

β'_4 values listed for other species if the relative HSAB acidities²⁵ of the various ions are taken into account.

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Oxidative Electropolymerization of Polypyridyl Complexes of Ruthenium

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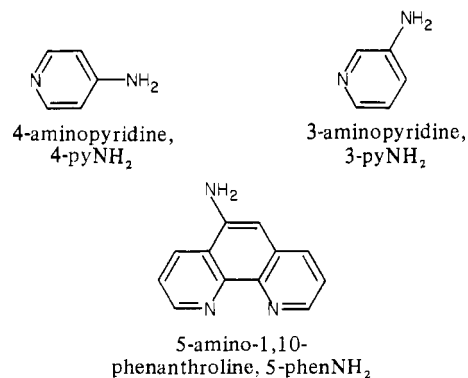
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It has been found that polypyridyl complexes of ruthenium that contain aromatic amine groups, e.g., [(bpy)₂Ru(4-pyNH₂)₂]²⁺ (bpy = 2,2'-bipyridine, 4-pyNH₂ = 4-aminopyridine), [(bpy)₂Ru(3-pyNH₂)₂]²⁺ (3-pyNH₂ = 3-aminopyridine), [(bpy)₂Ru(5-phenNH₂)₂]²⁺ (5-phenNH₂ = 5-amino-1,10-phenanthroline), [(bpy)Ru(5-phenNH₂)₂]²⁺, and [Ru(5-phenNH₂)₃]²⁺, undergo electrochemically induced, oxidative polymerization reactions. The resulting polymers form fairly stable, electrochemically active films on the oxidizing electrode, which can be Pt, SnO₂, or vitreous carbon. Complexes containing only one amine substituent are difficult to polymerize but can be copolymerized with [Ru(5-phenNH₂)₃]²⁺. Evidence is presented to suggest that the polymerization process is ligand based and affected by the addition of base to the polymerization media. Stability studies indicate that the films lose electrochemical activity upon repeated oxidative cycling in the presence of trace H₂O. Visible and IR spectroscopies were employed to probe the nature of the polymer link, and the results are discussed with respect to mechanistic studies of the oxidative electropolymerization of aniline.

Introduction

Recent work has shown that polypyridyl complexes of ruthenium and osmium containing conjugated olefinic groups form stable, electroactive polymeric films on the electrode following electrochemical reduction of a π^* molecular orbital of one of the polypyridyl ligands.^{1,9} This reduction presumably initiates a free-radical, anionic olefin polymerization process, which results in the polymer-coated electrodes.

One of our goals has been to invent a broadly based chemistry for the incorporation of metal complex sites into polymers^{1b,2} and polymer films. In this paper we introduce a new approach to the preparation of polymer films by electrochemical polymerization. The approach is based on the oxidative polymerization of ruthenium complexes that have an aromatic amine group or groups on the surrounding ligands; the ligands used here are



The reasoning for our experiments was based on the known oxidative electropolymerization of aniline and its derivatives;³ oxidation of aniline and related compounds to their radical cations results in polymeric film growth on the electrode surface. Since oxidation of a complex like [Ru(5-phenNH₂)₃]²⁺ results in the oxidation of the ligand, we anticipated that analogous polymerization reactions might occur following oxidation of the complexes. In fact, the strategy has proven successful and we have prepared polymeric films on Pt, SnO₂, and vitreous carbon electrodes from [Ru(5-phenNH₂)₃]²⁺ and similar complexes.

There is an important difference between films prepared by oxidative electropolymerization of [Ru(5-phenNH₂)₃]²⁺ and those from aniline. Poly(aniline) films prepared by oxidation in pyridine/acetonitrile solution tend to act as electrical insulators.^{3a,c} As insulators, they inhibit electron transfer between the electrode and redox couples in the external solution, including the oxidation of additional aniline monomer, which stops film growth. Poly(aniline) films prepared in 0.1 M H₂SO₄^{3b} are less readily passivated but still do not have well-defined electrochemical reactivity. In contrast, films of poly-[Ru(5-phenNH₂)₃]²⁺ display well-defined Ru^{III/II} electrochemical reactivity and continued film growth via film-mediated oxidation of additional monomer, as well as film-mediated oxidation of other redox couples in an external solution.

Experimental Section

Materials. Tetraethylammonium perchlorate (TEAP) was prepared with use of a literature procedure,⁴ purified by recrystallization from hot water four times, dried under vacuum at 100 °C for 10 h, and stored in a vacuum desiccator. Acetonitrile (Burdick and Jackson)

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and pyridine (Fisher, distilled from BaO) were stored over Davison 4-Å molecular sieves. Alumina (Woelm Pharmaceutical, activity 1), 2,6-lutidine (Aldrich), and ligands (Aldrich, Polysciences) were used as received. All other solvents were reagent grade. Ammonium hexafluorophosphate (Aldrich, 95%) was filtered as an aqueous solution prior to use.

Preparation of Complexes. The ruthenium complexes $[(bpy)_2Ru(vpy)_2](PF_6)_2$ ^{1a} (bpy is 2,2'-bipyridine; vpy is 4-vinylpyridine), $[Ru(bpy)_3](PF_6)_2$, and $[Ru(phen)_3](PF_6)_2$ ⁵ (phen is 1,10-phenanthroline), as well as the starting materials *cis*- $Ru(bpy)_2Cl_2 \cdot 2H_2O$ ⁶ and "(bpy)RuCl₄"⁷ were prepared as reported previously.

$[(bpy)_2Ru(4-pyNH_2)_2](PF_6)_2$. A 10-fold molar excess of 4-aminopyridine (1.81 g, 19.2 mmol) dissolved in 75 mL of ethanol was added to 0.500 g (10.96 mmol) of *cis*- $Ru(bpy)_2Cl_2 \cdot 2H_2O$ dissolved in 75 mL of hot H₂O (in aqueous solution the dominant form of the complex is $Ru(bpy)_2(H_2O)Cl^+$) and heated at reflux for 24 h. Most of the ethanol was removed by rotary evaporation, and a 5-fold molar excess of NH_4PF_6 (0.78 g, 48 mmol) dissolved in H₂O was added to the clear, cherry red solution. The resulting precipitate was collected by suction filtration, redissolved in a minimum amount of acetonitrile (<5 mL), and dropped into rapidly stirred diethyl ether (350 mL). The orange-red powder was collected by suction filtration, washed with ether, and allowed to dry overnight under vacuum; yield 0.81 g (95%). Anal. Calcd for $[(bpy)_2Ru(4-pyNH_2)_2](PF_6)_2$: C, 40.41; H, 3.17; N, 12.57. Found: C, 40.31; H, 3.31; N, 12.56. (Complexes of the type $[(bpy)_2Ru(py)_2]^{2+}$ are photolabile,⁸ and manipulations in solution involving this and related complexes were carried out in the absence of light.)

$[(bpy)_2Ru(3-pyNH_2)_2](PF_6)_2$. The procedure was as described above. The product is an orangish powder. Anal. Calcd for $[(bpy)_2Ru(3-pyNH_2)_2](PF_6)_2$: C, 40.41; H, 3.17; N, 12.57. Found: C, 40.12; H, 3.40; N, 12.39.

$[(bpy)_2Ru(5-phenNH_2)](PF_6)_2 \cdot H_2O$. A 10% molar excess of 5-amino-1,10-phenanthroline (0.21 g, 1.08 mmol) dissolved in 100 mL of hot ethanol was added to 0.500 g (0.96 mmol) of *cis*- $Ru(bpy)_2Cl_2 \cdot 2H_2O$ dissolved in 50 mL of hot H₂O. The solution was deaerated with argon for 20 min and then heated at reflux for 3 h under argon. Most of the ethanol was removed by rotary evaporation, and a 5-fold molar excess of NH_4PF_6 (0.98 g, 4.8 mmol) dissolved in H₂O was added to produce an orangish precipitate. The product was collected by suction filtration and purified by elution chromatography on an alumina column with a 2:1 toluene-acetonitrile solution. After elution and evaporation, the product was redissolved in a minimum amount of acetonitrile (<5 mL) and dropped into 350 mL of rapidly stirred diethyl ether. The orangish powder was collected by suction filtration, washed with diethyl ether, and dried overnight under vacuum; yield 0.78 g (90%). Anal. Calcd for $[(bpy)_2Ru(5-phenNH_2)](PF_6)_2 \cdot H_2O$: C, 41.93; H, 2.96; N, 10.70. Found: C, 42.20; H, 2.89; N, 10.51.

