Synthesis and Characterization of Cyclopentadienyl and Pentamethylcyclopentadienyl Ruthenium Complexes of Oligothiophenes

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We report the synthesis and characterization of 14 complexes of the general form [CpRu(oligothiophene)]PF_6 and [Cp*Ru(oligothiophene)]PF_6 (Cp = η^5-cyclopentadienyl; Cp* = η^5-pentamethylcyclopentadienyl). The complexes were synthesized from [CpRu(CH_3CN)$_3$]PF_6 or [Cp*Ru(CH_3CN)$_3$]PF_6 and the appropriate oligothiophene via procedures previously reported for other [Cp/Cp*Ru(η^6-arene)]PF_6 sandwich complexes. For the oligothiophenes 2,2′-bithiophene (Bth), 2,2′:5′,2″-terthiophene (Tth), 2,2′:5′,2″:5″,2‴-quaterthiophene (Qth), and 5,5″-dimethyl-2,2′:5′,2″-terthiophene (Me_2Tth), the Ru is bound η^5 to the outermost thiophene ring while the complexes of the oligothiophene 5,5″-diphenyl-2,2′:5′,2″-terthiophene (Ph_2Tth) have Ru bound η^6 to a pendant phenyl group. The complexes with ruthenium bound to an arene are very stable with respect to decomplexation; complexes with ruthenium bound to a thiophene ring are stable in the solid state and in dichloromethane solutions; in acetone, rearrangement reactions occur to produce equilibrium mixtures of free oligothiophene and mono- and diruthenated species. Detailed analysis of ^1H and ^{13}C NMR spectra, $^1H-^1H$ decoupling experiments, heteronuclear multiple-bond correlation (HMBC), and heteronuclear multiple-quantum coherence (HMQC) experiments enabled the assignment of all ^1H and ^{13}C resonances. These assignments show that binding ruthenium to a thiophene ring of an oligothiophene shifts the bound ring resonances upfield and the unbound thiophene rings downfield. The coordination of ruthenium exerts a larger electronic effect in oligothiophene complexes than in polyaromatic complexes (quaterphenyl). Complexation of a thiophene ring by ruthenium will affect the electronic structure of up to five thiophene rings: the bound ring and the next two unbound thiophene rings on either side.

Introduction

Interest in polythiophene grew in recent years due to a unique physical property it exhibits: high electrical conductivity in the solid state when partially oxidized.[1−6] To gain insight into the physical factors that determine the properties of polythiophene, smaller and more processable oligothiophenes have been studied as models.[1,7−10] These studies have been designed to "tune"[11−27] the physical properties of the oligothiophene by varying the substituents on the individual thiophene rings of the chain.[21−27] The success of this method has inspired us to investigate an alternative method of property tuning: coordination of transition metals to the π-system of the oligothiophene to form complexes. Transition metal complexes of single-ring thiophene and thiophene derivatives have been reported and studied as models for hydrodesulfurization catalysts,[28−43] but we are aware of no

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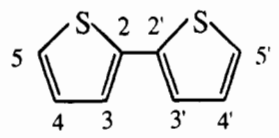
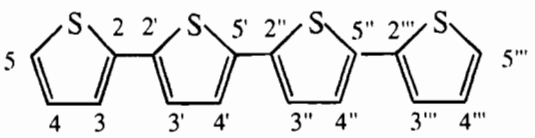
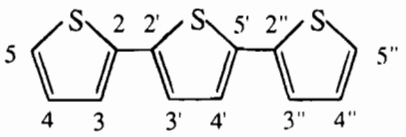


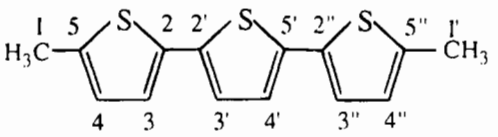
2,2'-bithiophene (Bth)



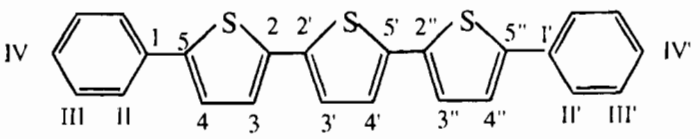
2,2':5',2":5",2"'-quaterthiophene (Qth)



2,2':5',2"-terthiophene (Tth)



5,5"-Dimethyl-2,2':5',2"-terthiophene (Me_2Tth)



5,5"-Diphenyl-2,2':5',2"-terthiophene (Ph_2Tth)

Figure 1. Structures, names, and numbering system used for the oligothiophenes.

reports of transition metal π-complexes of oligothiophenes.[44] This is quite surprising, as studies show that binding CpM^+ or Cp^*M^+ fragments (M = Fe, Ru, Os; Cp = cyclopentadienyl; Cp* = pentamethylcyclopentadienyl) to arenes modifies their properties.[45-48]

Herein, we report the synthesis and characterization of 14 complexes of the general forms [CpRu(oligothiophene)]PF_6 and [Cp*Ru(oligothiophene)]PF_6. For the oligothiophenes 2,2'-bithiophene (Bth), 2,2':5',2"-terthiophene (Tth), 2,2':5',2":5",2"'-quaterthiophene (Qth), and 5,5"-dimethyl-2,2':5',2"-terthiophene (Me_2Tth), we have found that the Ru is bound η^5 to the outermost thiophene ring while the complexes of the oligothiophene 5,5"-diphenyl-2,2':5',2"-terthiophene (Ph_2Tth) have the Ru bound η^6 to the pendant phenyl group (Figures 1 and 2). In addition to assigning the structures of these complexes, we also present our initial findings regarding the effect of the metal on the electronic structure of the oligothiophenes.

Experimental Section

General Considerations. All synthetic procedures were carried out under an inert atmosphere of Ar with Schlenk line techniques unless otherwise noted. Reaction solvents were of spectroscopic grade and were dried by distilling acetone from B_2O_3, dichloromethane from P_2O_5, and tetrahydrofuran from sodium. All solvents used in the workup of the reactions were of spectroscopic grade and were used as received. The acetone-d_6 and dichloromethane-d_2 used for NMR studies were dried over 3-Å molecular sieves and were degassed with Ar prior to use.

[$CpRu(CH_3CN)_3$]PF_6[49] and [$Cp^*Ru(CH_3CN)_3$]PF_6[50-53] were synthesized according to literature procedures and were stored in a dry N_2 atmosphere prior to use.

Characterization. ^1H and ^{13}C NMR spectra were recorded on either a VXR-300 or a VXR-500 instrument. The chemical shifts are reported in ppm (relative to TMS) and are referenced to the residual solvent peak. The heteronuclear multiple-bond correlation (HMBC), the heteronuclear multiple-quantum coherence (HMQC), and all $^1H-^1H$ decoupling experiments were performed on the VXR-500 spectrometer. Simulations of the NMR spectra were performed with the NMR program of Calleo Scientific Software Publishers. 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^+ values quoted are the values for the cationic complex without the PF_6^- anion(s). The theoretical isotopic patterns of the M^+ ions were calculated via the ISO program of VG Analytical, Ltd., and were compared to the observed M^+ isotopic pattern in order to verify the identity of the M^+ peak. Low-resolution electron impact (EI) mass spectra were obtained on an AEI MS-30 mass spectrometer. Elemental analyses were performed by MHW laboratories.

Synthesis of Oligothiophenes. The oligothiophenes 2,2'-bithiophene (Bth), 2,2':5',2"-terthiophene (Tth), and 2,2':5',2":5",2"'-quaterthiophene (Qth) were synthesized according to literature procedures.[11] The previously reported purification procedure for Qth provided only 85-90% purity. Synthetic reactions of this low-purity material with the ruthenation reactants yielded uncharacterizable mixtures of metal complexes. Higher purity Qth (>98% by ^1H NMR) of acceptable quality was obtained by Soxhlet extraction with $CHCl_3$ and repeated recrystallization from a 3:1 $CHCl_3$:acetone mixture. 2,5-Dibromothiophene[54] and 5,5"-dimethyl-2,2':5',2"-terthiophene[18] (Me_2Tth) were synthesized as reported earlier. 5,5"-Dibromo-2,2':5',2"-terthiophene was synthesized as reported earlier.[11] Repeated recrystal-

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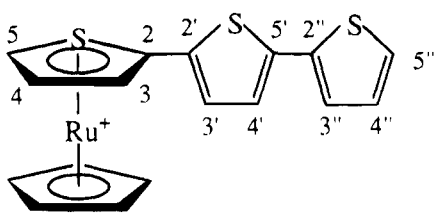
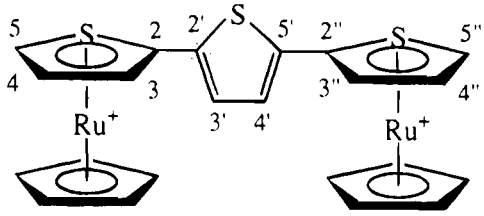
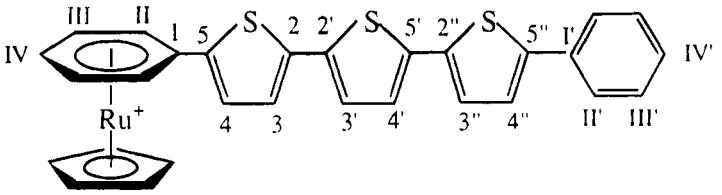


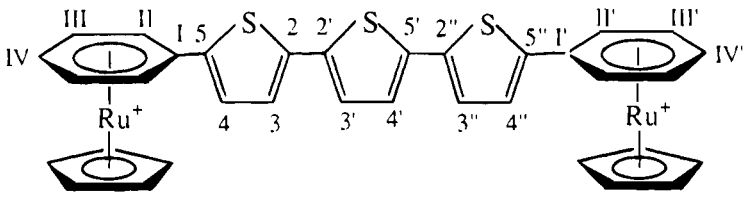
$[CpRu(\eta^5\text{-Tth})]PF_6$



$[(CpRu)_2(\eta^5,\eta^5\text{-Tth})](PF_6)_2$



$[CpRu(\eta^6\text{-}Ph_2Tth)]PF_6$



$[(CpRu)_2(\eta^6,\eta^6\text{-}Ph_2Tth)](PF_6)_2$

Figure 2. Structures and numbering system used for the oligothiophene complexes.

lization from $CHCl_3$ provides high-purity material (>98% by ^1H NMR). 2-Bromothiophene, thiophene, bromobenzene, and *p*-quaterphenyl were purchased from Aldrich Chemical Co. and were used as received.

5,5″-Diphenyl-2,2′:5′,2″-terthiophene (Ph_2Tth) has previously been synthesized,[55] but a more convenient synthesis has been worked out on the basis of the method of Zimmer et al.[11] The Grignard of bromobenzene (1.43 mL, 0.0135 mol) in 25 mL of ethyl ether was added to a suspension of 5,5″-dibromo-2,2′:5′,2″-terthiophene (1.756 g, 0.00542 mol) and $NiCl_2$(dppp) (40.1 mg, 0.0739 mmol) in 80 mL of anhydrous ethyl ether. After a reflux of 19 h, the rusty orange suspension was cooled to room temperature and filtered onto 1 cm of diatomaceous earth on a coarse frit, and the solid was washed with 15 mL of ethyl ether, 10 mL of hexanes, and then 30 mL of 95% ethanol. The orange solid and diatomaceous earth were transferred to a 1000 mL flask, and 800 mL of toluene was added. After heating to reflux, the suspension was filtered, and the brick red insoluble residue was washed with 500 mL of refluxing toluene. The toluene filtrate was reduced to 300 mL and allowed to cool. The bright orange precipitate which formed was filtered off and washed with cold toluene until no more red color was observed in the washings (washings were slightly yellow because Ph_2Tth is slightly soluble in toluene). After drying, 1.196 g (0.00299 mol, 55% yield) of Ph_2Tth was obtained as a bright orange powder. EI: 400.1 (M^+). Anal. Calcd for $C_{24}H_{16}S_3$: C, 71.96; H, 4.03; S, 24.01. Found: C, 71.80; H, 4.18; S, 24.00.

[CpRu(η^5-Bth)]PF_6. A 25 mL flask equipped with a N_2 adapter was charged with $[CpRu(CH_3CN)_3]PF_6$ (80.6 mg, 0.186 mmol) and Bth (74.2 mg, 0.447 mmol) and purged three times. Then 10 mL of CH_2Cl_2 was added and the solution stirred at room temperature for 45 h. The solution volume was reduced to 3 mL, and 12 mL of ethyl ether was added. Then twice more the solution volume was reduced to 3 mL, and 12 mL of ethyl ether was added. The yellow precipitate was filtered off and washed with 10 mL of hexanes, 10 mL of ethyl ether, and then 10 mL of pentane to give 71.3 mg (0.149 mmol, 80% yield) of [CpRu(Bth)]PF_6. FABMS: *m/e* 332.9 (M^+). Anal. Calcd for $C_{13}H_{11}F_6PS_2Ru$: C, 32.71; H, 2.32; S, 13.43. Found: C, 32.87; H, 2.31; S, 13.57.

