>+</sup> caused the red shift of the MLCT band at 491 nm to 504 and 524 nm, respectively. Thus, the MLCT band from Ru(II) to PD shifted to longer wavelength with the progress of the reduction of the *o*-quinoid group of the PD ligand of [1]<sup>*n*</sup> (*n* = +1, 0, -1). The re-oxidation of the CH<sub>3</sub>CN solution of [1]<sup>0</sup> at -0.2 V completely regenerated the UV-vis spectrum of [1]<sup>+</sup>, while the similar oxidation of [1]<sup>-</sup> at the same potential did not fully recover [1]<sup>+</sup> in the UV-vis spectrum. This observation indicates that [1]<sup>0</sup> was stable in solution, but [1]<sup>-</sup> gradually decomposes on prolonged electrolysis in CH<sub>3</sub>CN.

Electrochemical oxidation of [1](PF<sub>6</sub>) at +0.7 V in CH<sub>3</sub>CN caused complete disappearance of the MLCT band at 491 nm, indicating that the [1]<sup>+/1</sup> redox couple at *E*<sub>1/2</sub> = +0.59 V is assigned to the metal-centered Ru<sup>II</sup>/Ru<sup>III</sup> redox couple. It is of note that the redox potential of the Ru<sup>II</sup>/Ru<sup>III</sup> couple of [1]<sup>+</sup> (+0.94 V vs. Ag/AgCl)† is close to those of [Ru(trpy)(bpy)Cl]<sup>+</sup> and [Ru(trpy)(phen)Cl]<sup>+</sup> (*E*<sub>1/2</sub> = +0.83 and +0.80 V, respectively vs. Ag/AgCl).<sup>16,17</sup> This result indicates that 3d-orbital energies of Ru(II) in [1]<sup>+</sup> are close to those of [Ru(trpy)(bpy)Cl]<sup>+</sup> and [Ru(trpy)(phen)Cl]<sup>+</sup>, despite that the N–N chelate PD of [1]<sup>+</sup> has the strongly electron-deficient *o*-quinoid moiety.

The solution IR spectra of [1](PF<sub>6</sub>) in CD<sub>3</sub>CN under electrolysis also afforded fundamental information of the electronic states of the PD ligand. A CD<sub>3</sub>CN solution containing [1](PF<sub>6</sub>) (5 mmol dm<sup>-3</sup>) and *n*-Bu<sub>4</sub>NPF<sub>6</sub> (0.1 mol dm<sup>-3</sup>) showed the ν(CO) band of the PD ligand at 1700 cm<sup>-1</sup>, which completely disappeared under the controlled potential electrolysis of the solution at -0.7 V. Instead a new absorption band emerged at 1625 cm<sup>-1</sup>. Further electrolysis of the solution at -1.5 V caused the disappearance of the 1625 cm<sup>-1</sup> band. The re-oxidation of the resultant solution did not recover the IR spectrum of [1]<sup>+</sup> completely because of the lability of [1]<sup>-</sup> as described above. Taking into account that the *o*-quinoid moiety in PD of [1]<sup>+</sup> is

reduced to the semiquinoid and catecholato forms under controlled potential electrolysis at -0.7 and -1.5 V, respectively, [1]<sup>0</sup> with the semiquinoid group is stable in CH<sub>3</sub>CN, while [1]<sup>-</sup> with the catecholato group is not stable on prolonged electrolysis.

#### Effect of Lewis acids in a CH<sub>3</sub>CN solution

The N–N chelate PD ligand of [1]<sup>+</sup> is electrochemically active and underwent stepwise reduction as described above (eqn. (2)). We also examined the redox behavior of [1]<sup>+</sup> in the presence of HClO<sub>4</sub> to elucidate the interaction between the quinoid group and protons in CH<sub>3</sub>CN, since protons participate in redox reactions of dioxolene molecules.

