

Synthesis and Electrochemical and Spectroscopic Properties of a Series of Binuclear and Trinuclear Ruthenium and Palladium Complexes Based on a New Bridging Ligand Containing Terpyridyl and Catechol Binding Sites

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Received June 3, 1994[⊗]

The ligand 4'-(3,4-dimethoxyphenyl)-2,2':6',2''-terpyridine (L^2), containing a terpyridyl binding site and a masked catechol binding site, was prepared by a standard Kröhnke-type synthesis. From this the complexes $[\text{Ru}(\text{terpy})(L^2)][\text{PF}_6]_2$ (**1**) and $[\text{Ru}(L^2)_2][\text{PF}_6]_2$ (**2**), containing one and two dimethoxyphenyl substituents, were prepared: demethylation with BBR_3 afforded $[\text{Ru}(\text{terpy})(\text{H}_2\text{L}^1)][\text{PF}_6]_2$ (**3**) and $[\text{Ru}(\text{H}_2\text{L}^1)_2][\text{PF}_6]_2$ (**4**), respectively, which have one or two free catechol binding sites pendant from the $[\text{Ru}(\text{terpy})_2]^{2+}$ core. Binuclear complexes (based on **3**) and trinuclear complexes (based on **4**) were then prepared by attachment of other metal fragments at the catechol sites. In $[\text{Ru}(\text{terpy})(\mu\text{-L}^1)\text{Ru}(\text{bipy})_2][\text{PF}_6]_3$ (**5**) and $[\text{Ru}(\mu\text{-L}^1)_2\{\text{Ru}(\text{bipy})_2\}_2][\text{PF}_6]_4$ (**6**) the pendant $\{\text{Ru}(\text{bipy})_2(\text{O-O})\}^{n+}$ sites (O-O = catecholate, $n = 0$; *o*-benzosemiquinone, $n = 1$; *o*-benzoquinone, $n = 2$) are redox active and may be reversibly interconverted between the three oxidation levels. In $[\text{Ru}(\text{terpy})(\mu\text{-L}^1)\text{Pd}(\text{bipy})][\text{PF}_6]_2$ (**7**), $[\text{Ru}(\mu\text{-L}^1)_2\{\text{Pd}(\text{bipy})\}_2][\text{PF}_6]_2$ (**8**), $[\text{Ru}(\text{terpy})(\mu\text{-L}^1)\text{Pd}(4,4'\text{-tBu}_2\text{-bipy})][\text{PF}_6]_2$ (**9**), and $[\text{Ru}(\mu\text{-L}^1)_2\{\text{Pd}(4,4'\text{-tBu}_2\text{-bipy})\}_2][\text{PF}_6]_2$ (**10**) the pendant $\{\text{Pd}(\text{bipy})(\text{catecholate})\}$ fragments are known to be photocatalysts for production of $^1\text{O}_2$ in their own right. Electrochemical and UV/vis studies were performed on all complexes and consistently indicate the presence of interactions between the components in **5–10**. The EPR spectrum of **6** (which contains two semiquinone radicals) shows that the two spins are coupled by an exchange interaction, despite being well-separated and attached to mutually perpendicular terpyridyl fragments on either side of a central Ru(II) ion.

Introduction

There is currently considerable interest in synthesizing polynuclear assemblies in which a photoactive polypyridyl–ruthenium(II) complex¹ is covalently attached to potential quenching groups.^{2–4} There are two principal reasons for this: (i) electron-transfer³ or energy-transfer⁴ from the excited state of the ruthenium “antenna” to the quencher is intramolecular rather than intermolecular; (ii) spatial control of the separation and relative orientations of the interacting fragments may be achieved, allowing examination of the efficacy of intramolecular energy- and electron-transfer processes while steric parameters such as chromophore–quencher separation and relative spatial arrangement are varied in a controllable and predictable way.^{3b,d,h,4a–c,4m}

The archetypal ruthenium photosensitizer is $[\text{Ru}(\text{bipy})_3]^{2+}$ ($\text{bipy} = 2,2'\text{-bipyridine}$),¹ and many examples exist of bipyridine derivatives functionalized at the periphery which thereby permit the photochemically active core to be covalently incorporated into “supramolecular” species.^{2–5} This is, in principle, a straightforward process when there is only one peripheral binding site, i.e. in complexes of the type $[\text{Ru}(\text{bipy})_2(\text{bipy-X})]^{2+}$ where X is a peripheral functional group. If it is desired to

[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1995.

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have more than one attachment—as might be necessary, for example, in linear oligomers or dendrimers—then the tris-chelate geometry of the $[\text{Ru}(\text{bipy-X})_3]^{2+}$ -type core is problematic for three reasons. First, it is chiral, and if several such groups are incorporated into a molecule, then a mixture of a large number of (generally inseparable) stereoisomers will occur.^{4f} This problem was recently addressed by the separation of such diastereomeric mixtures^{6a} and by the use of resolved mononuclear complexes as building blocks,^{6b} but so far these methods have only been applied to binuclear complexes. Second, there is the additional possibility of *facial* and *meridional* geometric isomers with asymmetric bidentate ligands in a tris-chelate complex. Use of such complexes as building blocks therefore may lead to a mixture of geometric isomers of polynuclear species; even if the starting material is known to be a pure *fac* or *mer* isomer, the irregular disposition of peripheral binding sites is not appealing as a starting point for polynuclear arrays. The third problem is simply that monosubstituted bipy derivatives are not always easy to synthesize because of their asymmetry.

These considerations have led to functionalized $[\text{Ru}(\text{terpy-4'-X})_2]^{2+}$ fragments (terpy-X is a 4'-substituted derivative of 2,2':6',2''-terpyridine) receiving attention as building blocks for polynuclear arrays.⁷⁻¹¹ It is not chiral; the two peripheral sites are disposed in a simple linear arrangement about the ruthenium(II) core; and (symmetrical) 4'-substituted terpyridines are simple to prepare.⁸ Such $[\text{Ru}(\text{terpy-4'-X})_2]^{2+}$ fragments have been incorporated into photochemical triads,⁹ linear oligomers,^{4b,10} and dendrimers.¹¹ The major disadvantage of a $[\text{Ru}(\text{terpy})_2]^{2+}$ core compared to $[\text{Ru}(\text{bipy})_3]^{2+}$ is that its photochemical characteristics are not so desirable, as it has a much shorter excited-state lifetime and does not luminesce in fluid solution.^{1,12} However recent work showed that, with appropriate substituents on the ligands, derivatives of $[\text{Ru}(\text{terpy})_2]^{2+}$ may be luminescent in fluid solution and have photophysical properties which begin to approach those of $[\text{Ru}(\text{bipy})_3]^{2+}$.¹³ Complexes of the type $[\text{Ru}(\text{terpy-4'-X})_2]^{2+}$ can therefore, with appropriate fine-tuning, become building blocks with ideal structural and photophysical properties.

This paper describes the preparation of Ru(II) complexes of

the new bridging ligand 4'-(3,4-dihydroxyphenyl)-2,2':6',2''-terpyridine (H_2L^1), which contains a catechol binding site attached to the periphery of a terpy ligand. The complexes $[(\text{terpy})\text{Ru}(\text{H}_2\text{L}^1)]^{2+}$ (**3**) and $[\text{Ru}(\text{H}_2\text{L}^1)_2]^{2+}$ (**4**) were used as building blocks in the assembly of bi- and trinuclear species by attachment of additional metal fragments at the peripheral catecholate sites. The catechol group is an appealing peripheral binding site for several reasons. First, it forms stable, well-characterized complexes with many transition and main-group metals.¹⁴ Second, by using the templating effects of complexes such as $[\text{M}(\text{cat})_3]^{3-}$ ($\text{M} = \text{Fe}, \text{Cr}$; ^{14c} cat = dianion of catechol), it should be possible to assemble several photoactive polypyridyl-ruthenium chromophores around a single central metal ion for examination of the antenna effect.² Third, catechol is redox-active and undergoes reversible catecholate/semiquinone/quinone interconversions in many metal complexes,^{14,15} allowing the possibility of the energy- or electron-transfer characteristics of polynuclear complexes being switchable according to the redox level of the peripheral fragments. A preliminary communication describing part of this work has been published.^{7b}