$[(bpy)Ru(5-phenNH_2)_2](PF_6)_2 \cdot 2H_2O$. A 10% molar excess of 5-amino-1,10-phenanthroline (0.44 g, 2.25 mmol) suspended in 10 mL of DMF was added to 0.400 g (1.0 mmol) of "(bpy)RuCl₄" suspended in 15 mL of DMF. The mixture was deaerated with argon for 20 min and then heated at reflux overnight under argon. A 5-fold molar excess of NH_4PF_6 (0.78 g, 4.8 mmol) dissolved in 125 mL of H₂O was added to the reaction solution at room temperature. The resulting orange precipitate was collected and purified as described above; yield 0.47 g (50%). Anal. Calcd: C, 41.94; H, 3.11; N, 11.51. Found: C, 42.29; H, 2.69; N, 11.24.

$[Ru(5-phenNH_2)_3](PF_6)_2$. A 10% molar excess of 5-amino-1,10-phenanthroline (1.00 g, 5.12 mmol) suspended in 10 mL of DMF was added to 0.406 g (1.55 mmol) of $RuCl_3 \cdot 3H_2O$ suspended in 5 mL of DMF. The resulting mixture was deaerated with argon for 20 min and heated at reflux for 10 h under argon. After the mixture was cooled to room temperature, a 5-fold molar excess of NH_4PF_6 (1.26 g, 7.75 mmol) dissolved in 10 mL of H₂O was added, and the orangish precipitate was collected and purified as described above; yield 0.45 g (30%). Anal. Calcd for $[Ru(5-phenNH_2)_3](PF_6)_2$: C, 44.27; H, 2.79; N, 12.91. Found: C, 44.38; H, 2.98; N, 12.88.

Electrochemistry. Experiments were performed in acetonitrile with 0.1 M tetraethylammonium perchlorate (TEAP) supporting electrolyte in conventional three-compartment "H" cells for electropolymerization and in one-compartment cells for prepared films. Electrochemical potentials were recorded vs. the saturated sodium chloride electrode (SSCE). Where noted, 0.2 M 2,6-lutidine or 0.2 M pyridine was added to the monomer solution. In some cases, the electrochemistry was carried out in a drybox with freshly distilled acetonitrile and freshly dried TEAP and with added activated alumina to ensure removal of trace H₂O from the electrolyte solution. Cyclic voltammograms were obtained without *iR* compensation at 200 mV/s with a Princeton Applied Research Model 175 universal programmer and a Model 173 potentiostat and were recorded on a Hewlett-Packard 7015B X-Y recorder. Electrodes were either SnO₂ films on glass or platinum disks with Teflon shrouds. Pt surfaces were polished with 1-μm diamond paste (Buehler) on a Gould 550/1140 rpm polishing wheel (Buehler). Where necessary, solutions were degassed for ca. 20 min with solvent-saturated argon. Trace oxygen and H₂O were removed by passing the argon through a column packed with R3-11 catalyst (Chemical Dynamics Corp.), a column packed with potassium hydroxide, and finally a column packed with 4-Å molecular sieves (Davison).

Apparent surface coverages (Γ_T^{app} , mol/cm²) were calculated by using the equation $\Gamma_T^{app} = Q_c/nFA$ (where *n* is the number of electrons per molecule reduced, *F* is Faraday's constant, *A* is the area of the electrode in cm², and *Q_c* is the charge (area) under the reductive Ru^{III/II} wave as evaluated by planimetry). For the thicker films (>>10⁻⁸ mol/cm²) the procedure may underestimate the actual quantity of monomer sites in the film because of slow electrochemical response on the time scale of the experiment, but the accuracy is believed sufficient for the purposes of this study.

Statements as to the apparent number of "layers" of polymeric material are based on a hard-sphere model for Ru/polypyridine type complexes,⁹ in which a monolayer of polymeric material corresponds to ca. 8 × 10⁻¹¹ mol/cm². However, it should be noted that the uniformity of polymer film growth is unknown for these films, and complete coverage of the electrode may require many effective "layers".¹⁰

Relative rates of film growth were defined by the following procedure: (1) The surface coverage of a film prepared by oxidative electropolymerization for a particular amine complex was determined by cyclic voltammetry. (2) The coverage in (1) was divided by the coverage resulting from the reductive electropolymerization of the reference compound, $[(bpy)_2Ru(4-vpy)_2]^{2+}$ (4-vpy = 4-vinylpyridine), also determined by cyclic voltammetry. The reductive electropolymerization procedure involved cycling the electrode potential 10 times from -1.0 to -1.5 V in a 0.1 M TEAP/CH₃CN solution containing 0.0015 M $[(bpy)_2Ru(4-vpy)_2]^{2+}$ and measuring coverage on the basis of the Ru^{III/II} wave. In the oxidative polymerizations, the electrode potential was scanned 10 times over a 1.0-V range with scan limits set so that the Ru^{III/II} waves for the different monomers were all approximately in the same relative position between the scan limits. Equal concentrations (0.003 M) of polymerizable amine groups were present in the 0.1 M TEAP/CH₃CN solutions (vs. 0.001 M monomer was used if the complex possessed three amine groups, 0.0015 M if the complex possessed two amine groups, and 0.003 M if the complex possessed only one amine group). The film coverages on the electrodes were determined after the electropolymerization period in fresh 0.1 M TEAP/CH₃CN. The above protocol proved to be successful in obtaining a high degree of reproducibility in comparisons involving relative film growth rates.

Analytical Measurements. Elemental analyses were performed either by Integral Microlabs, Raleigh, NC, or by Galbraith Laboratories, Knoxville, TN. Ultraviolet and visible spectra of monomers in solutions and of polymeric films (dry) supported on polyvinyl chloride (PVC) were recorded with a Bausch and Lomb Model 210 spectrophotometer. The use of PVC as a support for polymeric films will be described in detail in a forthcoming publication.¹¹ Infrared spectra were obtained with a Beckman 4250 spectrophotometer either as KBr pellets or as thin films supported on PVC. XPS measurements

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Table I. Spectral and Electrochemical Data for Monomeric Complexes as PF_6^- Salts

complex	$E^{\circ}_{\text{soln}}, \text{V}^a$	vis abs max ^b	
		$\lambda_{\text{max}}, \text{nm}$	$\epsilon, \text{L}/(\text{mol cm})$
$[(\text{bpy})_2\text{Ru}(3\text{-pyNH}_2)_2]^{2+}$	+1.18	463 329	7.85×10^3 1.59×10^4
$[(\text{bpy})_2\text{Ru}(4\text{-pyNH}_2)_2]^{2+}$	+0.99	491	8.30×10^3
$[(\text{bpy})_2\text{Ru}(5\text{-phenNH}_2)_2]^{2+}$	+1.31	455 370	1.59×10^4 1.06×10^4
$[(\text{bpy})\text{Ru}(5\text{-phenNH}_2)_2]^{2+}$	+1.39 ^c	462 364	1.66×10^4 1.69×10^4
$[\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$... ^d	470 364	1.61×10^4 2.07×10^4

^a E°_{soln} is the average of $E_{\text{p,a}}$ and $E_{\text{p,c}}$ and was determined by cyclic voltammetry in 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$ at a platinum electrode vs. the saturated sodium chloride electrode. The scan rate was 200 mV/s. ^b In CH_3CN at 23 °C. ^c This value is approximate because direct ligand oxidative waves overlap the metal II/III oxidative wave (see text). ^d Electropolymerization was too rapid to see the $\text{Ru}^{\text{III/II}}$ wave for the solution couple.