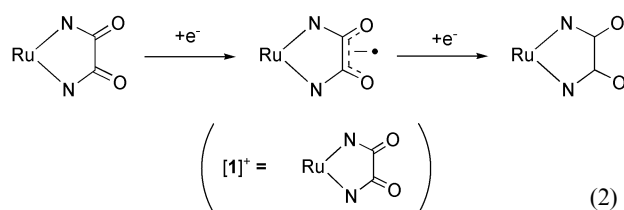


Fig. 4 shows the cyclic voltammograms of [1](PF<sub>6</sub>) in the presence of various amounts of a methanolic solution of HClO<sub>4</sub> (0.1 mol dm<sup>-3</sup>). The redox waves of the reversible [1]<sup>+/1</sup> redox couple at *E*<sub>1/2</sub> = -0.53 V (*E*<sub>pc</sub> = -0.57 V and *E*<sub>pa</sub> = -0.49 V) in CH<sub>3</sub>CN were not perturbed and those of the [1]<sup>0/1</sup> redox couple at *E*<sub>1/2</sub> = -1.27 V (*E*<sub>pc</sub> = -1.30 V and *E*<sub>pa</sub> = -1.23 V) slightly shifted to *E*<sub>1/2</sub> = -1.07 V (*E*<sub>pc</sub> = -1.11 V and *E*<sub>pa</sub> = -1.04 V) in the presence of a large excess of CH<sub>3</sub>OH. This observation is explained by the weak interaction between [1]<sup>-</sup> and CH<sub>3</sub>OH. The reversible [1]<sup>+/1</sup> and [1]<sup>0/1</sup> redox couples at *E*<sub>1/2</sub> = -0.53 V and *E*<sub>1/2</sub> = -1.27 V became pseudo-reversible upon an addition of 1 equiv. of HClO<sub>4</sub> to the solution, and two pairs of redox waves appeared at *E*<sub>pc</sub> = -0.04 V and *E*<sub>pa</sub> = +0.46 V, and *E*<sub>pc</sub> = -0.40 V and *E*<sub>pa</sub> = -0.22 V (cf. Fig. 4(a) and (b)). The change of the redox behavior of the [1]<sup>+/1</sup> and [1]<sup>0/1</sup> redox couples from reversible to pseudo-reversible in the presence of 1 equiv. of HClO<sub>4</sub> apparently results from an attack of H<sup>+</sup> to oxygen of PD of [1]<sup>0</sup>. Further addition of another 1 equiv. of HClO<sub>4</sub> to the solution caused merging of the two pairs of the pseudo-reversible redox couples, and a pair of cathodic and anodic waves emerged at *E*<sub>pc</sub> = -0.08 V and *E*<sub>pa</sub> = +0.46 V. Thus, [1]<sup>+</sup> underwent two-electron reduction at the potential in the presence of 2 equiv. of HClO<sub>4</sub> (eqn. (3)), where the cathodic peak potential of the [1]<sup>0/1</sup> redox couple anodically shifted by 1220 mV.

On the other hand, the redox waves of the [1]<sup>+/1</sup> redox couple (*E*<sub>1/2</sub> = +0.59 V) were not changed by the addition of 2 equiv. of

† Electrode potentials based on Ag/Ag<sup>+</sup> and Ag/AgCl reference electrodes are correlated with the following equation; *E*(Ag/AgCl) = *E*(Ag/Ag<sup>+</sup>) + 0.35 V.



(30 protons) for  $\text{PPh}_3$ . The assignments of all signals were also performed with H–H COSY experiments. The splitting pattern of the signals derived from PD and trpy was similar to that of  $[1]^+$ , suggesting that the structure of  $[2]^+$  and  $[3]^+$  in solution was similar to that of  $[1]^+$ . The UV-vis spectra of  $[2]^+$  and  $[3]^+$  showed strong absorption bands at 528 and 537 nm, respectively. The MLCT bands of  $[1]^+$ ,  $[1]^0$  and  $[1]^-$  in  $\text{CH}_3\text{CN}$  were observed at 491, 504 and 524 nm, the latter of which is quite close to those of  $[2]^+$  and  $[3]^+$ . Both  $[2]^+$  and  $[3]^+$ , therefore, contain  $[1]^-$  with the catecholato moiety and  $\text{Pd}(\text{II})(\text{PPh}_3)_2$  and  $\text{Pt}(\text{II})(\text{PPh}_3)_2$  frameworks, respectively.

