Synthesis and Electrochemical Oxidation of Bridged Ruthenium/Platinum Complexes of 1,10-Phenanthroline-5,6-diolate

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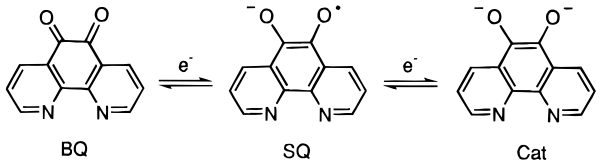
Introduction

Recent interest in the electrooxidation of methanol at Pt/Ru anodes[1] has led us to explore the synthesis and electrochemical properties of heterobimetallic Pt/Ru complexes.[2] Our initial studies involved compounds with bis(phosphine) and phosphido bridges. Efforts to vary the metal−metal interaction led us to consider rigid, aromatic bridging ligands. The aromatic systems would provide bridges that mediate metal−metal interaction through the π-system while the redox properties of the ligands could allow stabilization of a variety of oxidation states.

Pierpont has recently reported using the bridging ligand 1,10-phenanthroline-5,6-diolate (PhD)[3] to construct binuclear complexes such as $(PPh_3)_2Pt(O,O'\text{-PhD-}N,N')Ru(PPh_3)_2Cl_2$ (**1**).[4] Complex **1** exhibits two ligand waves [BQ/SQ and SQ/Cat (shown in eq 1 for the uncomplexed PhD ligand)] and the Ru-



(1)

(III/II) couple. Both O-bound and N-bound monometallic complexes of the PhD ligand have been reported,[5] providing a basis for comparison of the bimetallic species. Additional relevant studies address the interconversion of quinone, semiquinone, and catecholate forms of the ligand during redox processes of the complexes.[6] Since the metal and quinone orbital energy levels are generally quite close, the electronic structure of complexes can be sensitive to the nature of the ancillary ligands.[6e] This suggested the possibility of fine-tuning the redox properties of such complexes by ligand substitution.

These characteristics led us to investigate derivatives of $(PPh_3)_2Pt(O,O'\text{-PhD-}N,N')Ru(PPh_3)_2Cl_2$ (**1**). Abstraction of one of the chloride ligands of **1** in the presence of various two-electron donor ligands yields a series of cationic Pt/Ru binuclear complexes where the metal orbital energy levels shift with respect to the ligand π-system as a function of the electron demand of the new ligands. This effect can be observed in the changing positions of the Ru(III/II) waves *vs* the BQ/SQ and SQ/Cat ligand redox potentials.

Results and Discussion

Synthesis of Ru/Pt Complexes by Substitution Reactions of 1. Thallium(I) hexafluorophosphate reacts rapidly with **1** in a variety of solvents to abstract a chloride ligand from the Ru(II) center, providing a route to cationic derivatives. Treatment of a DME solution of **1** with excess $TlPF_6$ under an atmosphere of CO yielded the cationic substitution product **2** (Chart 1), which bears a highly π-acidic carbonyl ligand. The presence of a single carbonyl ligand in **2** is indicated by the infrared spectrum which shows one strong absorption at 1961 cm^{-1}. The ^1H NMR spectrum reveals splitting of the PhD protons and, thus, lowering of the symmetry from C_{2v} in **1** to C_s as expected upon substitution of a single chloride ligand. The ^{31}P NMR spectrum exhibits a Ru−P singlet and two doublets for the platinum phosphines (J_{PP} = 23 Hz), verifying substitution for chloride in the ruthenium equatorial plane. Electrospray mass spectrometry of **2** in acetonitrile solution shows the molecular cation, $[\mathbf{2} - PF_6^-]^+$, providing further evidence in support of the structural assignment for **2**.

