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Equilibrium and Kinetic Studies of Sulfur-Coordinated Thiophenes (Th) in $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$ and $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$: Models for Thiophene Adsorption on Hydrodesulfurization Catalysts

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A series of stable sulfur-bound thiophene complexes, $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$, where Cp = $\eta^5\text{-}C_5H_5$ and Th = T, 2-MeT, 3-MeT, 2,5-Me_2T, Me_4T, BT and DBT, are synthesized from the reaction of $Cp(CO)_2RuCl$ with Ag^+ and thiophenes. Equilibrium constants, K', for the displacement of thiophene (T) by methyl-substituted thiophenes and benzo[*b*]thiophene (BT), $Cp(CO)_2Ru(\eta^1(S)\text{-}T)^+ + Th \rightleftharpoons Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+ + T$, increase with an increasing number of methyl groups in the thiophene: T (1.00) < 2-MeT (3.30) < 3-MeT (4.76) < 2,5-Me_2T (20.7) < BT (47.6) < Me_4T (887). First-order rate constants (10^6k_1, s^{-1}) for phosphine substitution of the thiophenes in $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$, $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+ + PR_3 \rightarrow Cp(CO)_2Ru(PR_3)^+ + Th$, by a dissociative mechanism decrease in the following order: 3-MeT (450) > 2-MeT (410) > BT (100) > 2,5-Me_2T (23). Rate constants for thiophene dissociation in the analogous $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ complexes decrease in a slightly different order, T (1400) > 2-MeT (220) > 3-MeT (170) > 2,5-Me_2T (130) > BT (70) > DBT (17) > Me_4T (5.8), due to steric repulsions between the bulky PPh_3 and methyl groups in the 2- and 5-positions of the thiophene. In general, methyl groups on the thiophene (Th) increase K' and decrease k_1, which suggests that the electron-releasing methyl groups enhance thiophene binding to the metal. Thiophene binding on a Co–Mo/Al_2O_3 HDS catalyst also increases with the number of methyl groups in the thiophene. This trend is consistent with η^1(S) and/or η^5 coordination of thiophenes at metal sites on the catalyst surface.

Introduction

Catalytic hydrodesulfurization (HDS) is an important industrial process[2] for the removal of sulfur from petroleum feedstocks. A critical step in the mechanism(s) for the HDS of thiophene is its initial binding to a metal site on the catalyst surface. Organotransition-metal complexes of thiophene (T) and its methyl-substituted [2-methylthiophene (2-MeT), 3-methylthiophene (3-MeT), 2,5-dimethylthiophene (2,5-Me_2T) and tetramethylthiophene (Me_4T)] and benzo-substituted [benzo[*b*]thiophene (BT), dibenzothiophene (DBT)] derivatives provide models for possible modes[3] of thiophene adsorption. Of these modes, the sulfur-bound thiophene ($\eta^1(S)$-T) is one of the least studied since the thiophene S atom is such a weak donor. Thus, in known η^1(S)-bound thiophene complexes, $Cp(CO)_2Fe(Th)^+$ (Cp = $\eta^5\text{-}C_5H_5$, Th = T,[4] 2,5-Me_2T[5]), $(NH_3)_5Ru(T)^{2+}$,[6] $Cp(MeCN)_2Fe(2,5\text{-}Me_2T)^+$,[7] $W(CO)_3(PCy_3)_2(T)$,[8] $Cp'(CO)_2Re(T)$ (Cp′ = $\eta^5\text{-}C_5H_5$ or $\eta^5\text{-}C_5Me_5$),[9] $Cp(CO)(PPh_3)Ru(Th)^+$,[10] $(C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2^+$,[11] and $[Ru(HL)_2Cl][BF_4]$ (HL = 6-(2-thienyl)-2,2′-bipyridine),[12] the thiophene is easily displaced by other ligands (e.g. MeCN, C_4H_8S, and PPh_3).

Two recent studies of organometallic complexes containing the η^1(S)-bound thiophenes (Th) have examined the effect of methyl substitution on the ability of the thiophene ligand to coordinate to a metal center. Kinetic studies[13] of Th replacement in $Cp(CO)_2Re(\eta^1(S)\text{-}Th)$ by PPh_3 (eq 1) show that as the number of Me groups on the thiophene increases, the thiophene ligand binds more tightly to the Re. Thus, rate constants (10^7k_1, s^{-1}), which are determined by rate-limiting dissociation of the thiophene, decrease in the order T (3000) > 3-MeT (1200) > 2-MeT (91) > 2,5-Me_2T (13) > Me_4T (2.7) > DBT (1.6). This order is similar to that for the adsorption of