Experimental Section

General Details. ¹H NMR spectra were recorded on JEOL GX270 and GX400 spectrometers. Electron-impact (EI) and fast-atom-bombardment (FAB) mass spectra were measured on a VG-Autospec, in the latter case with 3-nitrobenzyl alcohol as matrix. EPR spectra were recorded on a Bruker ESP-300E spectrometer either at room temperature or at 77 K using a Dewar insert in the sample chamber. Electronic spectra were recorded on a Perkin-Elmer Lambda 2 spectrophotometer. Electrochemical experiments were performed using an EG&G PAR model 273A potentiostat. A standard three-electrode configuration was used, with platinum-bead working and auxiliary electrodes and a saturated calomel electrode (SCE) reference. Ferrocene was added at the end of each experiment as an internal standard; all potentials are quoted vs the ferrocene/ferrocenium couple (Fc/Fc^+). The solvent was CH_3CN , purified by distillation from CaH_2 , containing 0.1 mol dm^{-3} $[\text{NBu}_4][\text{PF}_6]$. Organic starting materials were purchased from Aldrich and used as received; $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and $\text{Na}_2\text{PdCl}_4 \cdot x\text{H}_2\text{O}$ were purchased from Johnson Matthey. 2,2':6',2''-Terpyridine,¹⁶ $[\text{Ru}(\text{bipy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$,¹⁷ $[\text{Ru}(\text{terpy})\text{Cl}_3]$,¹⁸ $[\text{Pd}(\text{bipy})\text{Cl}_2]$,¹⁹ 4,4'-di-*tert*-butyl-2,2'-bipyridine (4,4'-^tBu₂-bipy),²⁰ and 1-[2-oxo-2-(2-pyridinyl)ethyl]pyridinium iodide (**B**)²¹ were prepared according to published procedures. $[\text{Pd}(4,4'\text{-}^t\text{Bu}_2\text{-bipy})_2\text{Cl}_2]$ was prepared according to the method used for $[\text{Pd}(\text{bipy})\text{Cl}_2]$.¹⁹

Preparations. 1-(2-Pyridyl)-3-(3,4-dimethoxyphenyl)propen-1-one (A). To a solution of veratraldehyde (5.55 g, 33.1 mmol) and NaOH (1.8 g, 45 mmol) in EtOH/H₂O (50 cm³, 1:1) was added a solution of 2-acetylpyridine (4.00 g, 33.1 mmol) in EtOH (5 cm³) dropwise over 10 min with vigorous stirring. A thick yellow solid precipitated 10 min after addition was complete. The mixture was

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stirred for a further 40 min; then the yellow solid was collected by filtration, washed with aqueous ethanol, and dried *in vacuo*. Crude yield: 90%. The crude product is sufficiently pure for use in the next step; a sample for analysis was recrystallized from ethanol. IR, CH_2Cl_2 : $\nu(\text{CO}) = 1668 \text{ cm}^{-1}$. $^1\text{H NMR}$, CDCl_3 , δ (ppm): 3.94 (3 H, s, OCH_3), 3.97 (3 H, s, OCH_3), 6.90 (1 H, d, $J = 8.1 \text{ Hz}$, phenyl H^5), 7.30 (2 H, m, phenyl H^2 and H^6), 7.49 (1 H, ddd, $J = 7.5, 4.8, 1.3 \text{ Hz}$, pyridyl H^5), 7.88 (1 H, td, $J = 7.7, 1.8 \text{ Hz}$, pyridyl H^4), 7.92 (1 H, d, $J = 15.9 \text{ Hz}$, $\text{CH}=\text{CH}$), 8.16 (1 H, d, $J = 15.9$, $\text{CH}=\text{CH}$), 8.20 (1 H, dt, $J = 7.9, 1.1 \text{ Hz}$, pyridyl H^3), 8.75 (1 H, ddd, $J = 4.8, 1.8, 0.9 \text{ Hz}$, pyridyl H^6). EI MS: $m/z = 269$ (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_3$: C, 71.4; H, 5.2; N, 5.6. Found: C, 71.6; H, 5.1; N, 5.9.

4'-(3,4-Dimethoxyphenyl)-2,2':6,2''-terpyridine (L^2). A mixture of enone **A** (7.07 g, 26.3 mmol), pyridinium iodide salt **B** (8.56 g, 26.3 mmol), and ammonium acetate (20 g, large excess) in methanol (200 cm^3) was heated to reflux with stirring for 8 h affording a dark solution. After concentration *in vacuo*, the resulting slurry was partitioned between CH_2Cl_2 and water, and the organic layer was separated from the mixture. Further extractions of the aqueous phase with CH_2Cl_2 were performed; the combined organic extracts were then dried (MgSO_4), and the solvent was removed *in vacuo*. The resulting dark oil was purified by column chromatography on Al_2O_3 with CH_2Cl_2 as eluant. Fractions containing the product were identified by the appearance of an intense purple color when a drop of the solution was added to a methanolic solution of FeSO_4 ; these fractions were combined and evaporated to dryness, and the resulting orange solid was recrystallized from $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ to give pale yellow crystals of pure L^2 in 30–40% yield. $^1\text{H NMR}$, CDCl_3 , δ (ppm): 3.93 (3 H, s, OCH_3), 4.03 (3 H, s, OCH_3), 7.00 (1 H, d, $J = 8.4 \text{ Hz}$, phenyl H^5), 7.36 (2 H, ddd, $J = 7.5, 4.8, 1.3 \text{ Hz}$, pyridyl H^5), 7.40 (1 H, d, $J = 2.0 \text{ Hz}$, phenyl H^2), 7.51 (1 H, dd, $J = 8.4, 2.0 \text{ Hz}$), 7.89 (2 H, td, $J = 7.8, 1.8 \text{ Hz}$, pyridyl H^4), 8.67 (4 H, m, pyridyl H^3 and H^6), 8.73 (2 H, m, pyridyl H^6). EI MS: $m/z = 369$ (M^+). Anal. Calcd for $\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}_2\cdot\text{H}_2\text{O}$: C, 71.3; H, 5.4; N, 10.9. Found: C, 71.4; H, 5.5; N, 10.8.

[Ru(terpy)(L^2)] $[\text{PF}_6]_2$ (1**)**. A mixture of $[\text{Ru}(\text{terpy})\text{Cl}_3]$ (0.44 g, 1 mmol) and L^2 (0.37 g, 1 mmol) in ethylene glycol (50 cm^3) was heated to reflux for 2 h to give a deep orange solution. After cooling, the product was precipitated by addition of excess aqueous KPF_6 , filtered off, washed with water, and dried. Purification was with a preparative-scale TLC plate (alumina) using 3:2 acetonitrile/toluene as eluant. Yield: 83%. $^1\text{H NMR}$, CD_3CN , δ (ppm): 3.99 (3 H, s, OCH_3), 4.09 (3 H, s, OCH_3), 7.18 (4 H, m, H^5 of terpy and H^5 of L^2), 7.29 (1 H, d, $J = 8.3 \text{ Hz}$, phenyl H^5), 7.35 (2 H, m, H^3 of terpy), 7.44 (2 H, m, H^3 of L^2), 7.73 (1 H, d, $J = 2.2 \text{ Hz}$, phenyl H^2), 7.82 (1 H, dd, $J = 8.3, 2.2 \text{ Hz}$, phenyl H^6), 7.94 (4 H, m, H^4 of terpy and H^4 of L^2), 8.41 (1 H, t, $J = 8.2 \text{ Hz}$, H^4 of terpy), 8.50 (2 H, d, $J = 8.2 \text{ Hz}$, H^3 of terpy), 8.67 (2 H, d, $J = 7.6 \text{ Hz}$, H^6 of L^2), 8.76 (2 H, d, $J = 8.7 \text{ Hz}$, H^6 of terpy), 8.97 (2 H, s, H^3 of L^2).