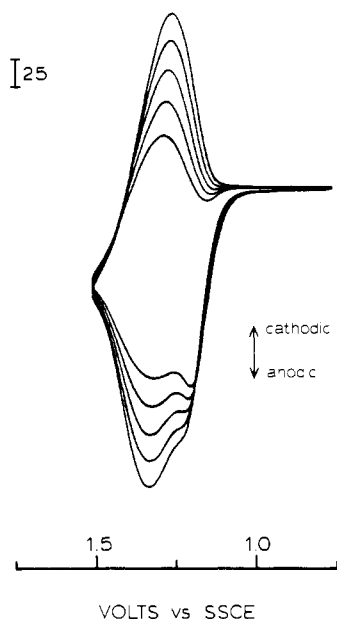


Figure 1. Oxidative electropolymerization of 1 mM $[\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$ at a platinum electrode by repeated potential scans (third through seventh shown) at 200 mV/s between +0.6 and +1.6 V vs. SSCE in 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$. The increase in wave size arises because of polymer film growth. The current scale is shown in the upper left-hand corner in μA .

were made with a Du Pont Model 605B electron spectrometer. Samples were prepared either by electropolymerizing onto a Pt-flag electrode or by pressing a powdered sample of the salt onto the face of an indium plate.

Results

Spectral and electrochemical properties of the monomeric complexes are summarized in Table I. The formal potential, E°_{soln} , reported for the monomer is that for the more reversible wave observed and is thought to correspond to the $\text{Ru}^{\text{III/II}}$ reaction. Irreversible ligand-based oxidative waves can also be observed as discussed below. Potential values for the $\text{Ru}^{\text{III/II}}$ couples were obtained from the first one to two potential scans, before the electrode was completely coated with polymer. Polymerization of $[\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$ proceeded too rapidly to obtain a reliable potential for the monomeric couple in solution.

Oxidative Electropolymerization. Repeatedly scanning the potential of a Pt electrode in a 0.1 M TEAP/ CH_3CN solution containing 0.001 M $[\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$ (not deaerated) over

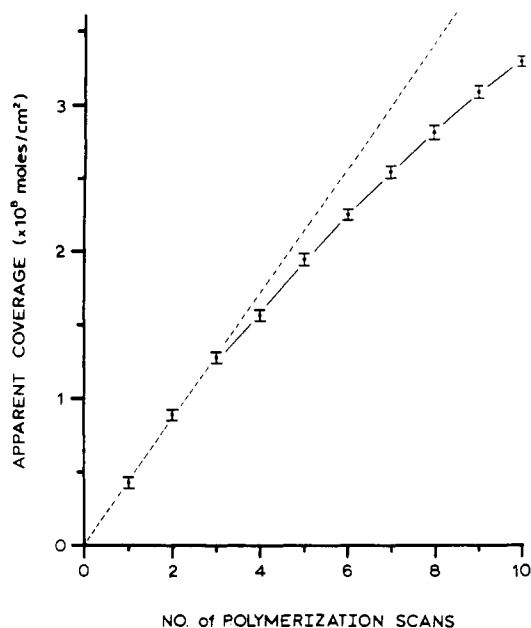


Figure 2. Plot of the apparent surface coverage of $[\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$ vs. the number of electropolymerization scans under the same scan conditions as described in Figure 1. Note that the apparent surface coverages were determined after each scan in a fresh electrolyte solution.

the range +0.6 to +1.6 V vs. SSCE results in a continuous increase in the size of the cyclic voltammogram wave for the $\text{Ru}^{\text{III/II}}$ couple, as shown in Figure 1. If after a period of scanning, the electrode is transferred, with thorough rinsing with acetone, to fresh electrolyte (containing no monomeric complex), the observed $\text{Ru}^{\text{III/II}}$ wave persists (see Figure 6A). Similar observations were made in our earlier work on reductive electropolymerization.^{1a} The behavior shown in Figure 1 suggests that an electroactive and presumably polymeric film of the complex forms on the electrode as a consequence of oxidation. The current observed in Figure 1 for the $\text{Ru}^{\text{III/II}}$ wave arises from the $\text{Ru}^{\text{III/II}}$ couple within the growing film and from the mediated oxidation of monomeric complex in the external solution, part of which becomes incorporated into the film as it grows.

The results shown in Figure 1 for $[\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$ can also be obtained with glassy-carbon or highly doped SnO_2 electrodes. The other complexes used in this study gave similar results. There is a prewave at the onset of the $\text{Ru}^{\text{II}} \rightarrow \text{Ru}^{\text{III}}$ oxidation wave and a slight positive shift in E°_{surf} as the film grows. Similar prewaves have been observed for electrode/film interfaces prepared by reductive electropolymerization and their origin is not well understood (vide infra).

Figure 2 shows how the charge under the $\text{Ru}^{\text{III/II}}$ surface wave increases with an increasing number of electropolymerizing potential scans for $[\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$. The apparent coverages were calculated from data like those shown in Figure 1 except that the cyclic voltammograms were obtained in a fresh electrolyte solution. The calculations were based on the area under the $\text{Ru}^{\text{III/II}}$ reductive waves. The apparent surface coverage by the Ru complex increases linearly over the first three potential scans, and less rapidly thereafter. After the third potential scan the equivalent of ca. 160 monolayers of electroactive complex sites (see Experimental Section) had been incorporated into the film. The extent of surface coverage is independent of scan rate over the range 50–200 mV/s, showing that the origin of the nonlinearity of Figure 2 is not from the onset of charge-transport limitations in the thickening film, which could arise if not all the Ru^{II} sites are oxidized during an oxidative potential scan. The falloff in rate of surface coverage is also not caused by depletion of the mo-

Table II. Apparent Film Coverages and Formal Potentials for Oxidatively Electropolymerized Complexes at a Scan Rate of 200 mV/s

monomer complex electropolymerized	potential scan lim, V	polymerization medium	E° , ^a surf vs. SSCE, ^d V	apparent film coverage mol/cm ² ^e	coverage rel to [(bpy) ₂ Ru(4-vpy) ₂] ²⁺ ^f
[(bpy) ₂ Ru(3-pyNH ₂) ₂] ²⁺	+0.37 ⇌ +1.37	a	+1.32	1.75 × 10 ⁻¹¹	0.062
		b	+1.31	9.72 × 10 ⁻¹⁰	1.99
		c	+1.51	8.11 × 10 ⁻¹¹	0.199
[(bpy) ₂ Ru(4-pyNH ₂) ₂] ²⁺	+0.37 ⇌ +1.37	a	+1.34	1.49 × 10 ⁻¹¹	0.074
		b	+1.33	4.74 × 10 ⁻¹⁰	4.07
		c	+1.40	4.75 × 10 ⁻¹¹	0.341
[(bpy) ₂ Ru(5-phenNH ₂) ₂] ²⁺	+0.55 ⇌ +1.55	a	+1.32	2.21 × 10 ⁻¹¹	0.092
		b	+1.35	2.99 × 10 ⁻¹¹	0.124
		c
[(bpy)Ru(5-phenNH ₂) ₂] ²⁺	+0.55 ⇌ +1.55	a	+1.34	2.37 × 10 ⁻¹⁰	0.991
		b	+1.43	1.43 × 10 ⁻⁹	5.99
		c	+1.62	5.41 × 10 ⁻¹⁰	2.27
[Ru(5-phenNH ₂) ₃] ²⁺	+0.60 ⇌ +1.60	a	+1.49	3.14 × 10 ⁻⁸	132
		b	+1.53	1.89 × 10 ⁻⁸	79
		c	+1.67	1.24 × 10 ⁻⁸	52
[(bpy) ₂ Ru(4-vpy) ₂] ²⁺	-1.00 ⇌ -1.50 ^f -1.00 ⇌ -1.70 ^g	a	+1.23	2.39 × 10 ⁻¹⁰	1.00
		a	+1.23	8.23 × 10 ⁻¹⁰	3.45

^a 0.1 M Et₄ClO₄/CH₃CN. ^b 0.1 M Et₄ClO₄/CH₃CN containing 0.2 M 2,6-lutidine. ^c 0.1 M Et₄ClO₄/CH₃CN containing 0.2 M pyridine. ^d SSCE, saturated sodium calomel electrode. ^e From 10 potential scans; see Experimental Section. ^f Through the first bpy reduction wave. ^g Through both bpy reduction waves.

monomer, which could result if extensive homogeneous polymerization induced by electrochemical oxidation had occurred. Essentially identical coverage vs. number of scans plots were obtained in a series of experiments using several different electrodes sequentially electropolymerized in the same monomer solution.