The acetonitrile analogue, **3**, may be obtained from reaction of **1** and $TlPF_6$ in acetonitrile. The ^1H and ^{31}P NMR spectra display the same splitting patterns as observed for **2**, with **3** displaying an additional proton resonance at 2.27 ppm corresponding to the methyl group of the acetonitrile ligand. The infrared spectrum of a KBr pellet of **3** shows a very weak absorption at 2266 cm^{-1} assigned as ν_{CN} for the nitrile, and electrospray mass spectrometry data revealed a signal corresponding to the cation, $[\mathbf{3} - PF_6^-]^+$. Formation of **3**-d_3 in quantitative yield may also be followed by ^1H NMR when CD_3CN is used as the reaction solvent.

Use of pyridine as the reaction solvent in an attempt to form the pyridine analogue of **2** and **3** resulted in NMR evidence for displacement of a ruthenium-bound PPh_3 and formation of a disubstituted derivative containing two inequivalent pyridine ligands. This product is likely to be the *cis*-bis(pyridine) species, $[(PPh_3)_2Pt(O,O'\text{-PhD-}N,N')Ru(PPh_3)Cl(py)_2]PF_6$, as similar results were obtained when excess 3,5-lutidine was added to a THF solution of **1** and $TlPF_6$ to yield the *cis*-bis(3,5-lutidine) complex, **4**. ^1H NMR spectroscopy reveals the resonances of two inequivalent lutidine ligands in **4**, and ^{31}P NMR confirms the additional substitution of one phosphine for lutidine at the ruthenium center. Elemental analysis of the compound is in good agreement with the molecular formulation for **4**. Attempts to obtain a monosubstituted lutidine derivative by addition of only 1 equiv of the amine to solutions of **1** and $TlPF_6$ resulted in loss of PPh_3 and formation of the disubstituted product in low yield. The observed displacement of phosphine by pyridine and lutidine is consistent with the known lability of ruthenium(II)-bound PPh_3 in the presence of pyridine.[7]

Electrochemistry of Heterobimetallic Complexes 1−4. The cyclic voltammogram of **1** was originally described by Pierpont.[4] Oxidation reveals a reversible Ru(III/II) couple ($E_{1/2}$

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(3) Abbreviations: PhD = 1,10-phenanthroline-5,6-dione; BQ = benzoquinone; SQ = semiquinone; Cat = catecholate; Lut = 3,5-lutidine.

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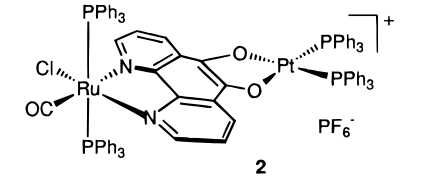
Chart 1



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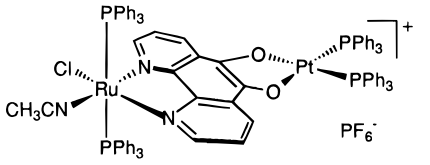

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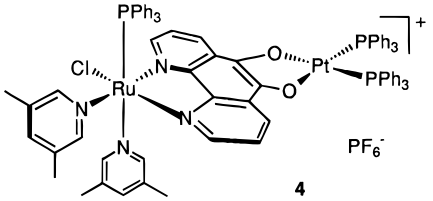

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Table 1. Summary of Redox Potentials for **1**−**4**[a]

compd	SQ/BQ[b]	Cat/SQ	Ru(III/II)	ref
1	1.18	0.70	0.27	3
1	1.37	0.73	0.31	*c*
2	1.29	0.71	*d*	*e*
3	1.28	0.60	1.46	*e*
4	1.30	0.64	1.11	*e*

[a] All values reported as V *vs* NHE. [b] Irreversible oxidation; potential given as E_{pa}. [c] Values observed under our experimental conditions. [d] Not observed. [e] This work.