[Cp*Ru(η^5-Bth)]PF_6. The preparation of this compound followed that of [CpRu(Bth)]PF_6. Starting with 90.1 mg (0.179 mmol) of $[Cp^*Ru(CH_3CN)_3]PF_6$ and 114.1 mg (0.689 mmol) of Bth gave 89.9 mg (0.0164 mmol, 92% yield) of [Cp*Ru(Bth)]PF_6 as a yellow powder.

Table 1. ^1H NMR Chemical Shifts[a] of Bithiophene and Its Complexes

		compound		
	mult	Bth[b]	[CpRu(Bth)]PF_6[c]	[Cp*Ru(Bth)]PF_6[c]
H(5)	dd	7.35	6.57	6.29
H(4)	dd	7.05	6.69	6.35
H(3)	dd	7.25	6.93	6.58
H(3′)	dd	7.25	7.53	7.48
H(4′)	dd	7.05	7.12	7.17
H(5′)	dd	7.35	7.73	7.69
Cp	s		5.55	
Cp*	s			1.93
$J_{5,4}$[d]		5.2	3.0	3.1
$J_{5,3}$		1.2	0.9	0.7
$J_{4,3}$		3.7	3.5	3.0
$J_{3',4'}$		3.7	3.7	3.6
$J_{3',5'}$		1.2	1.2	1.0
$J_{4',5'}$		5.2	5.1	5.2

[a] Recorded in acetone-d_6. Values are in ppm and are referenced to TMS (s = singlet, dd = doublet of doublets). [b] Spectrum recorded at 500 MHz. [c] Spectra recorded at 300 MHz. [d] Coupling constants are in Hz.

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Table 2. ^{1}H NMR Chemical Shifts[a] of Terthiophene (Tth) and Its Complexes in Acetone-d_6

			compound			
	mult	Tth[b]	[CpRu(Tth)]PF_6[c]	[Cp*Ru(Tth)]PF_6[b]	[$(CpRu)_2$(Tth)]$(PF_6)_2$[b]	[$(Cp^*Ru)_2$(Tth)]$(PF_6)_2$[c]
H(5)	dd	7.43	6.59	6.31	6.61	6.39
H(4)	dd	7.08	6.71	6.36	6.71	6.44
H(3)	dd	7.29	6.96	6.58	6.94	6.67
H(3′)		7.21[d]	7.49[e]	7.43[e]	7.50[d]	7.55[d]
H(4′)		7.21[d]	7.25[e]	7.30[e]	7.50[d]	7.55[d]
H(3″)	dd	7.29	7.38	7.40	6.94	6.94
H(4″)	dd	7.08	7.14	7.13	6.71	6.71
H(5″)	dd	7.43	7.56	7.54	6.61	6.61
Cp	s		5.59		5.58	
Cp*	s			1.97		1.98
$J_{5,4}$[f]		5.1	3.3	3.0	3.5	3.6
$J_{5,3}$		1.4	*g*	*g*	*g*	*g*
$J_{4,3}$		3.6	3.0	3.0	3.0	2.9
$J_{3',4'}$			3.9	3.75		
$J_{3'',4''}$		3.6	3.6	3.77	3.0	2.9
$J_{3'',5''}$		1.4	1.1	1.25	*e*	*e*
$J_{4'',5''}$		5.1	5.25	5.0	3.5	3.6

[a] The values are in ppm and are referenced to TMS (s = singlet, dd = doublet of doublets). [b] Spectrum recorded at 500 MHz. [c] Spectrum recorded at 300 MHz. [d] Resonance is a singlet. [e] Resonance is a doublet. [f] Coupling constants are in Hz. [g] This coupling was not observed.

FABMS: *m/e* 403.1 (M^+). Anal. Calcd for $C_{18}H_{21}F_6PS_2Ru$: C, 39.50; H, 3.87. Found: C, 39.72; H, 4.05.

[CpRu(η^5-Tth)]PF_6. A 50 mL Schlenk flask was charged with [CpRu$(CH_3CN)_3$]PF_6 (100.1 mg, 0.231 mmol) and Tth (126.7 mg, 0.510 mmol). After the system was purged three times, 18 mL of acetone was added and the reaction mixture was stirred at room temperature for 68 h. The solvent was removed in vacuum, and then 40 mL of hexanes was added. After 30 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 color was observed in the washings.

The solid was washed through the frit with acetone, the volume was reduced to 1 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 the solid was washed with hexanes until no green color washed off. After this procedure was repeated once more, the solid was washed through the frit with acetone, the solvent was removed by rotary evaporation, and then 20 mL of $CHCl_3$ was added. After the $CHCl_3$ suspension was stirred for 10 min, it was filtered through 1 cm of diatomaceous earth on a coarse frit, and the solid was washed with $CHCl_3$ until no color washed off. The solid on the frit was washed through the frit with acetone, the solvent was removed by rotary evaporation, and the above $CHCl_3$ washing procedure was repeated twice more. The remaining $CHCl_3$-insoluble residues were washed through with acetone, and the solvent was reduced to about 1 mL. Then 10 mL of heptane was added and the resulting precipitate was filtered off and washed with 5 mL of pentane to give 5.0 mg (0.0057 mmol, 5% yield) of [$(CpRu)_2$(Tth)]$(PF_6)_2$ as a yellow-green powder.

The $CHCl_3$ washings were combined, solvent was removed by rotary evaporation, and then 2 mL of CH_2Cl_2 was added. Next, 15 mL of heptane was added and the volume was reduced to 5 mL by rotary evaporation. The resulting precipitate was filtered off and washed with 10 mL of hexanes to give 98.8 mg (0.177 mmol, 77% yield) of [CpRu-(Tth)]PF_6 as a bright yellow powder. FABMS: *m/e* 414.9 (M^+). Anal. Calcd for $C_{17}H_{13}F_6PS_3Ru$: C, 36.49; H, 2.34; S, 17.19. Found: C, 36.42; H, 2.29; S, 17.13.

[Cp*Ru(η^5-Tth)]PF_6. The preparation of this compound is similar to that of [CpRu(Tth)]PF_6 except that the $CHCl_3$ used in the washing procedure was replaced by a 3:2 $CHCl_3$:hexanes mixture. The reaction of 98.3 mg (0.195 mmol) of [Cp*Ru$(CH_3CN)_3$]PF_6 and 102.2 mg (0.411 mmol) of Tth in 20 mL of acetone was stopped after 60 h, and workup of the reaction mixture provided two products. Recrystallization of the 3:2 $CHCl_3$:hexanes insoluble material from CH_2Cl_2/heptane gave 6.9 mg (0.0068 mmol, 7% yield) of [$(Cp^*Ru)_2$(Tth)]$(PF_6)_2$ as a bright yellow-green powder.

Recrystallization (CH_2Cl_2/heptane) of the 3:2 $CHCl_3$:hexanes soluble material gave 96.2 mg (0.153 mmol, 78% yield) of [Cp*Ru(Tth)]PF_6 as a yellow powder. FABMS: *m/e* 485.0 (M^+). Anal. Calcd for $C_{22}H_{23}F_6PS_3Ru$: C, 41.97; H, 3.68; S, 15.28. Found: C, 42.15; H, 3.65; S, 15.09.

Table 3. ^{1}H NMR Chemical Shifts[a] of Dimethylterthiophene and Its Complexes

		compound		
	mult	Me_2Tth[b]	[CpRu(Me_2Tth)]PF_6[b]	[Cp*Ru(Me_2Tth)]PF_6[c]
H(4)	m	6.75	6.62	6.21
H(3)	d	7.05	6.80	6.47
H(3′)	d	7.08	7.39	7.34
H(4′)	d	7.08	7.12	7.18
H(3″)	d	7.05	7.15	7.17
H(4″)	m	6.75	6.81	6.81
CH_3(I)	d	2.48	2.52	2.38
CH_3(I′)	d	2.48	2.49	2.50
Cp	s		5.56	
Cp*	s			1.94
$J_{4,3}$[d]		3.6	*e*	*e*
$J_{4,I}$		1.2	2.9	3.2
$J_{3',4'}$			3.9	4.0
$J_{4'',I'}$		1.2	1.0	1.2
$J_{3'',4''}$		3.6	3.9	3.5

[a] Recorded in acetone-d_6. The values are in ppm and are referenced to TMS (s = singlet, d = doublet, m = multiplet). [b] Spectrum recorded at 300 MHz. [c] Spectrum recorded at 500 MHz. [d] Coupling constants are in Hz. [e] This coupling was not observed.

[CpRu(η^5-Me_2Tth)]PF_6. A 50 mL Schlenk flask was charged with 77.5 mg (0.179 mmol) of [CpRu$(CH_3CN)_3$]PF_6 and 84.4 mg (0.305 mmol) of Me_2Tth and purged three times. Then 20 mL of CH_2Cl_2 was added and the solution was stirred at room temperature. After 60 h, the solvent was removed by rotary evaporation and 40 mL of ethyl ether was added. After 30 min of stirring, the suspension was filtered and the solid was washed twice with 15 mL of ethyl ether.

The solid was washed through the frit with acetone, the volume was reduced to 2 mL, and then 20 mL of hexanes was added. The emulsion was filtered onto 1 cm of diatomaceous earth on a coarse frit, and the solid was washed with ethyl ether until no yellow color came off. This precipitation/washing procedure was repeated. The solid was then washed through the frit with acetone and the solvent removed by rotary evaporation. The residue was dissolved in 3 mL of CH_2Cl_2, 10 mL of heptane was added, and the solution volume was reduced to 3 mL. The resulting precipitate was filtered off and washed with 10 mL of pentane to give 87.5 mg (0.149 mmol, 83% yield) of [CpRu(Me_2Tth)]-PF_6 as a yellow powder. FABMS: *m/e* 443.0 (M^+). Anal. Calcd for $C_{19}H_{17}F_6PS_3Ru$: C, 38.84; H, 2.92. Found: C, 38.61; H, 3.14.

[Cp*Ru(η^5-Me_2Tth)]PF_6. The preparation was similar to that of [CpRu(Me_2Tth)]PF_6. Starting with 51.8 mg (0.103 mmol) of [Cp*Ru$(CH_3CN)_3$]PF_6 and 44.0 mg (0.159 mmol) of Me_2Tth (in 10 mL of CH_2Cl_2) gave 53.8 mg (0.0818 mmol, 79% yield) of [Cp*Ru(Me_2-

Tth)]PF_6 as a dark yellow powder. FABMS: *m/e* 513.1 (M^+). Anal. Calcd for $C_{24}H_{27}F_6PS_3Ru$: C, 43.83; H, 4.14. Found: C, 43.66; H, 3.96.

[(CpRu)$_2$(η^5,η^5-Tth)](PF$_6$)$_2$. A 50 mL Schlenk flask was charged with [CpRu(CH_3CN)$_3$]PF_6 (67.8 mg, 0.156 mmol) and [CpRu(Tth)]-PF_6 (69.5 mg, 0.124 mmol). After the system was purged three times, 18 mL of acetone was added and the reaction mixture was stirred at room temperature for 48 h. The solvent was removed by rotary evaporation, and 40 mL of $CHCl_3$ was added. After the suspension was stirred for 30 min, it was filtered through 1 cm of diatomaceous earth on a coarse frit and the solid was washed with $CHCl_3$ until no yellow color was observed in the washings. The solid was washed through the frit with acetone, the volume was reduced to 3 mL, and then 20 mL of hexanes was added. The emulsion was filtered, and the solid was washed with $CHCl_3$ until the filtrate was colorless. The solid was washed through the frit with acetone and the volume reduced to 5 mL. Then 10 mL of heptane was added, the volume was reduced to 5 mL, and the resulting precipitate was filtered off and washed with 20 mL of $CHCl_3$ and then 10 mL of pentane to give 93.3 mg (0.107 mmol, 86% yield) of [(CpRu)$_2$(Tth)](PF$_6$)$_2$ as an olive green powder. FABMS: *m/e* 581.4 ($M^+ = C_{22}H_{18}S_3Ru_2$), 726.9 ($M^+ + PF_6$). Anal. Calcd for $C_{22}H_{18}F_{12}P_2S_3Ru_2$: C, 30.35; H, 2.08. Found: C, 30.15; H, 2.13.

[(Cp*Ru)$_2$(η^5,η^5-Tth)](PF$_6$)$_2$. The preparation of this compound was similar to that of [(CpRu)$_2$(Tth)](PF$_6$)$_2$ except that a 3:2 $CHCl_3$: hexanes mixture was used in place of $CHCl_3$ to wash the product. Starting with 59.6 mg (0.156 mmol) of [Cp*Ru(CH_3CN)$_3$]PF_6 and 69.5 mg (0.124 mmol) of [Cp*Ru(Tth)]PF_6 gave 93.3 mg (0.107 mmol, 86% yield) of [(Cp*Ru)$_2$(Tth)](PF$_6$)$_2$ as a bright yellow-green powder. Anal. Calcd for $C_{32}H_{38}F_{12}P_2S_3Ru_2$: C, 38.02; H, 3.79; S, 9.52. Found: C, 38.10; H, 4.00; S, 9.66.

