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Electrochemical Investigations of Oligomers and Polymers Containing Ruthenium- and Iron-Arene Complexes

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Summary: Cyclic voltammetry was employed to investigate the electrochemical behavior of numerous cyclopentadienyliron ($CpFe^+$) and pentamethylcyclopentadienylruthenium (Cp^*Ru^+) coordinated oligomers and polymers. The electrochemical behavior of the iron systems indicated the cyclopentadienyliron complexes had isolated redox centers and that changes in the reversibility of the redox couple occurred with changes in solvent and temperature. In contrast, the monometallic ruthenium systems showed large peak separations that suggested slow kinetics on the CV timescale. The cyclic voltammograms of the larger ruthenium-containing oligomers and polymers showed multiple redox steps indicating complex electrochemical behavior.

Keywords: arene complexes; electrochemistry; metal-polymer complexes; oligomers; polyethers

Introduction

Over the past decade, there has been considerable interest in the electrochemical properties and applications of organometallic oligomers and polymers.[1-8] Particular attention has been given to systems that contain arenes π-coordinated to cyclopentadienyliron moieties. The redox behavior of this class of materials has led to a thorough investigation of the electron-transfer reactions that these complexes undergo.[9-13] Much of this interest stems from the ability of these systems to exhibit mixed-valency[14, 15] and conductivity,[16] to act as electron reservoirs which initiate electron-transfer chain catalysis,[2] and to behave like molecular batteries[17] and metalloreceptors for anion recognition.[18]

Numerous electrochemical studies have been undertaken to explore the redox behavior of η^6-arene-η^5-cyclopentadienyliron complexes. The iron centers in these complexes undergo two

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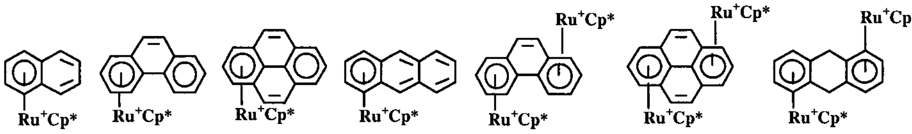
successive one-electron reductions (18/19 e^- and 19/20 e^-), with the reversibility of these couples being dependent on the solvent, working electrode, and temperature.[3, 9-11, 18, 19] Solodovnikov *et al* have also reported the formation of an extremely unstable 21e^- dianionic cyclopentadienyliron complex of naphthalene;[20] however, it is the neutral arene systems (19e^-) that are the most important electron reservoirs. This class of electron reservoir can be used as catalysts in the reduction of other species existing in solution via homogeneous charge transfer reactions.[1, 2, 19, 21] It has also been reported that the decoordination of unstable nineteen-electron complexes may take place by polyhapto ligand replacement in the presence of donor ligands such as $P(OMe)_3$.[22-24]

In addition to monometallic species, there has been considerable interest in the electrochemistry of bi- and poly-metallic complexes due to possible communication of the metal centers through coordinating ligands.[6-12, 25] The type of metal and bridging ligands present often dictates whether the metal centers are interacting with, or isolated from one another. For instance, Bard and co-workers have shown that for a bimetallic phenanthroline complex, the planar polycyclic ligand allows for electrochemical communication between the metal centers, with the electrochemical reversibility being dependent on the scan rate.[26] At low scan rates, two electrochemically irreversible waves were detected, whereas at much higher scan rates (20 V/s), complete reversibility was shown. For interacting systems of this nature, the degree of communication is often measured by the separation of formal potentials (ΔE^o), obtained by cyclic voltammetry.[27] In contrast to communicating systems, the cyclic voltammograms of complexes containing multiple isolated redox centers are the same as for a molecule with a single redox center.[28] Controlled potential coulometry is often employed to determine the number of electrons involved in these types of electron transfer processes.[29-31] Astruc has shown that only one electrochemically reversible wave is observed for tentacled cationic arene cyclopentadienyliron sandwich complexes with multiple isolated redox centers.[25] It was also reported that a complex containing six terminal ferrocene ($FeCp_2$) units and a core consisting of an arene cyclopentadienyliron complex exhibited two separate redox waves.[25] The neutral ferrocene complexes were oxidized while the cationic cyclopentadienyliron complex was reduced. For this material, the central $[FeCp(arene)]^+$ unit was used as a standard to determine the number of electrons involved in the ferrocene oxidations. More recently, Astruc has reported the preparation of a metallodendrimer containing sixty-four redox active cationic Fe(II) sites attached to the periphery of a polypropyleneimine dendrimer. Cyclic voltammetric studies indicated the presence of a single reversible redox couple due to the isolated centers. Sixty-four equivalents of a nineteen-electron permethylated arene complex were used to reduce the polycationic dendrimer, which resulted in the isolation of its neutral analog.[17]