[Ru(L^2) $_2$] $[\text{PF}_6]_2$ (2**)**. A mixture of commercial $\text{RuCl}_3\cdot x\text{H}_2\text{O}$ (assay 41.88% Ru: 0.12 g, 0.5 mmol) and L^2 (0.37 g, 1 mmol) in ethylene glycol (30 cm^3) was heated to reflux for 1 h. Addition of excess aqueous KPF_6 precipitated the complex which was filtered off, washed with water, and dried. TLC (alumina, MeCN/PhMe (1:1)) showed the material to be pure. Yield: 90%. $^1\text{H NMR}$, CD_3CN , δ (ppm): 3.99 (6 H, s, OCH_3), 4.10 (6 H, s, OCH_3), 7.19 (4 H, td, $J = 7.2, 1.5 \text{ Hz}$, pyridyl H^5), 7.30 (2 H, d, $J = 8.6$, phenyl H^5), 7.44 (4 H, d, $J = 5.7 \text{ Hz}$, pyridyl H^3), 7.73 (2 H, d, $J = 2.0 \text{ Hz}$, phenyl H^2), 7.82 (2 H, dd, $J = 8.6, 2.0 \text{ Hz}$, phenyl H^6), 7.95 (4 H, td, $J = 7.9, 1.5 \text{ Hz}$, pyridyl H^4), 8.68 (4 H, d, $J = 8.3 \text{ Hz}$, pyridyl H^6), 8.98 (4 H, s, pyridyl H^3).

[Ru(terpy)(H_2L^1)] $[\text{PF}_6]_2$ (3**) and **[Ru(H_2L^1) $_2$] $[\text{PF}_6]_2$ (**4**)**. These were prepared by demethylation of the parent complexes (**1** and **2**, respectively) with BBr_3 .²² To a solution of **1** or **2** in dry CH_2Cl_2 under N_2 at -78°C was added by syringe BBr_3 (10 equiv). The stirred solution was allowed to warm to -10°C over 2 h, and the reaction was then quenched by addition of water. After removal of the CH_2Cl_2 *in vacuo*, the complex precipitated on addition of KPF_6 and was filtered off, washed with water, and dried. Complete demethylation was verified by the absence of the OMe singlets at around 4 ppm in the $^1\text{H NMR}$ spectrum. Yields: 70–90%. $^1\text{H NMR}$ of **3**, CD_3CN , δ (ppm): 7.18 (4 H, m, H^5 of terpy and H^5 of L^1), 7.33 (2 H, d, $J = 4.7 \text{ Hz}$, H^3**

of terpy), 7.44 (2 H, d, $J = 4.7 \text{ Hz}$, H^3 of L^1), 7.56 (1 H, broad m, phenyl H^5), 7.65 (1 H, dd, $J = 8.2, 2.2 \text{ Hz}$, phenyl H^6), 7.72 (1 H, d, $J = 2.2 \text{ Hz}$, phenyl H^2), 7.93 (4 H, m, H^4 of terpy and H^4 of L^1), 8.41 (1 H, t, $J = 8.3 \text{ Hz}$, H^4 of terpy), 8.50 (2 H, d, $J = 8.3 \text{ Hz}$, H^3 of terpy), 8.63 (2 H, d, $J = 7.5 \text{ Hz}$, H^6 of L^1), 8.77 (2 H, d, $J = 8.4 \text{ Hz}$, H^6 of terpy), 8.93 (2 H, s, H^3 of L^1). $^1\text{H NMR}$ of **4**, CD_3CN , δ (ppm): 7.17 (6 H, m, pyridyl H^5 and phenyl H^5), 7.42 (4 H, d, $J = 4.8 \text{ Hz}$, pyridyl H^3), 7.64 (2 H, dd, $J = 8.3, 2.2 \text{ Hz}$, phenyl H^6), 7.72 (2 H, d, $J = 2.2 \text{ Hz}$, phenyl H^2), 7.93 (4 H, td, $J = 7.9, 1.4 \text{ Hz}$, pyridyl H^4), 8.63 (4 H, d, $J = 8.1 \text{ Hz}$, pyridyl H^6), 8.93 (4 H, s, pyridyl H^3).

[(terpy)Ru(μ - L^1)Ru(bipy) $_2$] $[\text{PF}_6]_3$ (5**)**. A mixture of **3** (273 mg, 0.28 mmol), $\text{Ru}(\text{bipy})_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$ (147 mg, 0.28 mmol), and KOH (100 mg, excess) was heated to reflux in ethanol (in the air) overnight to afford a dark blue solution. After addition of aqueous KPF_6 , the mixture was concentrated *in vacuo* and a dark solid was filtered off. This was redissolved in acetone, and the solution was treated with $[\text{Cp}_2\text{Fe}]\text{PF}_6$ (100 mg, 0.3 mmol), resulting in an immediate color change from inky blue to deep red. After evaporation to dryness, the mixture was loaded onto a preparative-scale SiO_2 plate using the minimum volume of acetone, and the plate was then eluted with a mixture of $\text{MeCN}/\text{H}_2\text{O}$ /saturated aqueous KPF_6 , 17:1:1. The major brown-red band was scraped off and the product leached out of the silica using the elution solvent. This solution was then concentrated *in vacuo* and extracted with CH_2Cl_2 to give **5** in 35% yield.

[Ru(μ - L^1) $_2$ {Ru(bipy) $_2$ }] $[\text{PF}_6]_4$ (6**)**. A mixture of **4** (204 mg, 0.19 mmol), $\text{Ru}(\text{bipy})_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$ (198 mg, 0.38 mmol), and KOH (100 mg, excess) was heated to reflux in ethanol (in the air) overnight to afford a dark blue solution. After treatment with KPF_6 , filtration, and oxidation with $[\text{Cp}_2\text{Fe}]\text{PF}_6$ as above, the brown-red product was purified by chromatography on a preparative-scale alumina TLC plate eluting with MeCN . Yield: 20%.