[CpRu(η^5-Qth)]PF$_6$. To a 100 mL three-neck flask equipped with an addition funnel, condenser, and N_2 adapter was added 158.7 mg (0.480 mmol) of Qth. After the mixture was purged three times, 35 mL of CH_2Cl_2 was added and the resultant mixture was heated to reflux. Meanwhile, a 25 mL two-neck flask equipped with a septum and N_2 adapter was charged with 97.1 mg (0.224 mmol) of [CpRu(CH_3CN)$_3$]-PF_6. After the mixture was purged three times, 6 mL of acetone was added and, via cannulation, this solution was transferred to the addition funnel. Once the CH_2Cl_2 solution had reached reflux, all of the ligand dissolved and the acetone solution was added dropwise over 30 min to the CH_2Cl_2 solution. After the reaction mixture was refluxed for 48 h, it was cooled to room temperature and transferred to a 200 mL flask and the solvent was removed by rotary evaporation. Then 15 mL of acetone was added, the suspension was filtered through 1 cm of diatomaceous earth, and the solid was washed with 5 mL of acetone (Qth is only sparingly soluble in acetone).

The filtrate was concentrated to 5 mL, and 30 mL of hexanes was added. The emulsion was filtered onto 1 cm of diatomaceous earth on a coarse frit, and the solid was washed with ethyl ether until little color came off. The solid was 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 four times to remove all excess Qth. The insoluble residue on the frit was washed with $CHCl_3$ until no color came off, and the washings were set aside for later workup. The $CHCl_3$-insoluble material was washed through the frit with acetone, the solvent volume was reduced to 2 mL, and 30 mL of hexanes were added. The emulsion was filtered onto 1 cm of diatomaceous earth on a coarse frit, and the solid was again washed with $CHCl_3$ until no color came off. The $CHCl_3$ washings were combined, and the solvent was removed by rotary evaporation. The residues were dissolved in 3 mL of acetone, 15 mL of heptane was added, and the volume was reduced to 5 mL. The resulting precipitate was filtered off and washed with 15 mL of ethyl ether to give 93.5 mg (0.146 mmol, yield 65%) of [CpRu(Qth)]PF_6 as an orange-yellow solid. FABMS: *m/e* 496.9 (M^+), 330.0 (M^+ − CpRu). Anal. Calcd for $C_{21}H_{15}F_6PS_4Ru$: C, 39.31; H, 2.36; S, 19.99. Found: C, 39.18; H, 2.61; S, 19.74.

The $CHCl_3$-insoluble material was washed through the frit with acetone and the volume reduced to 2 mL. To this was added 10 mL of heptane, and the volume was reduced to 5 mL. The resulting precipitate was filtered off and washed with 10 mL of ethyl ether to give 16.2 mg of a green powder that was identified by its ^{1}H NMR spectrum to be [(CpRu)$_2$(η^5,η^5-Qth)](PF$_6$)$_2$. Yield: 0.017 mmol, 15%. ^{1}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). In order to further verify the identity of this green solid, 1.1 equiv of [CpRu(CH_3CN)$_3$]PF_6 was reacted with 1 equiv of [CpRu(Qth)]PF_6 in acetone-d_6. After 20 h, the ^{1}H NMR spectrum was recorded and was found to be exactly the same as that reported for [(CpRu)$_2$(Qth)](PF$_6$)$_2$.

[Cp*Ru(η^5-Qth)]PF$_6$. The preparation was similar to that of [CpRu-(Qth)]PF_6. The reaction of 138.5 mg (0.419 mmol) of Qth in 30 mL of CH_2Cl_2 with 100.2 mg (0.199 mmol) of [Cp*Ru(CH_3CN)$_3$]PF_6 in 5 mL of acetone gave two products. Recrystallization (acetone/heptane) of the $CHCl_3$-soluble material gave 98.4 mg (0.138 mmol, 69% yield) of [Cp*Ru(Qth)]PF_6 as a yellow powder. FABMS: *m/e* 567.1 (M^+). Anal. Calcd for $C_{26}H_{25}F_6PS_4Ru$: C, 43.87; H, 3.54; S, 18.02. Found: C, 44.00; H, 3.71; S, 17.81.

Recrystallization (acetone/heptane) of the $CHCl_3$-insoluble material gave 9.6 mg of a green powder which was identified by its ^{1}H NMR spectrum as [(Cp*Ru)$_2$(η^5,η^5-Qth)](PF$_6$)$_2$. Yield: 0.009 mmol, 9% yield. ^{1}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, Cp*). In order to further verify the identity of this green solid, 1.1 equiv of [Cp*Ru(CH_3CN)$_3$]-PF_6 was reacted with 1 equiv of [Cp*Ru(Qth)]PF_6 in acetone-d_6. After 20 h, the ^{1}H NMR spectrum was recorded and was found to be exactly the same as that reported for [(Cp*Ru)$_2$(Qth)](PF$_6$)$_2$.

[CpRu(η^6-Ph$_2$Tth)]PF$_6$. To a 100 mL three-neck flask equipped with an addition funnel, condenser, and N_2 adapter was added 66.5 mg (0.166 mmol) of Ph_2Tth. After purging three times, 75 mL of THF was added and the mixture was heated to reflux. Meanwhile, a 25 mL two-neck flask equipped with a septum and N_2 adapter was charged with 53.8 mg (0.124 mmol) of [CpRu(CH_3CN)$_3$]PF_6. After purging three times, 8 mL of acetone was added; this solution was transferred (via cannulation) to the addition funnel. Once the THF solution had reached reflux, all of the ligand dissolved and the acetone solution was added dropwise over 30 min. After the reaction mixture was refluxed for 42 h, it was cooled to room temperature and the solvent removed by rotary evaporation. After 150 mL of acetonitrile was added, the suspension was stirred for 15 min and then filtered through 1 cm of diatomaceous earth to remove unreacted Ph_2Tth. The solvent was

Table 4. ^{1}H NMR Chemical Shifts[a] of Quaterthiophene and Its Complexes

		compound		
	mult	Qth[b]	[CpRu(Qth)]PF_6[b]	[Cp*Ru(Qth)]PF_6[b]
H(5)	dd	7.46	6.60	6.35
H(4)	dd	7.10	6.71	6.40
H(3)	dd	7.33	6.96	6.62
H(3′)	d	7.27	7.50	7.46
H(4′)	d	7.25	7.28	7.35[c]
H(3″)	d	7.25	7.34	7.35[c]
H(4″)	d	7.27	7.29	7.29
H(3‴)	dd	7.33	7.35	7.35[c]
H(4‴)	dd	7.10	7.12	7.12
H(5‴)	dd	7.46	7.50	7.51
Cp	s		5.59	
Cp*	s			1.98
$J_{5,4}$[d]		5.1	3.3	3.1
$J_{5,3}$		1.0	0.7	0.8
$J_{4,3}$		3.6	3.0	3.1
$J_{3',4'}$		3.6	3.9	3.9
$J_{3'',4''}$		1.0	3.9	3.9
$J_{3''',4'''}$		3.6	3.6	3.9
$J_{3''',5'''}$		1.0	1.0	1.2
$J_{4''',5'''}$		5.1	5.0	5.1

[a] Recorded in acetone-d_6. The values are in ppm and are referenced to TMS (s = singlet, d = doublet, dd = doublet of doublets). [b] Spectrum recorded at 300 MHz. [c] H(4′), H(3″), and H(3‴) overlap and produce a broad multiplet at 7.35 ppm. [d] Coupling constants are in Hz.

Table 5. ^{1}H NMR Chemical Shifts[a] of Diphenylterthiophene (Ph_2Tth) and Its Complexes in Dichloromethane-d_2

		compound				
	mult	Ph_2Tth[b]	$[CpRu(Ph_2Tth)]PF_6$[c]	$[Cp^*Ru(Ph_2Tth)]PF_6$[c]	$[(CpRu)_2(Ph_2Tth)](PF_6)_2$[b]	$[(Cp^*Ru)_2(Ph_2Tth)](PF_6)_2$[b]
H(I)	t	7.31	6.19	5.83	6.16	5.79
H(II)	dd	7.42	6.31	5.89	6.30	5.89
H(III)	dd	7.64	6.57	6.09	6.59	6.10
H(4)	d	7.30	7.44e	7.42i	7.44	7.43
H(3)	d	7.21	7.19f	7.26j	7.23	7.28
H(3′)		7.18[d]	7.20[f,g]	7.42[g,i]	7.27[g]	7.26[g]
H(4′)		7.18[d]	7.24[g,h]	7.26[g,j]	7.27[g]	7.26[g]
H(3″)	d	7.21	7.25[h]	7.21	7.23	7.28
H(4″)	d	7.30	7.31	7.31	7.44	7.43
H(III′)	dd	7.64	7.65	7.65	6.59	6.10
H(II′)	dd	7.42	7.43[e]	7.42[i]	6.30	5.89
H(I′)	t	7.31	7.33	7.33	6.16	5.79
Cp	s		5.33		5.35	
Cp*	s			1.87		1.85
$J_{II,I}$[k]		7.2	6.0	5.75	6.0	6.0
$J_{III,I}$		1.2	(*l*)	(*l*)	(*l*)	(*l*)
$J_{III,II}$		7.2	6.0	5.75	6.0	6.0
$J_{4,3}$		4.0	4.0	4.0	4.0	4.0
$J_{3',4'}$			4.0	4.0		
$J_{3'',4''}$		4.0	4.0	4.0	4.0	4.0
$J_{III',II'}$		7.2	7.6	7.5	6.0	6.0
$J_{III',I'}$		1.2	1.0	1.0	(*l*)	(*g*)
$J_{II',I'}$		7.2	7.6	7.5	6.0	6.0

[a] The values are in ppm and are referenced to TMS (s = singlet, d = doublet, dd = doublet of doublets, t = triplet). [b] Spectrum recorded at 300 MHz. [c] Spectrum recorded at 500 MHz. [d] Resonance is a singlet. [e] H(4) and H(II′) coincide as a multiplet. [f] H(3) and H(3′) coincide as a multiplet. [g] Resonance is a doublet. [h] H(4′) and H(3″) coincide as a multiplet. [i] H(4), H(3′), and H(II′) coincide as a multiplet. [j] H(3) and H(4′) coincide as a multiplet. [k] Coupling constants are in Hz. [l] This coupling was not observed.

removed by rotary evaporation, and 400 mL of $CHCl_3$-were added. The suspension was stirred for 30 min and filtered, and the filtrate was set aside.

The residues were dissolved in 300 mL of CH_2Cl_2, and 150 mL of hexanes was added. The resulting precipitate was filtered off and washed with 75 mL of $CHCl_3$, and the filtrate was combined with the previous $CHCl_3$ washings. The insoluble matter was washed through the frit with acetonitrile, the solvent removed by rotary evaporation, and the residue treated as before. This precipitation procedure was carried out a total of three times.

The $CHCl_3$-insoluble material was washed through the frit with acetonitrile and the solvent removed by rotary evaporation. Then 10 mL of acetone was added, followed by 15 mL of heptane. After reduction of the volume to 5 mL, the precipitate was filtered off and washed with 10 mL of pentane to give 12.5 mg (0.0122 mmol, 20% yield) of $[(CpRu)_2(Ph_2Tth)](PF_6)_2$ as a bright yellow powder.

The CH_2Cl_2/hexanes and $CHCl_3$ washings were combined, and the solvent was removed by rotary evaporation. The residues were dissolved in acetonitrile, and the solution was refiltered. After removal of the solvent, the material was dissolved in 15 mL of acetone, 30 mL of heptane was added, and the solution volume was reduced to 10 mL. The resulting precipitate was filtered off and washed with 10 mL of pentane to give 51.9 mg (0.0729 mmol, 59% yield) of $[CpRu(Ph_2Tth)]PF_6$ as a yellow solid. ^{13}C NMR (125.7 MHz, acetonitrile-d_3, 22 °C): 81.64 (*C*H, bound phenyl group), 83.64 (*C*H, bound phenyl group), 85.63 (*C*H, bound phenyl group), 97.30 (q-*C*, bound phenyl group), 124.51 (*C*H), 124.86 (*C*H), 124.90 (*C*H), 125.43 (*C*H), 125.56 (*C*H), 126.04 (*C*H), 128.06 (*C*H), 129.18 (*C*H), 129.21 (*C*H), 133.48 (q-*C*), 134.51 (q-*C*), 135.46 (q-*C*), 136.09 (q-*C*), 137.19 (q-*C*), 139.70 (q-*C*), 143.60 (q-*C*), 85.22 (*C*H of Cp). FABMS: *m/e* 567.0 (M^+), 400.0 (M^+ − CpRu). Anal. Calcd for $C_{29}H_{21}F_6PS_3Ru$: C, 48.94; H, 2.97; S, 13.52. Found: C, 47.98; H, 3.13; S, 12.04.