Abd-El-Aziz and coworkers have also reported the electrochemical behavior of a variety of cyclopentadienyliron-coordinated mono- and poly-metallic complexes.[10, 11, 32-36] Again, it was found that the first electron transfer was chemically reversible in all complexes while the second processes were dependent on the experimental conditions. In addition, organoiron polymers that contain ferrocenyl spacers in their backbones and cyclopentadienyliron cations pendent to their backbones have also been synthesized and studied.[32] For these systems, the neutral iron centers underwent reversible oxidation and the cationic iron centers underwent reversible reduction processes.

Electrochemical investigations of arene complexes with the Cp^*Ru^+ moiety are decidedly rare, and much less successful than the analogous $CpFe^+$ systems.[37, 38] There have only been a few studies on the electrochemical behavior of pentamethylcyclopentadienylruthenium-coordinated complexes.[39-41] The electrochemical reduction of mono- and bi-metallic (Cp*)(polyarene)ruthenium cations was reported in 1990 by Koelle (Figure 1).[40] Reduction of the ruthenium complexes was observed in CH_2Cl_2 and propylene carbonate, using either platinum or vitreous carbon working electrodes. The monocations exhibited varying degrees of reversibility, which were highly dependent on the scan rates used. The pyrene complex, $\mathbf{3}^+$, was chemically reversible at fairly low scan rates (1 V/s), while the phenanthrene and anthracene complexes required much higher scan rates (20 V/s) in order to exhibit reversible reduction processes. The dications ($\mathbf{5}^{2+}$ and $\mathbf{6}^{2+}$) behaved as interacting redox centers and reduced in two discrete steps with the degree of separation being dependent on the nature of the arene.[40] It was postulated that the lower aromaticity of the polyarenes allowed for electrochemical reduction to occur within the potential window, unlike monoarene cations which have been reported to show no electrochemical activity up to -2.5 V.[37, 42] The increased stability of the neutral bimetallic complexes over the corresponding monometallics was attributed to a redistribution of electrons which may occur for $\mathbf{5}^{2+}$ and $\mathbf{6}^{2+}$.



1^+ $E_{1/2}$ = - 1.58

2^+ $E_{1/2}$ = - 1.80

3^+ $E_{1/2}$ = - 1.66

4^+ $E_{1/2}$ = - 1.28

5^{2+} $E_{1/2}$ (1) = - 1.40, $E_{1/2}$ (2) = - 1.58

6^{2+} $E_{1/2}$ (1) = - 1.30, $E_{1/2}$ (2) = - 1.53

7^{2+} $E_{1/2}$ (1) = - 0.40, $E_{1/2}$ (2) = - 1.19

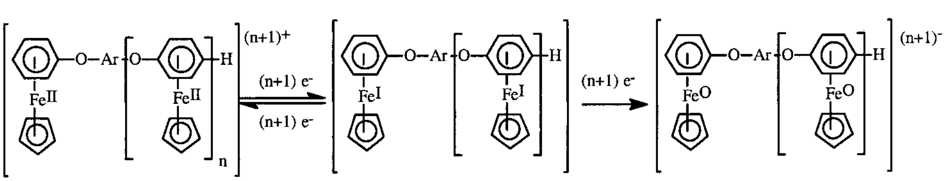
Figure 1. Half-wave potentials for (polyarene)Ru^+Cp^* complexes.

This article describes the electrochemical behavior of oligomers and polymers containing pendent cyclopentadienyliron and pentamethylcyclopentadienylruthenium cations. The effects of temperature, scan rate and the nature of the iron and ruthenium complexes are also examined.

