Electropolymerization of Ruthenium Bis(1,10-phenanthroline)(4-methyl-4'-vinyl-2,2'-bipyridine) Complexes through Direct Attack on the Ligand Ring System

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Mixed ligand complexes of the general type $RuP_2(4$ -methyl-4'-vinyl-2,2'-bipyridine)²⁺ (where P represents phenanthroline or a substituted phenanthroline) undergo rapid electropolymerization following initial two-electron reduction. The polymerization yields redox-conductive electrode coatings and appears to proceed via radical-radical coupling between the vinyl moiety and a phenanthroline carbon, with the 4- and 7-positions of the phenanthroline being the most reactive. When the phenanthroline ligands possess substituents in the 4- and 7-positions, polymerization still proceeds, but an unexpected reversible electrochemical response near -0.2 V vs. SSCE is generated. The response is attributed to an intermediate which can exist in a stable ligand-centered free-radical form. This radical species has been observed by EPR spectroscopy and is stabilized by 4,7disubstitution and/or the presence of proton donors. The mechanistic pathways involved in the electropolymerization are complex and lead to multiple products. Polymerized films display unusual electrochemistry, including prominent "charge-trapping" peaks for which a mechanistic system is proposed.

The reductive electropolymerization of ruthenium(II) tris(4methyl-4'-vinyl-2,2'-bipyridine) (Ru(vbpy)₃²⁺) and related complexes has received extensive recent study, primarily by Murray and co-workers.¹⁻¹² Electrochemical reduction of these complexes produces polymers that adhere strongly to the electrode surface to form stable electroactive coatings. Electrode coatings produced by this technique have been used to examine electron-transfer kinetics at the film-solution interface^{7,8} and to demonstrate several interesting bistable switching devices.⁹⁻¹² Revealing work of Calvert et al.⁶ suggested that the polymerization proceeds via several pathways, the most important of which is a radical-radical coupling process involving pairs of vinyl groups. This has two important consequences. First, the dominant pathway leads to products with saturated, four-carbon-atom links between the aromatic ring systems. Second, mixed ligand complexes containing only one vinylbipyridine ligand are much less active in the formation of coatings, presumably because, as with activated olefins,^{13,14} end-to-end, radical-radical coupling of two vinyl moieties produces only dimeric products that are soluble in the solvents employed.

To the extent that the 5-6 bond in 1,10-phenanthroline (phen) can be regarded as structurally analogous to the vinyl group in vbpy, one might expect unsubstituted phenanthroline complexes of Ru(II) to undergo reductive electropolymerization in a manner similar to Ru(II) complexes of vbpy. Although direct phen-phen



coupling apparently does not occur, we wish to report that vbpy-phen coupling is efficient, and mixed ligand complexes of the general type $\operatorname{RuP}_2(\operatorname{vbpy})^{2+}$ (where P is a phenanthroline or a substituted phenanthroline ligand) can be rapidly polymerized via electrochemical reduction. One advantage of these mixed ligand complexes is the greater flexibility available in ligand substitution, allowing for variation in parameters such as size, redox potential, and excited-state properties.^{15,16} In addition, since the expected products have two methylene groups separating the aromatic ring system, the rates of charge transport through the redox polymer products may be higher than those obtained with the previous polymers based on $M(\operatorname{vbpy})_3^{2+}$ (M = Ru, Os) complexes.⁶

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Experimental Section

Materials. The ligands 5-chloro-1,10-phenanthroline (5-Clphen), 5,6-dimethyl-1,10-phenanthroline (5,6-Me₂phen), 4,7dimethyl-1,10-phenanthroline (4,7-Me₂Phen), 4,7-diphenyl-1,10-phenanthroline $(4,7-Ph_2phen)$, and 3,4,7,8-tetramethyl-1,10-phenanthroline $(3,4,7,8-Me_4phen)$ were obtained from the G. F. Smith Chemical Co. and were used as received. 1,10-Phenanthroline (phen) (Baker) and 4,4'-dimethyl-2,2'-bipyridine (Me₂bpy) (Aldrich) were also used as received. Ruthenium trichloride was obtained from several sources (Aesar, Aldrich, Alfa) and was used without further purification in all cases. Ammonium hexabromoosmate was prepared from OsO4 (Aldrich) by using standard literature methods.¹⁷ Tetra-*n*-butylammonium perchlorate (Southwestern Analytical) and sodium perchlorate (Aldrich) were recrystallized twice and dried overnight in a vacuum oven. Acetonitrile (Burdick and Jackson UV) was distilled from CaH₂ prior to use.