Measurements in fresh electrolyte on polymer films, which were electropolymerized as outlined in the Experimental Section, gave the values for Ru^{III/II} formal potentials and apparent film coverages as summarized in Table II. Where noted, the 0.1 M TEAP/CH₃CN solutions used for electropolymerization contained pyridine (0.2 M) or 2,6-lutidine (0.2 M) in addition to the monomeric complex. The bases were added as proton acceptors since the chemical reactions thought to lead to oxidative polymerization involve the loss of protons (vide infra). The visual appearance of the polymer films (on Pt electrodes) ranges from transparent for thin films ($\Gamma_T^{\text{app}} < 10^{-9}$ mol/cm²) to glossy orange for films of medium coverage to dark, grainy orange for thick films ($\Gamma_T^{\text{app}} > 3 \times 10^{-8}$ mol/cm²).

The apparent surface coverages determined from the areas of the Ru^{III/II} reduction waves, obtained for the electropolymerized films in fresh electrolyte solution (see Experimental Section), are expressed in Table II in two ways: (1) as apparent coverages of electroactive ruthenium monomeric sites in the films; (2) as ratios of apparent coverages to apparent coverages obtained for the reductive electropolymerization of [(bpy)₂Ru(4-vpy)₂]²⁺ (see Experimental Section). Table II also gives formal potentials for the polymeric Ru^{III/II} couples as a function of the medium used for electropolymerization.

The apparent film coverages for several monomers in Table II correspond to monolayer (ca. 8×10^{-11} mol/cm²) or even submonolayer coverages under certain electropolymerization conditions. The low extent of surface coverage suggested the possibility of simple adsorption of the monomers rather than electropolymerization. However, when Pt electrodes were soaked in various electrolyte/base/monomer solutions, removed, and treated in the same fashion as in the electropolymerization experiments, there was no observable Ru^{III/II} surface electrochemistry. In a second experiment, Pt electrodes were potentiostated at +1.0 V in solutions containing the same monomers. Again, no evidence for surface-bound Ru^{III/II} couples was obtained by cyclic voltammetry in fresh electrolyte solution. In fact, observable Ru^{III/II} surface electrochemistry occurred only following oxidation of the monomeric complexes.

As a consequence, we attribute the results showing low coverages in Table II to the formation of a polymeric material, probably in small patches on the electrode, as opposed to adsorption via Pt/olefin interactions of the kind described in aqueous media by Land and Hubbard.¹²

Initial potential scans for electropolymerization of the monomers [(bpy)₂Ru(5-phenNH₂)₂]²⁺, [(bpy)Ru(5-phenNH₂)₂]²⁺, and [Ru(5-phenNH₂)₃]²⁺ and their protonated analogues are shown in Figure 3. Protonation was ensured by the addition of two drops of concentrated H₂SO₄ to the electrolyte solution. The disappearance of the shoulder (indicated by an asterisk) on the monomeric cyclic voltammetric oxidative wave when the complex is protonated is an important observation, since it suggests that the shoulders are due to irreversible oxidation of the amine groups on the pyridyl ligands. The wave itself represents the Ru^{III/II} couple. It is important to note that cycling the electrode potential through the Ru^{III/II} waves for the protonated complexes does not induce surface polymerization.

The suggestion of an initial ligand-based oxidation is supported by an experiment where the electrode potential was scanned repetitively into the leading edge (+0.60 ⇌ +1.10 V) of the first, apparently amine-based, oxidative wave for [Ru(5-phenNH₂)₃]²⁺ in the absence of acid (Figure 3C). Subsequent transfer of the electrode to a fresh electrolyte solution and determination of surface coverage showed that a limiting value of ca. nine "layers" of polymer (7.4×10^{-10} mol/cm²) was obtained on the electrode surface. Additional potential cycling in the same potential range in the monomer solution did not produce an increase in film coverage. However, once the potential scan range was extended to >+1.10 V, polymerization proceeded as described above. The experiments described here suggest that an amine-based oxidation is responsible for the electropolymerization. Polymerization is initiated but not sustained by simple amine-based oxidation; partial oxidation of the metal is subsequently needed. The necessity of Ru(II) → Ru(III) oxidation for sustained polymer growth is consistent with our earlier studies on reductive electropolymerization.¹⁰ As the thickness of the polymer film increases, diffusion of the monomer to the electrode surface, where direct amine-based oxidation could occur, is inhibited. However, oxidation of monomer in the external solution can

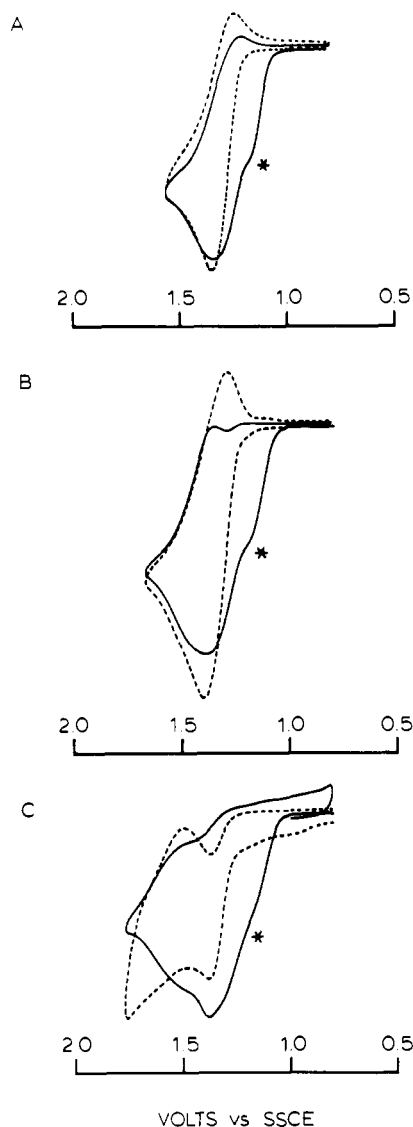


Figure 3. Initial potential scan cyclic voltammograms in 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$ in the $\text{Ru}^{\text{III/II}}$ region for monomeric (—) and protonated monomeric (---) complexes of (A) 3 mM $[(\text{bpy})_2\text{Ru}(5\text{-phenNH}_2)]^{2+}$, (B) 1.5 mM $[(\text{bpy})\text{Ru}(5\text{-phenNH}_2)_2]^{2+}$, and (C) 1.0 mM $[\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$. The scan rate is 200 mV/s.

occur by a three-stage process if the potential at the electrode is sufficient to oxidize Ru^{II} to Ru^{III} in the film. The three stages are as follows: (1) Oxidation of Ru^{II} to Ru^{III} in the film at the electrode; (2) electron-hole migration through the film to the film-solution interface; (3) oxidation of Ru^{II} to Ru^{III} in the external solution at the interface.

Several general trends are apparent from the data in Table II. Addition of 2,6-lutidine to the electropolymerization medium significantly increases the extent of electropolymerization for all cases except $[\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$. The latter complex, for which the apparent film-forming ability is the greatest of the complexes studied, shows a relative rate of electropolymerization that is actually *decreased* by the added base. In the other complexes studied, addition of pyridine, a weaker base than 2,6-lutidine, also increases the film-forming ability compared to that for no added base but to a lesser degree than for added 2,6-lutidine. In an assessment of the effects of the added bases, it should be noted that 2,6-lutidine is itself oxidized at +1.26 V,¹³ (which is within the potential scan range used for electropolymerization). It is thus conceivable that 2,6-lutidine becomes incorporated into the

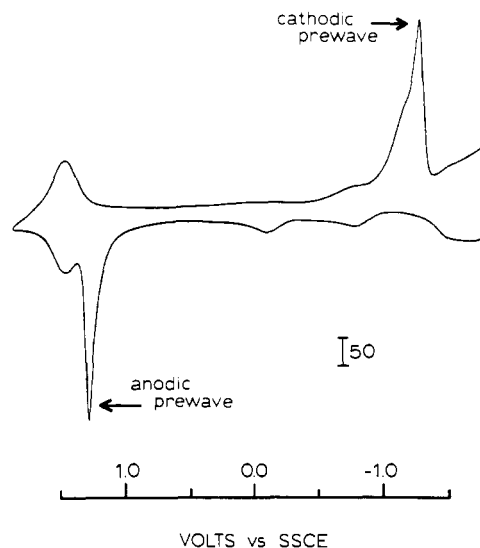


Figure 4. Cyclic voltammogram of a platinum electrode coated with poly- $[\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$ showing cathodic and anodic prewaves at 200 mV/s in 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$. The potential scan is 0 \rightarrow -1.8 \rightarrow +1.8 \rightarrow 0 V vs. SSCE. The current scale is shown in the lower right-hand corner in μA .

polymeric networks during electropolymerization. The extent to which this may occur is unknown. Pyridine is not oxidized at Pt in CH_3CN in the potential scan range used for electropolymerization.