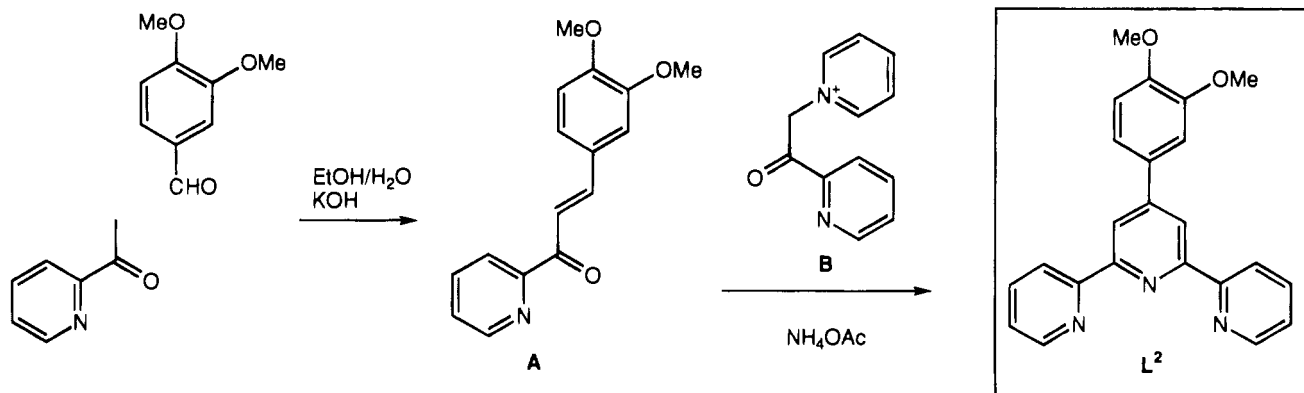
[(terpy)Ru(μ - L^1)Pd(bipy)] $[\text{PF}_6]_2$ (7**) and [(terpy)Ru(μ - L^1)Pd(4,4'- Bu_2 -bipy)] $[\text{PF}_6]_2$ (**8**)**. A mixture of **3** (245 mg, 0.25 mmol), KOH (100 mg, excess), and either $\text{Pd}(\text{bipy})\text{Cl}_2$ (83 mg, 0.25 mmol, for **7**) or $\text{Pd}(4,4'\text{-Bu}_2\text{-bipy})\text{Cl}_2$ (111 mg, 0.25 mmol, for **8**) in methanol (50 cm^3) was stirred at room temperature under N_2 for 4 h. Aqueous KPF_6 was then added and the mixture concentrated *in vacuo* until a purple precipitate appeared, which was filtered off, washed with water, and dried. Recrystallization from $\text{MeCN}/\text{Et}_2\text{O}$ gave pure **7** or **8** in 40% yield. $^1\text{H NMR}$ of **7**, CD_3CN , δ (ppm): 6.65 (1 H, d, $J = 8.1 \text{ Hz}$, phenyl H^5), 7.12 (2 H, td, $J = 5.6, 1.2 \text{ Hz}$, H^5 of terpy), 7.19 (2 H, td, $J = 5.6, 1.2 \text{ Hz}$, H^5 of L^1), 7.27 (1 H, d, $J = 2.3 \text{ Hz}$, phenyl H^2), 7.29 (2 H, dd, $J = 5.6, 0.7 \text{ Hz}$, H^3 of terpy), 7.32 (1 H, dd, $J = 8.1, 2.3 \text{ Hz}$, phenyl H^6), 7.49 (2 H, d, $J = 5.6 \text{ Hz}$, H^3 of L^1), 7.73 (2 H, m, H^2 of bipy), 7.91 (4 H, m, H^4 of terpy and H^4 of L^1), 8.24 (4 H, m, H^3 and H^4 of bipy), 8.38 (1 H, t, $J = 8.2 \text{ Hz}$, H^4 of terpy), 8.49 (2 H, d, $J = 7.8 \text{ Hz}$, H^6 of L^1), 8.64 (2 H, d, $J = 7.8 \text{ Hz}$, H^6 of terpy), 8.70 (2 H, m, H^6 of bipy), 8.74 (2 H, d, $J = 8.3 \text{ Hz}$, H^3 of terpy), 8.90 (2 H, s, H^3 of L^1). $^1\text{H NMR}$ of **8**, CD_3CN , δ (ppm): 1.48 (18 H, s, CH_3), 6.63 (1 H, d, $J = 7.9 \text{ Hz}$, phenyl H^5), 7.11 (2 H, td, $J = 6.6, 1.2 \text{ Hz}$, H^5 of terpy), 7.19 (2 H, td, $J = 6.6, 1.2 \text{ Hz}$, H^5 of L^1), 7.29 (4 H, m, H^3 of terpy, phenyl H^2 and H^6), 7.50 (2 H, d, $J = 5.5 \text{ Hz}$, H^3 of L^1), 7.69 (1 H, dd, $J = 6.0, 1.8 \text{ Hz}$, H^2 of Bu_2 -bipy), 7.72 (1 H, dd, $J = 6.0, 1.8 \text{ Hz}$, H^5 of Bu_2 -bipy), 7.90 (4 H, m, H^4 of terpy and H^4 of L^1), 8.27 (2 H, s, H^3 of Bu_2 -bipy), 8.38 (1 H, t, $J = 8.2 \text{ Hz}$, H^4 of terpy), 8.50 (3 H, m, H^6 of L^1 and one H^6 of Bu_2 -bipy), 8.55 (1 H, d, $J = 6.1 \text{ Hz}$, one H^6 of Bu_2 -bipy), 8.61 (2 H, d, $J = 8.2 \text{ Hz}$, H^6 of terpy), 8.74 (2 H, d, $J = 8.2 \text{ Hz}$, H^3 of terpy), 8.88 (2 H, s, H^3 of L^1).

[Ru(μ - L^1) $_2$ {Pd(bipy) $_2$ }] $[\text{PF}_6]_2$ (9**) and **[Ru(μ - L^1) $_2$ {Pd(4,4'- Bu_2 -bipy) $_2$ }] $[\text{PF}_6]_2$ (**10**)**. A mixture of **4** (264 mg, 0.25 mmol), KOH (100 mg, excess) and either $\text{Pd}(\text{bipy})\text{Cl}_2$ (173 mg, 0.52 mmol, for **9**) or $\text{Pd}(4,4'\text{-Bu}_2\text{-bipy})\text{Cl}_2$ (230 mg, 0.52 mmol, for **10**) in methanol (50 cm^3) was stirred at room temperature under N_2 for 6 h. After addition of aqueous KPF_6 and concentration *in vacuo*, a purple precipitate appeared, which was filtered off and dried. Crude **9** was dissolved in acetone and reprecipitated by dropwise addition of ether; crude **10** was dissolved in CH_2Cl_2 and reprecipitated by dropwise addition of hexane. The complexes were then filtered off and dried to give yields of 50–70%. $^1\text{H NMR}$ of **9**, CD_3SOCD_3 , δ (ppm): 6.65 (2 H, d, $J = 8.3 \text{ Hz}$, phenyl H^5), 7.25 (4 H, m, H^5 of L^1), 7.52 (4 H, m, H^2 and H^6 of phenyl, H^3 of L^1), 7.90 (4 H, m, H^5 of bipy), 8.01 (4 H, t, $J = 7.7 \text{ Hz}$, H^4 of L^1), 8.41 (4 H, m, H^4 of bipy), 8.63 (4 H, m, H^3 of bipy), 8.70 (4 H, m, H^6 of bipy), 9.12 (4 H, d, $J = 7.9 \text{ Hz}$, H^6 of L^1), 9.26 (4 H, s, H^3**

Table 1. Analytical and Mass Spectroscopic Data for the New Complexes

complex	anal./% ^a			FABMS <i>m/z</i> ^{a,c}		
	C	H	N	(M - PF ₆)	(M - 2PF ₆)	(M - 3PF ₆)
1	45.5 (45.9)	3.0 (3.0)	8.1 (8.5)	849 (849)	704 (704)	
2	48.5 (48.9)	3.2 (3.4)	7.3 (7.4)	985 (985)	840 (840)	
3·H ₂ O	44.3 (44.0)	2.9 (2.9)	8.3 (8.5)	821 (821)	675 (676)	
4·2H ₂ O	45.3 (45.5)	3.1 (3.1)	7.3 (7.6)	929 (929)	783 (784)	
5	44.2 (44.2)	2.8 (2.7)	9.4 (9.2)	1379 (1378)	1234 (1233)	1088 (1088)
6	44.7 (45.0)	2.9 (2.7)	8.9 (9.0)	2038 (2042)	1898 (1898)	1753 (1753)
7·2H ₂ O	43.3 (43.8)	2.8 (2.9)	9.3 (8.9)	1084 (1081)	937 (937)	
8·2H ₂ O	46.8 (47.2)	3.9 (3.8)	8.1 (8.2)	1195 (1193)	1050 (1048)	
9·4H ₂ O	45.1 (44.7)	2.8 (3.0)	8.4 (8.0)	<i>b</i>		
10·4H ₂ O	49.3 (49.5)	4.2 (4.4)	7.3 (7.4)	1675 (1673)	1530 (1528)	

^a Calculated values in parentheses. ^b This compound did not fly under FAB conditions. ^c The peaks in the FAB mass spectra may differ slightly from the expected values for two reasons: (i) protonation by the matrix that may occur to an unknown extent; (ii) the presence of broad peak clusters (up to 20 mass units broad for the trinuclear complexes) due to the large number of isotopes of Ru and Pd.

Scheme 1

of L¹). ¹H NMR of **10**, CD₃CN, δ (ppm): 1.51 (18 H, s, CH₃), 1.53 (18 H, s, CH₃), 6.44 (2 H, d, *J* = 8.3 Hz, phenyl H⁵), 6.52 (2 H, s, phenyl H²), 7.18 (6 H, m, H⁵ of L¹ and phenyl H⁶), 7.43 (4 H, d, *J* = 5.1 Hz, H³ of L¹), 7.74 (4 H, m, H⁵ of 'Bu₂-bipy), 7.90 (4 H, t, *J* = 7.2 Hz, H⁴ of L¹), 8.26 (4 H, s, H² of 'Bu₂-bipy), 8.42 (2 H, d, *J* = 6.0 Hz, two H⁶ of 'Bu₂-bipy), 8.52 (6 H, m, H⁶ of L¹, two H⁶ of 'Bu₂-bipy), 8.70 (4 H, s, H³ of L¹).