= 0.27 V *vs* NHE) followed by two successive one-electron oxidations of the PhD ligand. The first ligand-centered oxidation (Cat/SQ) is fully reversible at $E_{1/2}$ = 0.70 V *vs* NHE, whereas removal of a second electron from the ligand (SQ/BQ; E_{pa} = 1.18 V *vs* NHE) displays some irreversibility. This is likely to be due to dissociation of the bimetallic complex at the Pt−O bonds in the highly oxidized species. The positive shift of the SQ/BQ anodic peak of **1** under our conditions (Table 1) may be attributed to greater resistivity in our experimental setup. Cyclic voltammograms of the cationic derivatives **2**−**4** show SQ/Cat and BQ/SQ redox potentials which vary little from those of **1**. Fairly constant SQ/Cat and BQ/SQ potentials are expected, as varying the second metal from Pd to Ru to Rh in a series of heterobimetallic Pt−PhD derivatives has little influence on the ligand-centered waves.[4] However, **2**−**4** do display the positive shift of the Ru(III/II) couple expected for the more electropositive ruthenium metal centers (Table 1). At +1.46 V, the ruthenium couple for the acetonitrile derivative, **3**, lies positive of both ligand-centered oxidations and represents a dramatic 1150 mV shift from that of its neutral precursor, **1**. The highly positive value corroborates with previously known cationic Ru(II)−acetonitrile complexes[11] and reflects the heightened electron deficiency of the cation as well as the relative π-acidity of the nitrile ligand. In the disubstituted lutidine derivative, **4**, the metal-centered oxidation is between the two ligand-centered waves. The more modest 800 mV shift for the Ru(III/II) couple (+1.11 V) is reflective of the additional electron density at the ruthenium center in the amine complex as compared to the acetonitrile derivative. No ruthenium couple was observed for the carbonyl derivative, **2**, consistent with the very high π-acidity of the CO ligand which shifts the ruthenium couple beyond the limitations of the solvent/electrolyte window.

Conclusion

The ruthenium center of **1** undergoes substitution reactions in the presence of $TlPF_6$ with carbon monoxide, acetonitrile, pyridine, and lutidine to yield the corresponding cationic Ru(II)/Pt(II) binuclear complexes **2**−**4**. The redox potentials for the Ru(III/II) couples of **2**−**4** shift positive relative to that of **1** and reflect the electron demand of the ligand framework around ruthenium. The position of the Ru(III/II) wave with respect to the ligand waves of **1**−**4** is dependent on the nature of the substituting ligand L, ranging from negative of the Cat/SQ couple in the neutral **1** to positive of the SQ/BQ couple in the cationic complexes **2** and **3**. Thus, the site of the first oxidation (metal *vs* ligand) can be controlled by the choice of ligands on the Ru center.

Experimental Section

General Methods. Standard Schlenk/vacuum techniques were used throughout. Hexane, petroleum ether, chloroform, acetonitrile, and methylene chloride were distilled from CaH_2. Diethyl ether, THF, toluene, and dimethoxyethane were distilled from Na/Ph_2CO. All NMR solvents were degassed via freeze−pump−thaw cycles and stored over molecular sieves. All other starting materials were purchased in reagent grade and used without further purification. The elemental analysis of **4** was performed at the University of Florida. Electrochemical experiments were performed under nitrogen using an EG&G PAR Model 263A potentiostat/galvanostat. Cyclic voltammograms were recorded at room temperature in a standard three-electrode cell with a glassy carbon working electrode. All potentials are reported *vs* NHE and were determined in 0.1 M TBAH/CH_2Cl_2. Ferrocene ($E_{1/2}$ = 0.55 V *vs* NHE) was used in situ as a calibration standard. $(PPh_3)_2Pt(O,O'$-PhD-$N,N')Ru(PPh_3)_2Cl_2$,[4] $Pt(PPh_3)_4$,[9] and $Ru(PPh_3)_4Cl_2$[10] were synthesized as reported in the literature.