A second noticeable trend in Table II is a shift to more positive potentials for the $E^{\circ'}_{\text{surf}}$ values for the $\text{Ru}^{\text{III/II}}$ couples in polymeric films prepared in 0.1 M TEAP/ CH_3CN containing 0.2 M pyridine. These potential shifts range from +0.06 to +0.28 V compared to $E^{\circ'}_{\text{surf}}$ measured for films electropolymerized in the absence of pyridine. It is possible that pyridine enhances formation of azo linkages, as compared to imine linkages, in the polymeric films since the formation of azobenzenes is favored in the electrooxidation of substituted aromatic amines in acetonitrile with added pyridine.^{3a} An additional possibility is that oxidized ligand rings may experience nucleophilic attack by pyridine with the pyridinated ligands shifting the formal potential for the $\text{Ru}^{\text{III/II}}$ couples by inductive effects.

A third notable point from Table II is a substantial increase in the film-forming ability of the complex, $[(\text{bpy})_{3-n}\text{Ru}(5\text{-phenNH}_2)_n]^{2+}$, when the number of amine groups (n) in the complex is increased. Apparent coverages and relative coverages increase in the series $[(\text{bpy})_2\text{Ru}(5\text{-phenNH}_2)]^{2+} < [(\text{bpy})\text{Ru}(5\text{-phenNH}_2)_2]^{2+} < [\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$. A similar trend was observed for the reductive electropolymerization of vinyl-containing complexes. The poor film-forming ability of monovinyl complexes was ascribed⁹ to an inhibition of the polymer self-propagation due to steric effects and to early termination (at the dimer stage) of many of the coupled radicals.

We have noted above the shifts in $E^{\circ'}_{\text{surf}}$ for $\text{Ru}^{\text{III/II}}$ couples in the films (Table II) as a consequence of added pyridine. Even without added base, however, comparisons of $E^{\circ'}_{\text{surf}}$ in Table II to potentials for the corresponding monomeric couples (Table I) show rather large positive shifts in the potentials of the electropolymerized films. This is in contrast to $\text{Ru}^{\text{III/II}}$ potentials in reductively polymerized films, where $E^{\circ'}_{\text{soln}}$ and $E^{\circ'}_{\text{surf}}$ were essentially the same.¹ It is known that formal potentials for $\text{Ru}^{\text{III/II}}$ couples in monomeric polypyridyl ruthenium complexes are quite responsive to substituent group effects on the pyridyl ligands.¹⁴ The shifts to more positive

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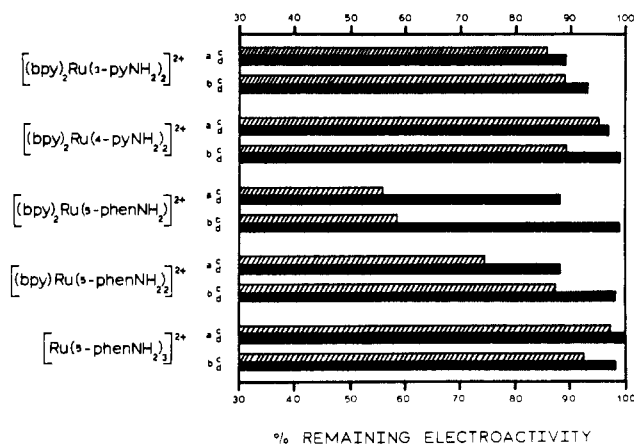


Figure 5. Bar graph showing the percentage of the charge (electroactivity) remaining under the $\text{Ru}^{\text{III/II}}$ surface wave after 10 cyclical 1.0-V potential scans through the $\text{Ru}^{\text{III/II}}$ surface wave for platinum electrodes coated with polymeric films of the indicated complexes. The electropolymerizations were carried out in 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$ (a) and in 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$ containing 0.2 M 2,6-lutidine (b). The potential scans were performed in fresh 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$ solutions under atmospheric conditions (c, hatched bar) and under drybox conditions (d, solid bar).

potentials for the electropolymerized complexes suggest that significant chemical changes in the amine substituent must occur as a consequence of oxidative polymerization, which is consistent with reasonable coupling reactions (*vide infra*).

We should note that all of the oxidatively polymerized films exhibit pronounced "prewaves" at the negative foot of the $\text{Ru}^{\text{II}} \rightarrow \text{Ru}^{\text{III}}$ oxidation and at the positive foot of the ligand-based (e.g., $\text{bpy} \rightarrow \text{bpy}^{\cdot-}$) reduction. An extraordinary example is shown in Figure 4. Continued observation of the prewaves after the initial potential scan depends on scanning through both waves. That is, if the potential scan range is restricted to the 0 \rightarrow +1.8-V region, the anodic prewave largely vanishes after the initial scan and the voltammogram is like that shown in Figure 6A. The origin of these voltammetric features is not well understood. Possibilities that have been suggested^{9,10} include structural rearrangements within the polymer film associated with the incorporation or loss of counterions upon oxidation or reduction and the presence of redox sites (of unknown chemical nature) within the films which are too immobile and/or too dilute to react with the platinum surface and undergo electron transfer only by mediation via the redox sites of the bulk polymer.

Finally, we should note that these films are not very stable toward reductive cycling through the potential region where ligand-localized reductions occur (Figure 4). The electroactivity of both the reductive ligand couples and the oxidative $\text{Ru}^{\text{III/II}}$ couple are lost upon repeated reductive cycling. However, the polymer film remains visible on the electrode, suggesting that the loss of electroactivity has its origin in a thin layer of polymer at the electrode-film interface, which must form an insulating barrier.

Oxidative Stability. The oxidative stability of the polymer films was investigated by scanning the electrode potential through the $\text{Ru}^{\text{III/II}}$ waves 10 times in a fresh 0.1 M $\text{TEAP}/\text{CH}_3\text{CN}$ solution and observing the decrease in charge under the $\text{Ru}^{\text{III}} \rightarrow \text{Ru}^{\text{II}}$ wave. The potential scan limits were set 1.0 V apart and were centered such that each film spent approximately the same fraction of the total time for a potential cycle in the Ru^{III} state. The first and tenth cyclic voltammograms were recorded and the areas compared to give the percent loss in coverage. The experiments were carried out in a conventional bench-top mode and also in a drybox with freshly distilled CH_3CN and freshly dried TEAP and with activated alumina added to the electrolyte solution to ensure

