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Synthesis and Charge-Dependent Binding Affinity of a New Redox-Active Polymeric Ligand

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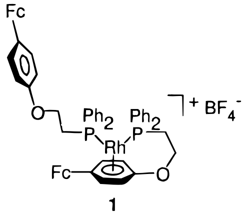
Summary: The synthesis and characterization of a new, polymeric, redox-active ligand with switchable binding affinities for transition metals are reported. Polymer **2** *is based on p-ferrocenylphenyl acrylate and complexes the (η^5-C_5Me_5)Ru^+ fragment. Oxidation of the polymeric ligand changes its binding constant for Ru by over two orders of magnitude.*

Inorganic polymers and transition-metal-containing polymers have a rich history and have been the subject of books and reviews.[1−4] The development of transition-metal-containing polymers has been spurred by interest in "heterogenizing" homogenous catalysts,[4−6] in addition to applications in materials science.[3] One ligating group that has been used for anchoring metal complexes to polymers is the arene group, which generally forms η^6 interactions with transition metals.[7−10] Polystyrene-supported group VI metal η^6-arene tricarbonyl complexes have been synthesized and successfully used as catalysts for the hydrogenation of methyl sorbate[7] and a variety of Friedel−Crafts reactions.[8] Other researchers have taken advantage of Ru η^6-arene chemistry for the synthesis of polymer-supported olefin hydrogenation catalysts[10] and for the preparation of novel organometallic polymers by transition-metal-activated nucleophilic, aromatic substitution reactions.[9]

In an extension of the chemistry and interest of metal arene complexes, recent work from our laboratories has focused on Rh(I) complexes of (phosphinoalkyl) arene ligands, in particular redox-switchable hemilabile ligands (RHLs).[11,12] Prior experiments have shown that the Rh−η^6-arene interaction is much weaker than the arene−metal interaction in the well-studied group VI metal arene complexes.[12] In fact, some coordinating solvents can displace Rh-bound aryl groups but not Cr-bound aryl groups.[13,14] It was further discovered that a redox group could be used to control the strength of the η^6-arene−Rh interaction in an RHL−Rh(I) complex, **1**.[11] Oxidation of the ferrocenyl groups in **1** increases the lability of the arene ligand[11] and leads to increased rates of catalytic olefin isomerization and intramolecular arene−arene exchange reactions.[15] Others have also investigated redox-active ligands for controlling transition-metal reactivity.[16−20] For example, the substitutionally inert (η^6-phenyl)ferrocene ligand (PhFc) has been used to modulate the charge-dependent, reversible uptake and release of $P(OEt)_3$ ligands at (PhFc)Cr-$(CO)_2P(OEt)_3$.[19] A long-term goal of ours is to extend the chemistry of RHLs to polymer-supported systems for the preparation of "heterogenized" transition-metal complexes with electrochemically controllable catalytic and/or small-molecule uptake and release properties. These ligands should ultimately allow one to design a new class of catalysts and materials for separation technologies that can be driven in an electrochemical fashion. With controllable lability of the arene ligand as a function of ligand oxidation state, one can envision a system in which one desired component of a mixture binds to an RHL−metal complex in its oxidized state but not in its reduced state. This paper focuses on the development of the polymer-supported redox-active aryl ligand **2** and its charge-dependent binding affinity for Ru. Primarily, it is concerned with determining the oxidation-state-dependent arene−Ru binding constant in the context of an electrode-surface-confined redox polymer.



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Polymer ligand **2** was synthesized by starting with polyacrylic acid, (Scheme 1). While several molecular

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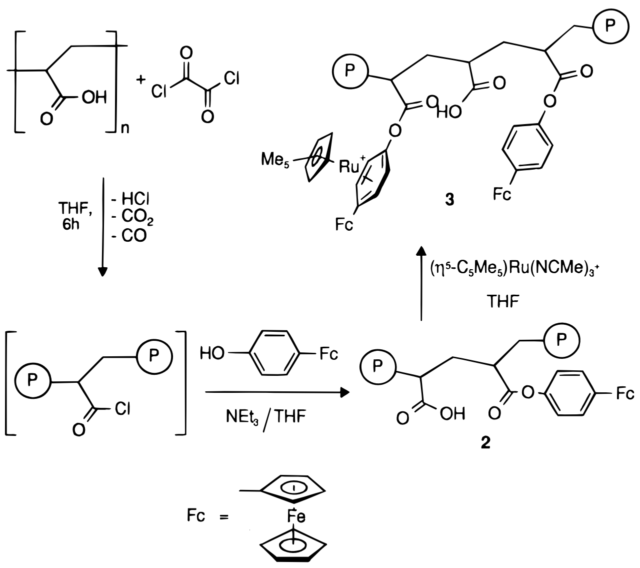
Scheme 1