4-Methyl-4'-vinyl-2,2'-bipyridine (vbpy). This ligand was prepared by a slight modification of the method of Spiro and

- (4) Pickup, P. G.; Murray, R. W. J. Electrochem. Soc. 1984, 131, 833.
 (5) Facci, J. S.; Schmehl, R. H.; Murray, R. W. J. Am. Chem. Soc. 1982, 104, 4959.
- (6) Calvert, J. M.; Schmehl, R. H.; Sullivan, B. P.; Facci, J. S.; Meyer, T. J.; Murray, R. W. Inorg. Chem. 1983, 22, 2151.
- (7) Leidner, C. R.; Murray, R. W. J. Am. Chem. Soc. 1984, 106, 1606.
 (8) Ikeda, T.; Leidner, C. R.; Murray, R. W. J. Electroanal. Chem. 1982, 138, 343.
- (9) Willman, K. W.; Murray, R. W. J. Electroanal. Chem. 1982, 133, 211.
 (10) Pickup, P. G.; Kutner, W.; Leidner, C. R.; Murray, R. W. J. Am.
- Chem. Soc. 1984, 106, 1991.
- (11) Abruña, H. D.; Denisevich, P.; Umaña, M.; Meyer, T. J.; Murray,
 R. W. J. Am. Chem. Soc. 1981, 103, 1.
- (12) Denisevich, P.; Willman, K.; Murray, R. W. J. Am. Chem. Soc. 1981, 103, 4727.
 - (13) Puglisi, V. J.; Bard, A. J. J. Electrochem. Soc. 1972, 119, 829.
- (14) Anderson, J. D.; Baizer, M. M.; Prill, E. J. J. Org. Chem. 1965, 30, 1645.
- (15) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. Top. Curr. Chem. 1978, 75, 1.

(16) Lin, C.-T.; Böttcher, W.; Chou, M.; Creutz, C.; Sutin, N. J. Am. Chem. Soc. 1976, 98, 6536.

(17) Dwyer, F. P.; Hogarth, J. W. Inorg. Synth. 1957, 5, 204.

⁽¹⁾ Ikeda, T.; Schmehl, R.; Denisevich, P.; Willman, K.; Murray, R. W. J. Am. Chem. Soc. 1982, 104, 2683.

⁽²⁾ Denisevich, P.; Abruña, H. D.; Leidner, C. R.; Meyer, T. J.; Murray, R. W. Inorg. Chem. 1982, 21, 2153.

⁽³⁾ Calvert, J. M.; Peebles, D. L.; Nowak, R. J. Inorg. Chem. 1985, 24, 3111.

Ghosh.¹⁸ First, 25 mL of 2.6 M n-BuLi (Aldrich) was carefully added to a solution containing 4 mL of diisopropylamine (Aldrich) in 15 mL of dry tetrahydrofuran (THF). The resulting mixture was stirred for 15 min. A solution of 5.0 g of Me₂bpy in 125 mL of dry THF was then slowly added via a dropping funnel to produce an orange-brown solution. A stream of formaldehyde, prepared by passing dry argon over 2.0 g of paraformaldehyde in a heated flask (~ 50 °C), was bubbled through the solution for 2 h. The reaction was then quenched with ice water and extracted with ether. Most of the solvent was removed from the organic layer, and the resulting yellow oil was filtered to remove any unreacted Me₂bpy. The product, 4-CH₃-4'-CH₂CH₂OH-bpy, was purified by column chromatography on deactivated alumina with ethyl acetate as the eluant. Dehydration was achieved by adding ~ 0.5 g of powdered NaOH to the oil in a vacuum sublimator and heating the mixture to 130 °C under vacuum. The product, vbpy, was collected as a white crystalline solid on the cold finger.

 RuP_2Cl_2 (*Except Ru*(3,4,7,8-*Me*₄*phen*)₂*Cl*₂). These compounds were prepared by using the method of Sprintschnik et al.¹⁹

 $Ru(3,4,7,8-Me_4phen)_2Cl_2$. This compound proved difficult to prepare by the method of ref 19 and was synthesized by the following procedure: 203 mg of RuCl₃·3H₂O (0.78 mmol) was added to 50 mL of ethanol and briefly refluxed to facilitate dissolution. 3,4,7,8-Me_4phen, 370 mg (1.57 mmole), was added along with a fivefold excess of hydroxylamine hydrochloride to serve as a reducing agent. After 1 h of refluxing, the reddishorange solution was cooled and filtered. The filtrate was concentrated and passed down a Sephadex LH-20 column using 2:1 MeOH/DMF as eluant. The chloride salt was obtained by addition of aqueous LiCl, followed by removal of methanol and overnight refrigeration.

 $RuP_2(vbpy)(PF_6)_2$. These compounds were prepared by refluxing stoichiometric amounts of vbpy with the appropriate RuP_2Cl_2 complex in methanol for 3 h. Purification was achieved by column chromatography on Sephadex LH-20 using either methanol or 1:1 MeOH/DMF as eluant. The hexafluorophosphate salts were obtained by addition of aqueous NH_4PF_6 to a methanolic solution of the complex, followed by slow removal of the methanol under vacuum. The resulting products were usually either crystalline or microcrystalline and were characterized by NMR and elemental analyses.