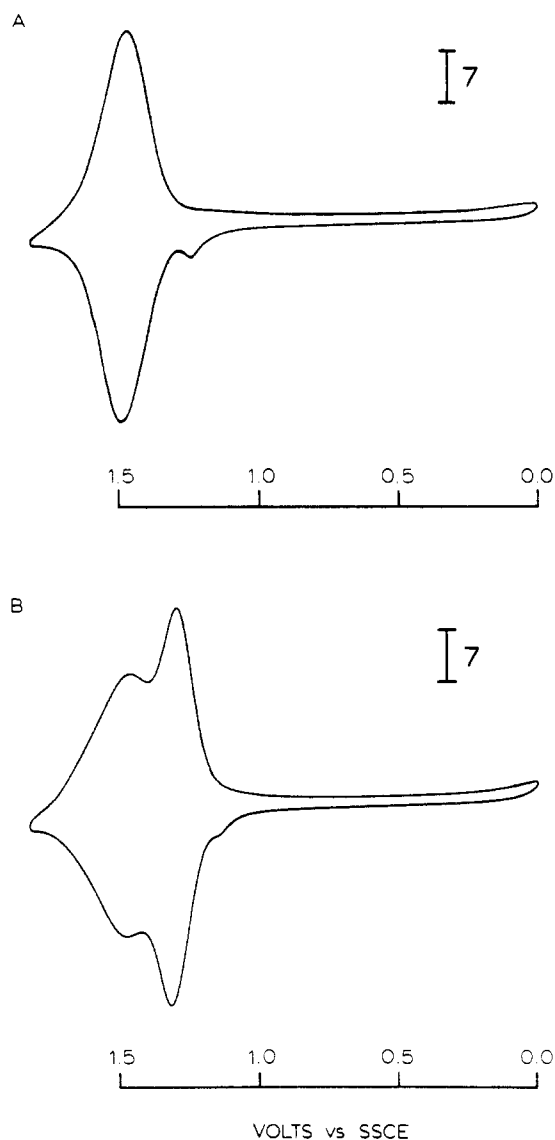


Figure 6. (A) Cyclic voltammogram of the poly- $[\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$ -coated electrode from Figure 1 in fresh 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$. The apparent surface coverage is 6.2×10^{-9} mol/cm². (B) Cyclic voltammogram of a platinum electrode co-electropolymerized in 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$ that is 1 mM in $[\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$ and 3 mM in $[(\text{bpy})_2\text{Ru}(5\text{-phenNH}_2)_2]^{2+}$. For both scans, the scan rate is 200 mV/s and the current scale is shown in the upper right-hand corner in μA .

the removal of trace H_2O . The results are summarized in Figure 5. The hatched bars are bench-top results, and the solid bars represent drybox data. The results show that removal of trace H_2O improves the oxidative stability of all the films and that film stability increases as the number of amine ligands is increased, as shown by the series $[(\text{bpy})_2\text{Ru}(5\text{-phenNH}_2)_2]^{2+} < [(\text{bpy})\text{Ru}(5\text{-phenNH}_2)_2]^{2+} \ll [\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$.

Films prepared by polymerization of $[\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$ are notably stable. Only a 1.7% loss in electroactivity was observed after more than 100 oxidative scans in the drybox. Because of this stability, subsequent film characterizations were based on poly- $[\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$ films.

We also compared film stabilities in the Ru^{II} and Ru^{III} states. In the resting Ru^{II} oxidation state, the poly- $[\text{Ru}(5\text{-phenNH}_2)_3]^{2+}$ films were stable indefinitely when stored in air or when soaked in 0.1 M $\text{TEAP}/\text{CH}_3\text{CN}$ (no loss after 20 h). Soaking in H_2O for 20 h resulted in a 5% loss in electroactivity, and a 30% loss was observed after soaking for 20 h in 0.5 M H_2SO_4 . However, potentiostating the films at +1.75 V, which has the effect of maintaining the Ru sites in

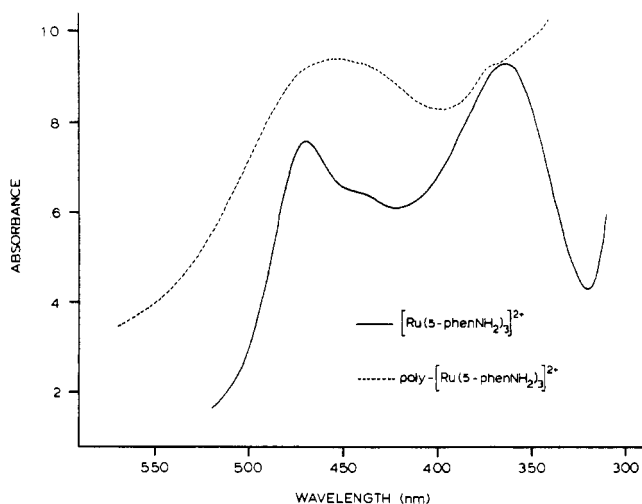


Figure 7. Visible absorption spectra for the monomer $[\text{Ru}(\text{5-phenNH}_2)_3]^{2+}$ dissolved in CH_3CN (—) and for a 5.9×10^{-8} mol/cm² poly- $[\text{Ru}(\text{5-phenNH}_2)_3]^{2+}$ film supported on polyvinyl chloride (---). The film was electropolymerized in 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$ containing 1 mM monomer.

the films in the +3 oxidation state, for 10 min in 0.1 M TEAP/ CH_3CN resulted in a 37% loss in electroactivity. A complete loss in electroactivity was observed following a single oxidative cycle in 0.5 M H_2SO_4 . (It should be noted that at these potentials H_2O is oxidized at the electrode.) The results show that instability occurs in the Ru^{III} oxidation state and is promoted in acidic media. As for the reductive instability noted above, there is no visible loss of material from the electrode as the electroactivity of the films decays. By inference, the loss of electroactivity must occur in that part of the film next to the electrode, which insulates the redox sites in the rest of the film toward charge transport to or from the electrode.

Copolymerization. It is possible to copolymerize more than one complex oxidatively, leading to multicomponent redox sites in the resulting films. The copolymerization scheme allows complexes to be incorporated which themselves are not readily polymerized, e.g., $[(\text{bpy})_2\text{Ru}(\text{5-phenNH}_2)]^{2+}$. Thus, when a Pt electrode is cycled repeatedly from +0.7 to +1.7 V in a 0.1 M TEAP/ CH_3CN solution that is 0.003 M in $[(\text{bpy})_2\text{Ru}(\text{5-phenNH}_2)]^{2+}$ and 0.001 M in $[\text{Ru}(\text{5-phenNH}_2)_3]^{2+}$ and then washed and transferred to fresh electrolyte solution, two distinct $\text{Ru}^{\text{III/II}}$ surface couples appear (Figure 6B; $E^{\circ'}_{\text{surf}} = +1.30$ and +1.46 V). Comparisons with the $\text{Ru}^{\text{III/II}}$ surface couple for a film of poly- $[\text{Ru}(\text{5-phenNH}_2)_3]^{2+}$ alone (Figure 6A; $E^{\circ'}_{\text{surf}} = +1.49$ V) show that the wave at +1.30 V must be due to copolymerized $[(\text{bpy})_2\text{Ru}(\text{5-phenNH}_2)]^{2+}$. The quantity of copolymerized $[(\text{bpy})_2\text{Ru}(\text{5-phenNH}_2)]^{2+}$ in Figure 6B is considerably greater than that which could be polymerized from a solution of this monomer under the same experimental conditions. Attempted copolymerizations using either $[\text{Ru}(\text{bpy})_3]^{2+}$ or $[\text{Ru}(\text{phen})_3]^{2+}$ with $[\text{Ru}(\text{5-phenNH}_2)_3]^{2+}$ were unsuccessful, showing the importance of the presence of an amine group in the complex for incorporation into the films.

Spectral Studies. The visible spectrum of poly- $[\text{Ru}(\text{5-phenNH}_2)_3]^{2+}$ was recorded as a polymeric film supported on polyvinyl chloride (which has no visible absorption) and is compared to the monomeric analogue in CH_3CN solution in Figure 7. Note that λ_{max} for the lowest energy absorption feature in the polymeric film is significantly blue shifted and broadened compared to that for the monomeric complex (454 and 470 nm, respectively). These observations are significant since it is known that both $\text{Ru}^{\text{III/II}}$ reduction potentials and metal-ligand charge-transfer (MLCT) bands for polypyridyl