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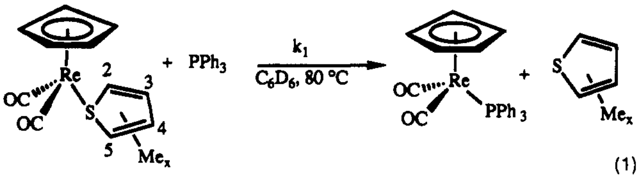
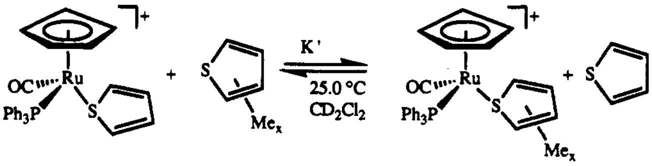


(1)

thiophenes on a sulfided Co–Mo/Al_2O_3 heterogeneous catalyst at 350 °C as measured by their relative adsorption coefficients,[14] K_{rel}: T (1.0) < 2-MeT (1.6) < 3-MeT (1.7) < 2,5-Me_2T (2.5). In an equilibrium study[10] of $\eta^1(S)$-Th displacement from Cp(CO)(PPh_3)Ru($\eta^1(S)$-Th)$^+$ (eq 2),



(2)

however, the following trend in K' values is observed: T (1.0) < 2,5-Me_2T (2.8) < 2-MeT (4.1) < 3-MeT (6.3). This order is the same as that for K_{rel} on the sulfided Co–Mo/Al_2O_3 except for the position of 2,5-Me_2T. The lower K' for 2,5-Me_2T in reaction 2 probably results from steric repulsion between an α-methyl group on 2,5-Me_2T and the bulky phosphine phenyl rings.[10]

To further explore this steric effect, a new series of thiophene complexes, $Cp(CO)_2Ru(\eta^1(S)\text{-Th})^+$ (Th = T (**1**), 2-MeT (**2**), 3-MeT (**3**), 2,5-Me_2T (**4**), Me_4T (**5**), BT (**6**), DBT (**7**), has been prepared. Here, a CO ligand replaces the bulky PPh_3 in the Ru coordination sphere, thereby greatly reducing steric effects of the 2- and 5-Me groups on Th. Equilibrium constants for this new series of thiophene complexes are compared with those in the previous study of Cp(CO)(PPh_3)Ru($\eta^1(S)$-Th)$^+$ (eq 2).[10] Also, kinetic studies of thiophene substitution in $Cp(CO)_2$Ru($\eta^1(S)$-Th)$^+$ and Cp(CO)(PPh_3)Ru($\eta^1(S)$-Th)$^+$ by phosphine ligands, PPh_3, PPh_2Me, and $PPhMe_2$, are reported; factors that affect the mechanisms and rates of these reactions are discussed.

Experimental Section

General Procedures. All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques.[15] Solvents were dried prior to use: methylene chloride, hexanes, and heptanes were distilled from CaH_2 and diethyl ether was distilled from sodium/benzophenone. Hexanes, heptanes, and methylene chloride were stored under nitrogen over molecular sieves. Neutral Al_2O_3, purchased from Aldrich, was deactivated with 5% deionized water after 24 h under vacuum. Deuterated solvents for NMR experiments were purchased from Cambridge and stored over molecular sieves in a desiccator. Thiophene was purified as previously described.[16] Solid thiophenes, DBT and BT, were purchased from Aldrich and sublimed prior to use. Starting materials $Ru_3(CO)_{12}$,[17] Me_4T,[18] $Cp(CO)_2RuCl$,[19] and Cp(CO)(PPh_3)Ru($\eta^1(S)$-Th)$^+$ (Th = T, 2-MeT, 3-MeT, 2,5-Me_2T, Me_4T, BT, DBT)[10] were prepared as previously described. Thiophene ligands 2-MeT, 3-MeT, and 2,5-Me_2T as well as $AgBF_4$, PPh_3, PPh_2Me, and $PPhMe_2$ were purchased from Aldrich and used without further purification.

Infrared spectra of the compounds in CH_2Cl_2 were taken using a Nicolet 710 FT-IR spectrometer. Fast atom bombardment (FAB) mass spectra of compounds in a CH_2Cl_2/3-nitrobenzyl alcohol matrix were obtained using a Kratos MS-50 mass spectrometer. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Nicolet NT-300, Bruker WM-200, or Varian VXR-300 spectrometer using CD_2Cl_2 as the solvent and the internal lock. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

General Procedure for the Preparation of [$Cp(CO)_2Ru(\eta^1(S)\text{-Th})$]$BF_4$ Complexes (1–7). To a solution of $Cp(CO)_2RuCl$ (50.2 mg, 0.195 mmol) and 0.97 mmol of Th in 20 mL of CH_2Cl_2 was added solid $AgBF_4$ (49.1 mg, 0.252 mmol); the solution was stirred at room temperature for 1 h. A white precipitate formed immediately, and the solution color lightened. After 1 h, the solution was filtered through Celite, and the volatiles were removed under vacuum (excess BT and DBT were removed with 3–5-mL diethyl ether washes). The residue was dissolved in 2 mL of CH_2Cl_2 and precipitated with 10 mL of diethyl ether at −20 °C, giving light yellow compounds, **1**–**7**, in 70–85% yields.