$[Cp^*Ru(\eta^6\text{-}Ph_2Tth)]PF_6$. This procedure is similar to that for $[CpRu(Ph_2Tth)]PF_6$. To 85.1 mg (0.212 mmol) of Ph_2Tth in 120 mL of refluxing THF was added 80.2 mg (0.159 mmol) of $[Cp^*Ru(CH_3CN)_3]PF_6$ in 10 mL of acetone. The reaction mixture was worked up as before except that a 1:1 CH_2Cl_2:hexanes mixture was used for the washings and precipitation procedures. Recrystallization (acetone/heptane) of the 1:1 CH_2Cl_2:hexanes insoluble material gave 30.8 mg (0.0265 mmol, 30% yield) of $[(Cp^*Ru)_2(Ph_2Tth)](PF_6)_2$ as a yellow powder. Recrystallization (acetone/heptane) of the 1:1 CH_2Cl_2:hexanes soluble material gave 76.6 mg (0.0980 mmol, 56% yield) of $[Cp^*Ru(Ph_2Tth)]PF_6$ as a bright yellow solid. ^{13}C NMR (125.7 MHz, acetonitrile-d_3, 22 °C): 87.02 (*C*H, bound phenyl group), 83.35 (*C*H, bound phenyl group), 83.29 (*C*H, bound phenyl group), 95.89 (q-*C*, bound phenyl group), 124.50 (*C*H), 124.88 (*C*H), 125.15 (*C*H), 125.43 (*C*H), 125.54 (*C*H), 126.05 (*C*H), 128.06 (*C*H), 128.52 (*C*H), 129.17 (*C*H), 133.49 (q-*C*), 134.39 (q-*C*), 134.57 (q-*C*), 135.49 (q-*C*), 137.13 (q-*C*), 139.00 (q-*C*), 143.58 (q-*C*), 96.81 (q-*C* of Cp*), 9.37 (*C*H$_3$ of Cp*). FABMS: *m/e* 637.1 (M^+). Anal. Calcd for $C_{34}H_{31}F_6PS_3Ru$: C, 52.23; H, 4.00; S, 12.30. Found: C, 52.10; H, 3.97; S, 12.19.

$[(CpRu)_2(\eta^6,\eta^6\text{-}Ph_2Tth)](PF_6)_2$. A 100 mL Schlenk flask equipped with a condensor was charged with 52.3 mg (0.0735 mmol) of $[CpRu(Ph_2Tth)]PF_6$ and 45.9 mg (0.106 mmol) of $[CpRu(CH_3CN)_3]PF_6$. After purging three times, 55 mL of acetone was added and the system heated to reflux. After 24 h, the reaction mixture was cooled to room temperature and the solvent removed by rotary evaporation. Then 150 mL of $CHCl_3$ was added and the suspension stirred for 30 min. The suspension was filtered and the solid washed with 50 mL more of $CHCl_3$. The solid was then washed through the frit with acetonitrile, and the solvent was removed by rotary evaporation. The residue was dissolved in 20 mL of acetone, 20 mL of heptane was added, and the volume was reduced to 10 mL. The precipitate was filtered off and washed with 10 mL of pentane to give 60.1 mg (0.0844 mmol, 80% yield) of $[(CpRu)_2(Ph_2Tth)](PF_6)_2$ as a bright yellow powder. ^{13}C NMR (75 MHz, acetonitrile-d_3, 22 °C): 81.54 (*C*H, bound phenyl groups), 83.55 (*C*H, bound phenyl groups), 85.16 (*C*H, bound phenyl groups), 96.97 (q-*C*, bound phenyl groups), 125.16 (*C*H), 126.02 (*C*H), 129.13 (*C*H), 135.69 (q-*C*), 136.49 (q-*C*), 139.11 (q-*C*), 85.53 (*C* H of Cp). FABMS: *m/e* 733.0 (M^+), 878.9 ($M^+ + PF_6$), 567.0 (M^+ − CpRu). Anal. Calcd for $C_{34}H_{26}F_{12}P_2S_3Ru_2$: C, 39.93; H, 2.56; S, 9.40. Found: C, 39.76; H, 2.40; S, 9.15.

$[(Cp^*Ru)_2(\eta^6,\eta^6\text{-}Ph_2Tth)](PF_6)_2$. The preparation was similar to that of $[(CpRu)_2(Ph_2Tth)](PF_6)_2$ but $[(Cp^*Ru)_2(Ph_2Tth)](PF_6)_2$ is slightly soluble in $CHCl_3$. The reaction of 64.2 mg (0.0821 mmol) of $[Cp^*Ru(Ph_2Tth)]PF_6$ and 59.4 mg (0.117 mmol) of $[Cp^*Ru(CH_3CN)_3]PF_6$ gave 81.7 mg (0.0702 mmol, 86% yield) of $[(Cp^*Ru)_2(Ph_2Tth)](PF_6)_2$ as a yellow powder. ^{13}C NMR (125.7 MHz, acetonitrile-d_3, 22 °C): 83.35 (*C*H, bound phenyl groups), 87.09 (*C*H, bound phenyl groups), 87.14 (*C*H, bound phenyl groups), 95.75 (q-*C*, bound phenyl groups), 125.58 (*C*H), 126.14 (*C*H), 128.57 (*C*H), 134.91 (q-*C*), 135.82 (q-*C*), 138.59 (q-*C*), 96.84 (q-*C* of Cp*), 9.35 (*C*H$_3$ of Cp*).

Table 6. ^{1}H NMR Chemical Shifts[a] of *p*-Quaterphenyl (QPh) and Its Complexes

		compound		
	mult	QPh[b]	[CpRu(QPh)]PF_6[b]	[Cp*Ru(QPh)]PF_6[b]
H(4)	t	7.38	6.23	5.84
H(3/5)	dd	7.49	6.36	5.94
H(2/6)	dd	7.69	6.61	6.26
H(2′/6′)	d	7.78	7.81	7.87
H(3′/5′)	d	7.74	7.69	7.68
H(2″/6″)	d	7.74	7.76[c]	7.79[d]
H(3″/5″)	d	7.78	7.76[c]	7.78[d]
H(2‴/6‴)	dd	7.69	7.69	7.68
H(3‴/5‴)	dd	7.49	7.50	7.49
H(4‴)	t	7.39	7.40	7.40
Cp	s		5.37	
Cp*	s			1.86
$J_{4,3}$[e]		7.5	6.5	6.0
$J_{3,2}$		7.5	6.0	6.0
$J_{2',3'}$		8.5	8.5	8.5
$J_{2'',3''}$		8.5	*c*	8.0
$J_{2''',3'''}$		7.5	7.5	7.5
$J_{3''',4'''}$		7.5	7.5	7.5

[a] Spectra recorded in dicholormethane-d_2. The values are in ppm and are referenced to TMS (s = singlet, d = doublet, dd = doublet of doublets, t = triplet). [b] Spectra recorded at 500 MHz. [c] This AB pattern appears as a singlet at 7.76 ppm. [d] These assignments may be reversed. [e] Coupling constants are in Hz.

FABMS: *m/e* 837.0 (M^+), 1018.0 ($M^+ + PF_6$), 637.0 ($M^+ - Cp^*Ru$). Anal. Calcd for $C_{44}H_{46}F_{12}P_2S_3Ru_2$: C, 45.44; H, 3.99; S, 8.27. Found: C, 45.31; H, 4.15; S, 8.49.

[CpRu(η^6-*p*-quaterphenyl)]PF_6. To a 200 mL three-neck flask equipped with a condensor, N_2 adapter, and septa was added 96.6 mg (0.315 mmol) of *p*-quaterphenyl. After purging three times, 115 mL of CH_2Cl_2 was added and the mixture was heated to reflux (about 75% of the ligand had dissolved). Meanwhile, a 25 mL two-neck flask equipped with a septum and N_2 adapter was charged with 90.4 mg (0.208 mmol) of [$CpRu(CH_3CN)_3$]PF_6. After purging three times, 10 mL of acetone was added and this solution was cannulated to the refluxing CH_2Cl_2 solution. Within minutes all the ligand dissolved. After the reaction mixture was refluxed for 42 h, it was cooled to room temperature and the solvent removed by rotary evaporation. Then 150 mL of acetonitrile was added, and the suspension was stirred for 15 min and filtered through 1 cm of diatomaceous earth to remove unreacted quaterphenyl. The solvent was removed by rotary evaporation, and 50 mL of $CHCl_3$ was added. The $CHCl_3$ suspension was placed on a short alumina column and eluted with $CHCl_3$ to remove a tan impurity. The residues on the alumina were eluted with acetone to remove the monoruthenated complex. The acetone volume was reduced to 10 mL by rotary evaporation, 20 mL of heptane was added, and the solvent volume reduced to 10 mL. The obtained precipitate was filtered off to give 33.3 mg (0.0539 mmol, 26% yield) of [CpRu(*p*-quaterphenyl)]PF_6 as a white solid. The identification of this product was made by comparison of its ^{1}H NMR spectrum to that of *p*-quaterphenyl as shown in Table 6.

[Cp*Ru(η^6-*p*-quaterphenyl)]PF_6. This procedure is similar to that for [CpRu(*p*-quaterphenyl)]PF_6. To 82.7 mg (0.270 mmol) of *p*-quaterphenyl in 115 mL of refluxing CH_2Cl_2 was added 87.1 mg (0.173 mmol) of [$Cp^*Ru(CH_3CN)_3$]PF_6 in 10 mL of acetone. After the reaction mixture was refluxed for 42 h, it was cooled to room temperature and the solvent removed by rotary evaporation. Then 150 mL of acetonitrile was added, and the suspension was stirred for 15 min and filtered through 1 cm of diatomaceous earth to remove unreacted quaterphenyl. The solvent was removed by rotary evaporation, and 80 mL of $CHCl_3$ was added, followed by 40 mL of ethyl ether. This suspension was placed on a short alumina column and eluted with a 2:1 $CHCl_3$:ether mixture until all of a tan impurity was removed. The residues on the alumina were eluted with acetonitrile and the acetonitrile, was removed by rotary evaporation. To the residues was added 200 mL of $CHCl_3$; the suspension was filtered onto diatomaceous earth on a coarse frit and washed with 200 mL more of $CHCl_3$. After removal of the $CHCl_3$ by rotary evaporation, 10 mL of acetone was added, followed by 25 mL of heptane. The solvent volume was reduced to 10 mL, and the resulting precipitate was filtered off to give 33.4 mg (0.0486 mmol, 28% yield) of [Cp*Ru(*p*-quaterphenyl)]PF_6 as a white solid. The identification of this solid was made by comparing of its ^{1}H NMR spectrum to that of *p*-quaterphenyl as shown in Table 6.

Table 7. ^{13}C NMR Chemical Shifts[a] of Bithiophene and Its Complexes

	compound		
	Bth[b]	[CpRu(Bth)]PF_6[c]	[Cp*Ru(Bth)]PF_6[c]
C(5)	125.69	78.76	78.96
C(4)	128.04	86.58	88.88
C(3)	123.84	84.72	85.11
C(2)	137.87	94.59	92.89
C(2′)	137.87	131.74	131.62
C(3′)	123.84	128.59	128.91
C(4′)	128.04	130.62	128.10[d]
C(5′)	124.69	129.77	128.10[d]
Cp		81.66	
Cp*			96.51
$Cp^*(CH_3)$			9.82

[a] Recorded in acetone-d_6. Values are in ppm and are referenced to TMS. [b] Spectrum recorded at 125.7 MHz. [c] Spectra recorded at 75 MHz. [d] C(4′) and C(5′) coincide.

Reaction of [$CpRu(CH_3CN)_3$]PF_6 with [CpRu(η^5-Bth)]PF_6. To an NMR tube were added 2.9 mg (0.00601 mmol) of [CpRu(Bth)]PF_6 and 4.6 mg (0.011 mmol) of [$CpRu(CH_3CN)_3$]PF_6. The tube was taken into a glovebox and capped with a septum, and then 0.7 mL of acetone-d_6 was added. ^{1}H NMR spectra of the reaction mixture taken after 26 and 48 h showed that only [$(CpRu)_2(\eta^5,\eta^5$-Bth)]$(PF_6)_2$ was present. ^{1}H NMR (500 MHz, acetone-d_6, 22 °C): 6.87 (d, 2H, H(3,3′), J = 3.0 Hz), 6.71 (dd, 2H, H(4,4′), J = 3.0, 3.1 Hz), 6.66 (d, 2H, H(5,5′), J = 3.0 Hz), 5.75 (s, 5H, Cp). (Each of the peaks actually appears as two overlapping peaks, each having the same coupling constant and coupling pattern. For example, the peak for H(3,3′) appears as two distinct doublets separated by only 0.001 ppm. This indicates that a mixture of conformational isomers is present with slightly different chemical shifts for each proton.)

Reaction of [$Cp^*Ru(CH_3CN)_3$]PF_6 with [Cp*Ru(η^5-Bth)]PF_6. To an NMR tube were added 2.4 mg (0.0044 mmol) of [Cp*Ru(Bth)]PF_6 and 6.9 mg (0.014 mmol) of [$Cp^*Ru(CH_3CN)_3$]PF_6. The tube was purged three times on a Schlenk line and capped with a septum, and then 0.7 mL of acetone-d_6 was added. The ^{1}H NMR spectrum of the reaction mixture taken after 40 h showed that the only species present was [$(Cp^*Ru)_2(\eta^5,\eta^5$-Bth)]$(PF_6)_2$. ^{1}H NMR (500 MHz, acetone-d_6, 22 °C): 6.85 (d, 2H, H(3,3′), J = 3.0 Hz), 6.64 (dd, 2H, H(4,4′), J = 3.0, 3.1 Hz), 6.53 (d, 2H, H(5,5′), J = 3.1 Hz), 1.99 (s, 30 H, Cp*). (Each of the peaks listed actually appears as two overlapping peaks, each having the same coupling constant and coupling pattern as was described for [$(CpRu)_2$(Bth)]$(PF_6)_2$.)