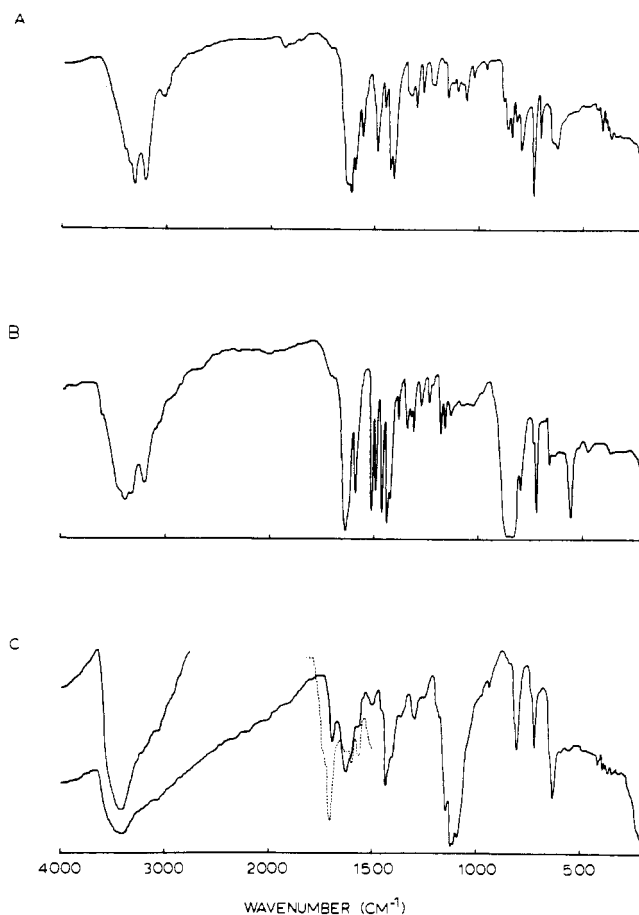


Figure 8. Infrared spectra of (A) the ligand 5-phenNH₂ (KBr pellet), (B) $[\text{Ru}(\text{5-phenNH}_2)_3](\text{PF}_6)_2$ (KBr pellet), and (C) poly- $[\text{Ru}(\text{5-phenNH}_2)_3](\text{ClO}_4)_2$ run as a polymer scraped from several SnO_2 electrodes (KBr pellet) (—) and as a polymeric film supported on polyvinyl chloride (---).

complexes of Ru^{II} are sensitive to substituents on the bound ligands¹⁴ (e.g., λ_{max} for $[\text{Ru}(\text{5-phenNO}_2)_3]^{2+}$ in CH_3CN is 448 nm¹³). The broadness of the visible spectrum for the polymeric film suggests that more than one type of ligand environment at ruthenium may be present, yet we see no evidence for more than one electrochemically active $\text{Ru}^{\text{III/II}}$ site in the surface electrochemistry (see Figure 6A).

The blue wavelength shifts and the more positive $\text{Ru}^{\text{III/II}}$ potentials suggest that polymerization involves the amine groups and that the polymerization process converts them into better electron-withdrawing groups. Better electron-withdrawing groups should lower the ligand-based π^* levels, leading to an enhanced $\pi^*-\text{d}(\text{Ru})$ mixing and a stabilization of the Ru^{II} state relative to the Ru^{III} state, where mixing with $\text{d}\pi(\text{Ru})$ should be less important.

The polymer film formed from $[\text{Ru}(\text{5-phenNH}_2)_3]^{2+}$ can be scraped off large SnO_2 electrodes and partially dissolved in Me_2SO by repeated grinding with a mortar and pestle. Droplets of these solutions placed on a Pt electrode and evaporated gave stable films. When the electrode was placed in fresh electrolyte, the $\text{Ru}^{\text{III/II}}$ electrochemistry was virtually identical with that in Figure 6A. Additionally, these redeposited films can be resupported on PVC; the resulting visible spectrum was the same as described above.

IR spectra of the ligand 5-phenNH₂, the monomer $[\text{Ru}(\text{5-phenNH}_2)_3](\text{PF}_6)_2$, and poly- $[\text{Ru}(\text{5-phenNH}_2)_3](\text{ClO}_4)_2$ are presented in Figure 8. The following are notable points: (i) Bands assignable to $\nu(\text{NH})$ stretching vibrations of the NH_2 groups appear at 3320 and 3200 cm^{-1} in spectra of both the ligand (A) and the monomeric complex (B); (ii) $\nu(\text{NH})$ bands are not present in the polymer (C); (iii) a new band at 1695

cm^{-1} appears in the spectrum of the polymer. The band at 1695 cm^{-1} is distinct from the phenanthroline $\text{C}=\text{N}$ ring mode at 1630 cm^{-1} and is more intense in the intact polymeric film than in KBr pellets (Figure 8C). Both the loss of $\nu(\text{NH})$ and the appearance of the 1695-cm^{-1} band are consistent with an oxidative conversion of the amine groups of the ligands into imine groups ($>\text{C}=\text{N}-$).¹⁵

An additional point about the IR results relates to the polyanionic, ion-exchange character of the polymeric films. The starting monomeric complexes were PF_6^- salts, and the electropolymerizations were carried out in ClO_4^- media. The monomer spectra show bands at 560 and 850 cm^{-1} , which are characteristic of the PF_6^- anion.¹⁶ However, the polymer films contain ClO_4^- instead of PF_6^- anions as shown by the absence of PF_6^- bands and by the appearance of bands at 1120 and 630 cm^{-1} , which are characteristic of the ClO_4^- anion¹⁶ (Figure 8C).

ESCA measurements of the polymer on a Pt-flag electrode confirmed the presence of ClO_4^- counterions and the absence of PF_6^- ($\text{Cl } 2p_{1/2,3/2} = 207.75\text{ eV}$, no F detected). However, the measurements could not distinguish between the phenanthroline, amine, and imine type nitrogen atoms.

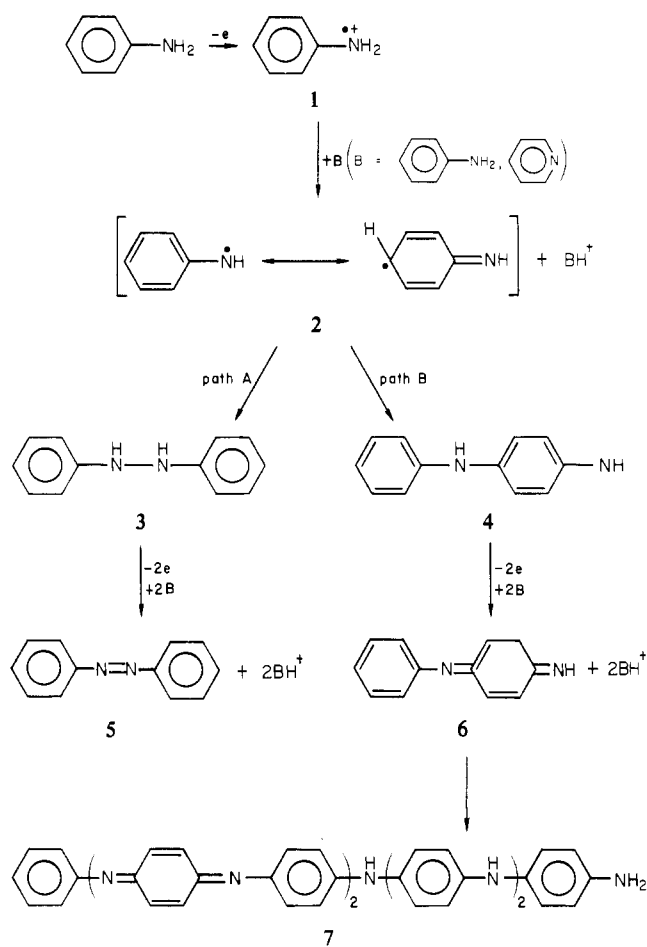
Discussion

The results described here show how to prepare electroactive metallopolymer films on electrodes by oxidative electropolymerization. The polymerization chemistry appears to be based on oxidative coupling of aromatic amine functional groups on the coordinated ligands. The growth rates of the films can be controlled and depend on such factors as the number of polymerizable groups, the presence of a proton-accepting base, and the number of oxidative scans. The film stability is notably less in the reduced (bpy^-) and in the Ru^{III} states.

Reasonable mechanisms exist for explaining the oxidative polymerizations observed here. Aniline is known to undergo oxidative electropolymerization at Pt electrodes in both aqueous sulfuric acid solution and acetonitrile solutions with or without added base.¹⁷ There have been conflicting reports as to what is actually deposited on the electrode. In $0.1\text{ M H}_2\text{SO}_4$, exhaustive oxidation of aniline was reported to lead, by both head-to-tail and head-to-head coupling, to an eight-unit oligomer, emeraldine.¹⁸ More recently, Diaz and Logan^{3b} reinvestigated the aqueous aniline oxidation, finding that poly(aniline) formed at constant potential is a poorly adherent powder, whereas an adherent film with a complicated electrochemistry was formed with potential cycling. The films were not characterized structurally.