 $Os(phen)_2Br_2$. (NH₄)₂OsBr₆ (605 mg, 0.86 mmol) and 1,10phenanthroline (340 mg, 1.72 mmol) were refluxed for 1 h in 20 mL of dimethylformamide (DMF). The solution was cooled and 50 mL of MeOH was added. Addition of 70 mL of dilute Na₂S₂O₄ produced a black precipitate, Os(phen)₂Br₂, which was recrystallized from CHCl₃ (yield: 534 mg, 88%). Os(phen)₂(vbpy)(PF₆)₂. Os(phen)₂Br₂ (321 mg, 0.45 mmol)

 $Os(phen)_2(vbpy)(PF_6)_2$. Os(phen)₂Br₂ (321 mg, 0.45 mmol) and vbpy (100 mg, 0.51 mmol) were dissolved in 40 mL of 5:1 H₂O/EtOH and refluxed for 3 days. The mixture was filtered, and the product was precipitated by the addition of aqueous NH₄PF₆ to the filtrate. The complex was purified by column chromatography on Sephadex LH-20 (1:1 MeOH/DMF) (yield: 313 mg, 67%).

Procedures. Electrochemical measurements were performed with a Princeton Applied Research Model 173 potentiostat, a Model 175 universal programmer, and a Model 179 digital coulometer. The glassy carbon electrodes were prepared by polishing small lengths of 5- or 6-mm-diameter GC-20 rod (Tokai) with wetted sandpaper, then with successively finer alumina (Buehler 3.0, 1.0, and 0.3 μ m). The electrode was cleaned in an ultrasonic bath between each step to remove any adhering particles. Heat-shrinkable polyolefin tubing (Alfa Wire Co.) was used to attach the short carbon rods to glass tubing so that only the polished surface was exposed to the solution. Electrical contact was made to the back of the rod by means of a small Hg pool and a copper lead. Regeneration of the electrode surface between



Figure 1. Cyclic voltammograms recorded continuously at 100 mV s⁻¹ with 0.4 mM $[Ru(phen)_2(vbpy)]^{2+}$ in acetonitrile. Glassy carbon electrode (0.2 cm²). Supporting electrolyte: 0.1 M NaClO₄.

experiments was accomplished by repeating the 0.3- μ m polishing (0.3- μ m alumina) and ultrasonic cleaning steps. No major differences in electrode behavior were observed when commercially available, premounted glassy carbon electrodes [Bioanalytical Systems, Inc.) were employed. Electrode potentials were measured and are quoted with respect to a sodium chloride saturated calomel electrode (SSCE).

Samples for electron spin resonance (ESR) experiments were prepared by electropolymerization of the desired complex onto a coiled Pt wire which served as the working electrode. Typically, the Pt wire was cycled continuously at 50 mV/s from 0 to 1.8 V vs. SSCE in a 0.5 mM solution of the complex in acetonitrile containing 0.1 M NaClO₄ as supporting electrolyte. After coating, the electrode was removed, rinsed with dry acetonitrile, and dried in a standard ESR tube under vacuum. The tube was then placed in the cavity and the ESR signal measured in the absence of solvent. Spectra were recorded on a Varian E-line Century Series X-band spectrometer operating in the absorption mode.

Results

A series of cyclic voltammograms recorded during the reductive electropolymerization of Ru(phen)₂(vbpy)²⁺ is shown in Figure 1. The continuous increase in the peak currents of the waves at -1.4 and -1.55 V results from accumulation of an electroactive polymer on the electrode surface. As with the polypyridine complexes described in previous studies,¹⁻¹² the deposition of polymer on the electrode is more rapid when the electrode potential is scanned over both of the reduction waves. Five additional Ru complexes and one Os complex, each containing two phenanthroline-based ligands and one vbpy ligand, were also electropolymerized in a similar fashion. These complexes and the formal potentials of the monomers and their polymeric products are listed in Table I. The reactivity of the M(phen)₂(vbpy) complexes contrasts sharply with that of the much less reactive M(bpy)2-(vbpy) analogues, which suggests that the reduced vbpy ligand may attack the phenanthroline ring system. It should be noted that $Ru(phen)_3^{2+}$ does not electropolymerize under these conditions, so that coupling between phen ligands on reduced complexes apparently does not occur at an appreciable rate.

⁽¹⁸⁾ Ghosh, P. K.; Spiro, T. G. J. Am. Chem. Soc. 1980, 102, 5543.
(19) Sprintschnik, G.; Sprintschnik, H. W.; Kirsh, P. P.; Whitten, D. G. J. Am. Chem. Soc. 1977, 99, 4947.

TABLE I: Formal Potentials of RuP₂(vbpy)²⁺ Monomers and Reductively Electropolymerized Polymers^a

Р	monomer			polymer		
	E _{3+/2+}	E_1	E_2	E3+/2+	E_1	E_2
phen	+1.22	-1.33	-1.51	+1.20	-1.30	-1.53
5-Clphen	+1.24	$(-1.29)^{b}$	c	+1.18	~-1.38	-1.60
5,6-Mephen	+1.12	$(-1.44)^{b}$	-1.62	+1.11	-1.41	-1.60
4.7-Phophene	+1.13	-1.38	-1.53	+1.14	-1.32	-1.49
4.7-Meaphen	+1.08	-1.44	-1.66	+1.08	-1.48	-1.66
3,4,7,8-	+1.02	-1.47	с	$+1.04^{d}$	-1.51	-1.69
Me ₄ phen						
phen	+0.72	-1.34	-1.52	+0.70	(-1.33) ^c	-1.52

^a Formal potentials are the average of cathodic and anodic peak potentials measured at a scan rate of 100 mV s⁻¹ at a glassy carbon electrode in CH₃CN with 0.1 M NaClO₄ as supporting electrolyte. $E_{3+/2+}$ corresponds to the M(III)/M(II) couples. E_1 and E_2 correspond to the first and second, ligand-centered, ^{6,15,20,21} reductions of the M(II) complex. ^b Adsorption of reduced material made measurement of the anodic peak potential imprecise. ^c Irreversible. ^dSecond, smaller couple also present at +1.24 V. ^ePh = phenyl. ^fOsmium(II) complex.