Results and Discussion

Oligomeric Cp Fe$^+$-Coordinated Complexes

As mentioned previously, studies of monoiron cyclopentadienyliron arene complexes have shown that these materials undergo two successive one-electron reductions.[10, 11] We have also conducted cyclic voltammetric studies on oligomeric ether complexes that contain between two and fifteen cationic cyclopentadienyliron moieties pendent to alternating aromatic rings.[39-41] All of these materials exhibited two separate reduction steps, with the electrochemical reversibility being dependent on the nature of the complex, working electrode, temperature and solvent. In all oligomers, the presence of only one electrochemically reversible wave ($E_{1/2}$ between –0.99 and –1.89 V vs Fc/Fc$^+$), corresponding to the generation of the neutral nineteen-electron species, indicated that the iron centers were isolated from one another. For bimetallic complexes, this was also verified using controlled potential coulometry.[40] The mechanism for electron transfer in these complexes follows the general form shown in Scheme 1.



Scheme 1. Mechanism of electron transfer in polyether complexes of CpFe$^+$.

We have also prepared oligomeric complexes that contain mixed ether/sulfide or ether/sulfone backbones and these complexes showed the presence of more than one redox couple due to the different environments of the iron centers.[34] In addition, we have found that it is possible to detect subtle differences in the environment of the iron centers in star-shaped polyaromatic ethers coordinated to cyclopentadienyliron cations as shown below.[35] The cyclic voltammogram of the complex shown in Figure 2 reveals the presence of two distinct redox processes. These two redox steps can be attributed to the inner three and outer three iron centers. The $E_{1/2}$ values for these two redox processes occurred at −1.20 and −1.30 V, respectively.

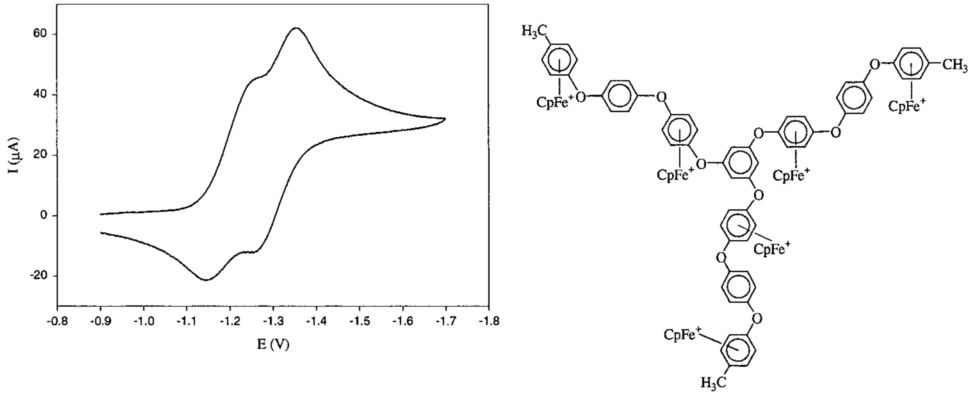


Figure 2. Cyclic voltammogram at glassy carbon of 2 mM complex in 0.1 M TBAP in DMF, ν = 0.1 V/s, T = 233K (Reproduced from "Aromatic Ether Star Oligomers Coordinated to Redox-active Cyclopentadienyliron Moieties", A.S. Abd-El-Aziz, E.K. Todd and T. Afifi, *Macromol. Rapid Commun.*, **23**, 113 (2002) Copyright © [2002] Wiley Periodicals, Inc.).

Our studies have also indicated that the coordinating ability of the solvent plays a role in the electrochemical behavior of Fe(I) complexes. In general, at low temperature (233 K) the rate of arene decomplexation was much higher in acetonitrile than in solvents such as DMSO, DMF, and acetone. This behavior is attributed to the fact that acetonitrile is a stronger coordinating solvent. The mechanism for decoordination of a bimetallic complex is shown is Scheme 1 but this can be extrapolated to the larger oligomers as well.

$$[\{(C_6H_5O)Fe^{II}Cp)\}_2C_6H_4]^{2+} + 2e^- \rightleftharpoons [\{(C_6H_5O)Fe^{I}Cp)\}_2C_6H_4]$$

$$[\{(C_6H_5O)Fe^{I}Cp)\}_2C_6H_4] + nS \xrightarrow{k} 2\,[S_n(Fe^{I}Cp)] + [(C_6H_5O)_2C_6H_4]$$

$$2\,[S_n(Fe^{I}Cp)]_2 \xrightarrow{fast} Fe^{II}(Cp)_2 + Fe^0 + 2nS$$

Scheme 1. Mechanism of electrochemical decoordination.