The cyclic voltammogram of  $[2](\text{PF}_6)$  in  $\text{CH}_2\text{Cl}_2$  is shown in Fig. 6. The redox potentials of  $[2]^+$  and  $[3]^+$ , and related complexes are also listed in Table 2. Complex  $[2]^+$  displayed the  $[2]^+/[2]^{2+}$ ,  $[2]^{2+}/[2]^{3+}$ , and  $[2]^{3+}/[2]^{4+}$  redox processes ( $E_{1/2} = +0.09$ ,  $+0.52$ , and  $+0.69$  V, respectively) in the potential range between 0 and  $+1.0$  V vs.  $\text{Ag}/\text{Ag}^+$ . The  $[2]^+/[2]^{2+}$  and  $[2]^{2+}/[2]^{3+}$  redox couples are associated with the bridging PD-based redox reactions. The pseudo-reversible  $[2]^{2+}/[2]^{3+}$  couple at  $E_{pc} = +0.52$  V is ascribed to partial dissociation of the  $\text{Pd}(\text{PPh}_3)_2$  fragment from  $[2]^{3+}$  in the CV time scale because of the extremely low binding ability of the *o*-quinoid form in  $[2]^{3+}$  to  $\text{Pd}(\text{II})$  (eqn. (6)).

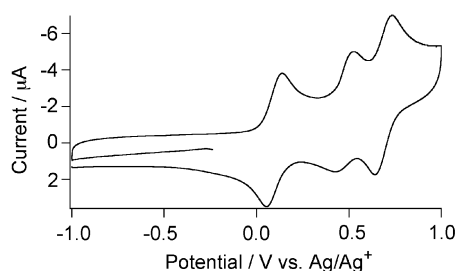
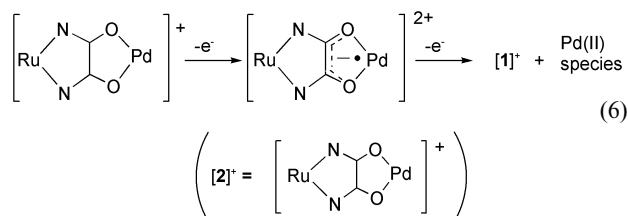


Fig. 6 Cyclic voltammogram of  $[2](\text{PF}_6)$  in  $0.1 \text{ mol dm}^{-3} n\text{-Bu}_4\text{NPF}_6\text{-CH}_2\text{Cl}_2$ .



The  $[2]^{3+}/[2]^{4+}$  redox couple at  $E_{1/2} = +0.69$  V is assigned to the metal-centered  $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$  redox reaction. When the electrode potential was maintained at  $+1.0$  V for several minutes, the  $[1]^{2+}/[1]^+$  and  $[1]^+/[1]^0$  redox couples were detected in the subsequent potential sweep from  $+1.0$  V to  $-1.0$  V. Thus, similarly to  $[2]^{3+}$ ,  $[2]^{4+}$  also was partly degraded to  $[1]^{2+}$  and  $\text{Pd}(\text{II})$  species in the CV time scale. The Pd complex of  $[2]^+$  underwent irreversible reduction at  $E_{pc} = -1.44$  V. The subsequent anodic potential sweep displayed the anodic peaks of the  $[1]^-/[1]^0$  and  $[1]^0/[1]^+$  redox couples due to dissociation of the  $\text{Pd}(0)$  fragment from  $[2]^0$ .

The redox behavior of the Pt complex of  $[3]^+$  was similar to that of  $[2]^+$ . The redox potential of the  $[3]^+/[3]^{2+}$  couple appeared at 160 mV more positive than that of the  $[2]^+/[2]^{2+}$  couple. The difference is ascribed to the acidity difference between  $\text{Pd}(\text{II})$  and  $\text{Pt}(\text{II})$ . In fact,  $[3]^+$  did not undergo reduction up to  $-1.8$  V indicating that the O–O chelation of  $\text{Pt}(\text{II})$  in  $[3]^+$  was more stable than that of the  $\text{Pd}(\text{II})$  complex.