weight ranges of polyacrylic acid are commercially available (as high as $M_w = 4\ 000\ 000$), a low-molecular-weight sample ($M_w = 2000$) was chosen for this prototype ligand to facilitate the polymer solubility and thus synthesis. The polymer was suspended in THF, and 3.3 equiv per functionality of oxalyl chloride was added dropwise with evolution of gas bubbles and complete dissolution of the solid. The side products were presumably HCl, CO_2, and CO[21] but were not experimentally confirmed. Removal of the solvent after 6 h left a white solid. A portion of this solid was reacted with triethylamine (3 equiv) and *p*-ferrocenylphenol (3 equiv) at room temperature for 9 h. The solvent and unreacted oxalyl chloride were removed *in vacuo*, leaving an orange-red sticky residue. Sonication of the residue in water removed triethylamine hydrochloride and yielded an orange powder, which contained polymeric product and unreacted *p*-ferrocenylphenol. Soxhlet extraction with ether removed the unreacted phenol (72% recovered). The residue from the Soxhlet extraction was an orange powder exhibiting a broad band in the IR at 1723 cm^{-1} (ν_{CO}), attributed to unmodified acid sites, and one at 1749 cm^{-1}, attributed to modified ester sites. Note that the band at 1723 cm^{-1} is shifted from the starting polyacrylic acid (ν_{CO} = 1708 cm^{-1}); this phenomenon may result from intramolecular interactions (e.g. hydrogen bonding, within the polymer). Further confirmation of the formulation for **2** was obtained from proton ^{1}H NMR spectroscopy. Unlike the starting polyacrylic acid, polymer **2** is soluble in deuterated acetone and its spectrum exhibits characteristic resonances for both the backbone and the attached ferrocenylarene. Integration of these resonances, for instance the phenyl resonance (δ 6.77) and the backbone methylene resonance (δ 1.15) indicated that the polymer was ~30% functionalized with ester sites.

Having prepared the polymer-supported redox-active arene ligand, we chose complexation of the (η^5-C$_5$Me$_5$)Ru$^+$ fragment as our initial synthetic target. (η^5-C$_5$Me$_5$)Ru$^+$ arene complexes are known to be very stable[22-27] and allow us to evaluate the general suitability of **2** for coordination to transition-metal fragments. The reagent, (η^5-C$_5$Me$_5$)Ru(NCMe)$_3$$^+$, provides facile entry into a wide variety of Ru$-\eta^6$-arene complexes with a variety of aryl substituents.[22-27] [(η^5-C$_5$Me$_5$)Ru(NCMe)$_3$][SbF$_6$] was synthesized according to the literature precedent, with the minor modification of exchanging the triflate salt for the hexafluoroantimonate salt.[22] Stirring the reagent (0.68 equiv per arene) in a THF solution of **2** for 14 h yielded the poly(ruthenium organometallic complex) **3**, which was precipitated from a concentrated THF solution by addition of ether (Scheme 1). The polymeric product had Ru-functionalized arene sites, unfunctionalized arene sites, and remaining carboxylic acid sites, as indicated by its ^{1}H NMR spectrum. Resonances for both free (δ 7.45, 7.03) and metal-coordinated (δ 5.67, 5.48) arene protons were present; the upfield shift of arene proton resonances in the ^{1}H NMR spectra of Ru$-\eta^6$-arene complexes is well-known.[22,24-27] The relative integration of the two types of arene resonances indicated that 63% of the ferrocenylarene sites had been functionalized with Ru. Significantly, the unfunctionalized ferrocenylarene sites can serve as an internal reference in electrochemical investigations, which probe reactions taking place at the arene-bound metal center. Other spectroscopic data are also consistent with the formulation of **3**.

