

# Electrochemical Investigation of Ruthenium and Osmium Oligothiophene Complexes: How Does Metal Binding Affect the Oligothiophene $\pi$ -System?

David D. Graf and Kent R. Mann\*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received March 22, 1996<sup>⊗</sup>

We have studied the electrochemistry of a series of oligothiophene complexes with one or more “Cp\*Ru<sup>+</sup>”, “CpRu<sup>+</sup>”, or “CpOs<sup>+</sup>” fragments (Cp = cyclopentadienyl; Cp\* = pentamethylcyclopentadienyl) attached to the oligothiophene  $\pi$ -system. This series varies the metal (Ru or Os), ancillary ligand (Cp or Cp\*), ring substituents (phenyl or methyl groups), and length of the oligothiophene (1–4 rings). The peak potentials for the oxidation of the free oligothiophenes and their complexes indicate that the electron hole produced upon oxidation of the complexes is delocalized on the uncomplexed rings of the oligothiophene. Oxidation of the complexes results in conductive films on the electrode but the composition of the electrodeposited films is unclear. The electron added upon reduction of the complexes is localized on the [Cp/Cp\*M(thiophene)]<sup>+</sup> unit formed by complexation of the oligothiophene. We propose that complexation of a thiophene ring converts it into a [Cp/Cp\*M(thiophene)]<sup>+</sup> unit and removes it from conjugation with the remaining, uncomplexed rings. The unbound rings function as a shortened, metal-substituted oligothiophene unit. Complexation of oligothiophenes by “Cp\*Ru<sup>+</sup>”, “CpRu<sup>+</sup>”, and “CpOs<sup>+</sup>” fragments is a rational method for controlling the properties of oligothiophenes.

## Introduction

Oligothiophenes are useful models for polythiophene because they are conductive when partially oxidized, they exhibit similar electrochemical properties, and their well-defined molecular structure can be directly related to the observed properties.<sup>1–30</sup> Many oligothiophene studies have varied the ring substituents

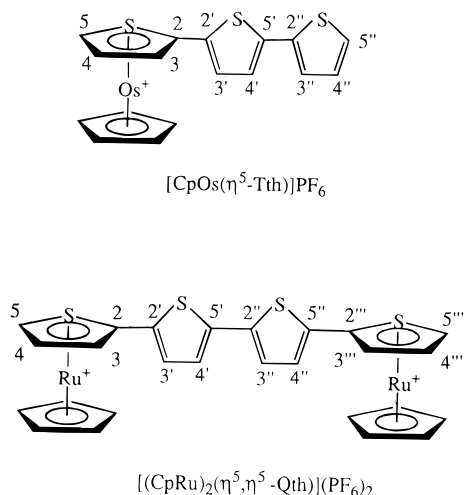
to control the physical properties.<sup>1–30</sup> Recently<sup>31,32</sup> we reported novel oligothiophene complexes (Figure 1) with one or more “Cp\*Ru<sup>+</sup>” or “CpRu<sup>+</sup>” fragments (Cp = cyclopentadienyl; Cp\* = pentamethylcyclopentadienyl) directly attached to the  $\pi$ -system or to pendant arene groups. We studied these complexes by NMR (<sup>1</sup>H and <sup>13</sup>C)<sup>31</sup> and optical spectroscopy<sup>32</sup> to determine whether transition metal substituents can modulate the physical properties of the oligothiophenes in ways that organic substituents can not. It became obvious during these studies that the electrochemical properties of these compounds would also be of interest. With additional osmium complexes of Tth (2,2':5',2''-terthiophene), Qth (2,2':5',2'':5'',2'''-quaterthiophene), and Me<sub>2</sub>Tth (5,5''-dimethyl-2,2':5',2''-terthiophene) synthesized here, this series of oligothiophene complexes systematically varies the metal (Ru or Os), ancillary ligand (Cp or Cp\*), length of the bound oligothiophene (1–4 rings), and substituents on the rings (phenyl or methyl groups). The electrochemical studies described herein show that the unbound thiophene rings function as a discrete oligothiophene unit with one or two [Cp/Cp\*M(thiophene)]<sup>+</sup> substituents. The properties of these complexes are dependent on the number of unbound thiophene rings and

\* To whom correspondence should be addressed.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, December 15, 1996.

- (1) Hill, M. G.; Penneau, J. F.; Zinger, B.; Mann, K. R.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1106.
- (2) Hill, M. G.; Penneau, J. F.; Zinger, B.; Mann, K. R.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1113.
- (3) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J.-F. *J. Am. Chem. Soc.* **1992**, *114*, 2728.
- (4) Bauerle, P.; Segelbacher, U.; Maier, A.; Mehring, M. *J. Am. Chem. Soc.* **1993**, *115*, 10217.
- (5) Guay, J.; Diaz, A.; Wu, R.; Tour, J. M.; Dao, L. H. *Chem. Mater.* **1992**, *4*, 1097.
- (6) Pham, C. V.; Burkhardt, A.; Shabana, R.; Cunningham, D. D.; Mark, H. B.; Zimmer, H. *Phosphorus, Sulfur, Silicon* **1989**, *46*, 153.
- (7) Amer, A.; Burkhardt, A.; Shabana, N. R.; Galal, A.; Mark, H. B.; Zimmer, H. *Phosphorus, Sulfur, Silicon* **1989**, *42*, 63.
- (8) Rossi, R.; Carpita, A.; Ciofalo, M. *Gazz. Chim. Ital.* **1990**, *120*, 793.
- (9) Shabana, R.; Amer, A.; Mark, B.; Zimmer, H. *Phosphorus, Sulfur, Silicon* **1990**, *53*, 299.
- (10) Eachern, A. M.; Soucy, C.; Leitch, L. C.; Aranson, J. T.; Morand, P. *Tetrahedron* **1990**, *44*, 2403.
- (11) Hoeve, W.; Wynberg, H. *J. Am. Chem. Soc.* **1991**, *113*, 5887.
- (12) Ikenoue, Y.; Uotani, N.; Patil, A. O.; Wudl, P. F.; Heeger, A. J. *Synth. Met.* **1989**, *30*, 305.
- (13) Barbarella, G.; Bongini, A.; Zambianchi, M. *Adv. Mater.* **1991**, *3*, 494.
- (14) Garnier, F.; Yasar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc.* **1993**, *115*, 8716.
- (15) Yassar, A.; Delabouglise, D.; Hmyene, M.; Nessak, B.; Horowitz, G.; Garnier, F. *Adv. Mater.* **1992**, *4*, 490.
- (16) Yu, Y.; Gunic, E.; Zinger, B.; Miller, L. L. *J. Am. Chem. Soc.* **1996**, *118*, 1013 and references therein.
- (17) (a) Bauerle, P. *Adv. Mater.* **1992**, *4*, 102. (b) Bauerle, P.; Pfau, F.; Schlupp, H.; Wurthner, F.; Gaudl, K. U.; Caro, M. B.; Fischer, P. *J. Chem. Soc., Perkin Trans. 2* **1993**, 489.
- (18) Guay, J.; Diaz, A.; Wu, R.; Tour, J. M.; Dao, L. H. *Chem. Mater.* **1992**, *4*(2), 254.
- (19) Garcia, P.; Pernaut, J.-M.; Hapiot, P.; Wintegens, V.; Valat, P.; Garnier, F.; Delabouglise, D. *J. Phys. Chem.* **1993**, *97*, 513.
- (20) Effenberger, F.; Wurthner, F.; Steybe, F. *J. Org. Chem.* **1995**, *60*, 2082.

- (21) Krishnaswamy, N. R.; Kumar, Ch S. S. R. *Indian J. Chem., Sect. B* **1993**, *32B*(7), 766.
- (22) Segelbacher, U.; Sariciftci, N. S.; Grupp, A.; Bauerle, P.; Mehring, M. *Synth. Met.* **1993**, *55–57*, 4728.
- (23) Hapiot, P.; Audebert, P.; Monnier, K.; Pernaut, J.-M.; Garcia, P. *Chem. Mater.* **1994**, *6*, 1549.
- (24) Audebert, P.; Garcia, P.; Hapiot, P.; Monnier, K.; Pernaut, J.-M. *J. Chim. Phys.* **1995**, *92*, 827.
- (25) Audebert, P.; Hapiot, P.; Pernaut, J.-M.; Garcia, P. *J. Electroanal. Chem.* **1993**, *361*, 283.
- (26) Bauerle, P.; Segelbacher, U.; Gaudl, K.-L.; Huttenlocher, D.; Mehring, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 76.
- (27) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, *5*, 620.
- (28) Bauerle, P.; Gotz, G.; Segelbacher, U.; Huttenlocher, D.; Mehring, M. *Synth. Met.* **1993**, *55–57*, 4768.
- (29) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Synth. Met.* **1993**, *61*, 81.
- (30) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, *5*, 430.
- (31) Graf, D. D.; Day, N. C.; Mann, K. R. *Inorg. Chem.* **1995**, *34*, 1562.
- (32) Graf, D. D.; Mann, K. R. Unpublished results.



**Figure 1.** Structures and numbering schemes of the ruthenium and osmium oligothiophene complexes.

on the nature of the metal containing substituent. By a careful choice of the metal, ancillary ligand, and oligothiophene, complexes can be synthesized with a desired set of electrochemical properties.