## Conclusion

Novel  $\text{Ru}(\text{II})$  complexes with a redox active ligand, 1,10-phenanthroline-5,6-dione,  $[\text{Ru}(\text{trpy})(\text{PD-}N,N')\text{Cl}](\text{PF}_6)$  ( $[1](\text{PF}_6)$ ),  $[(\text{PPh}_3)_2\text{Pd}(\text{O},\text{O}'\text{-PD-}N,N')\text{Ru}(\text{trpy})\text{Cl}](\text{PF}_6)$  ( $[2](\text{PF}_6)$ ) and

$[(\text{PPh}_3)_2\text{Pt}(\text{O},\text{O}'\text{-PD-}N,N')\text{Ru}(\text{trpy})\text{Cl}](\text{PF}_6)$  ( $[3](\text{PF}_6)$ ) were synthesized. The complex of  $[1]^+$  displayed two reversible redox couples due to the reduction of the PD ligand in  $\text{CH}_3\text{CN}$ . The quinoid group of  $[1]^+$  was endowed with an ability of coordination to Lewis acids by one- and two-electron reduction of the complex. Indeed, the redox behavior of  $[2](\text{PF}_6)$  and  $[3](\text{PF}_6)$  revealed that both complexes have the  $[1]^-$  and  $\text{M}(\text{II})$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) frameworks and two-electron oxidation of  $[2]^+$  and  $[3]^+$  resulted in degradation to  $[1]^+$  and the  $\text{M}(\text{II})$  species.

## Experimental

### Materials

2,2':6',6''-Terpyridine (trpy) was purchased from Aldrich. Other agents and solvents were purchased by Wako and used as received. Silica gel (Wakogel C-300HG) was used for column chromatography. 1,10-Phenanthroline-5,6-dione (PD)<sup>18</sup> and  $\text{Ru}(\text{trpy})(\text{DMSO})\text{Cl}_2$ <sup>19</sup> were prepared according to the previous reports.

### Synthesis of the complexes

**$[\text{Ru}(\text{trpy})(\text{PD-}N,N')\text{Cl}](\text{PF}_6)$  ( $[1](\text{PF}_6)$ ).**  $\text{Ru}(\text{trpy})(\text{DMSO})\text{Cl}_2$  (200 mg, 0.41 mmol) and PD (96 mg, 0.42 mmol) were added to ethanol ( $75 \text{ cm}^3$ ) and the reaction mixture was gently heated at  $75^\circ\text{C}$  for 8 h under  $\text{N}_2$ . After the solvent was evaporated under reduced pressure, the residue was dissolved in water ( $30 \text{ cm}^3$ ) followed by addition of a saturated aqueous solution of  $\text{KPF}_6$ . The brown precipitate was filtered off, washed with water and partially dried under reduced pressure. The crude complex was dissolved in  $\text{CH}_3\text{CN}$  ( $40 \text{ cm}^3$ ) and crystallized by addition of  $\text{Et}_2\text{O}$ . The brown crystals thus formed were collected by filtration, washed with  $\text{Et}_2\text{O}$  and dried under reduced pressure. Yield 252 mg (85%). Found: C, 44.59; H, 2.55; N, 10.10.  $\text{C}_{27}\text{H}_{17}\text{N}_5\text{O}_2\text{ClPF}_6\text{Ru}$  requires C, 44.73; H, 2.36; N, 9.66%. NMR:  $\delta_{\text{H}}$  (500 MHz;  $\text{CD}_3\text{CN}$ ; standard  $\text{SiMe}_4$ ) 10.37 (1H, d,  $J(\text{HH})$  4 Hz, PD), 8.70 (1H, d,  $J(\text{HH})$  7.8 Hz, PD), 8.51 (2H, d,  $J(\text{HH})$  8.5 Hz, trpy), 8.39 (2H, d,  $J(\text{HH})$  7.5 Hz, trpy), 8.14 (3H, t + t + d, PD and trpy), 7.91 (2H, t,  $J(\text{HH})$  8.0 Hz, trpy), 7.74 (2H, d,  $J(\text{HH})$  5.5 Hz, trpy), 7.62 (2H, d,  $J(\text{HH})$  5.5 Hz, PD), 7.29 (2H, t, trpy) and 7.15 (1H, t,  $J(\text{HH})$  6.8 Hz, PD). UV-vis:  $\lambda_{\text{max}}/\text{nm}$  ( $\text{CH}_3\text{CN}$ ) 491 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  12000), 371 (6750), 312 (34600) and 239 (45800). IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr) 1696 (C=O). ESI MS:  $m/z$  ( $\text{CH}_3\text{CN}$ ) 580 ( $[\text{M} - \text{PF}_6]^+$ ).