Estimates of the relative rates of the polymerization reactions can be obtained from the increase in charge consumed on successive reductive scans. The results of such measurements show that the rate of deposition obtained with the complexes listed in Table I is approximately the same except for Ru(4.7- $Ph_2phen)_2(vbpy)^{2+}$ which polymerizes much more slowly than the other six complexes. In fact, in DMF, no evidence for polymerization of this complex was observed, even after 60 min of continuous cycling. (All of the other complexes did electropolymerize in DMF, although their rates of polymerization were much lower than in acetonitrile.) This difference in reactivity needs to be accommodated by schemes proposed for the electropolymerization. Additional evidence useful for constructing a reaction scheme was obtained from the behavior of the Ru- $(3,4,7,8-Me_4phen)_2(vbpy)^{2+}$ complex. For this complex, the two cathodic waves corresponding to the reduction of the vbpy and Me_4 phen ligands, respectively, ^{15,20,21} are well separated. The first appears near -1.5 V and the second near -1.8 V. When the electrode is cycled between 0 and -1.6 V vs. SSCE, i.e., just beyond the peak for the reduction of the vbpy ligand, very little electropolymerization results. However, if the negative potential range is extended to −1.8 V, i.e., to the middle of the Me₄phen reduction wave, the polymerization proceeds at a much higher rate (Figure 2). Evidently reduction of both the vbpy and the Me₄phen ligands is necessary for rapid polymerization. Thus, it appears that radical or anionic chain growth pathways, which would require only a single reduced ligand, are relatively unimportant. A similar line of reasoning has been employed in arriving at a proposed mechanism for the electropolymerization of Ru(vbpy)₃²⁺ complexes.⁶

Three of the complexes yield polymers that display an unusual feature in their electrochemical responses. During electropolymerization of Ru(4,7-Me2phen)2(vbpy)2+, Ru(4,7-Ph2phen)2-(vbpy)²⁺, and Ru(3,4,7,8-Me₄phen)₂(vbpy)²⁺, a very prominent, reversible response develops in the region between -0.1 and -0.3V vs. SSCE (Figure 2). This response is surprising because the corresponding monomeric complexes exhibit no electrochemical activity in this potential region. Electropolymerized coatings that exhibit this unusual reversible response are blue rather than orange, the color obtained with the other Ru complexes. In aprotic solvents, the behavior is limited to complexes with substituents in the 4- and 7-positions. However, if the electropolymerizations are carried out in the presence of water, mineral acids, ammonium ions, or other proton donors, complexes with or without substituents in the 4- and 7-positions develop the same voltammetric response (see Figure 3) and yield blue instead of orange coatings. Depending on the exact conditions employed, the voltammetric responses in the potential region near -0.2 V can appear as a single



Figure 2. Cyclic voltammograms recorded continuously with 0.24 mM $[Ru(3,4,7,8-Me_4phen)_2(vbpy)]^{2+}$. Glassy carbon electrode (0.07 cm²). Other conditions as in Figure 1. (A) 75 cycles at potentials between +0.2 and -1.6 V; (B) 13 cycles between +0.2 and -1.8 V.



Figur: 3. Continuously recorded cyclic voltammograms for 0.2 mM $[Ru(5,6-Me_2phen)_2(vbpy)]^{2+}$. Supporting electrolyte: 0.1 M NaClO₄ + 0.1 mM HClO₄. Other conditions as in Figure 1.

reversible couple, as several well-defined reversible couples separated by several hundred millivolts, or as a broad, featureless wave. The behavior suggests that several different species and/or local environments may be involved.

The reversible response near -0.2 V remains relatively stable as long as the potential is not scanned to values more positive than ca. +1.4 V. However, a single scan of the potential to +1.5 V and back causes the response near -0.2 V to disappear, presumably because of an irreversible oxidation of the species responsible for the response. Consistent with this explanation is the fact that an irreversible oxidation peak, located slightly positive of the peak for the reversible oxidation of Ru(II) to Ru(III), is often observed on the first scan to +1.5 V and is absent on subsequent scans.

⁽²⁰⁾ Saji, T.; Aoyagui, S. J. Electroanal. Interfacial Electrochem. 1975, 58, 401.

⁽²¹⁾ Zuman, P. Substituent Effects in Organic Polarography; Plenum: New York, 1967.