$(PPh_3)_2Pt(O,O'$-PhD-$N,N')Ru(PPh_3)_2Cl_2$ (1). Spectroscopic data are as follows: ^{1}H NMR (CD_2Cl_2) δ 8.43 (d, 2H$_\alpha$, J_{HH} = 7.3 Hz), 7.8−6.92 (m, 62 H, PPh_3/others), 6.32 (dd, 2H, J_{HH} = 8.24 Hz, 2.9 Hz); ^{13}C NMR (CD_2Cl_2) δ 150.8 (s), 150.0 (d), 143.2 (s), 135.0 (t), 134.4 (t), 134.1 (s), 133.8 (s), 133.6 (s), 133.3 (s), 132.1 (s), 131.4 (s), 129.2 (t), 128.7 (m), 128.4 (m), 127.2 (s), 124.4 (s), 124.1 (s), 122.1 (m); ^{31}P NMR (CD_2Cl_2) δ 26.4 (s, RuP_2), 9.86 (s, J_{PPt} = 3586 Hz, PtP_2).

$[(PPh_3)_2Pt(O,O'$-PhD-$N,N')Ru(PPh_3)_2Cl(CO)]PF_6$ (2). CO was bubbled for 20 min through a DME slurry of **1** (0.55 g, 0.34 mmol) at room temperature. With continued CO bubbling, a DME solution of $TlPF_6$ (0.26 g, 0.74 mmol) was cannulated into the slurry. CO bubbling was continued for a total of 150 min, and then the reaction mixture was stirred under Ar for another 18 h. The mixture was cannula-filtered to give a dark red filtrate from which the product was obtained in 20% isolated yield by concentration of the DME solution and addition of diethyl ether: ^{1}H NMR (CD_2Cl_2) δ 8.41 (d, 1H PhD, J_{HH} = 5.1 Hz), 7.70−7.00 (m, 63H, PPh_3 + PhD), 6.82 (q, 1H, PhD), 6.28 (q, 1H PhD); ^{13}C NMR ($CDCl_3$) δ 204.3 (s), 152.9 (s), 149.9 (m), 147.2 (s), 138.7 (s), 138.2 (s), 135.8 (d), 134.3 (t), 132.5 (s), 131.5 (s), 131.2 (s), 131.1 (s), 130.9 (s), 130.6 (s), 130.0 (s), 129.4 (s), 129.3 (m), 128.6 (s), 128.4 (s), 124.2 (s), 123.5 (s); ^{31}P NMR (CD_2Cl_2) δ 27.9 (s, RuP_2), 10.2 (d, PtP, J_{PP} = 23 Hz, J_{PPt} = 3654 Hz), 8.3 (d, PtP, J_{PP} = 23 Hz, J_{PPt} = 3621 Hz), −144.1 (septet, PF_6); IR (CH_2Cl_2) ν_{CO} = 1961 cm^{-1}; MS (electrospray; CH_3CN) *m*/*z* 1619.2, [**2** − PF_6]$^+$; CV (CH_2Cl_2/TBAH) $E_{1/2}$(Cat/SQ) = 0.71 V, E_{pa}(SQ/BQ) = 1.29 V.

$[(PPh_3)_2Pt(O,O'$-PhD-$N,N')Ru(PPh_3)_2Cl(CH_3CN)]PF_6$ (3). CH_3CN (1 mL) was added to a test tube containing **1** (34 mg, 0.022 mmol) and $TlPF_6$ (11 mg, 0.034 mmol). The mixture was stirred at room temperature for 1 h and then chilled and filtered through Celite to give a red filtrate. The solvent was removed *in vacuo* to give a red solid. The product may be isolated in particulate form by dissolving it in