**$[(\text{PPh}_3)_2\text{Pd}(\text{O},\text{O}'\text{-PD-}N,N')\text{Ru}(\text{trpy})\text{Cl}](\text{PF}_6)$  ( $[2](\text{PF}_6)$ ).**  $[1](\text{PF}_6)$  (36 mg, 0.05 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  ( $15 \text{ cm}^3$ ) and the solution was deaerated by bubbling  $\text{N}_2$  for 30 min. To the solution,  $\text{Pd}(\text{PPh}_3)_4$  (62 mg, 0.05 mmol) was added under  $\text{N}_2$  and the reaction mixture was stirred at room temperature for 8 h under  $\text{N}_2$ . After the solvent was removed with a rotary evaporator, the residue was dissolved in a small amount of  $\text{CH}_2\text{Cl}_2$  followed by loading a silica gel column ( $2 \times 10 \text{ cm}$ ). The second band eluted with 1%  $\text{MeOH-CH}_2\text{Cl}_2$  was collected and the solvent was removed. The resulting precipitate was recrystallized by diffusion of diethyl ether into the  $\text{CH}_2\text{Cl}_2$  solution. The dark reddish-purple crystals thus formed were collected by filtration, washed with  $\text{Et}_2\text{O}$  and dried under reduced pressure. Yield 58 mg (85%). Found: C, 53.35; H, 3.69; N, 4.76.  $\text{C}_{63}\text{H}_{47}\text{N}_5\text{O}_2\text{ClPF}_6\text{PtRu}\cdot 4\text{H}_2\text{O}$  requires C, 52.99; H, 3.88; N, 4.90. NMR:  $\delta_{\text{H}}$  (500 MHz;  $\text{CD}_2\text{Cl}_2$ ; standard  $\text{SiMe}_4$ ) 9.95 (1H, d,  $J(\text{HH})$  5.0 Hz, PD), 8.32 (1H, d,  $J(\text{HH})$  8.0 Hz, trpy), 8.19 (2H, d,  $J(\text{HH})$  8.0 Hz, trpy), 8.00 (1H, t,  $J(\text{HH})$  8.5 Hz, trpy), 7.97 (2H, d,  $J(\text{HH})$  8.5 Hz, PD), 7.74 (2H, t + t, PD and trpy), 7.63–7.21 (33H, m, trpy, PD and  $\text{PPh}_3$ ), 7.08 (2H, t,  $J(\text{HH})$  5.0 Hz, trpy), 6.90 (1H, d,  $J(\text{HH})$  5.5 Hz, PD) and 6.71 (1H, t,  $J(\text{HH})$  7.0 Hz, PD). UV-vis:  $\lambda_{\text{max}}/\text{nm}$  ( $\text{CH}_2\text{Cl}_2$ ) 528 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  9970), 418 (11500), 318 (47700) and 283 (74800). ESI MS:  $m/z$  ( $\text{CH}_2\text{Cl}_2$ ) 1211 ( $[\text{M} - \text{PF}_6]^+$ ).

**[PPh<sub>3</sub>]<sub>2</sub>Pt(O,O'-PD-N,N')Ru(trpy)Cl](PF<sub>6</sub>) ([3](PF<sub>6</sub>)).** The Pt(II) complex of [3](PF<sub>6</sub>) was prepared by same method of [2](PF<sub>6</sub>) by using Pt(PPh<sub>3</sub>)<sub>4</sub> instead of Pd(PPh<sub>3</sub>)<sub>4</sub>. Yield 65 mg (89%). Found: C, 49.64; H, 3.46; N, 4.41. C<sub>63</sub>H<sub>47</sub>N<sub>5</sub>O<sub>2</sub>ClPF<sub>6</sub>PtRu·4H<sub>2</sub>O requires C, 49.89; H, 3.66; N, 4.62. NMR: δ<sub>H</sub> (500 MHz; CD<sub>2</sub>Cl<sub>2</sub>; standard SiMe<sub>4</sub>) 9.93 (1H, d, *J*(HH) 4.5 Hz, PD), 8.25 (1H, d, *J*(HH) 8.5 Hz, PD), 8.16 (2H, d, *J*(HH) 8.0 Hz, trpy), 7.93 (2H, t, *J*(HH) 8.0 Hz, trpy), 7.90 (2H, d, *J*(HH) 7.0 Hz, PD), 7.72 (3H, t, *J*(HH) 6.5 Hz, PD), 7.67 (2H, t, *J*(HH) 7.5 Hz, trpy), 7.5–7.12 (33H, m, trpy, PD and PPh<sub>3</sub>), 6.99 (2H, t, *J*(HH) 5.0 Hz, trpy), 6.90 (1H, d, *J*(HH) 5.5 Hz, PD) and 6.69 (1H, t, *J*(HH) 6.5 Hz, PD). UV-vis: λ<sub>max</sub>/nm (CH<sub>2</sub>Cl<sub>2</sub>) 537 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 10700), 408 (12500), 318 (40700) and 277 (67700). ESI MS: *m/z* (CH<sub>2</sub>Cl<sub>2</sub>) 1299 ([M – PF<sub>6</sub>]<sup>+</sup>).