Characterization of 1–7. [$Cp(CO)_2Ru(T)$]BF_4 (1). ^{1}H NMR: δ 7.67 (m, 2 H) and 7.33 (m, 2 H) T; 5.73 (s, 5 H) Cp. $^{13}C\{^1H\}$ NMR: δ 138.3 (s) and 133.0 (s) T; 192.7 (s), CO; 89.7 (s), Cp. IR: ν(CO) 2080, 2034 cm^{-1}.

[$Cp(CO)_2Ru(2\text{-MeT})$]BF_4 (2). ^{1}H NMR: δ 7.45 (dd, J = 5.4, 0.9 Hz, 1 H), 7.10 (m, 1 H), 6.99 (m, 1 H) and 2.45 (d, J = 1.2 Hz, 3 H), 2-MeT; 5.70 (s, 5 H) Cp. $^{13}C\{^1H\}$ NMR: δ 150.8 (s), 136.1 (s), 132.9 (s), 130.8 (s) and 14.3 (s), 2-MeT; 192.9 (s), CO; 89.8 (s), Cp. IR: ν(CO) 2080, 2033 cm^{-1}. Anal. Calcd for $C_{12}H_{11}BF_4O_2RuS$: C, 35.40; H, 2.72. Found: C, 34.90; H, 2.52.

[$Cp(CO)_2Ru(3\text{-MeT})$]BF_4 (3). ^{1}H NMR: δ 7.56 (dd, J = 5.1, 2.7 Hz, 1 H), 7.13 (m, 2 H) and 2.33 (d, J = 1.2 Hz, 3 H), 3-MeT; 5.72 (s, 5 H) Cp. $^{13}C\{^1H\}$ NMR: δ 145.0 (s), 138.1 (s), 136.3 (s), 130.9 (s), and 16.4 (s), 3-MeT; 192.9 (s), CO; 89.6 (s), Cp. IR: ν(CO) 2079, 2033 cm^{-1}. Anal. Calcd for $C_{12}H_{11}BF_4O_2RuS$: C, 35.40; H, 2.72. Found: C, 35.32; H, 2.69.

[$Cp(CO)_2Ru(2,5\text{-}Me_2T)$]$BF_4$ (4). ^{1}H NMR: δ 6.77 (s, 2 H) and 2.38 (s, 6 H), 2,5-Me_2T; 5.61 (s, 5 H) Cp. $^{13}C\{^1H\}$ NMR: δ 148.2 (s), 130.5 (s) and 14.6 (s), 2,5-Me_2T; 193.1 (s), CO; 90.1 (s), Cp. IR: ν(CO) 2080, 2034 cm^{-1}. Anal. Calcd for $C_{13}H_{13}BF_4O_2RuS$: C, 36.88; H, 3.09. Found: C, 36.44; H, 2.79.

[$Cp(CO)_2Ru(Me_4T)$]BF_4 (5). ^{1}H NMR: δ 2.26 (s, 6 H) and 2.05 (s, 6 H), Me_4T; 5.63 (s, 5 H) Cp. $^{13}C\{^1H\}$ NMR: δ 141.2 (s), 136.8 (s), 13.8 (s) and 12.6 (s), Me_4T; 193.5 (s), CO; 90.0 (s), Cp. IR: ν(CO) 2076, 2030 cm^{-1}. FAB: m/e 363 (M$^+$), 306 (M$^+$ − 2CO), 223 (M$^+$ − Me_4T). Anal. Calcd for $C_{15}H_{17}BF_4O_2RuS$: C, 40.07; H, 3.81. Found: C, 39.59; H, 3.44.

[$Cp(CO)_2Ru(BT)$]BF_4 (6). ^{1}H NMR: δ 7.93 (m, 2 H), 7.60 (m, 2 H) and 7.54 (s, 2 H), BT; 5.74 (s, 5 H) Cp. $^{13}C\{^1H\}$ NMR: δ 143.7 (s), 140.1 (s), 133.4 (s), 131.8 (s), 129.6 (s), 128.4 (s), 126.9 (s) and 124.9 (s), BT; 192.9 (s), CO; 89.9 (s), Cp. IR: ν(CO) 2079, 2032 cm^{-1}. FAB: m/e 357 (M$^+$), 301 (M$^+$ − 2CO), 223 (M$^+$ − BT). Anal. Calcd for $C_{15}H_{11}BF_4O_2RuS$: C, 40.65; H, 2.50. Found: C, 40.31; H, 2.41.