Figure 4. Cyclic voltammograms of a coating containing a mixture of two complexes. The coating was prepared by cycling the potential of a glassy carbon electrode (0.2 cm^2) between 0 and -1.8 V at 100 mV s⁻¹ for several minutes in an acetonitrile solution containing 0.1 M NaClO₄ and 0.3 mM of both Ru(vbpy)₃(PF₆)₂ and Os(phen)₃(PF₆)₂. The coated electrode was washed and transferred to a pure supporting electrolyte solution to record the voltammograms shown. (A) Potential scanned between 0 and -1.8 V: solid line, steady response obtained with unoxidized coating; dashed line, initial response obtained between 0 and +1.5 V: dashed line, initial response obtained with unoxidized coating; solid line, steady response obtained with solid line, steady response obtained with oxidized coating.

Coatings of Mixed Complexes. The attack of reduced vbpy radical anion ligands on reduced phenanthroline ligands is a general reaction that introduces the possibility of preparing mixed complexes. For example, reduction of an equimolar mixture of $Ru(vbpy)_3^{2+}$ and $Os(phen)_3^{2+}$ at a transparent SnO_2 electrode produces a coating that contains both ruthenium and osmium complexes as determined by UV-vis spectrophotometry. The $Os(phen)_3^{2+}$ centers appear to be covalently bound and not simply physically encapsulated by the polymer because $Os(bpy)_3^{2+}$ is not incorporated under identical conditions.

Interestingly, the Os(phen) $_{3}^{3+/2+}$ couple is not observed in cyclic voltammograms of electrodes coated with the mixed polymer. This result can be rationalized by considering the likely polymer structure: Reduced phenanthroline ligands can react with reduced vinylbipyridine ligands but not with each other, so that the Os metal centers will have only Ru sites as nearest neighbors. On the other hand, the reduced vinylbipyridine ligands can couple with each other as well as reduced phenanthroline ligands so that the Ru sites in the polymer can have both Os and Ru neighbors. Since electron transport in these films is believed to occur via electron exchange between neighboring oxidized and reduced sites, the structure of the mixed complex coatings prevents oxidation of the Os(II) sites near the Os(phen) $_{3}^{3+/2+}$ potential. However, the Os(II) sites should be oxidizable by cross-reaction with Ru(III) sites that are generated at more positive potentials.

In Figure 4 are shown cyclic voltammograms for a mixed coating that are consistent with this interpretation. The steady, irreversible response at potentials near -1.4 V (solid line) arises from the Ru complexes in the coating. If the electrode potential is scanned to positive values where Ru(III) is generated (Figure 4B, dashed line), a large anodic peak is obtained on the first but not subsequent scans (Figure 4B, solid curve). The large magnitude of the peak results form the Ru(III)-mediated oxidation of the Os(II) centers. The resulting Os(III) centers are not reduced directly during the return scan because Ru(II) cannot reduce Os(III). A corresponding cathodic peak appears on the first subsequent scan to more negative potentials (Figure 4A, dashed curve) where the Os(III) centers are reduced by crossreaction with the reduced Ru(II) complex. The enhanced anodic and cathodic peaks are present at the same positions during every scan if the range of the potential scan is expanded to +1.5 to -1.8

"Charge-trapping spikes" similar to those in Figure 4 have been previously described and analyzed by Murray and co-workers in the case of bilayer coatings where the reactants giving rise to the enhanced current peaks are contained in an outer layer of the coating that makes electronic contact with the electrode only via



Figure 5. Cyclic voltammograms for an electropolymerized coating prepared by cycling a glassy carbon electrode (0.07 cm^2) between 0 and -1.8 V for several minutes in 0.3 mM $[\text{Ru}(\text{phen})_2(\text{vbpy})]^{2+}$. Potential scanned between (A) 0 and +1.5 V, anodic charge-trapping spike present only on first scan; (B) +1.5 and -1.8 V, charge-trapping spikes present in every scan; (C) 0 and -1.8 V, cathodic charge-trapping spike present only on first scan. Other conditions as a Figure 1.

the inner layer.⁹⁻¹² In the present case, the Os(III)/(II) centers responsible for the charge-trapping spikes are distributed uniformly throughout a single layer and their charge-trapping behavior results from the chemistry responsible for the deposition of the polymeric coatings that forces the Os centers to be surrounded by Ru centers.

All electroactive species that were dispersed throughout a polymeric Ru(vbpy)32+ coating in a way that prevented uninterrupted direct electronic pathways to the electrode surface would be expected to show behavior similar to that in Figure 4 if their formal potentials were between those where the $Ru(vbpy)_3^{2+}$ centers are oxidized (+1.0 V) and reduced (-1.3 V). This fact may help to explain the otherwise surprising observation that charge-trapping spikes are sometimes observed with single-component coatings. For example, coatings prepared by reductive electropolymerization of M(phen)₂(vbpy) complexes behave similarly to the mixed Ru-Os coatings (Figure 5), although no "trappable" species were intentionally introduced. Evidently, the reaction sequence involved in the electropolymerization produces some isolated sites with formal potentials between +1.0 and -1.3V. It may be that the electrogenerated species that gives rise to the reversible voltammetric responses shown in Figures 2 and 3 may also be formed at sites that lack a direct pathway to the electrode so that their existence is only evident from the charge-trapping responses they produce. The observed behavior suggests that the use of complexes containing 4,7-substituted phenanthrolines and/or the presence of proton donors favors the production of untrapped species with formal potentials near -0.2 V while the generation of trapped species is more common in the absence of 4,7-substituents or proton donors.