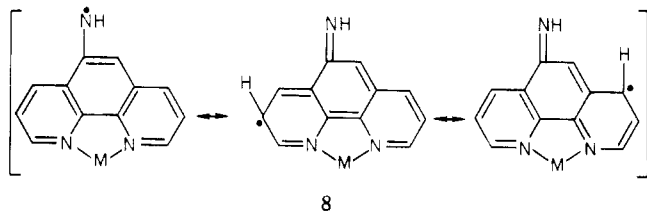
Oxidation of aniline in acetonitrile with added pyridine is not well understood because the reaction generally leads, by insulating film formation, to electrode passivation. Wawzonek and McIntyre^{3a} studied the macroscale oxidation of an aniline/*p*-chloroaniline/pyridine mixture and isolated primarily azobenzenes. Recently DuBois and co-workers^{3c} described the oxidative electropolymerization of aniline in a $\text{CH}_3\text{CN}/\text{NaClO}_4/\text{pyridine}$ medium by pulsed polarization. They characterized the thin films formed on the electrode by multiple-reflection IR spectrometry and found that emeraldine was formed after 30 min of pulsing. Their results seem to confirm the mechanism for aniline oxidation in acetonitrile proposed

Scheme I



by Breitenbach and Heckner¹⁹ outlined in Scheme I. In Scheme I, an initial one-electron oxidation gives the radical cation 1, which loses a proton to an added base to give 2. Radical coupling through path A leads to dimer 3 by N-N coupling; radical coupling through path B leads to dimer 4 by C-N coupling. The dimers 3 and 4 can themselves be oxidized, losing two electrons and two protons to give 5 and 6, respectively. Product 6 can undergo further coupling to give emeraldine 7.

We propose an analogous mechanism for the metal complex oxidative electropolymerizations. For the case of metal-bound 5-amino-1,10-phenanthroline, the first step would involve a ligand-based oxidation to give a radical cation, which can lose a proton to a base to give the radical 8. Important contrib-



uting resonance structures can be written with the unpaired electron at the amine nitrogen or at the 3- or 7-position of the ring, where N-N or C-N coupling could occur to give 9 or 10, respectively. Further oxidation of 10 with C-N coupling would lead to sustained polymerization. Sustained polymerization could also occur for the diazo-linked dimer 9 if the monomer complexes contained multiple amine-substituted ligands. That a variety of imine, diazo, and unreacted amine

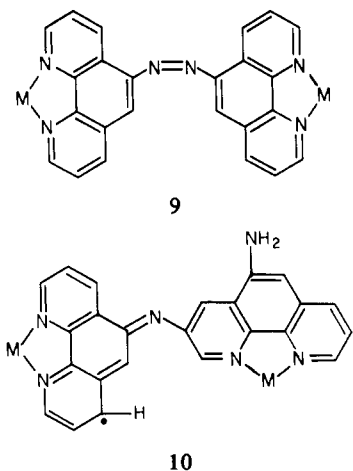
(15) Generally, $>\text{C}=\text{N}$ type linkages can occur from 1700 to 1650 cm^{-1} and conjugated $>\text{C}=\text{N}-$ linkages from 1670 to 1500 cm^{-1} : "CRC Handbook of Spectroscopy"; Robinson, J. W., Ed.; Chemical Rubber Publishing Co.: Cleveland, OH, 1974; Vol. II.

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sites may exist in the polymer films is suggested by the broad MLCT visible absorption manifold. As noted above, spectral shifts are expected to occur if chemical changes occur at the periphery of the coordinated polypyridines. Evidence for imine coupling links was obtained in the IR spectra, but N=N stretches (1370 and 1150 cm^{-1})²⁰ were not seen, perhaps due to the intrinsic weakness of the stretching mode. The presence or absence of azo linkages should be explored further with Raman spectroscopy.

The polymerization reactions proposed for the complexes are a speculation based on aromatic amine oxidations, and further detailed insights into the polymerization chemistry and polymer structure are eventually needed. However, the available evidence does seem to point to polymers based on

imine links of the type C=N=C. Based on this link, the phenanthroline ring system provides multiple coupling sites; note structure 10 above. Not accounted for in the above interpretation is the possible incorporation of 2,6-lutidine or pyridine into the polymer as suggested by the E°_{surf} shift effects described earlier.

Finally, we should note that this work is the first example of what we suspect will be a general technique for oxidative electropolymerization to produce electrodes coated with electroactive polymers. The procedure described yields relatively stable, electroactive polymeric films in aerated solutions for a variety of monomeric complexes in addition to the cases reported here. On the basis of preliminary studies, oxidative electropolymerization also occurs with tetrakis(*o*-amino-phenyl)porphine, *cis*-Os(5-phenNH₂)₂Cl₂, [(bpy)₂Ru(3-pyOH)₂]²⁺, and [(bpy)₂Ru(4-pyOH)₂]²⁺. Further work to support the implied generality of oxidative electropolymerization based on complexes containing amine or hydroxy substituents on bound ligands is currently under way.

Acknowledgments are made to the Army Research Office-Durham under Grant No. DAAG29-79-C-0044 and to the National Science Foundation under Grant No. CHE-7920114 for support of this research.

Registry No. [(bpy)₂Ru(4-pyNH₂)₂](PF₆)₂, 84537-84-8; [(bpy)₂Ru(3-pyNH₂)₂](PF₆)₂, 84558-23-6; [(bpy)₂Ru(5-phenNH₂)₂](PF₆)₂, 84537-86-0; [(bpy)Ru(5-phenNH₂)₂](PF₆)₂, 84537-88-2; [Ru(5-phenNH₂)₃](PF₆)₂, 84537-89-3; [(bpy)₂Ru(4-vpy)₂](PF₆)₂, 84537-90-6; poly-[(bpy)₂Ru(3-pyNH₂)₂](ClO₄)₂, 84537-92-8; poly-[(bpy)₂Ru(4-pyNH₂)₂](ClO₄)₂, 84623-06-3; poly-[(bpy)₂Ru(5-phenNH₂)₂](ClO₄)₂, 84537-93-9; poly-[(bpy)Ru(5-phenNH₂)₂](ClO₄)₂, 84537-94-0; poly-[Ru(5-phenNH₂)₃](ClO₄)₂, 84537-95-1; poly-[(bpy)₂Ru(4-vpy)₂](ClO₄)₂, 84537-96-2; [Ru(5-phenNH₂)₃](bpy)₂Ru(5-phenNH₂)₂ (copolymer), 84537-97-3; *cis*-Cl₂Ru(bpy)₂, 19542-80-4; Pt, 7440-06-4; SnO₂, 18282-10-5; 2,6-lutidine, 108-48-5; pyridine, 110-86-1.

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Organophosphazenes. 16. Synthesis and Reactions of (1-Alkoxyvinyl)fluorocyclotriphosphazenes¹

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The reactions of (1-lithioalkoxy)ethylenes with hexafluorocyclotriphosphazene (N₃P₃F₆) have been examined. In contrast to the case of similar reactions of propenyllithium with N₃P₃F₆, no evidence for degradation reactions via anionic attack on the olefinic center was observed and the reaction proceeds smoothly to yield N₃P₃F_{6-n}[C(OR)=CH₂]_n ($n = 1, 2$; R = CH₃, C₂H₅). The reaction follows a geminal pathway at the stage of disubstitution. The mixed phenyl/ethoxyvinyl derivative 2,2-N₃P₃F₄(C₆H₅)C(OC₂H₅)=CH₂ and dimethylamino/ethoxyvinyl derivatives 2,4-N₃P₃F₄[N(CH₃)₂]C(OC₂H₅)=CH₂ have been prepared. Evidence for both incoming group and ring substituent control of product stereochemistry has been observed. A model for ring substituent control is presented. The new (alkoxyvinyl)phosphazenes are characterized by mass spectrometry and NMR (¹H, ¹³C, ¹⁹F, ³¹P) spectroscopy. Examination of the ¹³C NMR spectra shows that the electron-withdrawing effect of the phosphazene results in a significant reduction of the electron-rich nature of the parent olefins.

In recent years there have been a number of investigations involving organophosphazenes.² Factors such as the complexities of reactions leading to these materials,^{3,4} electronic structure,⁵ and thermal stability^{6,7} all contribute to the interest

in this class of compounds. We have been interested in the preparation and synthetic transformations of phosphazenes with organofunctional substituents.⁸ These studies have led

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