## Experimental Section

**General Considerations.** All synthetic procedures were carried out under an inert atmosphere of Ar with Schlenk line techniques. Reaction and electrochemical solvents were of spectroscopic grade and were dried by distilling acetone from B<sub>2</sub>O<sub>3</sub>, acetonitrile from CaH<sub>2</sub>, and dichloromethane from P<sub>2</sub>O<sub>5</sub>. All solvents used in the workup of the reactions were of spectroscopic grade and were used as received. The acetone-*d*<sub>6</sub> and acetonitrile-*d*<sub>3</sub> used for NMR studies were dried over 3 Å molecular sieves and degassed with Ar prior to use.

The oligothiophenes Bth, Tth, Qth, and Me<sub>2</sub>Tth were synthesized as reported earlier.<sup>31</sup> Thiophene was purchased from Aldrich and purified by flash chromatography (activated alumina) prior to use. [CpRu(CH<sub>3</sub>CN)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub>, [Cp\*Ru(CH<sub>3</sub>CN)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub>,<sup>34–37</sup> and [CpOs(CH<sub>3</sub>CN)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub><sup>38</sup> were synthesized according to known procedures and were stored in a N<sub>2</sub> atmosphere prior to use. [CpRu( $\eta^5$ -Bth)]PF<sub>6</sub>, [Cp\*Ru( $\eta^5$ -Bth)]PF<sub>6</sub>, [CpRu( $\eta^5$ -Tth)]PF<sub>6</sub>, [Cp\*Ru( $\eta^5$ -Tth)]PF<sub>6</sub>, [CpRu( $\eta^5$ -Qth)]PF<sub>6</sub>, [Cp\*Ru( $\eta^5$ -Qth)]PF<sub>6</sub>, [CpRu( $\eta^5$ -Me<sub>2</sub>Tth)]PF<sub>6</sub>, [Cp\*Ru( $\eta^5$ -Me<sub>2</sub>Tth)]PF<sub>6</sub>, [(CpRu)<sub>2</sub>( $\eta^5$ , $\eta^5$ -Tth)](PF<sub>6</sub>)<sub>2</sub>, and [(Cp\*Ru)<sub>2</sub>( $\eta^5$ , $\eta^5$ -Tth)](PF<sub>6</sub>)<sub>2</sub> have been previously reported.<sup>31</sup> [CpRu( $\eta^5$ -thiophene)]PF<sub>6</sub> was prepared according to the literature procedure.<sup>39</sup>

**Characterization.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a VXR-300 or VXR-500 MHz instrument. The chemical shifts are reported in ppm (relative to TMS) and are referenced to the residual solvent peak. The <sup>1</sup>H and proton-decoupled <sup>13</sup>C NMR spectra were assigned by comparisons with our previous studies<sup>31</sup> and by selective decoupling experiments. The numbering system used for the NMR assignments is as reported earlier.<sup>31</sup> Low-resolution fast atom bombardment mass spectra (FABMS) of the complexes in a thioglycerol matrix were obtained by use of a VG 7070E-HF mass spectrometer. The FABMS M<sup>+</sup> values quoted are the values for the cationic complex without the PF<sub>6</sub><sup>-</sup> anion(s). The theoretical isotopic patterns of the M<sup>+</sup> ions were calculated via the ISO program of VG Analytical, Ltd., and were compared to those of the observed M<sup>+</sup> isotopic pattern to verify

the identity of the M<sup>+</sup> peak. Elemental analyses were performed by MHW Laboratories.

**Electrochemical Measurements.** Electrochemical experiments were performed with a BAS 100 electrochemical analyzer. Cyclic voltammetry (CV) and chronocoulometry (CC) experiments were performed at room temperature (23–24 °C) with a normal three-electrode configuration consisting of a highly polished glassy-carbon working electrode (A = 0.07 cm<sup>2</sup>), a Pt auxiliary electrode, and a Ag/AgCl reference electrode containing 1.0 M KCl. The 5 mL working compartment was separated from the reference compartment by a modified Luggin capillary. All three compartments were filled with a 0.1 M solution of supporting electrolyte. Tetrabutylammonium hexafluorophosphate (TBA<sup>+</sup>PF<sub>6</sub><sup>-</sup>) was purchased from Southwestern Analytical Chemicals and stored in vacuum prior to use. In all experiments, the electrolyte solution was passed down a column of activated alumina prior to the electrochemical experiments. The working compartment of the cell was bubbled with solvent-saturated argon to deaerate the solution. The working solutions were prepared by recording the background cyclic voltammograms of the electrolyte solution prior to addition of the solid sample. The electrode was removed from the solution and cleaned to remove conductive coatings that formed during some of the electrochemical experiments (oxidative scans).

Potentials are reported vs aqueous Ag/AgCl and are not corrected for the junction potential. The oxidation and reduction processes of the oligothiophenes and complexes tend to be irreversible no matter the scan rate used (50–2000 mV/s). Thus, the reported values for the oxidation and reduction processes of the oligothiophenes and complexes are given as the peak potentials only (*E*<sub>p,a</sub> or *E*<sub>p,c</sub>). Several of the oxidation processes overlapped with the electrolyte solution oxidation and thus could not be determined accurately by cyclic voltammetry studies. The peak potentials for these processes were determined by Osteryoung square wave analysis. As the peak potentials in general depend on the concentration and scan rate, the CV's for the complexes and uncomplexed oligothiophenes were recorded at similar concentrations (0.48–0.52 mM) and scan rates (100 mV/s). In this manner, the variation in the peak potentials due to concentration and scan rate could be reduced to a level where comparison of the data should be very reliable. We further note that the peak potentials contain both thermodynamic and kinetic factors. We were unable to quantify the kinetic factors (e.g. rates for the dimerization of the oxidized species and for the heterogeneous electron transfer from the electrode to the molecules) due to the extreme irreversibility of the electrochemical processes and the subsequent coupling of the oxidized species. The importance and relevance of these kinetic factors to the comparison of the peak potentials is addressed in the discussion section.

The *E*<sup>o</sup> value for the ferrocenium/ferrocene couple was determined for solutions and concentrations similar to those used in the study of the oligothiophenes and complexes to allow correlation of the *E*<sub>p,a</sub> and *E*<sub>p,c</sub> values to past and future studies. For a 0.54 mM dichloromethane solution of ferrocene, the oxidation and reduction waves occurred at +513 and +402 mV, respectively (*E*<sup>o</sup> = +458 mV). For a 0.30 mM dichloromethane solution of ferrocene, the oxidation and reduction waves occurred at +489 and +405 mV, respectively (*E*<sup>o</sup> = +448 mV). For a 0.54 mM propylene carbonate solution of ferrocene, the oxidation and reduction waves occurred at +426 and +343 mV, respectively (*E*<sup>o</sup> = +385 mV).

**[Cp\*Ru( $\eta^5$ -th)]PF<sub>6</sub>.** This complex was synthesized as for [CpRu( $\eta^5$ -th)]PF<sub>6</sub>.<sup>39</sup> To [Cp\*Ru(CH<sub>3</sub>CN)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub> (68.6 mg, 0.136 mmol) in 15 mL of CH<sub>2</sub>Cl<sub>2</sub> was added 0.20 mL of thiophene (2.5 mmol), and the solution was heated to reflux for 19 h. Workup of the reaction provided an acetone soluble fraction that was precipitated with diethyl ether to give 51.2 mg (0.110 mmol, 81% yield) of [Cp\*Ru(thiophene)]PF<sub>6</sub> as an ivory colored powder. <sup>1</sup>H NMR (300 MHz, acetone-*d*<sub>6</sub>, 25 °C): 6.25 (m, 2H, H(3,4)), 6.22 (m, 2H, H(2,5)), 2.08 (s, 15H, CH<sub>3</sub>-Cp\*) FABMS: *m/e* 321.0 (M<sup>+</sup>) Anal. Calcd for C<sub>14</sub>H<sub>19</sub>F<sub>6</sub>PSRu: C, 39.49; H, 3.87. Found: C, 39.65; H, 4.04

**[CpOs( $\eta^5$ -Tth)]PF<sub>6</sub>.** A 50 mL Schlenk flask equipped with a reflux condenser was charged with [CpOs(CH<sub>3</sub>CN)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub> (52.5 mg, 0.100 mmol) and Tth (50.2 mg, 0.202 mmol). After the system was purged three times, 20 mL of acetone was added, and the reaction was heated at reflux for 6 days during which the initial purple/red solution changed to a brown solution. The solvent was removed in vacuum, and then

(33) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485.

(34) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274.

(35) Fagan, P. J.; Mahoney, W. S.; Calabrese, J. C.; Williams, I. D. *Organometallics* **1990**, *9*, 1843.

(36) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

(37) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981.

(38) Freedman, D. A.; Gill, T. P.; Blough, A. M.; Koefod, R. S.; Mann, K. R. Unpublished results.

(39) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897.

40 mL of hexanes was added. After 10 min of stirring, the suspension was filtered through a coarse frit packed with 1 cm of diatomaceous earth. The solid was then washed with hexanes until no more green/yellow color was observed with the washings.