Discussion

On the basis of the results we have described, a possible reaction sequence to account for the reductive electropolymerization of $\operatorname{RuP}_2(vbp\bar{y})^{2+}$ complexes (where P represents a phenanthrolinebased ligand) can be proposed (Scheme I). After an initial one-electron reduction (reaction 1, Scheme I), dimerization could occur via radical-radical coupling of the vinyl moieties (reaction 2), followed by rapid protonation of the coupled product (reaction 3).^{6,13,14} However, such vinyl-vinyl coupling is relatively inefficient^{6,13,14} so that most of the singly reduced monomer (II) is likely to survive long enough to undergo a second one-electron reduction at the electrode^{6,13,14} (reaction 4) to yield a complex containing a pair of reduced ligands. An alternative type of radical-radical coupling can now occur, in which a reduced vinyl group on one complex attacks the reduced phenanthroline ring of a second complex (reaction 5). This facile vbpy-phen radical-radical coupling is the novel feature of the RuP₂(vbpy)²⁺ complexes.

SCHEME I



Previously reported examples involved only vinyl-vinyl coupling.⁶ Our results suggest that conventional radical and/or anionic chain growth pathways are inefficient with the $RuP_2(vbpy)^{2+}$ complexes because the electropolymerization proceeds very slowly when only a single ligand is reduced. One reason may be that the 2-position, which is the site most susceptible to radical attack in the free ligands,²² is sterically hindered in the coordinated ligands. The radical-radical coupling reaction (reaction 5 in Scheme I) is expected to be much faster^{6,23} than radical or anionic chain growth, and its rate is further enhanced by the high concentration of radicals near the electrode surface.

A similar reactivity pattern is exhibited by both pyridinium and quinoline derivatives, which generally dimerize via 2-2' or 4-4'radical-radical coupling following electroreduction.²⁴⁻²⁷ These precedents, along with the much lower rate of reductive electropolymerization of $Ru(4,7-Ph_2phen)_2(vbpy)^{2+}$, suggest that the coupling involves the 4- or 7-position of the phenanthroline ligand, as depicted in Scheme I. Further evidence implicating the 4- and 7-positions comes from previous photolysis²⁸ and radiolysis²⁹

(29) Venturi, M.; Emmi, S.; Fuochi, P. G.; Mulazzani, Q. G. J. Phys.

studies, where free-radical attack on coordinated phenanthroline, initially thought to occur at the 5- or 6-postions,²⁸ was shown to occur at the 4-position.²⁹ Interestingly, and in accord with the present results, the analogous bipyridine complexes are essentially unreactive.29

The coupling reaction depicted in reaction 5 of Scheme I produces a neutral but very basic species that would be expected to extract a proton from extraneous water or from the acetonitrile solvent itself (reaction 6) to produce VII. The reduced vinylbipyridine and phenanthroline ligands in species VII would be reoxidized at potentials near -1.3 V during the scan of the potential to more positive values (reaction 7). The oxidation product, VIII, is analogous to intermediates that are formed in nucleophilic substitution reactions of pyridine with alkyllithium reagents^{30,31} and with alkali amides (Chichibabin reaction).^{32,33}

Species VIII also resembles the product obtained when quinoline is reduced in nonaqueous solvents.²⁷ This reaction proceeds in the two one-electron steps shown in reaction A. The quinoline



radical anion formed first is rapidly protonated by even traces of water, and the product is easier to reduce than quinoline itself so that a second electron is consumed. Both experimental and theoretical evidence is available^{27a,d} to support assignment of the 4-position in the quinoline molecule as the site of the protonation.

Cyclic voltammograms for the quinoline system exhibit an anodic peak at a potential much more positive than that where the quinoline reduction peak appears.²⁷ The anodic peak is attributable to the reverse of reaction A, which must proceed at the more positive potential required for oxidation of the doubly reduced anion that closely resembles species VIII in Scheme I. Thus, reaction A is reversible, but the cathodic and anodic peak potentials are widely separated.

The assumption that species VIII behaves analogously to the doubly reduced anion of the quinoline system provides a possible explanation for the electrochemical response near -0.2 V in Figures 2 and 3. The reasoning is outlined in Scheme II. The half-reaction for the $RuP_2(vbpy)^{2+}$ system that is analogous to the second electron-transfer step of reaction A is reaction 8 in Scheme II. With the quinoline system, the anodic peak has no cathodic counterpart near the same potential²⁷ while a reversible response near -0.2 V is obtained with the RuP₂(vbpy)²⁺ system. We believe this difference helps to support our interpretation because the presence of substituents in the 4- and 7-positions of the original complex would make it impossible for intermediate IX in Scheme II ($\mathbf{R} \neq \mathbf{H}$) to deprotonate to form intermediate X. As a result, IX should persist at the electrode surface where it would give rise to a cathodic wave near the same potential where it was formed (half-reaction 8). When the 4- and 7-positions are occupied by hydrogen, intermediate IX (R = H) can deprotonate to form X (reaction 9), which would be rapidly oxidized (reaction 10) at the potential where reaction 8 proceeds. However, if reaction 9 were reversible, the presence of excess protons could prevent the deprotonation of IX and thereby result in reversibility for reaction 8, even when $\mathbf{R} = \mathbf{H}$. This provides an explanation for the ability of added acid to stabilize the reversible response near -0.2 V in Figures 2 and 3.