Oligomeric Ru$^+$Cp* and Heterometallic Ru$^+$Cp*-Fe$^+$Cp Complexes

The synthesis of a number of aromatic ether and thioether complexes containing pendent pentamethylcyclopentadienylruthenium moieties has been described.[43] Cyclic voltammetric studies of the complexes shown in Figure 3 have been performed in various solvents, at different temperatures, and with different working electrodes. Studies of the monometallic complexes performed in DMF using either a platinum disk or glassy carbon working electrode have indicated that the monometallic complexes **4.1-4.3** undergo quasi-reversible redox processes with a large ΔEp at all temperatures (213 K - 363 K) and electrodes studied.[3, 14] It was noted that the ΔEp value decreased with an increase in temperature which suggests that the kinetics of the processes were slow on the CV timescale.

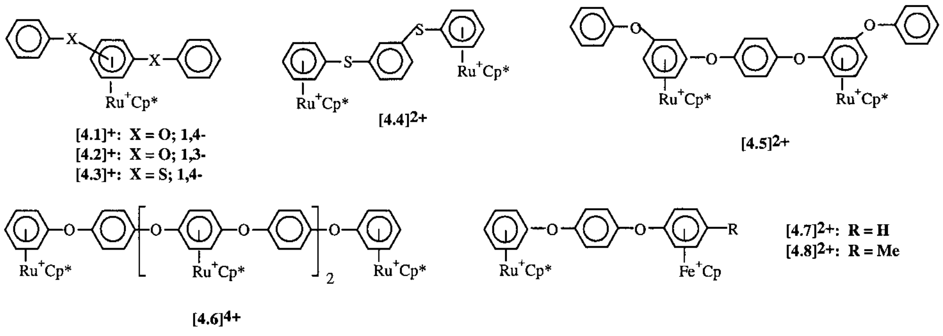


Figure 3. Structures of arene complexes of Cp*Ru$^+$ and complexes containing Cp*Ru$^+$ and CpFe$^+$ moieties.

Figure 4 shows typical cyclic voltammograms obtained for complex [**4.3**]$^+$ at different temperatures. The E_{pc} and E_{pa} values for this complex range from -2.58 V to -2.17 V and -0.81 V to -1.50V (vs Fc/Fc$^+$) as the temperature increases from 213 K to 333 K. Upon moving from the monometallic species to the bimetallic and tetrametallic complexes, the cyclic voltammograms of these materials became more complex. For the bimetallic ruthenium complexes, two or three reduction peaks were observed depending on the working electrode used, but only one oxidation peak was present. However, as in the case of the monometallic species, the peak separation did decrease with an increase in temperature.

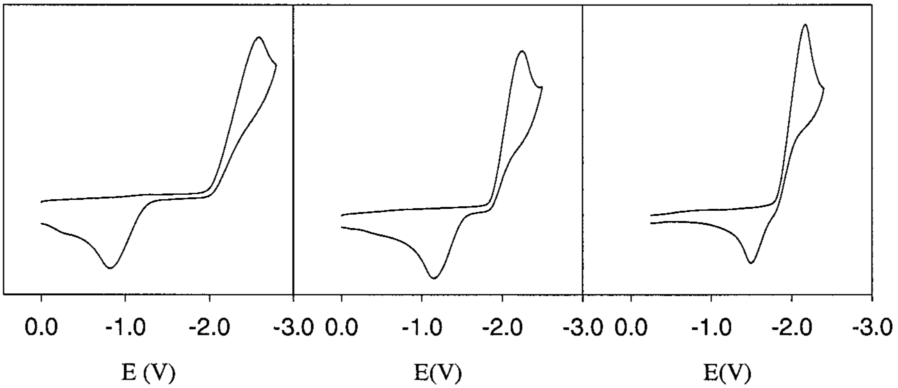


Figure 4. Cyclic voltammograms at Pt of 2.0 mM [**4.2**]$^+$ in DMF containing 0.1 M $TBAPF_6$; ν = 0.5 V/s at (a) 213 K, (b) 273 K, and (c) 333 K.