Reaction of [$CpRu(CH_3CN)_3$]PF_6 with [$(CpRu)_2(\eta^5,\eta^5$-Tth)]$(PF_6)_2$. To an NMR tube were added 3.5 mg (0.0040 mmol) of [$(CpRu)_2$(Tth)]$(PF_6)_2$ and 4.1 mg (0.0094 mmol) of [$CpRu(CH_3CN)_3$]PF_6. The tube was taken into a glovebox and capped with a septum, and then 0.7 mL of acetone-d_6 was added. The ^{1}H NMR spectra of the reaction mixture taken after 26 and 48 h were found to have peaks corresponding to [$(CpRu)_2$(Tth)]$(PF_6)_2$, but several new peaks were also observed in the aromatic region of the spectra. ^{1}H NMR (500 MHz, acetone-d_6, 22 °C): 7.01 (d, 4H, J = 3.0 Hz), 6.81 (dd, 2H, J = 3.0, 3.1 Hz), 6.70 (d, 2H, J = 3.1 Hz). These new peaks have about 30% of the intensity of the [$(CpRu)_2$(Tth)]$(PF_6)_2$ peaks; analysis of the spectrum indicates that they arise from the η^5 binding of a third $CpRu^+$ group to the middle ring of Tth (H(3′) shifts upfield and all the other protons shift downfield). We assign this spectrum to [$(CpRu)_3(\eta^5,\eta^5,\eta^5$-Tth)]$(PF_6)_3$; the 7.01 ppm peak corresponds to H(3′) and H(3″,4″), and the 6.81 and 6.70 ppm peaks correspond to H(3,3″) and H(5,5″), respectively. These assignments are tentative, but the coupling pattern and changes in chemical shift are in support of our assignment.

Reaction of [$Cp^*Ru(CH_3CN)_3$]PF_6 with [$(Cp^*Ru)_2(\eta^5,\eta^5$-Tth)]$(PF_6)_2$. To an NMR tube were added 2.7 mg (0.0027 mmol) of

$[(Cp^*Ru)_2(Tth)](PF_6)_2$ and 3.1 mg (0.0061 mmol) of $[Cp^*Ru(CH_3CN)_3]PF_6$. The tube was taken into a glovebox and capped with a septa, and then 0.7 mL of acetone-d_6 was added. ^1H NMR spectra of the reaction mixture taken after 26 and 48 h were found to have peaks corresponding to $[(Cp^*Ru)_2(Tth)](PF_6)_2$, but several new peaks were also observed in the aromatic region of the spectra. ^1H NMR (500 MHz, acetone-d_6, 22 °C): 6.86 (d, 2H, J = 3.0 Hz), 6.72 (dd, 2H, J = 3.0, 3.1 Hz), 6.55 (d, 2H, J = 3.1 Hz), 6.50 (d, 2H, J = 3.1 Hz). These new peaks have only 15% of the intensity of the $[(Cp^*Ru)_2(Tth)](PF_6)_2$ peaks; analysis of the spectrum indicates that they arise from the η^5 binding of a third Cp^*Ru^+ group to the middle ring of Tth (H(3′) shifts upfield and all the other protons shift downfield). We assign this spectrum to $[(Cp^*Ru)_3(Tth)](PF_6)_3$; the 6.86, 6.72, 6.55, and 6.50 ppm peaks are assigned to H(3′), H(3″,4″), H(3,3″), and H(5,5″), respectively. These assignments are tentative, but the coupling pattern and changes in chemical shift are in support of our assignment.

Reaction of $[CpRu(CH_3CN)_3]PF_6$ with $[(CpRu)_2(\eta^5,\eta^5\text{-Qth})](PF_6)_2$. To an NMR tube were added 2.7 mg (0.0028 mmol) of $[(CpRu)_2(Qth)](PF_6)_2$ and 3.9 mg (0.0089 mmol) of $[CpRu(CH_3CN)_3]PF_6$. The tube was purged three times on a Schlenk line and capped with a septa, and then 0.7 mL of acetone-d_6 was added. An ^1H NMR spectrum of the reaction mixture after 40 h showed peaks in the aromatic region corresponding to $[(CpRu)_2(Qth)](PF_6)_2$. A few other peaks (5% of the intensity of $[(CpRu)_2(Qth)](PF_6)_2$ peaks) were also observed. The low intensity of these peaks and the possibility of overlap with the larger $[(CpRu)_2(Qth)](PF_6)_2$ peaks did not allow us to determine whether a third metal was bound to Qth.

Reaction of $[CpRu(CH_3CN)_3]PF_6$ with $[(CpRu)_2(\eta^6,\eta^6\text{-}Ph_2Tth)](PF_6)_2$. To an NMR tube were added 1.0 mg (0.00098 mmol) of $[(CpRu)_2(Ph_2Tth)](PF_6)_2$ and 2.0 mg (0.0046 mmol) of $[CpRu(CH_3CN)_3]PF_6$. The tube was taken into a glovebox and capped with a septa, and then 0.7 mL of acetone-d_6 was added. ^1H NMR spectra of the reaction mixture taken after 26 and 48 h showed peaks in the aromatic region corresponding to $[(CpRu)_2(Ph_2Tth)](PF_6)_2$. Several other new peaks having nearly 50% of the intensity of the $[(CpRu)_2(Ph_2Tth)](PF_6)_2$ peaks were also observed. These new peaks are as follows. ^1H NMR (500 MHz, acetone-d_6, 22 °C): 7.74 (d, 1H, J = 4.0 Hz), 7.70 (d, 1H, J = 4.0 Hz), 7.61 (d, 1H, J = 4.0 Hz), 7.60 (d, 1H, J = 4.0 Hz), 7.46 (d, 1H, J = 4.0 Hz), 7.23 (d, 1H, J = 3.5 Hz), 7.16 (d, 1H, J = 3.5 Hz), 7.10 (s), 6.96 (d, 1H, J = 7.0 Hz), 6.77 (d, 2H, J = 7.0 Hz), 6.53 (m), 6.43 (m). The integration of each peak has been normalized to that of the peak at 7.70 ppm in order to show their relative integration values (the integration and values for the peaks at 6.53 and 6.43 ppm could not be determined since they overlapped with those of $[(CpRu)_2(Ph_2Tth)](PF_6)_2$). The peaks with J = 3.5 and 4.0 Hz are due to the thiophene rings while those with J = 7 are from the phenyl groups. As there are more new resonances observed for the three thiophene rings (eight) than for protons on the thiophene rings (six), at least two new species are present in solution with one or more $CpRu^+$ groups bound to the inner thiophene rings. Thus, it is not possible to definitively assign the mode of binding (η^1, η^2, η^5, etc.) of $CpRu^+$ to the thiophene rings.

Equilibrium Study of the Reaction of $[CpRu(CH_3CN)_3]PF_6$ with Tth. To three NMR tubes were added Tth (0.1−0.2 mmol) and $[CpRu(CH_3CN)_3]PF_6$ (0.1−0.2 mmol) in the appropriate amounts to create ligand to metal ratios of 1.35, 0.81, and 0.54. The tubes were purged three times on a Schlenk line and sealed with septa, and then 0.7 mL of acetone-d_6 was added. The equilibrium was studied by monitoring the ^1H NMR on a Varian VXR-500 spectrometer using the residual acetone peak as the internal lock and standard. An NMR spectrum of each reaction was recorded after 24 and 48 h and an additional spectrum was obtained after 67 h for the study with a ligand to metal ratio of 1.35. The integration values for the *resolved* peaks corresponding to each species were obtained for each spectrum and normalized. After normalization, the values for each species were averaged and used to calculate the relative proportion of each species in solution.

Results and Discussion

Synthesis. The complexes reported here have been synthesized via procedures previously reported for other $[Cp/Cp^*Ru(\eta^6\text{-arene})]PF_6$ sandwich complexes synthesized by our group.[43,56,57] These general procedures give the desired oligothiophene complexes in 60−90% isolated yields. Initial attempts designed to produce the monoruthenated products gave mixtures of products with one and two Cp/Cp^*Ru^+ groups coordinated to the oligothiophene. Even the use of a 100% excess of ligand did not prevent the formation of diruthenated complexes. After further study, we determined that a series of equilibria (reactions 1 and 2) were responsible for the observed

$$[CpRu(CH_3CN)_3]PF_6 + \text{oligomer} \rightleftharpoons [CpRu(\text{oligomer})]PF_6 + 3CH_3CN \quad (1)$$

$$[CpRu(CH_3CN)_3]PF_6 + [CpRu(\text{oligomer})]PF_6 \rightleftharpoons [(CpRu)_2(\text{oligomer})](PF_6)_2 + 3CH_3CN \quad (2)$$

results. These equilibria are similar to those reported by Angelici et al. for the related $[CpRu(\eta^5\text{-thiophene})]PF_6$ complexes.[58] In these complexes, bound thiophene exchanges with other alkylthiophenes in coordinating solvents such as acetone.[58] As solubility factors dictated the use of acetone for most of our synthetic procedures, the combination of equilibria 1 and 2 complicated the syntheses by requiring the separation of the residual reactants and the mono- and diruthenated complexes. A general procedure for the purification of both the mono- and diruthenated complexes from the reaction mixtures gave the complexes in very reasonable yields with only small (10−15%) losses due to purification. It should be noted that the syntheses of the complexes of Bth and Me_2Tth could be performed in dichloromethane with a large excess of the ligand. This method minimizes the effect of the equilibria and eliminates the extensive purification procedures necessary in other cases.

The insolubility of the higher oligomers (Qth, Ph_2Tth) in most solvents suitable for the reactions (i.e. acetone, dichloromethane) was another problem encountered. The synthesis of the higher oligomer complexes at room temperature or at reflux generally gave mixtures of the mono- and diruthenated products in a ratio of about 1:1 or 1:2. To minimize this solubility problem, the ligand was first dissolved in a refluxing solvent (about 1 mL/1 mg of ligand), and then a solution of the $[Cp/Cp^*Ru(CH_3CN)_3]PF_6$ in acetone was added. This increased the mono- to diruthenated complex ratio to 3:1 or better. This procedure worked well and allowed the isolation of the monoruthenated complexes of the higher oligomers in 56−69% yields.

The stability of the oligothiophene complexes depends on the ruthenium binding site. Complexes that contain the metal bound to a thiophene ring are moderately air stable but slowly decompose in air after several weeks in the solid state or after several days in solution. Complexes with the metal bound to a pendant phenyl group are very air stable and suffer no observable decomposition after 6 months in the solid state or after weeks in solution. The stability of the complexes in solution under an inert atmosphere depends on the type of solvent used. In noncoordinating solvents (e.g. dichloromethane), all the complexes are stable and no decomposition or change is observed after several weeks. In contrast, the complexes with the metal bound to a thiophene ring are unstable in coordinating solvents (under Ar). In acetone, these complexes convert to an equilibrium mixture after 1 or 2 days, while in acetonitrile, they decomplex within minutes to free oligothiophene and $[Cp/Cp^*Ru(CD_3CN)_3]PF_6$. The complexes with the metal bound to a pendant phenyl group are very stable in

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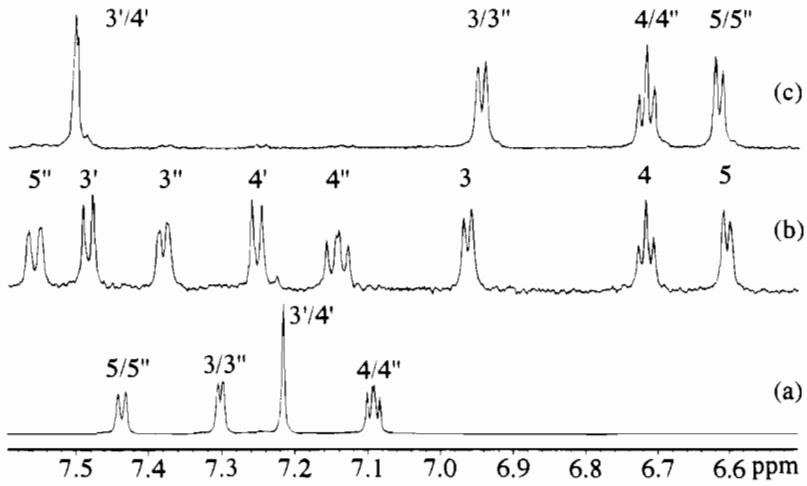

Figure 3. Aromatic regions of the ^{1}H spectra of (a) Tth, (b) [CpRu(Tth)]PF_6, and (c) [$(CpRu)_2$(Tth)]$(PF_6)_2$.

coordinating solvents with no observable changes in the ^{1}H NMR spectra after several weeks.