Further evidence supporting the assignment of the reversible response near -0.2 V in Figures 2 and 3 to reaction 8 in Scheme II was obtained from an EPR experiment: The coating resulting

⁽²²⁾ Brown, R. D. J. Chem. Soc. 1956, 272.

⁽²³⁾ Szwarc, M. Carbanions, Living Polymers, and Electron Transfer Processes; Interscience: New York, 1968; pp 367-378.

⁽²⁴⁾ Raghavan, R.; Iwamoto, R. T. J. Electroanal. Chem. 1978, 92, 101. (25) See, for example; *Pyridine and Its Derivatives*; Klingsberg, E., Ed.; Interscience: New York, 1960, and supplements, Parts I and II, Abramovitch,

R. A., ed.; Interscience: New York, 1974, and references therein. (26) See, for example: Quinolines, Jones, G., Ed.; Wiley: New York, 1977

⁽²⁶⁾ See, for example: *Quinoines*, Jones, G., Eu.; whey: New FOR, 1977
(Part I); 1982 (Part II), and references therein.
(27) (a) Smith W. H.; Bard, A. J. J. Am. Chem. Soc. 1975, 97, 6491. (b)
Millefiori, S. J. Heterocycl. Chem. 1970, 7, 145. (c) Fujinga, T.; Izutsu, K.;
Takaoka, K. J. Electroanal. Chem. 1966, 12, 203. (d) Chaudhuri, J.; Kume,
S.; Jagar-Grodzinski, J.; Szwarc, M. J. Am. Chem. Soc. 1968, 90, 6421.
(28) DeArmond, K.; Halper, W. J. Phys. Chem. 1971, 75, 3230.
(20) Varture M.: Empris S.: Fucchi P. G.: Mulazzani O. G. J. Phys.

Chem. 1980, 84, 2160.

⁽³⁰⁾ Foster, R.; Fyfe, C. A. Tetrahedron 1969, 25, 1389.

⁽³¹⁾ Giam, C. S.; Stout, J. L. Chem. Commun. 1969, 142.

⁽³²⁾ Bergstrom, F. W. J. Org. Chem. 1937, 2, 411 and references therein. (33) Bergstrom, F. W.; Sturz, H.; Tracy, H. J. Org. Chem. 1946, 11, 239 and references therein.



from the reductive electropolymerization of Ru(4,7-Me₂phen)₂- $(vbpy)^{2+}$ was maintained for several minutes at +0.2 V where radical IX in Scheme II is expected to be stable. Transfer of the washed and dried film to the EPR spectrometer produced a single-line signal with g = 2.003. The signal disappeared if the electrode potential was set between -0.5 and -1.0 V for several minutes before recording the spectrum. The EPR signal could be removed and restored several times (with some loss of intensity) by cycling the electrode potential between +0.2 and -0.8 V. These results indicate that reaction 8 in Scheme II is reversible and that the radical, IX, is apparently fairly stable within the polymeric coating. No hyperfine structure was detected in the EPR spectrum at temperatures as low as 10 K, presumably because of very rapid exchange interactions within the polymer.^{34,35} A Dysonian line shape³⁶ was observed for several samples, even at room temperature, suggesting that the polymeric coatings possess at least some electronic conductivity in the dry state.^{36,3}

In the absence of acid, with complexes where R = H, the anodic wave near -0.2 V is present only for the first few scans of the electropolymerization. Apparently, these first few scans produce a thin layer of polymeric material on the electrode surface that interferes with the continued oxidation of VIII via reactions 8-10 in Scheme II. This behavior may result from the following sequence of events: During the cathodic portion of the first cycle, vbpy-phen coupling proceeds as shown in Scheme I (eq 5). The return scan eventually produces intermediate VIII, which undergoes an irreversible oxidation (reactions 8-10 in Scheme II), leading to a layer of polymeric XI on the electrode surface in which the basic ruthenium polypyridine structure remains intact. Thus, since this is a redox polymer, and ruthenium polypyridines are electroinactive between about +1.0 V and -1.3 V, the layer of polymeric XI acts as an electrical insulator in this potential region.⁹⁻¹² Electropolymerization can still proceed, because the necessary reduction of additional monomer in solution occurs at more negative potentials (-1.5 V) where the film is redox-conductive. However, the anodic waves at -0.2 V disappear because the insulating layer next to the electrode surface prevents the

⁽³⁴⁾ Servant, R.; Palangie, E. Adv. Mol. Relaxation Interact. Processes 1978, 13, 231.

⁽³⁵⁾ Gaudiello, J. G.; Ghosh, P. K.; Bard, A. J. J. Am. Chem. Soc. 1985, 107, 3027.

⁽³⁶⁾ Dyson, F. J. Phys. Rev. 1955, 98, 349.