Mass spectroscopic and analytical data for the complexes are summarized in Table 1.

Results and Discussion

Syntheses of Ligand and Complexes. The Kröhnke-type synthesis⁸ of L² is outlined in Scheme 1. Condensation of 2-acetylpyridine with the appropriate aromatic aldehyde in a 1:1 ratio afforded the enone **A** as a yellow solid. A subsequent Michael reaction of this with 1-[2-oxo-2-(2-pyridinyl)ethyl]pyridinium iodide **B** (which is effectively a stabilized enolate of 2-acetylpyridine) generates a 1,5-dicarbonyl which is ring-closed *in situ* with ammonium acetate to give L² in approximately 30% overall yield. This route is further exemplified by the preparation of 4'-(4-pyridyl)terpy.^{7c} A more common route, in which 2 equiv of 2-acetylpyridine reacts with the aromatic aldehyde to give a 1,5-dicarbonyl directly (exemplified by the preparations of 4,4',4''-triphenylterpy,^{13b} 4'-ferrocenylterpy,^{7d} and 4-phenylterpy²³) does not work in this case, giving only cyclic products²⁴ arising from 3:1 and 3:2 condensation of 2-acetylpyridine with the 3,4-dimethoxybenzaldehyde; these will be described elsewhere.²⁵

L² was then used to prepare the complexes [Ru(terpy)L²][PF₆]₂ (**1**) and [Ru(L²)₂][PF₆]₂ (**2**) by standard methods. It is worth noting that, of the various literature methods for the preparation of terpy²⁶ (used to prepare [Ru(terpy)Cl₃], a precursor for **1**), we have found that of Jameson and Guise¹⁶ to be by far the best. Demethylation of **1** and **2** with BBr₃ in CH₂Cl₂²² gave [Ru(terpy)(H₂L¹)] [PF₆]₂ (**3**) and [Ru(H₂L¹)₂][PF₆]₂ (**4**), respectively in high yield. Unmasking of the peripheral catechol groups *after* coordination of the terpy binding sites to the Ru(II) cores prevents possible competition of the catechol ligands for the Ru(II) during complex formation and takes advantage of the fact that the {Ru(terpy)₂}²⁺ core is extremely stable and not affected by the HBr liberated in the workup.

For our initial investigations into the use of complexes **3** and **4** as building blocks for polynuclear complexes, we have attached {Ru(bipy)}²⁺ and {Pd(bipy)}²⁺ fragments to the catechol binding sites to give binuclear complexes (based on **3**) and trinuclear complexes (based on **4**). The complexes [Ru(bipy)₂(cat)]^{15c} and [Pd(bipy)(cat)]²⁷ (cat = dianion of catechol) are known and have characteristic spectroscopic and electrochemical properties which should assist in characterization of the polynuclear complexes of which they are components and, upon observation of how these properties are perturbed, will permit investigation of interactions between the different components of these complexes. Thus, reaction of **3** with [Ru(bipy)₂Cl₂]₂·2H₂O in the presence of KOH afforded **5**, in which the coordinated dioxolene fragment is in the semiquinone oxidation state. Initial TLC investigation of the reaction mixture showed the presence of two major products: a dark blue species

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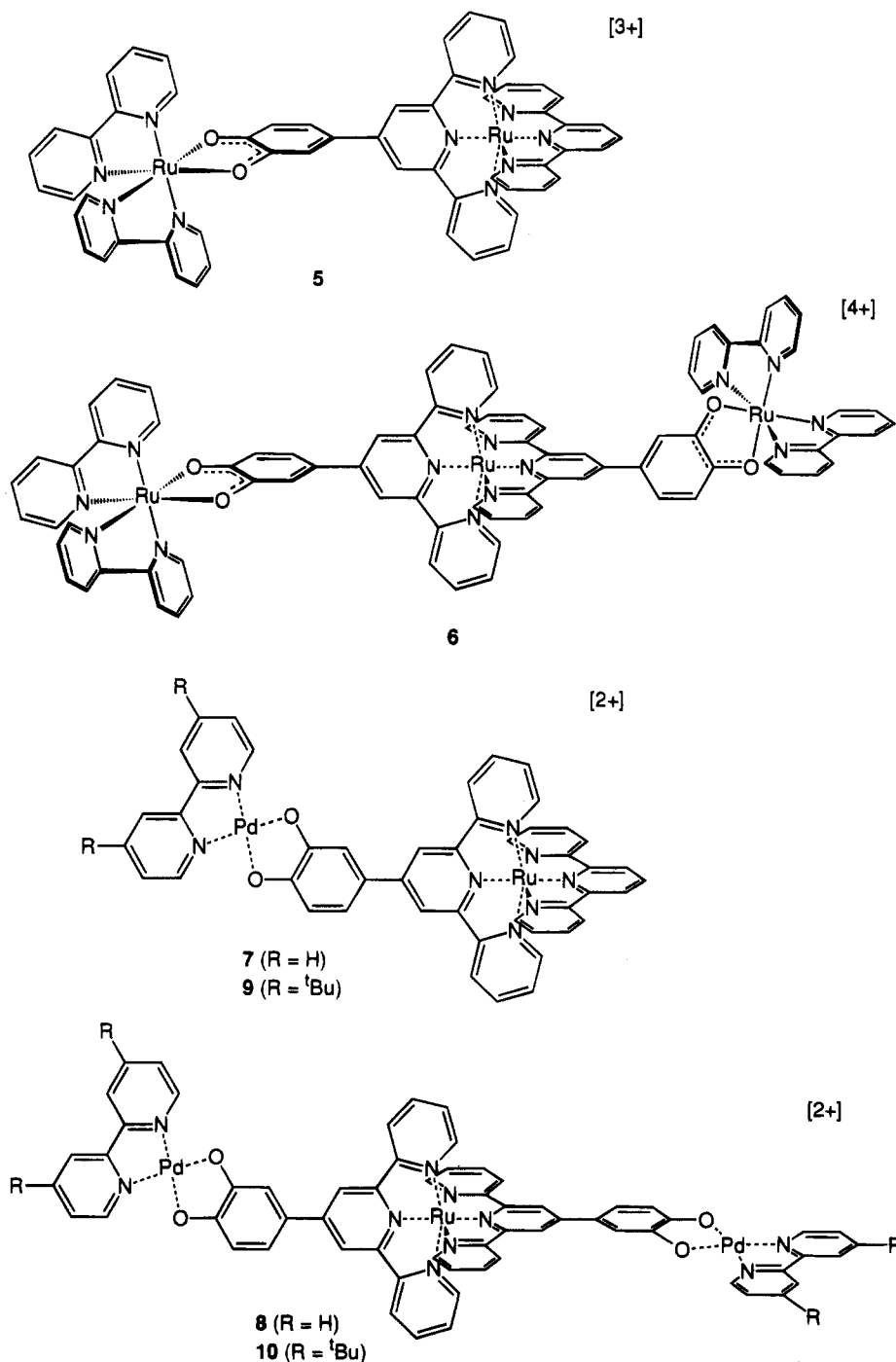


Figure 1. Structures of the new polynuclear complexes.

$[(\text{terpy})\text{Ru}(\mu\text{-L}^1)\text{Ru}(\text{bipy})_2]^{2+}$, in which the coordinated dioxolene fragment has remained in its reduced catecholate state, and a red-orange product $[(\text{terpy})\text{Ru}(\mu\text{-L}^1)\text{Ru}(\text{bipy})_2]^{3+}$, in which aerial oxidation of the coordinated catecholate to semiquinone has occurred. The mononuclear complex $[\text{Ru}(\text{bipy})_2(\text{cat})]$ shows similar behavior.^{15c} In order to simplify the workup, the crude mixture was treated with the mild oxidizing agent $[\text{Cp}_2\text{Fe}][\text{PF}_6]$ [$\text{Cp} = \eta^5\text{-cyclopentadienyl}$] before chromatographic purification, resulting in complete conversion to the air-stable semiquinone **5**. Similarly, reaction of **4** with 2 equiv of $[\text{Ru}(\text{bipy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ and KOH , followed by treatment with $[\text{Cp}_2\text{Fe}][\text{PF}_6]$ to complete the partial aerial oxidation, afforded the air-stable trinuclear diradical **6**, in which both dioxolene fragments are in the semiquinone form.