The solid was washed through the frit with acetone, the volume reduced to 5 mL by rotary evaporation, and then 40 mL of hexanes was added. The resulting emulsion was again filtered onto 1 cm of diatomaceous earth on a coarse frit and washed with hexanes until no green/yellow color washed out. After this procedure was repeated once more, the solid was washed with  $\text{CHCl}_3$  until no more yellow color was observed in the washings. The reddish residue on the frit was washed through the frit with acetone, the solvent was removed, and then 25 mL of  $\text{CHCl}_3$  was added. After 10 min of stirring, the suspension was filtered and washed with  $\text{CHCl}_3$  until no more yellow color was observed in the washings. A purple/red solid was deposited onto the diatomaceous earth. The  $\text{CHCl}_3$  washings were combined, solvent was removed by rotary evaporation, and then 2 mL of  $\text{CH}_2\text{Cl}_2$  was added. Next, 15 mL of heptane was added and the solvent was reduced to 5 mL. The resulting precipitate was filtered off and washed with 10 mL of hexanes to give 38.4 mg (0.0592 mmol, 59% yield) of  $[\text{CpOs}(\text{Tth})]\text{PF}_6$  as a dull yellow powder.  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ , 25 °C): 7.54 (dd, 1H, H(5''),  $J = 5.2, 0.9$  Hz), 7.44 (d, 1H, H(3')  $J = 3.9$  Hz), 7.36 (dd, 1H, H(3''),  $J = 3.6, 0.9$  Hz), 7.25 (d, 1H, H(4'),  $J = 3.9$  Hz), 7.13 (dd, 1H, H(4''),  $J = 3.6, 0.9$  Hz), 7.03 (d, 1H, H(3),  $J = 3.0$  Hz), 6.80 (dd, 1H, H(4),  $J = 3.0, 2.7$  Hz), 6.75 (d, 1H, H(5),  $J = 2.7$  Hz), 5.91 (s, 5H, Cp).  $^{13}\text{C}$  NMR (125.7 MHz, acetone- $d_6$ , 25 °C): 140.34 (C(2')), 135.56 (C(2'')), 131.70 (C(3')), 131.23 (C(5')), 128.41 (C(4'')), 126.24 (C(5'')), 125.02 (C(4' or 3'')), 124.78 (C(4' or 3'')), 84.58 (C(2)), 76.98 (C(4)), 75.92 (C(3)), 64.94 (C(5)), 78.53 (Cp). FABMS:  $m/e$  505.0 ( $\text{M}^+$ , 100%). Anal. Calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_6\text{P}_3\text{Os}$ : C, 31.48; H, 2.02; S, 14.83. Found: C, 31.67; H, 2.06; S, 14.66.

**$[\text{CpOs}(\eta^5\text{-Me}_2\text{Tth})]\text{PF}_6$ .** The preparation was similar to that of  $[\text{CpOs}(\text{Tth})]\text{PF}_6$ . To 55.5 mg (0.106 mmol) of  $[\text{CpOs}(\text{CH}_3\text{CN})_3]\text{PF}_6$  and 50.9 mg (0.184 mmol) of  $\text{Me}_2\text{Tth}$  was added 20 mL of acetone, and the solution was refluxed for 6 days. After the hexanes washing, recrystallization ( $\text{CH}_2\text{Cl}_2/\text{heptane}$ ) of the  $\text{CHCl}_3$ -soluble material provided 49.8 mg (0.0736 mmol, 69% yield) of  $[\text{CpOs}(\text{Me}_2\text{Tth})]\text{PF}_6$  as a dark yellow powder. (300 MHz, acetone- $d_6$ , 25 °C): 7.36 (d, 1H, H(3'),  $J = 3.9$  Hz), 7.13 (d, 2H, H(4'/3'')  $J = 3.6$  Hz), 6.92 (d, 1H, H(3),  $J = 2.7$  Hz), 6.80 (m, 1H, H(4'')), 6.75 (d, 1H, H(4),  $J = 2.7$  Hz), 2.56 (s, 3H,  $\text{CH}_3$ (bound ring)), 2.49 (d, 3H,  $\text{CH}_3$ (unbound ring),  $J = 0.9$  Hz), 5.90 (s, 5H, Cp).  $^{13}\text{C}$  NMR (125.7 MHz, acetone- $d_6$ , 25 °C): 140.75 (C(2',5''), overlapping peaks), 133.30 (C(2'')), 131.64 (C(3')), 130.71 (C(5'')), 126.72 (C(4'')), 124.95 (C(4')), 123.97 (C(3'')), 83.68 (C(5)), 78.80 (C(2), tentative assignment due to overlap with Cp peak), 78.63 (C(4)), 75.72 (C(3)), 15.45 ( $\text{CH}_3$ , methyl on bound ring), 14.35 ( $\text{CH}_3$ , methyl on unbound ring) 78.81 (Cp). FABMS:  $m/e$  532.9 ( $\text{M}^+$ , 100%) Anal. Calcd for  $\text{C}_{19}\text{H}_{17}\text{F}_6\text{P}_3\text{Ru}$ : C, 33.72; H, 2.53; S, 14.22. Found: C, 33.52; H, 2.58; S, 13.96.

**$[\text{CpOs}(\eta^5\text{-Qth})]\text{PF}_6$ .** To a 100 mL three-neck flask equipped with an addition funnel, condenser, and  $\text{N}_2$  adapter was added 60.2 mg (0.182 mmol) of Qth. After the flask was purged three times, 75 mL of acetone was added and heated to reflux. Meanwhile, a 10 mL flask was charged with 50.5 mg (0.0965 mmol) of  $[\text{CpOs}(\text{CH}_3\text{CN})_3]\text{PF}_6$  in a  $\text{N}_2$  atmosphere glovebox, capped with a septum, and removed from the box. After the Qth was dissolved in the refluxing acetone, the  $[\text{CpOs}(\text{CH}_3\text{CN})_3]\text{PF}_6$  was dissolved in 6 mL of acetone and transferred to the Qth solution via cannula. After the reaction was held at reflux for 48 h, the red-orange solution was cooled to room temperature and transferred to a 100 mL flask and the solvent removed by rotary evaporation. Then 20 mL of fresh acetone was added, and the suspension was stirred for 5 min, filtered through 1 cm of diatomaceous earth, and finally washed with 15 mL of acetone to leave an orange residue (Qth is sparingly soluble in acetone).

The filtrate was concentrated to 10 mL, and then 400 mL of hexanes was added. The emulsion was filtered onto 1 cm of diatomaceous earth on a coarse frit and washed with about 100 mL of diethyl ether. The solid was then washed through the frit with acetone and the filtrate subjected to the precipitation/washing procedure again. This precipitation/washing procedure was carried out a total of three times to remove all excess Qth. The insoluble residue on the frit was then washed with  $\text{CHCl}_3$  until no color came off while leaving a brown residue on the

diatomaceous earth. The  $\text{CHCl}_3$  was removed from the filtrate by rotary evaporation. The  $\text{CHCl}_3$ -soluble residue was dissolved in 5 mL of  $\text{CH}_2\text{Cl}_2$ , 40 mL of heptane was added, and the solvent volume was reduced to 10 mL. The resulting precipitate was filtered off and washed with 50 mL of diethyl ether to give 44.6 mg (0.610 mmol, yield 63%) of  $[\text{CpOs}(\text{Qth})]\text{PF}_6$  as a yellow solid.  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ , 25 °C): 7.50 (dd, 1H, H(5'''),  $J = 5.1, 0.9$  Hz), 7.46 (d, 1H, H(3')  $J = 3.9$  Hz), 7.35 (dd, 1H, H(3'''),  $J = 3.9, 0.9$  Hz), 7.32 (d, 1H, H(3''),  $J = 3.9$  Hz), 7.28 (d, 1H, H(4'),  $J = 3.9$  Hz), 7.27 (d, 1H, H(4''),  $J = 3.9$  Hz), 7.12 (dd, 1H, H(4'''),  $J = 5.1, 0.9$  Hz), 7.03 (d, 1H, H(3),  $J = 2.7$  Hz), 6.80 (dd, 1H, H(4),  $J = 2.7, 2.7$  Hz), 6.74 (d, 1H, H(5),  $J = 2.7$  Hz), 5.92 (s, 5H, Cp).  $^{13}\text{C}$  NMR (75.4 MHz, acetone- $d_6$ , 25 °C): 142.53 (C(2')), {139.86, 137.45, 136.18} (C(2'',5'',2'')), assignment is uncertain), 131.86 (C(3')), 131.38 (C(5')), 128.33 (C(4'')), 125.89 (C(4')), 125.62 (C(5'')), 124.90 (C(3'')), 124.83 (C(4'')), 124.45 (C(3'')), 80.361 (C(2)), 76.97 (C(4)), 75.89 (C(3)), 64.73 (C(5)), 78.60 (Cp). FABMS:  $m/e$  587.1 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{21}\text{H}_{15}\text{F}_6\text{P}_3\text{Os}$ : C, 34.52; H, 2.07; S, 17.55. Found: C, 34.66; H, 2.29; S, 17.47.

**$[(\text{CpRu})_2(\eta^5, \eta^5\text{-Qth})](\text{PF}_6)_2$ .** To a 50 mL Schlenk flask was added 57.0 mg (0.0888 mmol) of  $[\text{CpRu}(\eta^5\text{-Qth})]\text{PF}_6$  and 49.0 mg (0.113 mmol) of  $[\text{CpRu}(\text{CH}_3\text{CN})_3]\text{PF}_6$ . After the reaction was purged three times, 15 mL of acetone was added and the reaction was stirred at room temperature. After 48 h, the solution was transferred to a 100 mL flask and the solvent removed by rotary evaporation. Then 75 mL of  $\text{CHCl}_3$  was added, and after 10 min of stirring, the solution was filtered onto 1 cm of diatomaceous earth on a coarse frit. The  $\text{CHCl}_3$ -insoluble residues in the flask were dissolved in 10 mL of acetone, and then 80 mL of hexanes was added. The resulting emulsion was filtered onto 1 cm of diatomaceous earth on a coarse frit and again washed with  $\text{CHCl}_3$  until almost no color was present in the washings. The  $\text{CHCl}_3$ -insoluble residues were dissolved in acetone, and the acetone/hexanes precipitation and  $\text{CHCl}_3$  washing procedure was repeated. This precipitation/washing procedure was carried out a total of four times.