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minimal THF followed by precipitation with hexane (91% isolated yield): ^{1}H NMR (CD_2Cl_2) δ 8.57 (d, 1H, PhD, J_{HH} = 4.4 Hz), 7.70−7.00 (m, 63H PPh_3 + PhD), 6.78 (q, 1H, PhD), 6.37 (q, 1H, PhD), 2.27 (s, 3H, CH_3CN); ^{13}C NMR ($CDCl_3$) 152.3 (m), 150.2 (m), 149.9 (s), 148.5 (s), 141.0 (s), 140.2 (s), 134.7 (m), 133.8 (s), 133.4 (m), 132.6 (m), 132.9 (m), 131.2 (m), 130.9 (s), 130.6 (s), 130.0 (s), 129.0 (s), 128.5 (m), 128.1 (d), 127.7 (m), 127.3 (s), 126.2 (s), 124.3 (m), 123.9 (m), 123.5 (s), 121.5 (s), 4.2 (s); ^{31}P NMR (CD_2Cl_2) δ 27.4 (s, RuP_2), 10.9 (d, PtP_A, J_{PP} = 23.7 Hz, J_{PPt} = 3621 Hz), 8.0 (d, PtP_B, J_{PP} = 23.7 Hz, J_{PPt} = 3581 Hz), −144.0 (septet, PF_6^-, J_{PF} = 711 Hz); IR (KBr) ν_{CN} = 2266 cm^{-1}; MS (electrospray; CH_3CN) *m/z* 1632.0, [**3** − PF_6]$^+$; CV (CH_2Cl_2/TBAH) $E_{1/2}$(Ru(III/II)) = 1.46 V, $E_{1/2}$(Cat/SQ) = 0.60 V, E_{pa}(SQ/BQ) = 1.28 V.

[(PPh_3)$_2$Pt(*O*,*O*′-PhD-*N*,*N*′)Ru(PPh_3)Cl(lutidine)$_2$]PF_6 (4). THF (15 mL) was added to a Schlenk flask containing **1** (0.33 g, 0.20 mmol) and $TlPF_6$ (71 mg, 0.20 mmol). The solution was stirred at room temperature for 1 d, and then 3,5-lutidine (230 μL, 2.0 mmol) was added to the flask. The solution was stirred at room temperature for a second day, and then the THF was removed *in vacuo* to give a red solid. The sample was redissolved in 3 mL of CH_2Cl_2, chilled on ice, and cannula-filtered to give a red filtrate. The CH_2Cl_2 was removed *in vacuo* to yield the red solid product (30% isolated yield): ^{1}H NMR (CD_2Cl_2) δ 9.20 (d, 1 H, PhD, J_{HH} = 4.80 Hz), 8.21 (s, 2H, lutidine), 7.95 (d, 1H, PhD, J_{HH} = 4.80 Hz), 7.87 (s, 2H, lutidine), 7.70−6.80 (m, 61 H), 2.12 (s, 6 H, CH_3), 1.92 (s, 6H, CH_3); ^{13}C NMR (CD_2Cl_2) δ 155.3 (s), 150.0 (s), 148.9 (s), 145.7 (s), 143.6 (s), 141.9 (s), 138.9 (s), 138.2 (s), 135.0 (m), 134.4 (s), 133.8 (m), 133.2 (s), 132.6 (s), 131.6 (s), 129.5 (s), 128.6 (m), 127.8 (d), 127.2 (s), 125.5 (m), 124.7 (m), 122.5 (d), 18 (s). ^{31}P NMR (CD_2Cl_2) δ 48.7 (s, RuP_2), 10.4 (d, PtP, J_{PP} = 23.8 Hz, J_{PPt} = 3650 Hz), 8.1 (d, PtP, J_{PP} = 23.8 Hz, J_{PPt} = 3570 Hz), −144.1 (septet, PF_6, J_{PF} = 710 Hz); MS (electrospray; CH_3CN) *m/z* 1477, [**4** − PF_6 − 1 lutidine + CH_3CN]$^+$. Anal. Calcd for $C_{80}H_{69}N_4O_2P_4ClF_6PtRu$: C, 56.93; H, 4.12; N, 3.32. Found: C, 56.99; H, 3.76; N, 2.97. CV (CH_2Cl_2/TBAH): $E_{1/2}$(Ru(III/II)) = 1.11 V, $E_{1/2}$(Cat/SQ) = 0.64 V, E_{pa}(SQ/BQ) = 1.30 V.

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