Reaction of **3** and **4** with 1 or 2 equiv, respectively, of $[\text{Pd}(\text{bipy})\text{Cl}_2]$ gave **7** or **9**, in which the $\{\text{Ru}(\text{terpy})\}_2^{2+}$ core is attached to one or two $\{\text{Pd}(\text{bipy})(\text{cat})\}$ substituents. These

complexes are relatively insoluble, so we also prepared **8** and **10** using $[\text{Pd}(4,4'\text{-}^t\text{Bu}_2\text{-bipy})_2\text{Cl}_2]$ as starting material, in which the ^tBu substituents make the complexes much more soluble. Structures of the new polynuclear complexes are given in Figure 1.

All of the new complexes were characterized by FAB mass spectrometry and elemental analysis (Table 1) with the exception of **9**, which did not fly under FAB conditions. For the Ru–Pd complexes **7–10** the elemental analyses were erratic and tended to give low values for carbon; the analyses were repeated several times, and the most repeatable results consistently suggest the presence of two water molecules *per* $\{\text{Pd}(\text{bipy})(\text{cat})\}$ group. The purity of these complexes was confirmed independently by ¹H NMR spectrometry and TLC analysis. The proton resonances for the mixed-ligand complexes **1** and **3** could be confidently assigned to the specific ligands by comparison with the two homoleptic complexes. Thus, comparison of the spectra of

Table 2. Electronic Spectral Data for the New Complexes^a

complex	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$) ^b					
	A	B	C	D	E	F
1			486 (21)	307 (63)	282 (39)	272 (41)
2			486 (15)	308 (47)	280 (sh)	272 (34)
3			494 (33)	308 (74)	283 (60)	
4			494 (35)	308 (61)	283 (69)	
5	967 (20)		482 (21)	305 (71)	294 (75)	
6	982 (24)		491 (20)		293 (88)	
7		524 (19)	c	311 (60)		274 (33)
8		515 (12)	c	310 (40)		273 (28)
9		537 (28)	c	310 (74)		274 (57)
10		539 (41)	c	310 (95)		274 (75)

^a Key: (A) Ru(d π) \rightarrow semiquinone mlct process; (B) catecholate \rightarrow bipy llct process. (C) Ru(d π) \rightarrow bipy mlct process. (D–F) ligand-based $\pi \rightarrow \pi^*$ transitions. ^b Spectra recorded in MeCN. ^c Expected Ru(d π) \rightarrow bipy mlct process obscured by intense catecholate \rightarrow bipy llct process (column B).

[Ru(terpy)₂]²⁺ and [Ru(L₂)₂]²⁺ (2) allowed easy assignment of the spectrum of [Ru(terpy)(L²)]²⁺ (1) since the signals for each ligand are not much perturbed; this is generally true of asymmetric complexes of the type [Ru(terpy-X)(terpy-Y)]²⁺.²⁸ The more complex ¹H NMR spectra of 7–10 were assigned with the aid of two-dimensional ¹H–¹H correlation (COSY) spectra. Complexes 5 and 6 are paramagnetic and gave highly broadened, but not shifted, spectra.

UV/Visible Spectroscopy. Details of the electronic spectra are summarized in Table 2. For the mononuclear complexes 1–4 the spectra are generally as expected. Addition of dimethoxyphenyl groups to the [Ru(terpy)₂]²⁺ core results in an increase of the intensity of the characteristic metal-to-ligand charge-transfer (mlct) band at ca. 490 nm; demethylation of 1 and 3 does not significantly affect any of the peak positions. The spectra of 5 and 6 both show an intense Ru(d π) \rightarrow semiquinone(π^*) mlct band, similar to that observed in mononuclear [Ru(bipy)₂(sq)]⁺ (890 nm; $\epsilon = 6400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$),^{15c} but red-shifted and about 3 times more intense (Figure 2a). This red-shift indicates that the orbitals based on the semiquinone fragments of 5 and 6 are lower in energy than those of [Ru(bipy)₂(sq)]⁺, which may be ascribed to the more extended delocalization of L¹. The increased intensity suggests that the semiquinone fragments of 5 and 6 are more electron-deficient than that of [Ru(bipy)₂(sq)]⁺, resulting in an increased transition dipole moment for the Ru(d π) \rightarrow semiquinone(π^*) charge transfer.

The spectra of 7–10 all have a very strong band near 500 nm, which is a ligand-to-ligand charge transfer (llct) from catecholate to bipyridine and is characteristic of the [Pd(bipy)-(cat)] fragment. However for mononuclear [Pd(bipy)(cat)] this transition, although occurring at a similar position (535 nm), has an extinction coefficient ϵ of only $1300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$;²⁷ it is therefore increased in intensity by approximately 1 order of magnitude (*per* chromophore) in 7–10 (Figure 2b). This suggests that the catecholate fragments of 7–10 are more electron-rich than that of [Pd(bipy)(cat)], thereby increasing the transition dipole moment. It is interesting that, whereas the semiquinone fragments of 5 and 6 appear to have been rendered more electron-deficient by attachment to the [Ru(terpy)₂]²⁺ core, the catecholate fragments of 7–10 appear to have been rendered more electron-rich. It seems that the “direction” of the electronic interaction between the [Ru(terpy)₂]²⁺ core and the pendant metal complex depends on the oxidation state of the dioxolene ligand fragment. The expected Ru(d π) \rightarrow terpy(π^*) mlct transitions at 450–500 nm are obscured by the more intense llct processes at the palladium center.

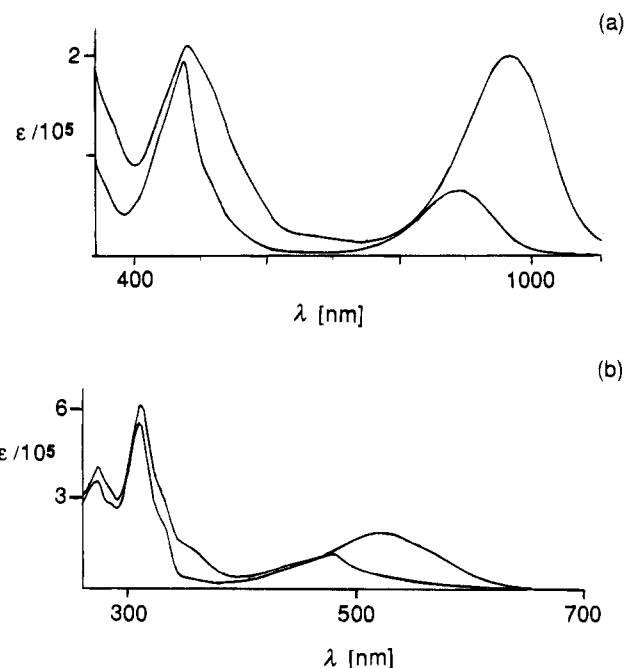


Figure 2. Electronic spectra, in MeCN: (a) 5 (upper trace) and a 1:1 mixture of [Ru(bipy)₂(sq)][PF₆] and [Ru(terpy)₂][PF₆]₂ at the same concentration (lower trace); (b) 7 (upper trace) and a 1:1 mixture of [Pd(bipy)(cat)] and [Ru(terpy)₂][PF₆]₂ at the same concentration (lower trace).