The  $\text{CHCl}_3$ -insoluble material absorbed on the diatomaceous earth was washed with  $\text{CH}_2\text{Cl}_2$  until the washings were nearly colorless. The insoluble residue was washed through the frit with acetone, the solvent removed, and the residue again washed with  $\text{CH}_2\text{Cl}_2$  until the washings were nearly colorless. This washing procedure was carried out a total of four times until the  $\text{CH}_2\text{Cl}_2$  washings were colorless and a  $\text{CH}_2\text{Cl}_2$  insoluble brown/orange solid was left on the diatomaceous earth. The  $\text{CH}_2\text{Cl}_2$  washings were combined, and solvent was removed. The residues were then dissolved in 5 mL of acetone, and then 15 mL of heptane was added and the solvent volume reduced to 5 mL. The resulting precipitate was filtered off and washed with 15 mL of diethyl ether and then 10 mL of pentane to give 70.1 mg (0.0736 mmol, 83% yield) of  $[(\text{CpRu})_2(\text{Qth})](\text{PF}_6)_2$  as a yellow/green solid.  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ , 25 °C): 7.55 (d, 2H, H(3',4''),  $J = 3.9$  Hz), 7.36 (d, 2H, H(4',3''),  $J = 3.9$  Hz), 6.96 (d, 2H, H(3,3''),  $J = 3.3$  Hz), 6.72 (dd, 2H, H(4,4''),  $J = 3.3, 3.0$  Hz), 6.60 (d, 2H, H(5,5''),  $J = 3.0$  Hz), 5.58 (s, 10H, Cp).  $^{13}\text{C}$  NMR (75.4 MHz, acetone- $d_6$ , 25 °C): 138.79 (C(2'/5'')), 132.17 (C(5'/2'')), 131.58 (C(3'/4'')), 126.10 (C(4'/3'')), 93.44 (C(2'/2'')), 86.76 (C(4/4'')), 84.55 (C(3'/3'')), 78.98 (C(5'/5'')), 81.87 (Cp). FABMS:  $m/e$  662.8 ( $\text{M}^+ = \text{C}_{26}\text{H}_{20}\text{S}_4\text{Ru}_2$ ), 808.8 ( $\text{M}^+ + \text{PF}_6$ ), 497.0 ( $\text{M}^+ - \text{CpRu}$ ). Anal. Calcd for  $\text{C}_{26}\text{H}_{20}\text{F}_{12}\text{P}_2\text{S}_4\text{Ru}_2$ : C, 32.78; H, 2.12; S, 13.46. Found: C, 33.00; H, 2.10; S, 13.37.

**$[(\text{Cp}^*\text{Ru})_2(\eta^5, \eta^5\text{-Qth})](\text{PF}_6)_2$ .** The preparation was similar to that of  $[(\text{CpRu})_2(\text{Qth})](\text{PF}_6)_2$ .  $[\text{Cp}^*\text{Ru}(\text{Qth})]\text{PF}_6$  (53.3 mg, 0.0749 mmol) was reacted with 55.0 mg (0.109 mmol) of  $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$  in 15 mL of acetone. Because  $[(\text{Cp}^*\text{Ru})_2(\text{Qth})](\text{PF}_6)_2$  is slightly soluble in  $\text{CHCl}_3$ , the  $\text{CHCl}_3$  washings were performed until the washings were light yellow in color. At this point, the  $^1\text{H}$  NMR spectrum of the  $\text{CHCl}_3$ -insoluble material was obtained to determine if all of the  $[\text{Cp}^*\text{Ru}(\text{Qth})]\text{PF}_6$  had been removed. Once the monoruthenated material had been removed, the  $\text{CHCl}_3$ -insoluble residue was repeatedly washed with  $\text{CH}_2\text{Cl}_2$  as for  $[(\text{CpRu})_2(\text{Qth})](\text{PF}_6)_2$ , and then the  $\text{CH}_2\text{Cl}_2$ -soluble material was recrystallized (acetone/heptane) to give 71.0 mg (0.0650 mmol, 87% yield) of  $[(\text{Cp}^*\text{Ru})_2(\text{Qth})](\text{PF}_6)_2$  as a yellow powder.  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ , 25 °C): 7.50 (d, 2H, H(3',4''),  $J = 3.9$  Hz), 7.45 (d, 2H, H(4',3''),  $J = 3.9$  Hz), 6.61 (d, 2H, H(3,3''),  $J = 3.0$  Hz), 6.39 (dd, 2H, H(4,4''),  $J = 3.0, 3.0$  Hz), 6.35 (d, 2H, H(5,5''),  $J = 3.0$  Hz), 1.98 (s, 30 H,  $\text{CH}_3\text{-Cp}^*$ ).  $^{13}\text{C}$  NMR (75.4

MHz, acetone- $d_6$ , 25 °C): 137.38 (C(2'/5'')), 131.71 (C(5'/2'')), 129.15 (C(3'/4'')), 126.38 (C(4'/3'')), 91.83 (C(2/2'')), 89.09 (C(4/4'')), 85.06 (C(3/3'')), 79.27 (C(5/5'')), 96.71 (Cp\*, q-C), 9.84 (Cp\*, -CH<sub>3</sub>). FABMS: *m/e* 803.1 (M<sup>+</sup> = C<sub>36</sub>H<sub>40</sub>S<sub>4</sub>Ru<sub>2</sub>), 949.0 (M<sup>+</sup> + PF<sub>6</sub>), 567.1.0 (M<sup>+</sup> - Cp\*<sup>+</sup>Ru). Anal. Calcd for C<sub>36</sub>H<sub>40</sub>F<sub>12</sub>P<sub>2</sub>S<sub>4</sub>Ru<sub>2</sub>: C, 39.56; H, 3.69; S, 11.73. Found: C, 39.49; H, 3.90; S, 11.90.

## Results and Discussion

**Synthesis and Comparison of Ru and Os Oligothiophene Complexes.** All of the ruthenium complexes we study here have been previously reported<sup>31</sup> except for the diruthenated Cp and Cp\* complexes of Qth. These new complexes were synthesized in high yields by following the procedures developed for the diruthenated complexes of Tth.<sup>31</sup> The new osmium complexes were slightly more difficult to synthesize than the ruthenium analogs. Attempts to synthesize the Tth and Me<sub>2</sub>Tth osmium complexes by reacting Tth (or Me<sub>2</sub>Tth) and [CpOs(CH<sub>3</sub>CN)<sub>3</sub>]PF<sub>6</sub> in acetone at room temperature for a few hours gave very similar purple-red solutions that were very different from the characteristic brown solutions of the  $\eta^5$  ruthenium analogs. After 48 h at room temperature, the workup of a typical reaction mixture gave a red-purple solid that was insoluble in dichloromethane. This insolubility sharply contrasts with the high solubility of the ruthenium analogs in the same solvent. The <sup>1</sup>H NMR spectrum of the red-purple solid showed that it was not the desired  $\eta^5$  complex but was a complicated mixture of complexes. Increasing the reaction times to a week at room temperature yielded similar red-purple solids; when reactions were refluxed for several days, the initial red solutions gradually changed to brown solutions. Workup of these brown solutions produced some of the red-purple solids but also gave very reasonable yields of the yellow  $\eta^5$  products ([CpOs( $\eta^5$ -Tth)]PF<sub>6</sub> (60%) and [CpOs( $\eta^5$ -Me<sub>2</sub>Tth)]PF<sub>6</sub> (69%)), starting with Tth and Me<sub>2</sub>Tth, respectively. Only traces of the diosmium product [(CpOs)<sub>2</sub>( $\eta^5, \eta^5$ -Tth)](PF<sub>6</sub>)<sub>2</sub> were detected in the Tth reactions. Under similar reaction conditions the Tth/ruthenium systems typically give 10–20% yields of diruthenated products.

Attempts to separate and identify the exact nature of the red-purple solids were largely unsuccessful. For example, a typical <sup>1</sup>H NMR spectrum showed a nearly continuous set of overlapping peaks in the thiophene hydrogen region (7.5–6.5 ppm) and at least six peaks in the region where the Cp resonance was expected to occur. It is likely that the red-purple materials are a mixture of complexes with osmium binding to the sulfurs in an  $\eta^1$  or  $\eta^1, \eta^1$  bridging fashion and/or osmium binding  $\eta^2$  or  $\eta^4$  to the olefinic part of the thiophene rings. Complexes with these binding modes are likely to be the kinetically favored products at room temperature; however, at reflux temperatures, enough energy is supplied to convert most of these intermediate osmium complexes to the more thermodynamically stable  $\eta^5$  forms. This type of kinetic selectivity and thermal rearrangement has been previously reported for related ruthenium complexes.<sup>40</sup>

A first attempt to synthesize [CpOs(Qth)]PF<sub>6</sub> again followed that of the ruthenium analogs: Qth was first dissolved in refluxing dichloromethane, and then the [CpOs(CH<sub>3</sub>CN)<sub>3</sub>]PF<sub>6</sub> was added in a small amount of acetone. A dark brown-red solution with a dark precipitate resulted after 1 day at reflux. Workup of the mixture provided less than a 20% yield of impure [CpOs(Qth)]PF<sub>6</sub>. The conditions were then changed so that Qth was first dissolved in refluxing acetone and [CpOs(CH<sub>3</sub>CN)<sub>3</sub>]PF<sub>6</sub> was added. The initial golden solution darkened to a golden brown over 2 days. After 48 h at reflux, the reaction was worked up to give a 55% yield of [CpOs(Qth)]PF<sub>6</sub> and traces

of a red solid whose <sup>1</sup>H NMR spectrum indicated it was a mixture of complexes similar to those found for the Tth and Me<sub>2</sub>Tth complexation reactions. The reactivity difference of [CpOs(CH<sub>3</sub>CN)<sub>3</sub>]PF<sub>6</sub> and Qth in acetone and dichloromethane may result from greater solubility of the kinetically formed intermediate complexes in acetone and/or to the ability of the acetone to coordinate and facilitate the conversion to the  $\eta^5$  form.