Studies of the tetrametallic complex ([**4.6**]$^{4+}$) showed even more complex behavior that varied with both solvent and working electrode. For complexes [**4.7**]$^{2+}$ and [**4.8**]$^{2+}$, it was expected that a reversible one-electron reduction corresponding to the iron center, and a quasi-reversible reduction corresponding to the ruthenium center would be present. It was indeed observed that a reversible one-electron redox couple corresponding to the iron center and a quasi-reversible process attributed to the reduction of the ruthenium center was present when scanning from -0.7 V to -3.2 V. It was also found that the second redox couple corresponding to the ruthenium complex became more prominent as the temperature of the electrochemical experiment was increased (Figure 5). No second redox couple was observed for the iron center.

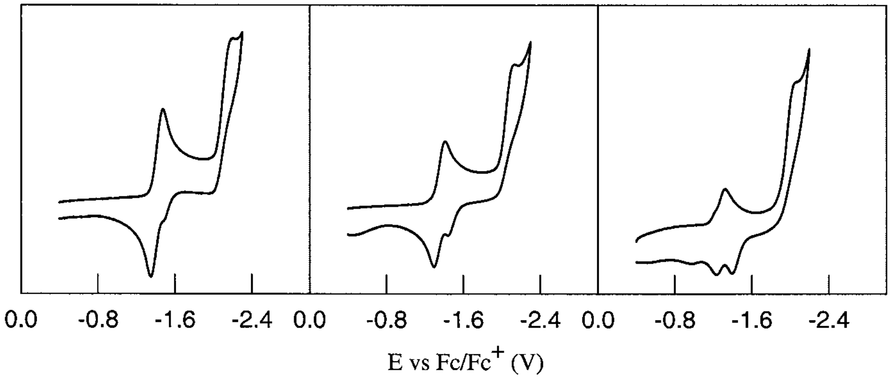


Figure 5. Cyclic voltammograms at Pt of 2.0 mM [**4.7**]$^{2+}$ in DMF containing 0.1 M TBAP; ν = 0.2 V/s at (a) 233 K, (b) 253 K, and (c) 273 K.

Polymeric Complexes

Homo- and hetero-metallic polymers containing pendent $CpFe^+$ and Cp^*Ru^+ moieties have been prepared by a number of synthetic routes including nucleophilic aromatic substitution, polycondensation, radical polymerization and ring-opening metathesis polymerization.[36, 43-49] Typically, the cyclopentadienyliron-coordinated polymers exhibited reversible redox couples similar to the smaller oligomers with $E_{1/2}$ values between -0.99 V and -1.45 V. It was important that the cyclic voltammetric behavior of the polymers be compared to their monomeric and oligomeric analogs. For example, Figure 6 shows the cyclic voltammograms of an aryl ether complex and polymer obtained in a DMF solutions containing TBAP as the supporting electrolyte. These CVs were measured at –20 °C with a scan rate of 1 V/s. It was found that the reduction processes for this diiron complex displayed good reversibility and had a cathodic peak potential (E_{pc}) of -1.28 V, and an anodic peak potential (E_{pa}) of -1.08 V. The half-wave potential ($E_{1/2}$) for this reduction process was at -1.18 V. The cyclic voltammograms of the polymeric analog showed poorer reversibility relative to the diiron complex, in particular at low scan rates. The CV of the organoiron polymer had an E_{pc} = -1.61 V, E_{pa} = -1.18 V and $E_{1/2}$ = -1.40 V.