Table 3. Electrochemical Data for the New Complexes^a

complex	dioxolene-based couples	{Ru(terpy) ₂ } ^{2+/3+}	Ligand-based reductions		
1	+1.20	+0.85 (80)	-1.67	-1.92	-2.36
2	+0.75	+0.95 (70)	-1.67	-1.94	-2.42
3	+1.19	+0.81 (70)	-1.63	-1.83	-2.30
4	+0.73	+0.94 (60)	-1.90	-2.07	-2.48
5	-0.50 (70), +0.26 (60)	+0.97 (90)	-1.73	-2.00	-2.10 -2.42
6	-0.50 (80), +0.25 (90)	+0.98 (130)	-1.82	-1.94	
7	+0.18	+0.93 (90)	-1.71	-2.08	
8	+0.13	+0.93 (90)	-1.81	-2.06	
9	+0.14	+0.97 (60)	-1.83		
10	+0.13	+0.97	-1.83	-2.01	

^a All cyclic/square-wave voltammograms were recorded in MeCN at a scan rate of 0.2 V s^{-1} . Potentials are given in volts vs the ferrocene/ferrocenium couple, Fc/Fc⁺; peak–peak separations for chemically reversible waves are given in parentheses. For irreversible processes, the peak potentials are taken from Osteryoung square-wave voltammograms.

Electrochemistry. The electrochemical properties of the complexes were studied by cyclic voltammetry and Osteryoung square-wave voltammetry and are summarized in Table 3. Addition of 4'-(3,4-dimethoxyphenyl) substituents to the [Ru(terpy)₂]²⁺ core in 1 and 3 results in a drop of the Ru(II)/Ru(III) couple of 40 mV *per* substituent ($E_{1/2}$ for the [Ru(terpy)₂]^{2+/3+} couple is +0.89 V vs Fc/Fc⁺); these substituents therefore stabilize the Ru(III) state by acting as electron-donor groups. Complexes 1 and 3 also show a second, irreversible, oxidation at ca. +1.20 V vs Fc/Fc⁺, which we assign to oxidation of the dimethoxyphenyl group (Figure 3a). For 1 a return wave is apparent which is smaller than the outward wave, indicating only partial decomposition: for 3 the process is completely irreversible with no return wave. Electrochemical oxidation of 1,2-dimethoxybenzene is known to afford either soluble oligomers or polymers bound to the electrode surface,²⁹ *via* coupling of the initially-generated radical cation.³⁰ Electrolysis of 1 generated a reversible product wave at $E_{1/2} = +0.91 \text{ V vs Fc/Fc}^+$ (Figure 3), which may be due to

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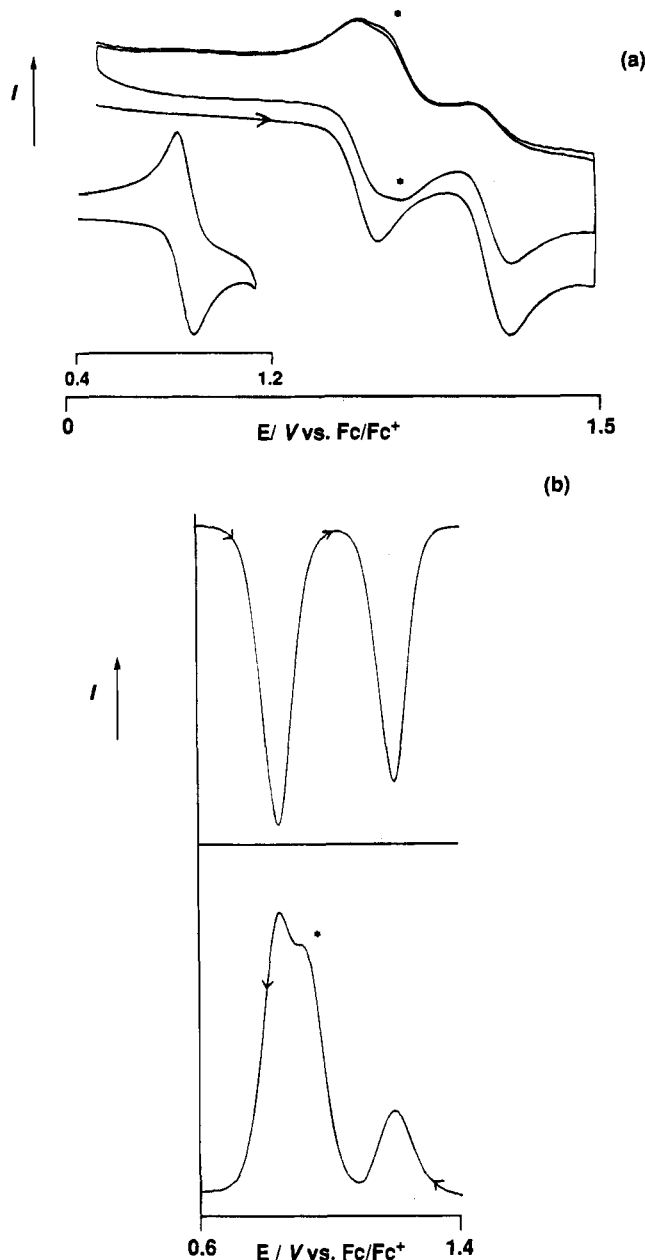


Figure 3. (a) Two cycles of the cyclic voltammogram of **1**, with a delay of 60 s at the positive extreme, and (b) Osteryoung square-wave voltammograms of **1** swept in different directions, both showing the appearance of a product wave (labeled*) due to the second oxidation process. The inset in (a) is the initial Ru(II)/Ru(III) wave alone.

a small oligomer of some kind (cf. formation of a cyclic trimer from either chemical^{31a} or electrochemical^{31b} oxidation of 1,2-dimethoxybenzene): the product wave would be a ligand-based oxidation, at a potential lower than that for oxidation of the single dimethoxyphenyl group of **1** due to formation of a more extended conjugated system.²⁹ Similar behavior occurs for **3**; after sweeping to potentials more positive than the second oxidation wave, a reversible product wave appeared at +0.97 V vs Fc/Fc⁺. A much weaker product wave was also apparent at +0.17 V vs Fc/Fc⁺. We are currently attempting to prepare these species on a larger scale and characterize them.

In complexes **2** and **4** the metal-based oxidations have reverted to the value for unsubstituted [Ru(terpy)₂]²⁺. In

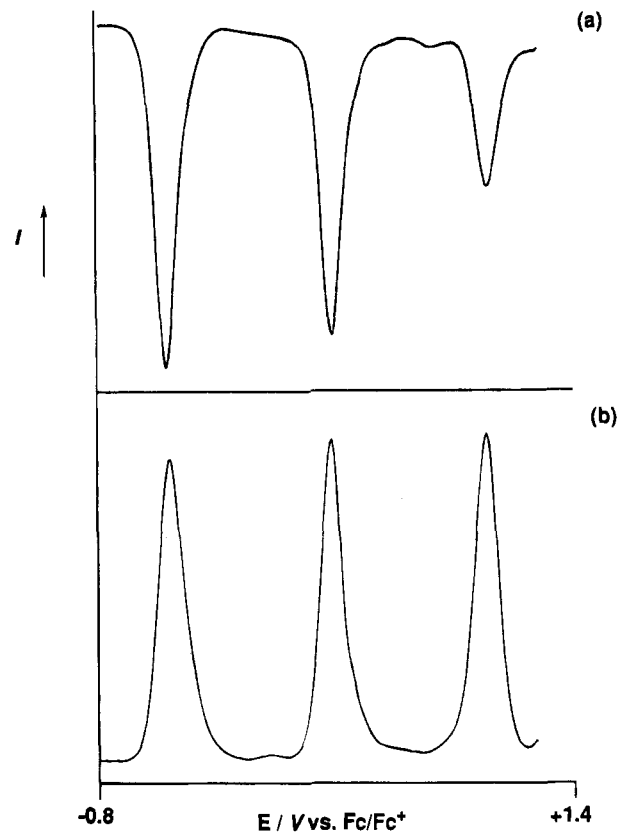


Figure 4. Osteryoung square-wave voltammograms of (a) **6** and (b) **5**, showing (from left to right) the catecholate/semiquinone, semiquinone/quinone, and [Ru(terpy)₂]^{2+/3+} couples.

addition, the pendant catechol groups undergo a totally irreversible oxidation at a lower potential than the metal centers. There is no evidence for any product waves associated with these irreversible oxidations. The irreversibility is doubtless due to loss of protons on oxidation which cannot be regained in a nonprotic solvent.