The stability of the new osmium oligothiophene complexes in coordinating solvents was studied. Previously the ruthenium oligothiophene complexes were shown to be relatively unstable in coordinating solvents.<sup>31</sup> Acetone- $d_6$  and acetonitrile- $d_3$  solutions of the osmium complexes were monitored by <sup>1</sup>H NMR spectroscopy. An acetonitrile solution of [CpOs( $\eta^5$ -Tth)]PF<sub>6</sub> showed about 10% conversion to [CpOs(CH<sub>3</sub>CN)<sub>3</sub>]PF<sub>6</sub> and Tth after 1 week at room temperature; the acetone solution exhibited no changes after 3 weeks. In comparison, acetonitrile solutions of [CpRu(Tth)]PF<sub>6</sub> revert to [CpRu(CH<sub>3</sub>CN)<sub>3</sub>]PF<sub>6</sub> and Tth within minutes and acetone solutions equilibrate to Tth, [CpRu(Tth)]PF<sub>6</sub>, and [(CpRu)<sub>2</sub>(Tth)](PF<sub>6</sub>)<sub>2</sub> in about a day.<sup>31</sup> The osmium complexes are much more inert to decomplexation and scrambling reactions than the ruthenium analogs.

The NMR (<sup>1</sup>H and <sup>13</sup>C) spectra of the osmium complexes show trends similar to those of the ruthenium analogs.<sup>31</sup> The proton and carbon resonances for the bound ring are shifted upfield from those of the free oligothiophene; the proton and carbon resonance shifts are 1–5% smaller and 5–10% larger than those observed for the CpRu analogs, respectively. The coupling constants for the protons of the bound ring are decreased by nearly the same amount for the ruthenium and osmium complexes. The proton and carbon resonances of the unbound rings exhibit a downfield shift that is similar for the osmium and ruthenium analogs. These results support our earlier conclusion<sup>31</sup> that the upfield shift of the <sup>1</sup>H and <sup>13</sup>C resonances for the bound ring largely results from the presence of the metal center (heavy atom effect). The downfield shift of the protons and carbons of the unbound rings of the oligothiophene is caused by the larger ring currents induced by rearomatization of these rings. The proton and carbon resonances of the thiophene ring farthest from the metal in [CpOs(Qth)]PF<sub>6</sub> and the ruthenium analogs exhibit no shifts. This supports another previous conclusion<sup>31</sup> that the metal center exerts an influence over the bound ring and the two neighboring unbound rings in the chain.

**Electrochemical Behavior of the Oligothiophenes.** The electrochemical properties of th, Bth, Tth, Qth, and Me<sub>2</sub>Tth were studied in dichloromethane to allow comparisons with the complexes. Each of the uncomplexed oligothiophenes exhibits one or two irreversible oxidation processes between 0.0 and +1.8 V (the solvent limit) that are coupled to several broad reduction processes (Table 1). For several of the oligothiophenes, an oxidation process overlapped with the solvent oxidation and the peak potential could not be determined accurately by cyclic voltammetry studies. The peak potentials for these processes were thus determined by Osteryoung square wave analysis. Reductive processes due to the bulk species were not observed inside the solvent limit (–1.9 V). The oxidations that produce the radical cations of Bth, Tth, and Qth and the dications of Tth and Qth are irreversible because the oxidized forms rapidly polymerize and coat the electrode. The broad coupled processes are reductions of the oxidized polymeric electrode coating and/or other oxidized oligomeric species at the electrode.<sup>7,41,42</sup> The first oxidation of Me<sub>2</sub>Tth is quasi-

(41) Delabouglise, D.; Hmyene, M.; Horowitz, G.; Yassar, A.; Garnier, F. *Adv. Mater.* **1992**, *4*, 107.

(42) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

**Table 1.** Cyclic Voltammetry Data for Oxidation Processes of th, Bth, Tth, Qth, Me<sub>2</sub>Tth, and Complexes<sup>a</sup>

	dichloromethane		propylene carbonate	
	$E_{p,a}$ (mV) <sup>b</sup>	$E_{p,c}$ (mV) <sup>c</sup>	$E_{p,a}$ (mV) <sup>b</sup>	$E_{p,c}$ (mV) <sup>c</sup>
thiophene	+1890 <sup>d</sup>	<i>e</i>		
[CpRu(th)]PF <sub>6</sub>	<i>f</i>	<i>e</i>	<i>e</i>	
[Cp*Ru(th)]PF <sub>6</sub>	+1746	<i>e</i>	+1695	
Bth	+1404	+1002, +845, +525		
[CpRu(Bth)]PF <sub>6</sub>	+1790 <sup>d</sup>	+1118, +1580		
[Cp*Ru(Bth)]PF <sub>6</sub>	+1635	+1332		
Tth	+1128, +1744 <sup>d</sup>	+942, +765, +528		
[CpOs(Tth)]PF <sub>6</sub>	+1506	+1225, +1175, +780		
[CpRu(Tth)]PF <sub>6</sub>	+1557	+1308, +1116	+1419	+620
[Cp*Ru(Tth)]PF <sub>6</sub>	+1410, +1640	+1308, +1090, +760	+1326, +1640 <sup>d</sup>	+825, +590
[(CpRu) <sub>2</sub> Tth](PF <sub>6</sub> ) <sub>2</sub>			+1686	+762
[(Cp*Ru) <sub>2</sub> Tth](PF <sub>6</sub> ) <sub>2</sub>			+1500, +1628 <sup>d</sup>	+546
Qth	+1008, +1328 <sup>d</sup>	+975, +528		
[CpOs(Qth)]PF <sub>6</sub>	+1218	+1074, +780		
[CpRu(Qth)]PF <sub>6</sub>	+1278, +1700 <sup>d</sup>	+1450, +1086, +801	+1146, +1456 <sup>d</sup>	+798, +590
[Cp*Ru(Qth)]PF <sub>6</sub>	+1212, +1525	+1359, +1080, +816, +525	+1116, +1368 <sup>d</sup>	+790, +635
[(CpRu) <sub>2</sub> Qth](PF <sub>6</sub> ) <sub>2</sub>			+1458	+756
[(Cp*Ru) <sub>2</sub> Qth](PF <sub>6</sub> ) <sub>2</sub>			+1311	+621, 490
Me <sub>2</sub> Tth	+975, +1348 <sup>d</sup>	+870, +234		
[CpOs(Me <sub>2</sub> Tth)]PF <sub>6</sub>	+1390, +1540 <sup>d</sup>	+1385, +1135, +816		
[CpRu(Me <sub>2</sub> Tth)]PF <sub>6</sub>	+1374, +1500 <sup>d</sup>	+1416, +1263		
[Cp*Ru(Me <sub>2</sub> Tth)]PF <sub>6</sub>	+1275, +1468 <sup>d</sup>	+1210, +225		

<sup>a</sup> Solution concentrations were 0.48–0.52 mM. <sup>b</sup> Measured at a scan rate of 100 mV/s in the range of 0.0 to 1.8 V. Scans were initiated toward positive potentials from 0.0 V. <sup>c</sup>  $E_{p,c}$  of reduction processes coupled to the irreversible oxidation processes. <sup>d</sup> Determined by Osteryoung square wave analysis as the values could not be reliably determined from the CV data (as discussed in the text). <sup>e</sup> No observed reduction processes. <sup>f</sup> No oxidation processes observed between 0.0 and 1.8 V.

reversible in agreement with other studies of  $\alpha$ -capped (e.g. C(5)-substituted) oligothiophenes where the polymerization of the oxidized species is slowed or inhibited by the end group substitution.<sup>1–5,16–30</sup>