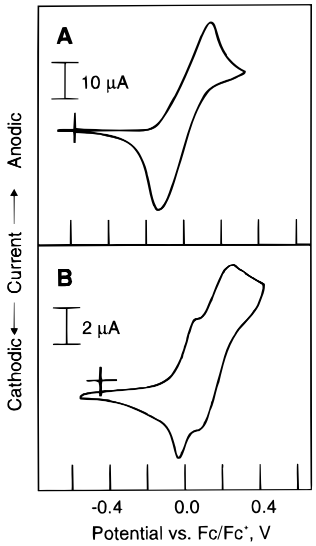


Figure 1. Cyclic voltammetry at a 1 mm gold-disk electrode in 0.1 M ^{n}Bu$_4$NPF$_6$ in CH$_2$Cl$_2$ at 200 mV/s: (A) polymer **2**; (B) polymer **3**.

Cyclic voltammetry studies of **2** and **3** in 0.1 M ^{n}Bu$_4$NPF$_6$ in dichloromethane at gold-disk electrodes indicated changes in the polymer upon introduction of the ruthenium fragment. Polymer **2** exhibited a reversible wave at $E_{1/2}$ = 7 mV vs Fc/Fc$^+$ (Figure 1). The minor shift compared to unmodified ferrocene indicates that the phenyl group introduces little electronic perturbation upon the ferrocenyl group. A cast film of **2** was prepared by evaporating a drop of a concentrated

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dichloromethane solution of **2** onto a gold thin film (2000 Å on an oxidized Si(100) wafer with a 50 Å Ti adhesion layer[28]). This film was insoluble in a 0.1 M $NaClO_4$ aqueous solution and exhibited a voltammetric response comparable to dissolved **2**. Furthermore, no change in the behavior was noted upon repeated scanning (30 cycles), which reflects the stability of these films in both oxidation states (Fc/Fc^+). Coordination of (η^5-C_5Me_5)-Ru^+ to the phenyl groups of **2** resulted in an anodic shift in the potential; thus, polymer **3** exhibited two reversible waves at $E_{1/2} = -17$ and 116 mV vs Fc/Fc^+. The first wave was at the same potential, within experimental error, as for polymer **2** and was attributed to unmodified ferrocenylarene sites in the polymer. The wave at higher potential was assigned to ferrocenyl oxidation and reduction for the ferrocenyl groups adjacent to the ruthenium-coordinated arenes. In support of this assignment we synthesized the literature complex [(η^5-C_5Me_5)Ru(η^6-$C_6H_5OC(O)Me$)][O_3SCF_3][25] (**4**) and examined its electrochemical behavior under the same conditions as for **3**. Complex **4** exhibited no oxidations within the voltammetric window of dichloromethane; thus, the ruthenium center of **3** was expected to be electrochemically silent within the potential window of interest and the electrochemical response of **3** was ferrocenyl-based. Likewise, [(η^5-C_5Me_5)Ru(η^6-C_6H_6)][O_3SCF_3][27,29] showed no oxidations within the same window.

From the shift in the formal potential of ruthenium-coordinated versus uncoordinated ferrocenylarenes one can determine a change in binding constant for the polymeric ligand in its oxidized versus reduced states. Using an equation derived from the Nernst equation, $\Delta E_{1/2} = (RT/nF)\ \ln(K_{red}/K_{ox})$,[30] and the experimental data, $\Delta E_{1/2} = 133$ mV, we calculate $K_{red}/K_{ox} = 1.78 \times 10^2$. Thus, the binding affinity of **2** for Ru may be controlled, by more than 2 orders of magnitude, through changes in its oxidation state. A nice aspect of this electrochemical analysis is that it allows one to extract information about equilibrium binding constants without directly measuring reactant and product concentrations under equilibrium conditions. Future work will focus on preparing an RHL version of **2** with the arene tethered to a substitutionally inert ligand (e.g. Cp); this will allow for electrochemical control over three coordination sites at a metal center without expelling the ligand from the metal's coordination sphere.

Experimental Section

All reactions were carried out under inert conditions using standard Schlenk or glovebox techniques. Dichloromethane was dried and distilled over calcium hydride; ether was dried and distilled over sodium−benzophenone. ^1H NMR spectra were recorded on either a Varian Gemini 300 MHz or a Varian VXR 300 MHz NMR spectrometer. Fourier-transform infrared spectra were recorded on a Nicolet 520SX spectrometer. Polyacrylic acid ($M_w \approx 2000$) was used as received from Aldrich Chemical Co. [(η^5-C_5Me_5)Ru$(NCMe)_3{}^+$][$SbF_6{}^-$] was synthesized by the established literature procedure for [(η^5-C_5Me_5)Ru$(NCMe)_3{}^+$][$O_3SCF_3{}^-$][22] with the minor modification of using $AgSbF_6$, in place of AgO_3SCF_3. Due to the heterogeneous nature of the polymers reported herein and the uncertainty of the exact degree of polymer modification, elemental analyses were not obtained. ^1H NMR was a more useful tool in determining polymer compositions.