In contrast to that for [Ru(terpy)₂]²⁺, reductive cyclic voltammetry for **1–4** showed only poorly-defined, irreversible (or only partly reversible) processes, some of which were obscured by absorption/desorption processes at the electrode surface. The peak potentials quoted in Table 3 for these were taken from the square-wave voltammograms.

Complexes **5** and **6** comprise a [Ru(terpy)₂]²⁺ core to which is attached one and two [Ru(bipy)₂(sq)]⁺ fragments, respectively, and all of the expected redox processes occur. [Ru(bipy)₂(sq)]⁺ undergoes reversible ligand-based redox processes (cat/sq and sq/q couples, where cat and sq are as previously defined and q is 1,2-benzoquinone) at -0.69 and +0.16 V and an irreversible Ru(II)/Ru(III) oxidation at +1.25 V vs Fc/Fc⁺.^{15c} In **5**, the catecholate/semiquinone and semiquinone/quinone redox couples of the bridging ligand occur at -0.51 and +0.26 V, respectively, and the irreversible Ru(II)/Ru(III) couple of the [Ru(bipy)₂(dioxolene)] fragment of **5** is at approximately +1.4 V vs Fc/Fc⁺ (it is difficult to measure accurately as it is broad and merging with the high background current at the limit of the solvent window). The shift of these toward more positive potentials compared to the case of [Ru(bipy)₂(sq)]⁺ may be ascribed to the presence of an additional +2 charge at the adjacent metal center in the binuclear complex and is consistent with the relative electron deficiency of the dioxolene fragment inferred from the electronic spectra. In addition, there is a reversible Ru(II)/Ru(III) couple of the {Ru(terpy)}²⁺ core at +0.94 V. The intensities of all three reversible waves—two from the [Ru(bipy)₂(dioxolene)] fragment of the complex and one from the {Ru(terpy)₂]²⁺ fragment—are similar in the cyclic

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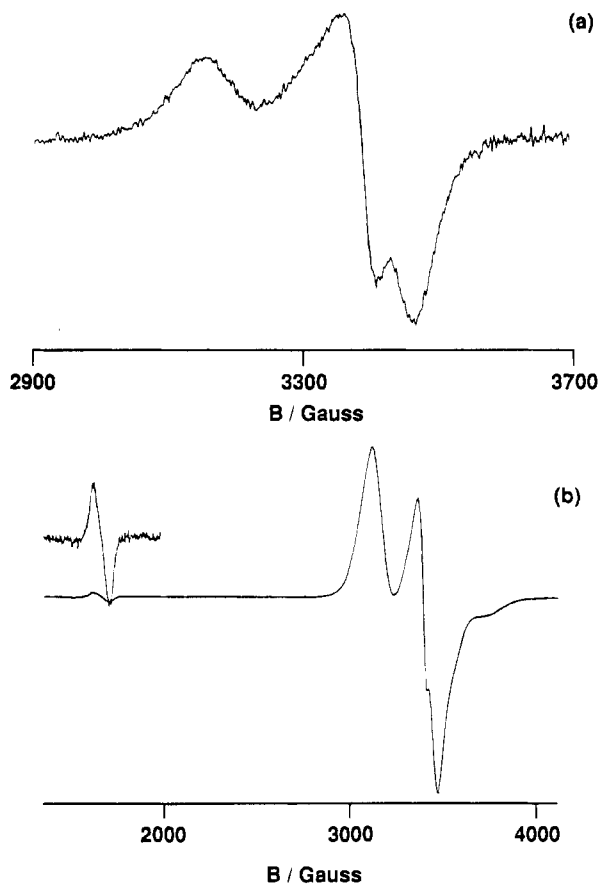


Figure 5. EPR spectra of (a) **5** and (b) **6** as frozen glasses (dmf/thf, 1:1) at 77 K.

and square-wave voltammograms. For **6** the potentials of the redox processes are very similar to those of **5**, but the waves corresponding to the reversible catecholate/semiquinone and semiquinone/quinone redox couples of the two bridging ligands (i.e. two simultaneous one-electron transfers) are now approximately twice as intense as that of the $\{\text{Ru}(\text{terpy})_2\}^{2+/3+}$ couple (Figure 4).

Complexes **7–10** all display an irreversible oxidation, characteristic of the mononuclear $\{\text{Pd}(\text{bipy})(\text{cat})\}$ fragment²⁷ but at rather less positive potentials. The catechol fragment is therefore more electron-rich in **7–10** than in $\{\text{Pd}(\text{bipy})(\text{cat})\}$, which is consistent with the electronic spectroscopic results. The expected Ru(II)/Ru(III) couple is also present and is reversible for **7–9** but not fully reversible for **10** (weak return wave).

Reductive voltammetry for **5–10**, as for **1–4**, displays only an ill-defined overlapping assembly of generally irreversible processes; peak potentials from the square-wave voltammograms are included in Table 3.

EPR Spectroscopy. Complexes **5** and **6**, being paramagnetic due to the presence of coordinated semiquinone groups, were examined by EPR spectroscopy. The results are shown in Figure 5. The spectrum of **5** (in a frozen dmf/thf glass at 77 K) comprises three signals at $g = 2.14, 2.00,$ and 1.95 consistent with the low symmetry. For **6** (a diradical) under the same conditions the main part of the signal is essentially similar (g

$= 2.17, 1.99, 1.95$ for the three main features), but a double-quantum transition from the triplet state is also apparent at half-field ($g = 4.06$). It is perhaps surprising that this occurs with two semiquinone fragments relatively far apart and attached to ligands which are mutually orthogonal. Exchange interactions are known to be propagated through the central metal ion in the triradical $[\text{Ga}^{\text{III}}(\text{DTBSQ}^{\cdot-})]$ (DTBSQ = di-*tert*-butyl-*o*-benzosemiquinone radical anion) although in this case the paramagnetic ligands are much closer together than in **6**.³² No hyperfine coupling to ruthenium was observed. There is currently considerable interest in preparing and examining polyradicals which contain several interacting spins in a spatially well-defined array,³³ and this result suggests that polynuclear complexes containing $\{\text{Ru}(\text{bipy})_2(\text{sq})\}$ fragments may be good candidates for components of such systems; we are currently looking into this.

Possible Photocatalytic Activity of 7–10. It is worth noting here that $[\text{Pd}(\text{bipy})(\text{cat})]$ and related complexes are known to be photocatalysts for the production of singlet oxygen.^{27,34} Irradiation into the llct band generates the excited state $[\text{Pd}^{\text{II}}(\text{sq}^{\cdot-})(\text{bipy}^{\cdot-})]$, which is quenched in solution by $^3\text{O}_2$ to give $^1\text{O}_2$. Complexes **7–10** fulfill, in principle, the basic requirements of a photochemical device in that the catalytically-active llct excited state of the $\{\text{Pd}(\text{bipy})(\text{cat})\}$ fragment could be sensitized by energy transfer from the adjacent $\{\text{Ru}(\text{terpy})_2\}$ fragment. Detailed photophysical studies on **7–10** will accordingly be reported in due course.

Conclusions. Using the new bridging ligand H_2L^1 , we have prepared derivatives of $[\text{Ru}(\text{terpy})_2]^{2+}$ bearing one or two pendant catechol binding sites at the periphery and have demonstrated how these may be used as building blocks for binuclear and trinuclear complexes which contain a photoactive core linked to redox-active or potentially catalytically active metal fragments. Electrochemical, UV/vis, and EPR measurements indicate the presence of significant interactions between the component parts. Photophysical studies to investigate (i) the extent to which luminescence quenching of the $[\text{Ru}(\text{terpy})_2]^{2+}$ core depends on the oxidation state of the peripheral metal fragments in **5** and **6** and (ii) the possibility of inter-component energy transfer in **7–10** enhancing their $^1\text{O}_2$ -producing ability will be described in due course.

Acknowledgment. We thank the SERC for a Ph.D. studentship (to B.W.) and for a grant to purchase the EPR spectrometer and also Dr. J. P. Maher for recording the EPR spectra.

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