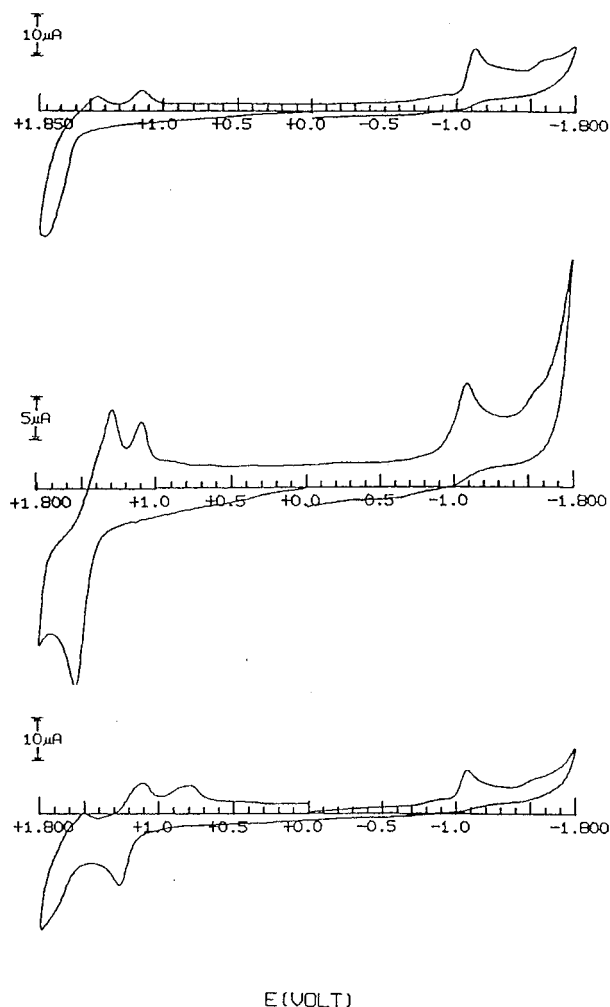
The  $E_{p,a}$  values of the oligothiophene oxidation processes are highly dependent on two main factors: the number of conjugated thiophene rings and their substituents. As the number of rings increases, the degree of conjugation increases, and the  $E_{p,a}$  for the oxidation processes decrease due to stabilization of the radical cation and/or dication in the order th > Bth > Tth > Qth (Table 1). Further, the change in the  $E_{p,a}$  value for the first oxidation process decreases as the chain length increases. For example, the difference in  $E_{p,a}$  for the first oxidation processes for the th/Bth, Bth/Tth and Tth/Qth pairs decreases from 486 to 276 to 120 mV, respectively. The addition of a thiophene ring to a short oligomer leads to a larger increase in conjugation than if a ring is added to a long oligomer that already has a high degree of conjugation. In regard to substituent effects, addition of either methyl or phenyl substituents to the 5 and 5'' positions of Tth decrease the  $E_{p,a}$  of the oxidation process by 153 mV (Table 1) and 181 mV,<sup>32</sup> respectively.

**Electrochemical Properties of the Oligothiophene Complexes.** The electrochemical properties of the monoruthenated complexes of Bth, Tth, Qth, and Me<sub>2</sub>Tth were also studied in dichloromethane. At least one oxidation (Table 1) was observed in the range of 0.0 to +1.8 V (the solvent limit). For several of the complexes, an oxidation process overlapped with the solvent oxidation and the peak potential could not be determined accurately by cyclic voltammetry studies. The peak potentials for these processes were thus determined by Osteryoung square wave analysis. All of the oxidations are electrochemically irreversible and are coupled to one or more broad reduction processes similar (but *not* identical) to those observed for the uncomplexed oligothiophenes (Figure 2). For the complexes of th in dichloromethane, only the complex of Cp\*Ru<sup>+</sup> exhibits an oxidation within the solvent window of 0.0 to +1.8 V. The

diruthenated complexes of Tth and Qth were not studied in dichloromethane due to very low solubility but were studied in propylene carbonate. The monoruthenated complexes of Tth and Qth were also studied in propylene carbonate in order to understand solvent effects. In propylene carbonate, each of the complexes exhibits at least one oxidative process in the region of 0.0 to +1.8 V. Each of the oxidations is electrochemically irreversible and is coupled to one or more broad reduction processes.

For all of the complexes studied, the irreversible oxidations lead to coating of the electrode surface. It is likely the coating is conductive because the amount of deposited material increases with repeated CV scans. For example, repeated CV scans of [CpRu(Tth)]PF<sub>6</sub> show that the reductive current increases with successive scans as more material is added to the electrode coating (supporting information). The composition and properties of these electrodeposited films is unclear at present. For example, we have yet to determine whether the metal is still bound in these electrodeposited coatings and to what degree oligomerization and/or polymerization occurs. The composition and properties of these polymeric materials will be the subject of future work.

The number of electrons involved in the oxidation processes of the complexes was investigated by chronocoulometry studies which were used to calculate the diffusion coefficients from a linear Anson plot ( $Q$  vs  $t^{1/2}$ ). Assuming a one-electron process, the calculated diffusion coefficient in dichloromethane for each complex is in the range of  $(1.0–4.0) \times 10^{-4}$  cm<sup>2</sup>/s while for a two-electron process, the calculated diffusion coefficient is in the range of  $(3.0–9.0) \times 10^{-5}$  cm<sup>2</sup>/s. The slope of the Anson plot for [Cp\*Ru(Tth)]PF<sub>6</sub> (0.51 mM) in dichloromethane was found to be  $5.45 \times 10^{-5}$  C/s<sup>1/2</sup> which gives a value of  $1.41 \times 10^{-2}$  cm/s<sup>1/2</sup> for  $nD^{1/2}$ . Using this value, the calculated diffusion coefficients for  $n = 1, 2, 3, 4,$  and  $5$  electrons are 19, 5.0, 2.2, 1.2, and  $0.8 \times 10^{-5}$  cm<sup>2</sup>/s, respectively. For comparison, chronocoulometry experiments with similar concentrations of ferrocene in dichloromethane designed to mimic the conditions



**Figure 2.** CV's of (top) [CpRu(Bth)]PF<sub>6</sub> (0.50 mM), (middle) [CpRu(Tth)]PF<sub>6</sub> (0.50 mM), and (bottom) [CpRu(Qth)]PF<sub>6</sub> (0.49 mM). These were recorded in 0.1 M TBA<sup>+</sup>PF<sub>6</sub><sup>-</sup>/CH<sub>2</sub>Cl<sub>2</sub> at a scan rate of 100 mV/s; scans were initiated in the positive direction from 0.0 V.

used for the complexes give experimental diffusion coefficients of  $(2.4\text{--}3.0) \times 10^{-5}$  cm<sup>2</sup>/s for  $n = 1$ , in good agreement with previously measured values for ferrocene.<sup>43</sup> The ferrocene results indicate that the high  $nD^{1/2}$  value obtained for [Cp\*Ru(Tth)]PF<sub>6</sub> is accurate and results from a large  $n$  value rather than a large  $D$  value. By using a value of  $D$  of  $9.62 \times 10^{-6}$  cm<sup>2</sup>/s that was calculated for the diffusion coefficient of [Cp\*Ru(Tth)]BF<sub>4</sub> from the molecular volume and Stokes–Einstein equation,<sup>44</sup> an  $n$  value between 4 and 5 is calculated for the oxidation of [Cp\*Ru(Tth)]PF<sub>6</sub>. The transfer of this many electrons in a simple irreversible electron transfer process is not reasonable for this or any other complex studied. It is likely that the high apparent  $n$  values are characteristic of the polymerization reactions that form the electrode coating. The passage of large amounts of charge has been observed during the electropolymerization of other five-membered heterocycles, such as pyrrole.<sup>42</sup> The large observed charges ( $Q$ ) per oxidation/diffusion event are the result of normal diffusion coefficients

(43) Gagne, R. R.; Koval, C. A.; Kisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

(44) The calculated diffusion coefficients for [Cp\*Ru(Tth)]PF<sub>6</sub> were obtained from the Stokes–Einstein equation:  $D$  (cm<sup>2</sup>/s) =  $(1 \times 10^7) / (RT/6\pi rN\eta)$  where  $R$  = gas constant,  $T$  = temperature (K),  $r$  = molecular radius (cm),  $\eta$  = solvent viscosity (P), and  $N$  = Avogadro's number. The molecular radius,  $r$ , was estimated to be  $5.2 \times 10^{-9}$  cm from the observed molecular volume of the crystal structure data<sup>32</sup> for [Cp\*Ru( $\eta^5$ -Tth)]BF<sub>4</sub>. The viscosity value used for CH<sub>2</sub>Cl<sub>2</sub> was  $4.21 \times 10^{-3}$  P.

but large apparent  $n$  values. Chronocoulometry experiments with the  $\alpha$ -unblocked and uncomplexed oligothiophenes give large  $n$  values, but  $\alpha$ -blocked oligothiophenes are known to undergo single electron oxidations.<sup>1–5,45,46</sup> It is likely that the oxidations of the complexes are most likely one-electron processes, followed by polymerization (or oligomerization) that enable further oxidation processes. These results indicate that the electron is being removed from the oligothiophene portion of the complex as the unbound thiophene rings would be expected to undergo coupling reactions upon being oxidized. This would give rise to an electrodeposited film and the passage of large amounts of charge as we observed.