### Physical measurements

<sup>1</sup>H NMR and H–H COSY experiments were performed with a JEOL GX-500 spectrometer. Infrared spectra were recorded on a Shimadzu FT IR-8100 spectrophotometer. UV-vis spectra were measured with a Shimadzu UV-3100PC UV-vis-NIR scanning spectrophotometer. ESI MS spectra were measured with a Shimadzu LCMS-2010 liquid chromatograph mass spectrometer. Elemental analyses were carried out at Research Center for Molecular-scale Nanoscience, Institute for Molecular Science. Cyclic voltammetry was performed with an ALS/Chi model 660 electrochemical analyzer. Cyclic voltammograms were recorded at a scan rate of 100 mV s<sup>-1</sup> at room temperature. The working and the counter electrodes were a glassy carbon and a Pt wire, respectively. The reference electrode was an Ag/AgNO<sub>3</sub> (0.01 mol dm<sup>-3</sup>), against which the half-wave potential of Fc/Fc<sup>+</sup> (Fc = ferrocene) was +0.06 V. The sample solutions in CH<sub>3</sub>CN or CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 mol dm<sup>-3</sup> *n*-Bu<sub>4</sub>NPF<sub>6</sub> were deoxygenated by an N<sub>2</sub> stream. Spectroelectrochemical UV-vis measurements were performed with a thin-layer electrode cell with a platinum minigrid working electrode sandwiched between two glass side of an optical cell (path length 0.5 mm) by using a Hokuto Denko HA-501 potentiostat and a Shimadzu UV-3100PC UV-vis-NIR scanning spectrophotometer. Spectroelectrochemical IR measurements in solution were performed with a thin-layer electrode cell with an Au mesh working electrode sandwiched between two KBr plates,<sup>20</sup> by using a Hokuto Denko HA-501 potentiostat and a Shimadzu FT IR-8100 spectrophotometer.

### X-Ray crystallography

Data for [1](PF<sub>6</sub>)·3/2CH<sub>3</sub>CN were collected on a Rigaku/MSC Mercury CCD diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71070$  Å) at 173 K, and processed using Crystal Clear.<sup>21</sup> The structure was solved by a heavy-atom Patterson method (PATTY),<sup>22</sup> and expanded using Fourier Techniques (DIRDIF94).<sup>23</sup> The structure was refined by full-matrix least-square refinement on *F*<sup>2</sup>. All non hydrogen atoms, except one solvent molecule, were refined anisotropically. All hydrogen atoms, with the exception of those of crystal solvents, were located on the calculated positions and not refined. All calculations were performed using the teXsan crystallographic software package.<sup>24</sup> Crystallographic data for [1](PF<sub>6</sub>)·3/2CH<sub>3</sub>CN: C<sub>30</sub>H<sub>21.5</sub>ClF<sub>6</sub>N<sub>6.5</sub>O<sub>2</sub>PRu, *M* = 786.53, *T* = 173 K, orthorhombic, space group *Pbca* (no. 61), *a* = 13.585(5), *b* = 15.898(6), *c* = 30.27(1) Å, *U* = 6538(4) Å<sup>3</sup>, *Z* = 8,  $\mu$ (Mo-K $\alpha$ ) = 6.84 cm<sup>-1</sup>, 7447 reflections measured, *R*<sub>1</sub> = 0.078, *wR*<sub>2</sub> = 0.190 (*I* > 3 $\sigma$ (*I*)).

CCDC reference number 209006.

See <http://www.rsc.org/suppdata/dt/b3/b304912d/> for crystallographic data in CIF or other electronic format.

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