Synthesis of Polymer 2. Polyacrylic acid ($M_w \approx 2000$; 1.01 g) was dispersed in 50 mL of tetrahydrofuran (THF) that was dried over KOH. Upon addition of oxalyl chloride (4 mL, 3.3 equiv) to this mixture, the polymer dissolved and gas was evolved from the reaction. After 6 h the solvent was removed *in vacuo*, leaving a white solid. A portion of this solid (0.381 g) was dissolved in 40 mL of THF that was dried over sodium−benzophenone. Triethylamine (1.8 mL, 3 equiv) and *p*-ferrocenylphenol (3.51 g, 3 equiv) were added to the solution, which was stirred at room temperature for 9 h. The solvent was removed *in vacuo*, leaving an orange-red sticky residue. Sonication in the presence of water (2 × 15 mL) yielded an orange powder, which contained polymeric product and unreacted *p*-ferrocenylphenol. Soxhlet extraction with ether (used as received from Fisher Scientific) removed the unreacted phenol (2.54 g, 72% recovered). The residue from the Soxhlet extraction was an orange powder (0.917 g). IR (Nujol mull): ν_{CO} 1723 cm^{-1} (br), 1749 cm^{-1} (br). ^1H NMR (acetone-d_6): δ 7.37 (d, $J_{H-H} = 8.65$ Hz, Ph); 6.78 (d, $J_{H-H} = 8.65$ Hz, Ph), 4.61 (dd, $J_{H-H} = 1.85$ Hz, substituted Cp), 4.23 (dd, $J_{H-H} = 1.85$ Hz, substituted Cp), 3.99 (s, unsubstituted Cp), 2.9 (br, backbone methyne), 1.2 (br, backbone methylene). Note that a 20 s delay time was used in the acquisition of the ^1H NMR to obtain accurate integrations. As expected, the ratio of the integration of each phenyl resonance and each substituted Cp resonance to the integration of the unsubstituted Cp was ~2/5. Comparison of the integration of the backbone methylene resonance to each of these revealed a ratio of ~3/1; i.e., the polymer was 32% functionalized with ester groups. CV (CH_2Cl_2, 0.1 M $^nBu_4NPF_6$, gold-disk electrode): $E_{1/2} = 7$ mV vs Fc/Fc^+.

Synthesis of 3: Ruthenium Coordination to Polymer 2. In 10 mL of THF (distilled from sodium only[22]) polymer **2** (91 mg) and [(C_5Me_5)Ru$(NCMe)_3$][SbF_6] (76 mg, 0.128 mmol) were stirred at room temperature for 14 h. The solution was concentrated *in vacuo* to 4 mL, and excess ether was added to precipitate the product as a sticky residue, which was further washed with ether. The product is comprised of a mixture of Ru-functionalized arene sites, unfunctionalized arene sites, and carboxylic acid sites. IR (Nujol mull): ν_{CO} 1730 cm^{-1} (v br), 1749 cm^{-1} (br). ^1H NMR (CD_2Cl_2): δ 7.45 (br, Ru-free Ph), 7.03 (br, Ru-free Ph), 5.67 (br, Ru-bound arene), 5.48 (br, Ru-bound arene), 4.61 (br, substituted Cp adjacent to Ru-free arene), 4.48 (substituted Cp next to Ru-bound arene), 4.38 (br, substituted Cp adjacent to Ru-bound arene), 4.31 (br, substituted Cp adjacent to Ru-free arene), 4.09 (s, unsubstituted Cp adjacent to Ru-bound arene), 4.02 (s, unsubstituted Cp adjacent to Ru-free arene), 3.11 (v br, backbone methyne), 1.72 (s, CH_3), 1.29 (br, backbone methylene). CV (CH_2Cl_2, 0.1 M $^nBu_4NPF_6$, gold-disk electrode): $E_{1/2}$(Ru-free arylferrocene) = −17 mV; $E_{1/2}$(Ru-bound arylferrocene) = 116 mV vs Fc/Fc^+.

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