We were also interested in determining how many metal atoms could be coordinated to an oligothiophene chain. Previous studies with *p*-quaterphenyl and *p*-sexiphenyl[52] had shown that under forcing conditions, all of the phenyl rings could be complexed by a Cp^*Ru^+ fragment. With NMR-scale reactions, [CpRu(Bth)]PF_6, [Cp*Ru(Bth)]PF_6, [$(CpRu)_2$(Tth)]$(PF_6)_2$, [$(Cp^*Ru)_2$(Tth)]$(PF_6)_2$, [$(CpRu)_2$(Qth)]$(PF_6)_2$, and [$(CpRu)_2$(Ph_2-Tth)]$(PF_6)_2$ were reacted with a large excess of either [CpRu(CH_3-$CN)_3$]PF_6 or [Cp*Ru($CH_3CN)_3$]PF_6. Analysis of the ^{1}H NMR spectra for these reactions showed that a $CpRu^+$ or a Cp^*Ru^+ group readily binds to *both* thiophene rings of Bth but the middle thiophene ring of [$(CpRu)_2$(Tth)]$(PF_6)_2$ and [$(Cp^*Ru)_2$(Tth)]$(PF_6)_2$ was only complexed to a small degree (15−30% based on NMR integration values). In addition, binding a third (or fourth) metal to the inner two thiophene rings of [$(CpRu)_2$(Qth)]$(PF_6)_2$ was not observed. Further, there was some interaction (η^1, η^2, η^5) of one or more $CpRu^+$ fragments with the inner three thiophene rings of [$(CpRu)_2$(Ph_2Tth)]$(PF_6)_2$, but the binding mode and/or isomeric distribution was not determinable. In summary, the binding of metal atoms to the "end" rings of the oligothiophene chain occurs under mild conditions; with more forcing conditions (i.e. as in the *p*-quaterphenyl and *p*-sexiphenyl cases[52]), binding additional metal atoms to each inner thiophene ring of the chain is probably possible.

Structural Determination. Thiophene binds to metals in a variety of ways;[33,59] several examples of sandwich compounds of Ru and Fe with η^5-thiophene and η^5-alkylthiophenes[28−30,33,60−66] have been characterized. In the complexes of Bth, Tth, Qth, and Me_2Tth, the ruthenium always binds η^5 to an end ring of the thiophene chain. In the complexes of Ph_2Tth, the ruthenium binds η^6 to the pendant phenyl group, rather than to a thiophene ring. The evidence for these structural assignments is discussed below.

The ring-binding mode of the ruthenium in the complexes of Bth, Tth, Me_2Tth, and Qth was determined by interpretation of the NMR (^{1}H, ^{13}C) data for the complexes and by application of the 18-electron rule. If the Cp/Cp^*Ru^+ fragment is bound to a thiophene ring in an η^1-S, η^2-olefin, or η^4-butadiene fashion, then the NMR (^{1}H, ^{13}C) spectra of the complexes should show the presence of other ligands (i.e. CH_3CN, acetone), while η^5 binding should allow no auxiliary ligands. In all of the complexes reported, the NMR (^{1}H, ^{13}C) spectra in noncoordinating solvents (i.e. CD_2Cl_2) only show the presence of the η^5-Cp/Cp* ring, the bound η^5-oligothiophene, and the residual solvent peak. Thus, the NMR spectra imply that these are true sandwich complexes with the ruthenium bound η^5 to both the Cp/Cp* and thiophene rings. This assignment is further supported, as the mass spectral data and the elemental analyses also agree with the formulation of an η^5 thiophene ring (i.e. no extra ligands). This argument also holds for the complexes of Ph_2Tth with the ruthenium bound η^6 to a pendant phenyl group and η^5 to the cyclopentadienyl ligand.

NMR (^{1}H, ^{13}C) spectroscopy was used to determine the attachment site of the metal on the oligothiophene. The aromatic regions of the ^{1}H spectrum of Tth, [CpRu(Tth)]PF_6 and [$(CpRu)_2$(Tth)]$(PF_6)_2$ are shown in Figure 3. The ^{1}H NMR spectrum of uncomplexed Tth (C_{2v} symmetry) shows four peaks of equal area that are assigned to four pairs of magnetically equivalent protons. The ^{1}H NMR spectra of [CpRu(Tth)]PF_6 exhibits eight peaks of equal area that are assigned to eight magnetically inequivalent protons of the bound oligothiophene. The ruthenium must bind to the outer thiophene ring to produce the complex with effectively C_1 symmetry and eight magnetically inequivalent protons. If the ruthenium binds to the inner ring, the resulting complex (C_s symmetry) would have four pairs of magnetically equivalent protons as in the free oligothiophene. Further, the ^{1}H NMR spectrum of [$(CpRu)_2$(Tth)]$(PF_6)_2$ exhibits four peaks of equal area, indicative of the symmetric complex (C_s) with both outer rings complexed. These symmetry arguments are consistent with the ^{13}C spectra (Table 8) of these complexes.

^{1}H NMR evidence indicates that the metal is bound to a pendant phenyl group in the complexes of Ph_2Tth. The ^{1}H NMR spectrum of free Ph_2Tth is very easy to assign due to large differences in coupling constants and patterns for the phenyl (J_{HH} > 7 Hz) and thiophene (J_{HH} = 4 Hz) ring protons. Comparison of the ^{1}H spectrum of Ph_2Tth to those of the [CpRu(Ph_2Tth)]PF_6 and [Cp*Ru(Ph_2Tth)]PF_6 complexes shows that the chemical shift of the protons on one phenyl group are shifted upfield (1.5 ppm for Cp*, 1.1 ppm for Cp) while all other protons for the oligothiophene shift downfield or remain the same. In addition, the ^{1}H spectra of [$(CpRu)_2$(Ph_2Tth)]$(PF_6)_2$

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Table 8. ^{13}C NMR Chemical Shifts[a] of Terthiophene (Tth) and Its Complexes in Acetone-d_6

	compound				
	Tth[b]	[Cp*Ru(Tth)]PF_6[b]	[CpRu(Tth)]PF_6[c]	[$(CpRu)_2$(Tth)]$(PF_6)_2$[b]	[$(Cp^*Ru)_2$(Tth)]$(PF_6)_2$[b]
C(5)	125.83 (188)	78.96 (207)	78.61	79.42	68.30
C(4)	128.93 (168)	88.91 (185)	86.60	86.89	85.30
C(3)	124.78 (168)	84.32 (187)	84.27	84.98	79.55
C(2)	137.43	92.36	94.01	92.48	89.25
C(2′)	136.82	139.16	140.72	135.50	133.59
C(3′)	125.37 (168)	128.89 (170)	131.33	131.31	129.30
C(4′)	125.37 (168)	125.01 (170)	124.67	131.31	129.30
C(5′)	136.82	130.08	130.38	135.50	133.59
C(2″)	137.43	135.60	135.41	92.48	89.25
C(3″)	124.78 (168)	125.12 (170)	125.23	84.98	79.55
C(4″)	128.98 (168)	128.49 (170)	128.45	86.89	85.30
C(5″)	125.83 (188)	126.27 (189)	126.43	79.42	68.30
Cp			81.75	82.09	
Cp*		96.55			96.87
Cp*(CH_3)		9.85 (128)[d]			9.91

[a] The values are in ppm and are referenced to TMS. Numbers in parentheses are J_{CH} coupling constants and are reported in Hz. [b] Spectrum recorded at 125.7 MHz. [c] Spectrum recorded at 75 MHz. [d] Resonance is a quadruplet.

Table 9. ^{13}C NMR Chemical Shifts[a] of Dimethylterthiophene and Its Complexes

	compound		
	Me_2Tth[b]	[CpRu(Me_2Tth)]PF_6[c]	[Cp*Ru(Me_2Tth)]PF_6[c]
C(5)	139.28	93.33	95.74
C(4)	126.37	87.19	89.85
C(3)	123.66[d]	84.01	84.75
C(2)	135.79	93.07	92.08
C(2′)	134.50	140.99[e]	139.41
C(3′)	123.66[d]	131.13	128.53
C(4′)	123.66[d]	125.15[f]	125.02[f]
C(5′)	134.50	129.96	129.68
C(2″)	135.79	133.16	133.35
C(3″)	123.66[d]	123.86[f]	124.18[f]
C(4″)	123.66[d]	126.76	126.78
C(5″)	139.28	140.99[e]	140.84
CH_3(I)	14.30	15.05	13.07
CH_3(I′)	14.30	14.36	14.36
Cp		82.01	
Cp*			96.04
Cp*(CH_3)			9.57

[a] Spectra recorded in acetone-d_6. Values are in ppm and are referenced to TMS. [b] Spectrum recorded at 75 MHz. [c] Spectrum recorded at 125.7 MHz. [d] These carbons coincide. [e] C(2′) and C(5″) coincide. [f] Assignments are tentative and may be switched.

Table 10. ^{13}C NMR Chemical Shifts[a] of Quaterthiophene and Its Complexes

	compound		
	Qth[b]	[CpRu(Qth)]PF_6[c]	[Cp*Ru(Qth)]PF_6[c]
C(5)	125.05	78.69	78.98 (207)
C(4)	128.32	86.62	88.92 (187)
C(3)	124.16	84.30	84.82 (185)
C(2)	137.22	93.94	92.93
C(2′)	136.06	140.18	138.58
C(3′)	124.67	131.43	128.96 (165)
C(4′)	124.75	126.08	125.96 (164)
C(5′)	136.63	130.60	130.31
C(2″)	136.63	137.64[d]	136.15[e]
C(3″)	124.75	124.83	125.12 (170)
C(4″)	124.67	124.75	124.85 (173)
C(5″)	136.06	136.12[d]	134.25[e]
C(2‴)	137.22	138.78[d]	137.44[e]
C(3‴)	124.16	124.49	124.45 (170)
C(4‴)	128.32	128.30	128.31 (169)
C(5‴)	125.05	125.64	125.61 (189)
Cp		81.78	
Cp*			96.59
Cp*(CH_3)			9.85[f] (129)

[a] Values are in ppm and are referenced to TMS. Numbers in parentheses are J_{CH} coupling constants in Hz. [b] Spectrum recorded at 75 MHz in dichloromethane-d_2. [c] Spectra recorded at 125.7 MHz in acetone-d_6. [d] Assignments are tentative and may be switched. [e] Assignments are tentative and may be switched. [f] This is a quadruplet.

and [$(Cp^*Ru)_2(Ph_2Tth)$]$(PF_6)_2$ show that both sets of phenyl protons shift upfield while the thiophene ring protons shift downfield. These results are only consistent with those obtained for some related η^6-arene complexes[30,47,56,57] with the ruthenium bound to a pendant phenyl group.

The preference of the ruthenium for the outer ring of the oligothiophene chain was expected, as other studies have shown that the thermodynamic product contains the metal bound to the outermost ring when Cp/Cp^*Ru^+ fragments bind to a *fused* polycyclic arene.[57] This preference has been rationalized on the basis that the outermost ring is less delocalized (i.e. more aromatic), forms the strongest bond to the ruthenium, and causes the least disruption of the remaining π-system.[57] By analogy, the outermost ring in the oligothiophenes is also the "least delocalized", as it is directly conjugated to only one other ring while the interior rings are directly conjugated to two other rings and are "more delocalized". Thus, the outer rings are the least delocalized (i.e. diluted), are more aromatic in nature, and are the thermodynamically preferred binding site of the Cp/Cp^*Ru^+ fragment.

Detailed Assignment of ^1H and ^{13}C NMR Spectra. The complete assignment of the ^1H and ^{13}C NMR spectra allowed a detailed view of the interaction of Ru with the oligothiophenes. In particular, it allowed an answer to this question: How many rings are affected by η^5-Ru binding? As discussed above, the pattern of the NMR (^1H, ^{13}C) spectra of these complexes is indicative of where and how the ruthenium is bound to the oligothiophene but the exact assignment of each peak is ambiguous. For example, the ^1H NMR spectrum of [Cp*Ru(Tth)]PF_6 exhibits eight peaks, all of which could be assigned, except H(3′) and H(4′), on the basis of coupling constants, chemical shifts, $^1H-^1H$ decoupling experiments, and literature reports for similar complexes.[66-69] Analysis of the ^{13}C spectrum of [Cp*Ru(Tth)]PF_6 was even less straight-forward and based on literature reports;[66-69] only the peaks corresponding to C(2), C(3), C(4), C(5), and Cp* could be assigned. To definitively assign the spectra of all the oligothiophene complexes, we elected to first assign the ^1H and ^{13}C spectra of the [Cp*Ru(Tth)]PF_6 complex, as it contains all the types of

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Table 11. Calculated Values for the Equilibrium Reactions at 22 °C

	K_1/K_2			$\Delta G°$ (kJ/mol)[b]		
ligand: metal ratio[a]	22 h	44 h	67 h	22 h	44 h	67 h
1.35	27 ± 12	27 ± 12		−8.1 ± 0.9	−8.1 ± 0.9	
0.81	30 ± 12	30 ± 12		−8.3 ± 0.9	−8.3 ± 0.9	
0.54	21 ± 6	23 ± 6	21 ± 6	−7.5 ± 0.8	−7.7 ± 0.8	−7.5 ± 0.8

[a] The ratio of Tth to $[CpRu(CH_3CN)_3]PF_6$ in the studies discussed in the text. [b] $\Delta G° = -RT\ln(K_1/K_2)$.