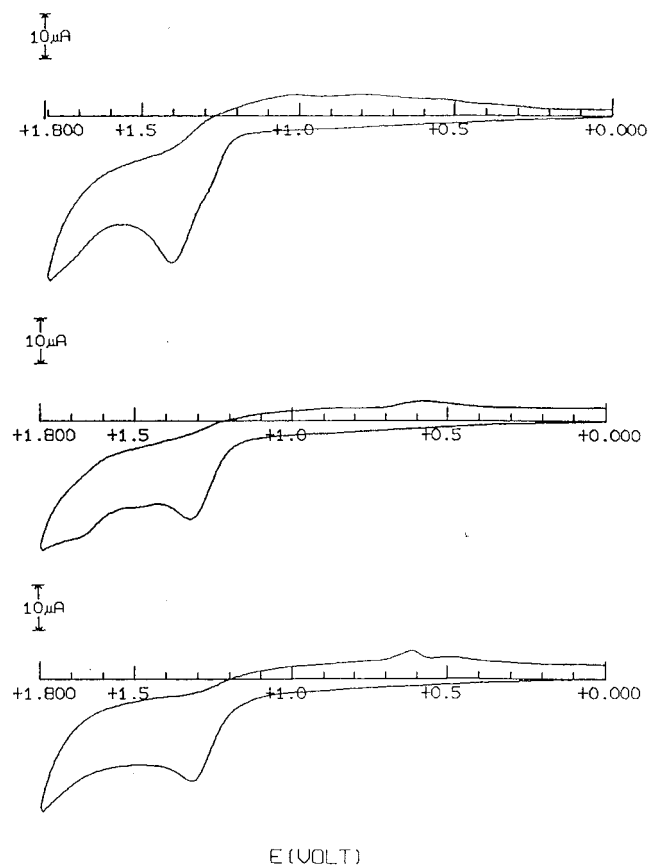
Comparison of the electrochemical data for the complexes and free oligothiophene adds insight into the electronics of the systems, but these comparisons must be viewed with some caution. The  $E_{p,a}$  and  $E_{p,c}$  values for the complexes and oligothiophenes are based on apparent redox potentials and incorporate both thermodynamic and kinetic factors. The extreme irreversibility of the redox processes did not allow for the quantitation of the kinetic factors in the  $E_{p,a}$  and  $E_{p,c}$  values. Thus, comparison of the peak potentials which differ to a large degree will be the most reliable while comparisons of values with smaller differences will be somewhat less reliable. Though the exact difference between the  $E_{p,a}$  and  $E_{p,c}$  values has some uncertainty, the general trends developed through comparison of all the data should be valid and do provide very reasonable results.

The  $E_{p,a}$  values for the oxidation processes in these complexes depend on the type of metal fragment bound to the oligothiophene. With respect to the free oligothiophene, binding one "CpRu<sup>+</sup>" increases  $E_{p,a}$  by 399, 386, 429, and 207 mV for the complexes of Me<sub>2</sub>Tth, Bth, Tth, and Qth, respectively. For "CpOs<sup>+</sup>", the increase is 415, 378, and 210 mV for the complexes of Me<sub>2</sub>Tth, Tth, and Qth, respectively. Binding of a "Cp\*Ru<sup>+</sup>" group increases the potential of the oxidation processes by 300, 231, 282, and 204 mV for the complexes of Me<sub>2</sub>Tth, Bth, Tth, and Qth, respectively. These results show that binding either one "CpRu<sup>+</sup>" or "CpOs<sup>+</sup>" fragment to an oligothiophene produces a similar increase in the  $E_{p,a}$  for the oxidation that is larger than that observed for a "Cp\*Ru<sup>+</sup>" group. These results also show that coordinating a metal fragment onto the longer Qth backbone has a smaller effect on the potential for the oxidation process than that of the shorter oligothiophenes. This is in agreement with our earlier NMR studies:<sup>31</sup> the effect of the metal center is greatest for short oligothiophenes (three or less rings). The oxidation of the th complexes is quite different in that only [Cp\*Ru(th)]<sup>+</sup> exhibits an oxidative process within the solvent window and this process is 150 mV lower than for th. This oxidation process is likely oxidation of the ruthenium center or the Cp\* ancillary ligand (vide infra).

Solubility and stability of the complexes in propylene carbonate allowed an investigation of the effect of binding a second metal to Tth and Qth. Relative to the free ligand in dichloromethane, the binding of one metal to Tth increases  $E_{p,a}$  for the oxidation by 290 and 200 mV for the mono-Cp and -Cp\* complexes, respectively, while for Qth the increase is 140 and 110 mV, respectively. When the second metal center is bound to Tth, the  $E_{p,a}$  for oxidation increases by 560 and 372 mV for the diruthenated Cp and Cp\* complexes, respectively, while for Qth the increase is 450 and 300 mV, respectively. The binding of the second metal to Tth gives about twice the

(45) Fichou, D.; Horowitz, G.; Xu, B.; Garnier, F. *Synth Met.* **1990**, *39*, 243.

(46) Alberti, A.; Favaretto, L.; Seconi, G. *J. Chem. Soc., Perkin Trans. 2* **1990**, 931.



**Figure 3.** CV's of the oxidation of (top) Bth in dichloromethane (0.48 mM), (middle)  $[\text{Cp}^*\text{Ru}(\text{Tth})]\text{PF}_6$  in dichloromethane (0.51 mM), and (bottom)  $[(\text{Cp}^*\text{Ru})_2(\text{Qth})](\text{PF}_6)_2$  in propylene carbonate (0.50 mM). These were recorded in 0.1 M  $\text{TBA}^+\text{PF}_6^-$  at a scan rate of 100 mV/s; scans were initiated in the positive direction from 0.0 V.

increase observed for the first metal, but for Qth, the binding of the second metal has a larger effect, about three times that of adding only the first metal.

The  $E_{p,a}$  values for oxidation of the complexes follow the same trends observed for the free oligothiophenes. For the complexes of Bth, Tth, and Qth with the same metal and ancillary ligand,  $E_{p,a}$  for oxidation decreases as the length of the bound oligothiophene increases (Figure 2). The first  $E_{p,a}$  observed for the complexes is 250–400 mV higher than the  $E_{p,a}$  observed for the corresponding, uncomplexed oligothiophene (i.e. Qth vs  $[\text{Cp}^*\text{Ru}(\text{Qth})]\text{PF}_6$ ). The positive shift caused by complexation moves  $E_{p,a}$  very close (only 10 to 150 mV more positive) to values observed for a free oligothiophene with *one less thiophene ring* than the bound oligothiophene (i.e.  $E_{p,a}$  for Tth is very close to  $E_{p,a}$  of  $[\text{Cp}^*\text{Ru}(\text{Qth})]\text{PF}_6$ ). Complexation severely curtails the conjugation of the complexed thiophene ring with the remaining, uncomplexed rings. This idea is also supported by comparing the  $E_{p,a}$  for oxidation of Bth with  $[\text{CpRu}(\text{Tth})]\text{PF}_6$ ,  $[\text{Cp}^*\text{Ru}(\text{Tth})]\text{PF}_6$ , and  $[\text{CpOs}(\text{Tth})]\text{PF}_6$ . These compounds exhibit oxidation processes at 1404, 1557, 1410, and 1506 mV, respectively (Figure 3). Further support of this idea comes from the  $E_{p,a}$ s of the diruthenated complexes that are very similar to those of the free oligothiophene which has *two less thiophene rings than the bound one*. For example,  $E_{p,a}$  for oxidation of Bth in dichloromethane is +1404 mV and for  $[(\text{CpRu})_2(\text{Qth})](\text{PF}_6)_2$  and  $[(\text{Cp}^*\text{Ru})_2(\text{Qth})](\text{PF}_6)_2$  in propylene carbonate, the  $E_{p,a}$ s are +1458 and +1311 mV, respectively (Figure 3). Although these  $E_{p,a}$ s are measured in different solvents, the comparisons are still valid as the effect of solvent on the monoruthenated complexes is small (100 mV lower in propylene carbonate than in dichloromethane).

**Table 2.** Cyclic Voltammetry Data for Reduction Processes of th, Bth, Tth, Qth,  $\text{Me}_2\text{Tth}$ , and Complexes<sup>a</sup>

	$E_{p,c}$ (mV) <sup>b</sup>	
	dichloromethane	propylene carbonate
thiophene	c	
$[\text{CpRu}(\text{th})]\text{PF}_6$	-1206	-1305
$[\text{Cp}^*\text{Ru}(\text{th})]\text{PF}_6$	-1509	-1545
Bth	c	
$[\text{CpRu}(\text{Bth})]\text{PF}_6$	-1137	
$[\text{Cp}^*\text{Ru}(\text{Bth})]\text{PF}_6$	-1407	
Tth	c	
$[\text{CpOs}(\text{Tth})]\text{PF}_6$	-1135	
$[\text{CpRu}(\text{Tth})]\text{PF}_6$	-1071	-1152
$[\text{Cp}^*\text{Ru}(\text{Tth})]\text{PF}_6$	-1359	-1320
$[(\text{CpRu})_2(\text{Tth})](\text{PF}_6)_2$		-987
$[(\text{Cp}^*\text{Ru})_2(\text{Tth})](\text{PF}_6)_2$		-1158
Qth	c	
$[\text{CpOs}(\text{Qth})]\text{PF}_6$	-1116	
$[\text{CpRu}(\text{Qth})]\text{PF}_6$	-1074	-1149
$[\text{Cp}^*\text{Ru}(\text{Qth})]\text{PF}_6$	-1341	-1305
$[(\text{CpRu})_2(\text{Qth})](\text{PF}_6)_2$		-1056
$[(\text{Cp}^*\text{Ru})_2(\text{Qth})](\text{PF}_6)_2$		-1176
$\text{Me}_2\text{Tth}$	c	
$[\text{CpOs}(\text{Me}_2\text{Tth})]\text{PF}_6$	-1179	
$[\text{CpRu}(\text{Me}_2\text{Tth})]\text{PF}_6$	-1233	
$[\text{Cp}^*\text{Ru}(\text{Me}_2\text{Tth})]\text{PF}_6$	-1470	

<sup>a</sup> Solution concentrations were 0.48–0.52 mM. <sup>b</sup> Measured at a scan rate of 100 mV/s in the range of 0.0 to -1.8 V. Scans were initiated toward negative potentials from 0.0 V. <sup>c</sup> No reduction processes observed in the range 0.0 to -1.8 V.