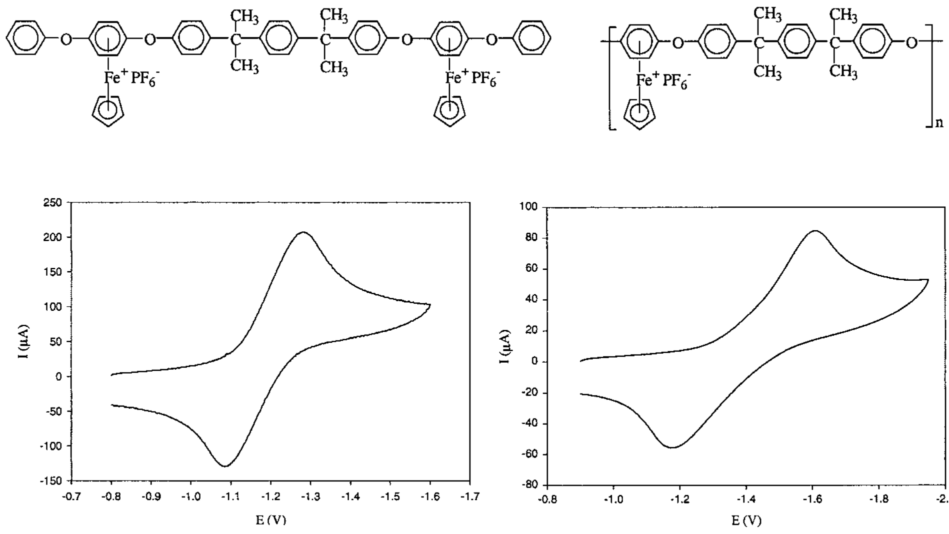


Figure 6. Cyclic voltammogram of a bimetallic complex and polymer containing aryl ether linkages.

For analogous pentamethylcyclopentadienylruthenium-coordinated polymers (Figure 7), it was found that the shape of the cyclic voltammogram depended on the scan rate and temperature. At 213 K, the cyclic voltammograms showed multiple reduction peaks at low scan rates (0.05, 0.2, 0.5 V/s) that started to coalesce as the scan rate was increased to 5 V/s. It was observed that as the scan rate increased, the voltammogram started to resemble the shape of the analogous monometallic Cp^*Ru^+ systems. It is also important to note that the heterometallic polymers only possessed one redox couple for the iron center with no electrochemical activity of the ruthenium center being observed. This may be a consequence of the multiple ruthenium centers becoming very difficult to reduce, and therefore no electrochemical activity is seen within the potential window of the experiment.

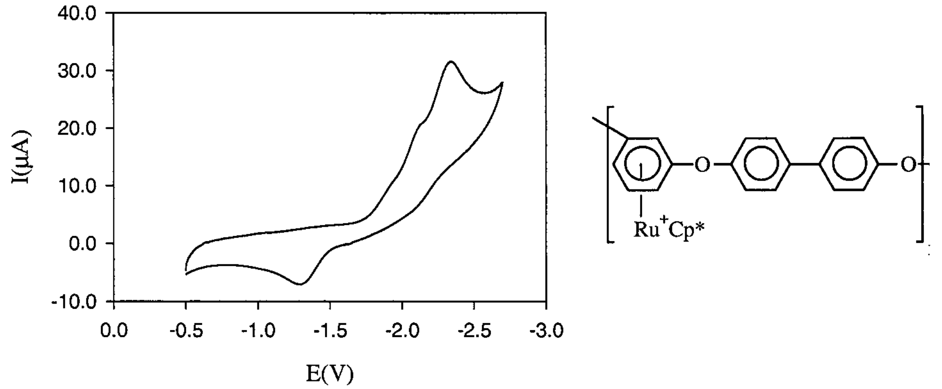


Figure 7. Cyclic voltammogram at Pt of 2.0 mM ruthenium polymer in DMF containing 0.1 M TBAP; v = 1.0 V/s at 213 K.

Conclusion

Extensive electrochemical studies of oligomeric and polymeric arene complexes with pendent cyclopentadienyliron and pentamethylcyclopentadienylruthenium moieties have been conducted. For the cyclopentadienyliron-coordinated systems it was found that the iron centers behaved as isolated redox centers. The reversibility of the couples were found to be dependent on different factors (solvent, temperature). In contrast, it was found that the ruthenium systems exhibited quite complex electrochemical behavior regardless of the experimental conditions employed.

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