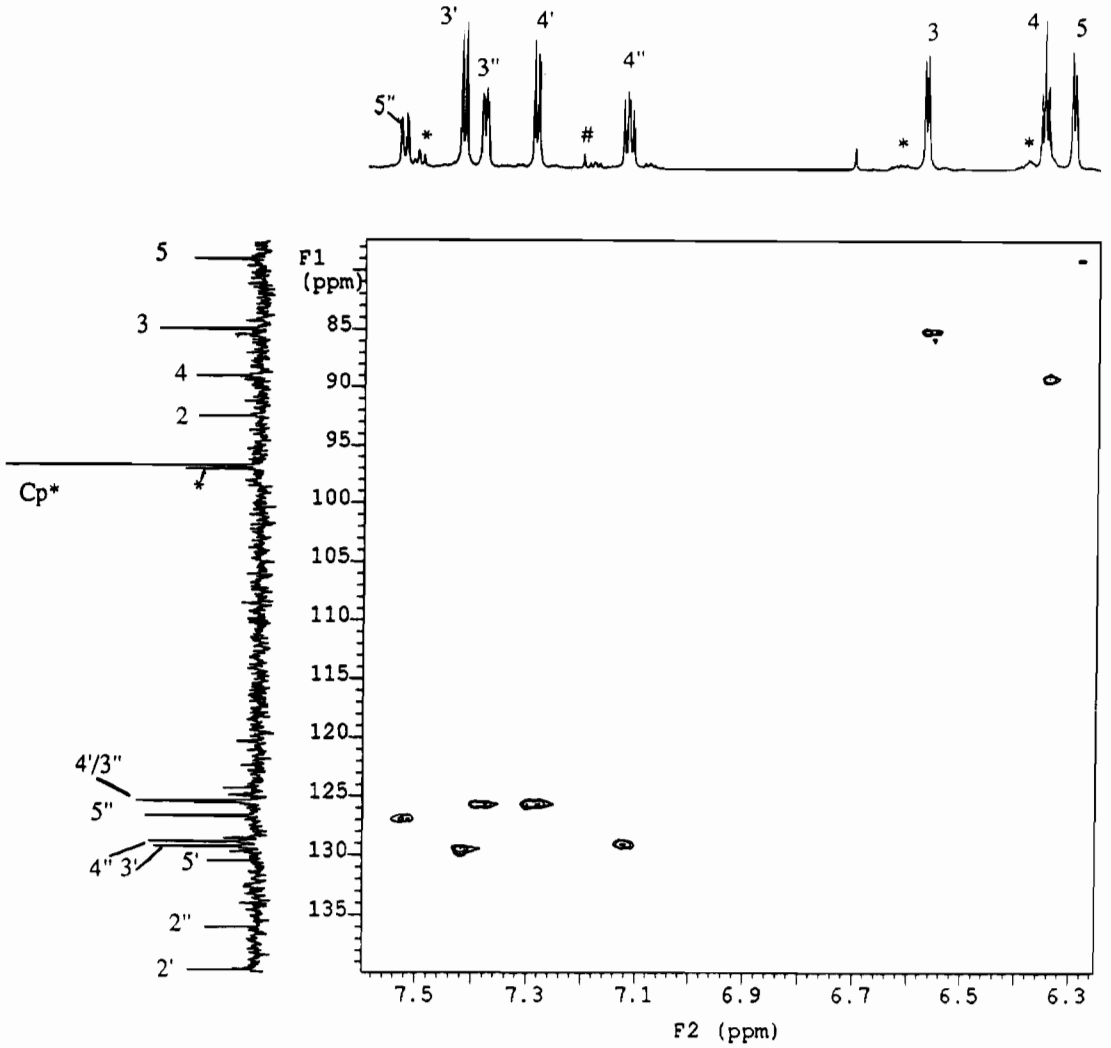

Figure 4. $^1H\{^{13}C\}$ 2D HMQC spectrum of $[Cp^*Ru(Tth)]PF_6$ obtained in acetone-d_6. The ^1H spectrum was obtained after the completion of this experiment (2 h); this spectrum shows the presence of free Tth (marked as #) and $[(Cp^*Ru)_2(Tth)](PF_6)_2$ (marked as *).

ambiguities possible. The assignments of the $[Cp^*Ru(Tth)]PF_6$ spectra were successfully accomplished by analyzing the proton-coupled, NOE-enhanced $^{13}C\{^1H\}$ spectrum and the 2D heteronuclear HMQC and HMBC spectra.

The $^{13}C\{^1H\}$ spectra of $[Cp^*Ru(Tth)]PF_6$ and Tth were obtained and compared. In both spectra, the J_{CH} values for the carbon α to the sulfur were about 20 Hz larger than J_{CH} for all other carbons in the oligothiophene (Table 8). Thus, C(5″) (and C(5)) were unambiguously assigned and verified. The HMQC spectrum (Figure 4; correlates a carbon and its attached proton) allowed definitive assignments of the ^{13}C peaks for C(4), C(3″), and C(4″). The remaining unassigned resonances (H(3′), H(4′), C(3′), C(4′), C(2′), C(5′), and C(2″)) were assigned with an HMBC experiment. The HMBC experiment (Figure 5) correlates a proton to carbons with long-range coupling to that proton (typically crosspeaks are observed for ^2J, ^3J, and ^4J couplings). The HMBC spectrum of the complex exhibited crosspeaks for a given proton to all other carbons in that ring and sometimes to a quaternary carbon in the next thiophene ring (e.g. H(3) couples to C(5), C(4), C(2), and C(2′)). Two important crosspeaks in the HMBC spectrum were found between H(3′) and C(2) and between H(4′) and C(2″). These long-range couplings (^3J) allowed the definitive assignment of H(3′) and H(4′) as well as C(3′) and C(4′). In addition, the HMBC spectrum allowed the assignment of the quaternary carbons C(2), C(5′), and C(2″). The final assignments of the proton and carbon spectra are shown in Tables 2 and 8. The assignment of the NMR (^1H, ^{13}C) spectra of the other complexes were based on the detailed assignment for $[Cp^*Ru(Tth)]PF_6$, $^1H-^1H$ decoupling experiments for each complex, and a proton-coupled, NOE-enhanced $^{13}C\{^1H\}$ spectrum of $[Cp^*Ru(Qth)]PF_6$. A further interpretation of these results as they relate to the effect of η^5-Ru binding on the electronic structure of the oligothiphenes is provided below.

Equilibrium Studies. As discussed earlier, the equilibria shown in eqs 1 and 2 are similar to those reported by Angelici et al. for the $[CpRu(\eta^5\text{-thiophene})]PF_6$ complex.[58] To further verify the nature of these equilibria, NMR-scale reactions with

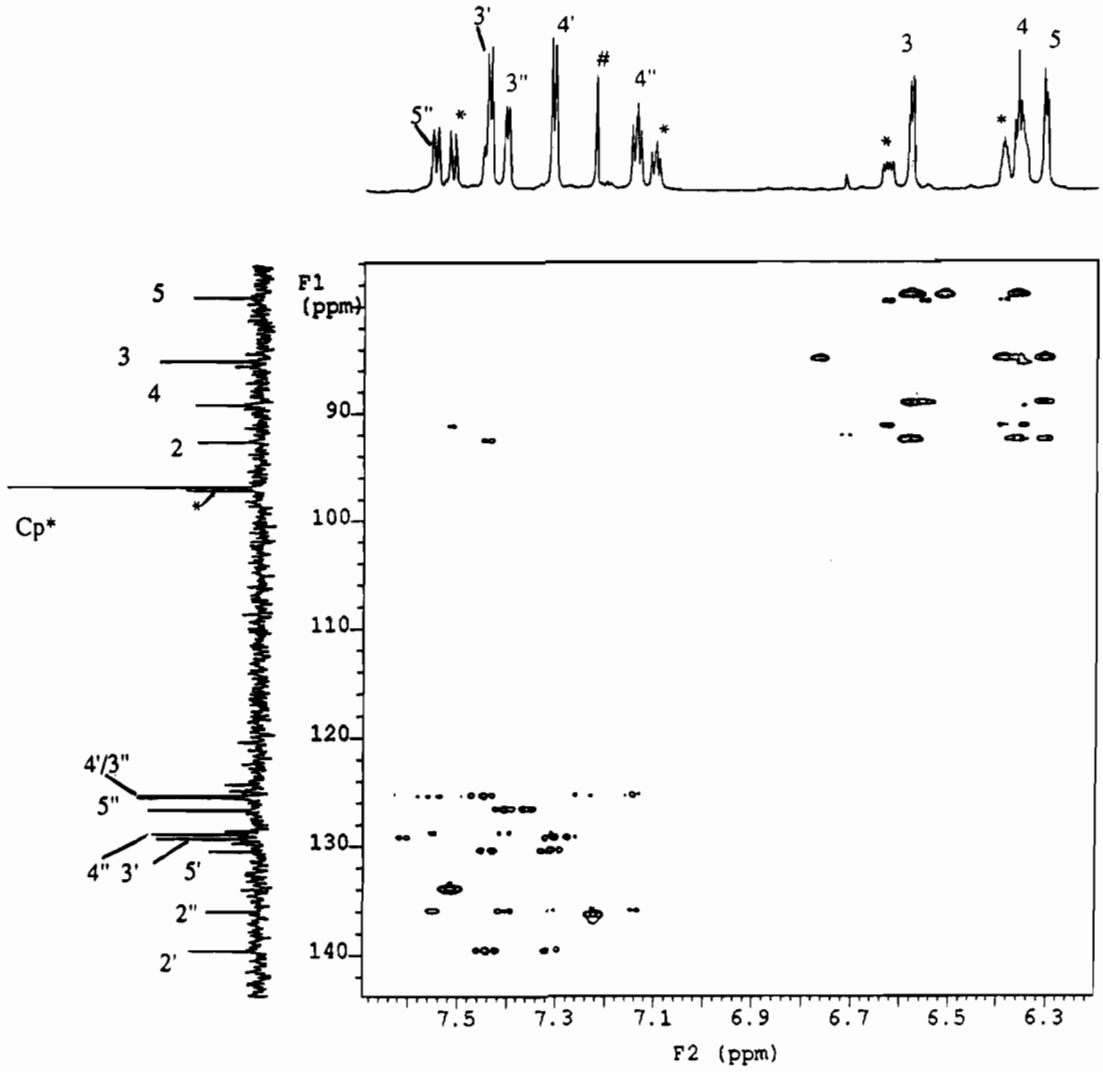

Figure 5. $^1H\{^{13}C\}$ 2D HMBC spectrum of $[Cp^*Ru(Tth)]PF_6$ obtained in acetone-d_6. The ^1H spectrum was obtained after the completion of this experiment (12 h); this spectrum shows the presence of a large amount of free Tth (marked as #) and $[(Cp^*Ru)_2(Tth)](PF_6)_2$ (marked as *).

1.35, 0.81, and 0.54 equiv of Tth and 1 equiv of $[CpRu(CH_3CN)_3]PF_6$ in acetone-d_6 were studied. Analysis of the ^1H spectra allowed the calculation of the ratio of K_1/K_2 from the normalized integration values for each species in the equilibrium reaction.[70]

The constant value obtained for K_1/K_2 (25 ± 9; $\Delta G° = -7.9 \pm 0.5$kJ/mol) supports our observation that equilibria 1 and 2 occur during the synthesis of these complexes. In addition, the intermediate value of K_1/K_2 and the calculated difference in ΔG for the two equilibria show that there is only a slightly larger preference for the formation of the monoruthenated complexes over the diruthenated complexes. It is likely that this small preference arises from the decrease in inter-ring conjugation that occurs upon binding a metal to one end of the oligothiophene chain. As discussed earlier, the $CpRu^+$ fragment has a higher thermodynamic preference for the most aromatic ring; thus, the ratio K_1/K_2 is a rough measure of how the aromaticity of an outer ring changes when the oligothiophene is complexed. For example, if binding a ruthenium group to one end of an oligothiophene tends to *increase* the aromaticity of the ring at the other end of the oligothiophene, then there should be a preference for two $CpRu^+$ groups to bind to the oligothiophene (i.e. K_1/K_2 is small). On the other hand, if binding a ruthenium group to one end of an oligothiophene tends to *decrease* the aromaticity of the ring at the other end of the oligothiophene, then there should be a preference for the binding of only one ruthenium group to the thiophene ring chain (i.e. K_1/K_2 is large). The intermediate value of K_1/K_2 indicates that binding ruthenium to one end of the oligothiophene chain slightly activates the other end of the chain toward binding another ruthenium group.

Analogous equilibria also occur when the Cp or Cp* complexes of Bth, Tth, Me_2Tth, and Qth are dissolved in a coordinating solvent such as acetone. For example, the ^1H NMR spectrum of $[CpRu(Tth)]PF_6$ in acetone-d_6 shows that, after 14 h, about 15–20% of this species is converted to $[(CpRu)_2(Tth)](PF_6)_2$ and Tth. In contrast, when $[CpRu(Tth)]PF_6$ is dissolved in CD_2Cl_2, the ^1H NMR spectrum of the complex shows no changes after 4 days. In ^1H NMR experiments with the monoruthenated complexes of Bth, Tth, Qth, and Ph_2Tth dissolved in CD_3CN, the complexes of Bth, Tth, and Qth converted to the free oligothiophene and $[Cp/Cp^*Ru(CD_3CN)_3]PF_6$ within minutes; under identical conditions, the complexes

(70) Free Tth and $[CpRu(Tth)]PF_6$ each contain four resolved peaks available for average integration values; differences in proton relaxation rates gave integration values for the protons of a given species that were inconsistent *within* a spectrum but were consistent *between* spectra of all three concentrations. For instance, the integration values for the proton resonances for H(5″) and H(5) in both Tth and $[CpRu(Tth)]PF_6$ were consistently lower than the integration values for the other protons of these compounds in each spectrum. This problem was magnified for the determination of the concentration of $[(CpRu)_2(Tth)](PF_6)_2$ because the only resolved peak for this species is H(5,5″). The calculated value of K_1/K_2 is an upper limit because this integration value is probably too small. The high uncertainty quoted for the K_1/K_2 value is the result of these NMR spectral problems.

of Ph_2Tth yielded no change in the spectra after 2 weeks. These results agree with Angelici's reports[58] of the solvent effects on the thiophene ring exchange reaction that occurs between $[CpRu(thiophene)]^+$ and alkylthiophenes.