The complexes of  $\text{Me}_2\text{Tth}$  also exhibit effects due to substitution of the  $\alpha$  protons of Tth with methyl groups superimposed on metal binding effects:  $E_{p,a}$  for oxidations of the  $\text{Me}_2\text{Tth}$  complexes are about 200–250 mV lower than those of the Tth analogs. The electrochemical results again indicate that the oxidation processes of the complexes are centered on the unbound thiophene rings that constitute a discrete oligothiophene unit. Each complex exhibits reductions coupled to the irreversible oxidation processes. These reductions are likely due to oligomeric/polymeric species formed on the electrode by coupling of the oxidized complexes. The structure and composition of these oligomeric/polymeric products will be studied in the future.

The complexes exhibit irreversible reductions between 0.0 and -1.8 V that are not coupled to the oxidations previously discussed (Table 2). The free oligothiophenes do not exhibit reductions in this potential range. For the monoruthenated complexes in dichloromethane or propylene carbonate, there is one distinct irreversible reduction and a smaller reduction near the solvent limit. Chronocoulometry experiments performed on the first reductive process of the monoruthenated complexes yield a linear Anson plot ( $Q$  vs  $t^{1/2}$ ). Assuming a one electron process, the calculated diffusion coefficients for the complexes in dichloromethane are in the range of  $(2.0\text{--}6.0) \times 10^{-5}$  cm<sup>2</sup>/s. These values are consistent with those found for ferrocene<sup>43</sup> and the ruthenium complexes of 5,5''-diphenyl-2,2':5',2''-terthiophene.<sup>32</sup> The monoruthenated complexes undergo one-electron reductions in dichloromethane or propylene carbonate. For the diruthenated complexes in propylene carbonate, two distinct irreversible reductions are observed on either side of a smaller reduction. Due to the overlapping nature of these peaks, chronocoulometry experiments for the diruthenated complexes proved to be unreliable. The measured CV peak currents for the reductions of the diruthenated complexes are 1.2–1.6 times larger than those of similar concentrations of the monoruthenated complexes. It is unclear whether the reductions of the di-

ruthenated complexes are one- or two-electron processes, but the latter interpretation is most likely based on the studies of the diruthenated complexes of 5,5''-diphenyl-2,2':5',2''-terthiophene.<sup>32</sup> For both the mono and diruthenated complexes, the products of the second reduction process are unknown.

The  $E_{p,c}$ s for the reduction processes depend on the metal and ancillary ligand (Cp or Cp\*). The  $E_{p,c}$ s for the reduction of the CpRu and CpOs complexes are similar and are generally 270–300 mV more positive than those of the Cp\*Ru complexes.  $E_{p,c}$  for reduction decreases very slightly with an increase in the oligothiophene chain length as shown by the series of CpRu complexes of th (–1509 mV), Bth (–1407 mV), Tth (–1359 mV), and Qth (–1341 mV) (Figure 2). The  $E_{p,c}$ s for reduction are also weakly dependent on the oligothiophene's substituents as shown by the higher  $E_{p,c}$  for the complexes of Me<sub>2</sub>Tth than of Tth.  $E_{p,c}$  values for reduction of the diruthenated complexes are 70 to 130 mV positive of the monoruthenated complexes in propylene carbonate. All of these results are consistent with reduction of the [Cp/Cp\*M(thiophene)]<sup>+</sup> unit.

**A Model for the Electrochemical Behavior of the Metal Complexes.** The electrochemical results for the complexes can be understood with a simple model: **Binding a metal to a thiophene ring effectively removes the ring from  $\pi$  conjugation with the remaining unbound thiophene rings and results in an effective decrease in the thiophene ring conjugation length by one ring per bound metal center.** For example, [Cp\*Ru(Tth)]PF<sub>6</sub> and [(Cp\*Ru)<sub>2</sub>(Qth)](PF<sub>6</sub>)<sub>2</sub> both behave electrochemically as if they contain a Bth unit (i.e. two unbound thiophene rings) (Figure 3). Slight additional shifts in  $E_{p,a}$  are expected as the unbound oligothiophene unit has one or two positively charged [Cp/Cp\*M(thiophene)]<sup>+</sup> end group substituents. This model suggests that  $E_{p,a}$ s for the oxidation processes will depend on three main factors: (1) the length of the unbound oligothiophene unit, (2) the electron-accepting/donating character of the [Cp/Cp\*M(thiophene)]<sup>+</sup> substituent, and (3) the effect of positive charge. The first factor will be largest for the smallest oligothiophenes. The second factor predicts that the Cp\* complexes should be the most electron rich and will be easiest to oxidize. We have recently assessed the effect of the positive charge with the complexes of 5,5''-diphenyl-2,2':5',2''-terthiophene (Ph<sub>2</sub>Tth) that contain the metal bound to the pendant phenyl group.<sup>32</sup> In these complexes where the terthiophene core is oxidized, the pendant positive charge increases  $E^{\circ}$  for the first oxidation potential by about 150 mV *per metal center* and the second  $E^{\circ}$  by slightly less than 150 mV *per metal center*. The last two factors, the charge and electron-donating/accepting effect of the metal fragment are substituent effects that should decrease in magnitude with increasing conjugation length.

The increase in  $E_{p,a}$  for the oxidation of a complex is highest for those complexes with the least number of unbound rings, the Cp\* ancillary complexes exhibit the lowest oxidation potentials, and the overall increase is greater than expected for simply adding positively charged substituents. Further, the increase in  $E_{p,a}$  for the complexes of Tth and Bth complexes is greater than for complexes of Qth with the same type and number of metal fragment(s). When one metal is bound to Bth or Tth, the remaining uncomplexed thiophene rings have a smaller degree of conjugation than those of the analogous Qth complexes. The similarity of the  $E_{p,a}$  increase for the Bth and Tth complexes likely results from the close proximity of the metal to the single uncomplexed thiophene ring of the Bth complexes.

This model also accounts for the  $E_{p,a}$  for oxidation of [Cp\*Ru(th)]PF<sub>6</sub>: as this complex has no unbound thiophene rings, its  $E_{p,a}$  for oxidation should not follow the trends of the complexes containing unbound thiophene rings. The oxidation of [Cp\*Ru(th)]PF<sub>6</sub> likely occurs at the ruthenium center or the Cp\* ancillary ligand. This is supported by the observation of an oxidation process at 1630–1640 mV for the Cp\*Ru complexes of Bth and Tth that is not consistent with a further oxidation of the conjugate, uncomplexed thiophene rings of these complex. This oxidation is only observed for the electron rich Cp\* complexes.

This model also is consistent with the reduction processes that are localized on the metal fragment. Each complex has a [Cp/Cp\*M(thiophene)]<sup>+</sup> substituent whose  $E_{p,c}$  for reduction depends on the metal, ancillary ligand ( $E_{p,c}$  of Cp\* is more negative than for Cp), and electron-accepting character of the oligothiophene substituent (i.e. larger conjugation lengths increase the electron-accepting character). In this case, the  $E_{p,c}$  for reduction of [Cp/Cp\*M(thiophene)]<sup>+</sup> is in line with that for the reduction of the other complexes. The reduction process is not significantly influenced by the thiophene ring chain length.

**Conclusions.** We have studied a series of oligothiophene complexes that vary the metal (Ru or Os), ancillary ligand (Cp or Cp\*), ring substituents (phenyl or methyl groups), and length of the oligothiophene (1–4 rings). The kinetic stability of these complexes depends on the metal center; the Os complexes are much more kinetically stable than the Ru analogs. Electrochemical studies indicate that the electron hole produced upon oxidation of the complexes is delocalized on the uncomplexed rings of the oligothiophene while the electron added upon reduction is localized on the [Cp/Cp\*M(thiophene)]<sup>+</sup> unit formed by complexation. Oxidation of the complexes results in conductive films on the electrode, but the composition of the electrodeposited films is unclear. We propose an electronic structural model that can explain these results: Complexation of a thiophene ring converts it into a [Cp/Cp\*Ru(thiophene)]<sup>+</sup> unit and removes it from conjugation with the remaining, uncomplexed rings. The remaining unbound rings act as a shortened, metal-substituted oligothiophene unit. Complexation of oligothiophenes by “Cp\*Ru<sup>+</sup>”, “CpRu<sup>+</sup>”, and “CpOs<sup>+</sup>” fragments presents a novel and rational method for controlling the properties of oligothiophenes. Future work will attempt to use this type of complexation to modulate the properties of oligothiophene-derived solids.

**Acknowledgment.** This research was supported by the National Science Foundation under Grant No. CHE-9307837. D.D.G. thanks the National Science Foundation for a Pre-Doctoral Fellowship. We thank Johnson-Matthey, Inc., for a generous loan of ruthenium trichloride.

**Supporting Information Available:** Figures showing (1) CVs for Bth, Tth, and Qth (CH<sub>2</sub>Cl<sub>2</sub>/0.1 M TBA<sup>+</sup>PF<sub>6</sub><sup>-</sup>), (2) CVs for the in-situ formation of the electrode coating via cyclic oxidation/reduction of [CpRu(Tth)]PF<sub>6</sub> (CH<sub>2</sub>Cl<sub>2</sub>/0.1 M TBA<sup>+</sup>PF<sub>6</sub><sup>-</sup>), and (3) CVs of the reductive processes of [CpRu(Tth)]PF<sub>6</sub> and [(CpRu)<sub>2</sub>(Tth)](PF<sub>6</sub>)<sub>2</sub> recorded in 0.1 M TBA<sup>+</sup>PF<sub>6</sub><sup>-</sup>/propylene carbonate (3 pages). Ordering information is given on any current masthead page.