⁽³⁷⁾ Murray, D. P.; Kispert, L. D.; Frommer, J. E. J. Chem. Phys. 1985, 83, 3681 and references therein.

oxidation of any material in the outer layers at this potential. In essence, a bilayer electrode⁹⁻¹² is produced, with an inner layer consisting of structures such as XI and the outer layer consisting of structures such as VIII.

In cases where radical IX contains no substituents in the 4- or 7-positions of the phenanthroline rings (R = H), it may be converted to the final product, XI, by another pathway that depends on the electrode potential. At sufficiently positive potentials, the oxidation of IX (reaction 11, Scheme II) could precede a rapid deprotonation^{38,39} (reaction 12). This second pathway may account for the irreversible oxidation often observed when the potential was swept to +1.5 V. However, the subsequent disappearance of the response near -0.2 V is more difficult to explain because the reverse of reactions 10 and 9 would permit radical IX to be regenerated. This disappearance of the response at -0.2 V following a potential excursion to +1.5 V is not yet understood.

Another feature of these films that is difficult to understand, particularly for the unsubstituted complexes in the absence of acid, is the stability of the prominent charge-trapping peaks. If the complex exists in the radical form (IX) for an appreciable amount of time, deprotonation and oxidation would be expected to occur (eq 9 and 10) leading eventually to a film containing only polypyridine units (structure XI). The charge-trapping peaks should then disappear because the film would consist entirely of one species. However, this is not observed; the trapping peaks are stable to repeated cycling for hours in very dry solvents. The origin of this behavior is unclear. It might indicate that additional species, such as reduced ligand sites (structure XIII), can lead to the appearance of the charge-trapping peaks.

In addition to the one-electron oxidation/reduction depicted in reaction 8 of Scheme II, intermediate VIII can undergo several other reactions. For example, when R = H, elimination of hydride from the C-4 position (reaction 13) may proceed to produce a binuclear complex (XI) containing a phenanthroline ligand substituted in the 4-position. Such hydride elimination reactions are well-known in the nucleophilic substitutions of pyridine. $^{25,30\text{--}33}$ In the present case, hydride elimination would lead to the same product (XI) that is obtained by the sequence of reactions 8 to 10 or 8, 11, 12 in which the polypyridine ligands that occupy the coordination sphere of the ruthenium remain essentially unperturbed. For this reason, the electrochemical behavior of the polymer coating resulting from either pathway would be expected to mimic that of the monomeric precursor from which it was generated. In fact, the formal potentials of the surface wave for the polymer films match those of the corresponding monomeric complexes (Table I), which indicates that species XI is the major component of the polymeric coatings.

A final pathway available to intermediate VIII involves protonation to yield structure XIII or a related isomer in which the phenanthroline ligand has been partially reduced (reaction 14). The electrochemistry of a polymer coating containing such reduced ligands would be expected to differ significantly from that of the original monomeric complex because the formal potential of the Ru^{III/II} couple would be more negative if one (or more) of the coordinated N atoms became saturated.⁴⁰ Although no such products were observed by the electrochemical methods employed here, their presence could not be precluded. If their concentrations were low, the redox activity of these sites would be evident only through charge-trapping peaks.9-12 At present, it is impossible to assess how much, if any, of the charge-trapping behavior that is observed arises from species such as XIII or further reduction products. However, a large contribution from such species might account for the otherwise unexpected stability of the chargetrapping peaks.

Summary and Conclusions

Complexes of the general type $RuP_2(vbpy)^{2+}$ (where P is a phenanthroline-based ligand) have been found to undergo rapid polymerization following two-electron electroreduction. The mechanism of the polymerization appears to involve radical-radical coupling of the vinylbipyridine and phenanthroline ligands, with the 4- and 7-positions of phenanthroline being the most reactive. The coupling process leads to a complicated reaction sequence in which a variety of products are possible, some of which can be interconverted by electrochemical oxidation or reduction. The net result is the deposition on the electrode of an electroactive, redox-conductive film containing several chemically distinct species. The presence of these species can be inferred from charge-trapping peaks and, under favorable conditions, they can be observed directly in cyclic voltammograms of the electrode coatings. In some cases, the electropolymerization apparently produces a bilayer electrode in essentially a single step.

One attractive feature of the coupling reactions described here is their potential utilization in the production of binuclear metal complexes. For example, electroreduction of a mixture of Ru-(bpy)₂(vbpy)²⁺ and Ru(bpy)₂(phen)²⁺ would be expected to produce $[(bpy)_2Ru(vbpy-phen)Ru(bpy)_2]^{n+}$. Such chemistry might then be extended to the synthesis of mixed-metal binuclear, trinuclear, and tetranuclear species, as well as electron donoracceptor complexes. It is clear from the present results that careful control of reaction conditions will be necessary to constrain the reaction sequence to the desired pathway in the face of the numerous alternative possibilities.

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 ⁽³⁸⁾ Rollick, K. L.; Kochi, J. K. J. Am. Chem. Soc. 1982, 104, 1319.
 (39) Grodkowski, J.; Neta, P.; Schlesener, C. J.; Kochi, J. K. J. Phys. Chem. 1985, 89, 4374.

⁽⁴⁰⁾ Mahoney, D. F.; Beattie, J. K. Inorg. Chem. 1973, 12, 2561.