Effect of the Metal upon the Oligothiophene. Insight into the metal's effect on the electronic structure of the thiophene chain can be gained from further interpretation of the ^1H and ^{13}C NMR spectra of the complexes. In agreement with other reports,[58,66-69] the protons of the bound thiophene and phenyl rings shift upfield from their free ligand values. This upfield shift is typically 5% greater for the Cp* complexes than for the Cp complexes. In the complexes with the phenyl group bound, *all* protons on the ring shift upfield by the same amount (20% for Cp*, 15% for Cp); but in those complexes where a thiophene ring is bound, the upfield shift of the protons is dependent on the position of the proton with respect to the sulfur. The upfield shift of the α (H(5)) protons is typically 5% more than that of the β protons (H(3/4)), in agreement with observations made for other η^5-thiophene complexes.[58,66-69] For the complexes of Me_2Tth, the change in chemical shift of the methyl groups depends on whether the ruthenium is bound to a Cp or a Cp* ligand. The methyl group on the bound ring shifts *downfield* by 0.04 ppm for the Cp complex but shifts *upfield* by 0.04 ppm for the Cp* complex.

The changes in chemical shifts observed for the bound thiophene rings are very similar to those reported in previous ^1H NMR studies of η^5-thiophene complexes of the $Cr(CO)_3$ and $Mn(CO)_3^+$ fragments. The two main explanations given for this upfield shift of the bound ring[66,71,72] are (1) a decrease in the π-electron density, and its resulting ring current, and (2) a magnetic anisotropy effect that arises from the metal−thiophene ring bond dipole.[66,71,72] In addition to the upfield shift of the protons on the bound ring, decreasing the π-electron density of an arene also leads to a deshielding effect of the protons due to the loss of electron density at the atoms.[64,69,70] Thus, in complexes with π-bound arenes, competing factors create upfield shifts (reduction in ring current, magnetic anisotropy) and downfield shifts (loss of π-electron density in the arene). All of these factors are likely to contribute to the net upfield shift of the protons on the bound ring.

A competition between these effects results in differences in the ^1H spectra of the Cp* and Cp complexes of each oligothiophene. As discussed before, the Cp* complexes have a larger upfield shift for the protons than do the Cp analogs. As the comparable magnetic anisotropies in the Cp and Cp* complexes should create a similar upfield shift, the differences in the ^1H upfield shifts for the Cp and Cp* complexes must largely result from the differences in the amount of π-density removed from the bound thiophene ring. As Cp is a poorer electron donor than Cp*, the Cp complexes of ruthenium should extract more π-electron density from the thiophene ring than the Cp* complexes. Thus, the Cp complexes should have a larger decrease in the π-electron density of the bound ring and a larger deshielding effect but at the same time the decrease in the ring current of the bound ring should result in a larger shielding effect. In the Cp complexes, the net loss of π-electron density (deshielding) is larger than the net loss in ring current (shielding), while in the Cp* complexes, the resultant is reversed.

Comparison of the ^{13}C spectra of Bth, Tth, Me_2Tth, and Qth to those of their complexes also show changes in chemical shifts similar to those observed in the ^1H spectra. (The insolubility of Ph_2Tth precluded the collection of its ^{13}C spectrum for comparison to that of its complexes.) The carbons of the bound thiophene ring exhibit upfield shifts that are again about 5% greater for the α carbons (36−38%) than for the β carbons (31−33%). In contrast to the shifts in the ^1H spectra, the upfield shifts of the bound carbons are similar for the monoruthenated Cp and Cp* complexes but are greater for the Cp* complexes with two ruthenium groups bound to the oligothiophene. The upfield chemical shifts of the carbons of the bound thiophene ring are in agreement with those reported earlier for other thiophene[66,68] and arene[72,73] complexes of transition metals. The upfield shifts of the bound carbons have been attributed to a change in the hybridization of the carbons (sp^2 to sp^3) upon binding to the metal,[73] to a change in the C−C bond order,[74] or to an increase of the net negative charge on the carbons.[75]

Analysis of the J_{HH} and J_{CH} coupling constants for the bound thiophene and phenyl rings also gives interesting results. The J_{HH} coupling constants are found to decrease in the bound thiophene ring, but the decrease in the value again depends on whether the proton is α or β to the sulfur atom. The $J_{5,4}$ coupling constants decrease by 30−40% while the $J_{3,4}$ coupling constants decrease by 15−20% in accord with results reported earlier for other η^5 complexes of thiophene.[66-69] In addition, the J_{HH} couplings for the unbound thiophene and phenyl rings are similar to those of the free ligand. Last, comparison of the J_{CH} values for Tth, Qth, $[Cp^*Ru(Tth)]PF_6$, and $[CpRu(Qth)]PF_6$ shows that the J_{CH} values for the bound thiophene ring increase by 10% (for C(5,4,3)) while all other J_{CH} values for the ligand remain the same.

The decrease in J_{HH} coupling constants for a thiophene ring bound to a transition metal has previously been attributed[66,67,71] to a decrease in the electron density present at the ring's protons due to the bound metal. The larger decrease in the J_{HH} values for the α protons than for the β protons has also been attributed[66,67] to a greater interaction of the metal with the α CH unit than with the β CH units. An increase in the J_{CH} values for the bound ring in arene complexes of Cr(0) has been attributed[71] to a decrease in the π-electron density of the bound arene that increases the effective nuclear charge of the carbons and slightly decreases that of the protons.

Perhaps the most interesting results are obtained through analysis of the chemical shift changes of the protons on the unbound rings. Relative to those of the free oligothiophene, the protons on the unbound thiophene rings exhibit a downfield shift that decreases as the distance from the ruthenium increases. This downfield shift is slightly greater for the Cp complexes than for the Cp* analogs and extends over the nearest, and the next nearest, unbound thiophene rings in both cases. For example, the ^1H NMR spectra of $[Cp^*Ru(Qth)]PF_6$ and $[CpRu(Qth)]PF_6$ show that the protons on the ring furthest from the metal (three thiophene rings away) show no significant changes in their chemical shifts. Further, the ^1H spectra of the $[CpRu(Ph_2Tth)]PF_6$ and $[Cp^*Ru(Ph_2Tth)]PF_6$ complexes show that the chemical shifts for the unbound phenyl group and its adjacent thiophene ring exhibit no significant changes from those observed for free Ph_2Tth. The chemical shifts of the ^{13}C resonances for the nearest and next nearest unbound thiophene rings also exhibit a significant downfield shift. Unfortunately, direct comparisons of ^{13}C chemical shifts in the third ring away from the ruthenium are not possible because the spectra of Qth and its complexes could not be recorded in the same solvent. Thus, the small differences in the ^{13}C resonances (0.2−0.5 ppm) for the carbons in the third ring away from the ruthenium in

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free Qth and its complexes may not reflect the presence of the metal but may in fact simply arise from solvent effects. In addition, comparisons of the ^{13}C spectra of Ph_2Tth and its complexes were precluded by the extreme insolubility of Ph_2-Tth in all suitable NMR solvents.

The large downfield shifts in the ^1H NMR spectra for the unbound rings of the oligothiophene are also observed for related ruthenium complexes of polycyclic arenes.[30,43,57] Several different factors determine these downfield shifts: the presence of the ruthenium (heavy atom effect), effects arising from the electrons in the ruthenium−thiophene bond, and changes in the electronics of the nearby aromatic ring (e.g. changes in ring currents, electron density at each atom, inter-ring twist angle, etc.). To investigate the role some of these factors play in the observed spectral changes, we synthesized the monoruthenated complexes of *p*-quaterphenyl (QPh). We chose QPh for its similarities to Qth (both have four individual rings with aromaticity) and its differences (Qth has a high degree of inter-ring conjugation while QPh has a smaller level of inter-ring conjugation, perhaps due to inter ring nonplanarity). Because the ruthenium group binds to the outer ring of both QPh and Qth, comparisons of the ^1H NMR spectra of the complexes of Qth and QPh should give insights into the conjugation effects within the ligand.

The ^1H NMR spectra (Table 6) of the $[CpRu(QPh)]PF_6$ and $[Cp^*Ru(QPh)]PF_6$ complexes exhibit upfield shifts of the bound phenyl group (15% for Cp, 20% for Cp*) and changes in J_{HH} coupling constants for the bound ring similar to those for complexes of Qth. In contrast to those of the Qth complexes, only small changes in the chemical shifts of the unbound phenyl ring resonances are observed in the complexes of QPh. For example, the proton H(2′) on the ring adjacent to the metal in QPh exhibits a downfield shift of 0.03 ppm (0.3%) for Cp and 0.09 ppm (1%) for Cp* while, in the complexes of Qth, the similarly positioned H(3′) exhibits a downfield shift of 0.25 ppm (3%) for Cp and 0.20 ppm (3%) for Cp*. In addition, the proton H(3′) on the unbound ring adjacent to the metal in QPh is found to shift *upfield* by 0.07−0.08 ppm (1%) while the equivalent proton for Qth (H(4′) shifts *downfield* by 0.02−0.03 ppm (0.5%). The interpretation of these chemical shifts for the second unbound ring from the ruthenium is more difficult because the H(3′) and H(2″/6″) protons on QPh constitute an AB pattern that is resolved as two doublets for QPh and $[Cp^*Ru(QPh)]PF_6$ but appears as a singlet for $[CpRu(QPh)]PF_6$. Simulation of these ^1H spectra gives a difference in chemical shifts for H(3′) and H(2″/6″) of 0.04 ppm for QPh, about 0.02 ppm for $[Cp^*Ru(QPh)]PF_6$, and only about 0.01 ppm for the $[CpRu(QPh)]PF_6$. In addition, the average chemical shift of this AB pattern for $[Cp^*Ru(QPh)]PF_6$ and $[Cp^*Ru(QPh)]PF_6$ is about the same as the average chemical shift of the AB pattern for QPh (7.76 ppm). Thus, there is a minimal change in the chemical shift (0.01−0.03 ppm, 0.1−0.3%) for protons H(3′) and H(2″/6″) in the complexes of QPh while, in the complexes of Qth, the similarly positioned protons H(3″) and H(4″) exhibit larger downfield shifts of 0.05−0.03 ppm (0.5−1%). These changes suggest that the ruthenium creates a larger deshielding effect at the unbound thiophene ring two rings away than for the equivalent unbound phenyl rings. Last, the ^1H NMR spectra of the complexes of both Qth and QPh show that there are no significant changes in the chemical shifts of the unbound ring three rings away from the ruthenium.

The larger downfield shift of the unbound rings in the Qth complexes most likely results from an adjustment of their aromaticity, caused by changes in inter-ring conjugation. Complexing the outer thiophene ring effectively reduces its inter-ring conjugation and allows the unbound thiophene ring adjacent to the metal to conjugate to only one other thiophene ring. This adjacent ring should have more localized aromaticity, a larger ring current, and a larger deshielding effect for its protons. The downfield shift of the second ring from the ruthenium may also occur through rearomatization or from the increased ring current of the adjacent thiophene ring.

Because the inter-ring conjugation of QPh is less than that of QTh, the binding of ruthenium to the outer ring of QPh leads to a smaller change in aromaticity (i.e. ring current) and a smaller deshielding effect for the nearby rings. In summary, a larger degree of "rearomatization" is most likely responsible for the larger downfield shift of the protons on the unbound rings of Qth compared to those of QPh.

Conclusions

We have synthesized mono- and diruthenated complexes of the form $[(CpRu)_n(oligothiophene)](PF_6)_n$ and $[(Cp^*Ru)_n(oligothiophene)](PF_6)_n$. The $CpRu^+$ and Cp^*Ru^+ fragments bind preferentially η^5 to the outer thiophene ring(s) of the oligothiophene chain. An equilibrium occurs between mono- and diruthenated complexes when acetonitrile is present or when the complexes are dissolved in a coordinating solvent. Detailed NMR experiments indicate that the electronic structure of the complexed oligothiophene is affected by the ruthenium and extends over the bound ring and the nearest neighbor and the next nearest neighbor unbound thiophene rings. Similar effects are observed in complexes of quaterphenyl, but these are of lesser magnitude because inter-ring conjugation is smaller in the polybenzenoid case. We predict that binding a ruthenium in the middle of a long thiophene ring chain will influence a total of five thiophene rings (the bound and the next two nearest rings in each direction). In the future, we intend to study these and related oligothiophene complexes with electrochemical techniques and electronic absorption/emission spectroscopy to gain a better understanding of how the ruthenium affects the oligothiophene electronic structure.

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