[$Cp(CO)_2Ru(DBT)$]BF_4 (7). ^{1}H NMR: δ 8.16 (m, 2 H), 7.93 (m, 2 H), and 7.68 (m, 4 H), DBT; 5.74 (s) Cp. $^{13}C\{^1H\}$ NMR: δ 140.6 (s), 137.1 (s), 130.3 (s), 130.1 (s), 125.8 (s) and 123.7 (s), DBT; 192.9 (s), CO; 90.1 (s), Cp. IR: ν(CO) 2078, 2034 cm^{-1}. Anal. Calcd for $C_{19}H_{13}BF_4O_2RuS$: C, 46.27; H, 2.66. Found: C, 45.81; H, 2.52.

Synthesis of Cp(CO)(PPh_2Me)RuCl (8). This complex was prepared by the method used previously for the synthesis of Cp(CO)(PPh_3)RuCl.[20] A solution of 0.136 g of $Ru_3(CO)_{12}$ (0.213 mmol) and 1.0 mL of freshly distilled cyclopentadiene (15.2 mmol)

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in 60 mL of heptanes was refluxed for 3 h. To the hot solution was added 120 μL of PPh_2Me, and the solution was refluxed for another 30 min. The solvent was removed under vacuum, and the residue was dissolved in 15 mL of $CHCl_3$ and stirred for 12 h. Following removal of the solvent, the residue was chromatographed on neutral alumina. The complex of interest was collected as the third yellow band using a 1:1 mixture of CH_2Cl_2 and hexanes as the eluting solvent. Following recrystallization from CH_2Cl_2 and hexanes, 0.120 g of $Cp(CO)(PPh_2Me)RuCl$ was recovered as orange crystals in 44% yield. IR: ν(CO) 1956 cm^{-1}. ^1H NMR: δ 4.90 (s, 5 H, Cp), 7.60–7.35 (m, Ph), 2.14 (d, $^2J_{HP}$ = 10 Hz, Me). $^{13}C\{^1H\}$ NMR: δ 200.8 (d, $^2J_{CP}$ = 21.4 Hz, CO); 137.7 (d, $^1J_{CP}$ = 46.1 Hz), 136.4 (d, $^1J_{CP}$ = 51.2 Hz), 132.4 (d, J_{CP} = 10.9 Hz), 131.3 (d, J_{CP} = 10.3 Hz), 130.4 (d, J_{CP} = 2.5 Hz), 130.0 (d, J_{CP} = 2.6 Hz), 128.5 (d, J_{CP} = 10.2 Hz) and 128.3 (d, J_{CP} = 10.2 Hz), PPh; 85.4 (d, $^2J_{CP}$ = 2.1 Hz, Cp); 16.7 (d, $^1J_{CP}$ = 33.9 Hz, PMe). The IR and ^1H NMR spectra are very similar to those of the corresponding PPh_3 complex.[20]

Synthesis of [Cp(CO)(PPh₂Me)Ru(η¹(*S*)-3-MeT)]BF₄ (9). To a solution of 50.1 mg of $Cp(CO)(PPh_2Me)RuCl$ (0.117 mmol) and 75 μL (0.59 mmol) of 3-MeT in 20 mL of CH_2Cl_2 was added 38.5 mg (0.198 mmol) of solid $AgBF_4$. The solution was stirred for 1 h at room temperature, during which time a precipitate formed and the solution color changed from orange to yellow. The solution was filtered through Celite, and the volatiles were removed under vacuum. The residue was dissolved in 2 mL of CH_2Cl_2 to give a solution to which was added 15 mL of Et_2O; 8 separated as an oil. IR: ν(CO) 1993 cm^{-1}. ^1H NMR: δ 7.04 (dd, J = 5.1, 2.7 Hz, 1 H), 6.96 (dd, J = 5.4, 1.2 Hz, 1 H), 6.66 (m, 1 H) and 2.19 (d, J_{HH} = 1.2 Hz, 3 H), 3-MeT; 5.05 (s, 5 H, Cp); 7.65–7.40 (m, 10 H) and 2.27 (d, $^2J_{PH}$ = 9.5 Hz, 3 H) PPh_2Me. $^{13}C\{^1H\}$ NMR: δ 143.5 (s), 138.0 (d, $^3J_{CP}$ = 2.1 Hz), 135.1 (s), 131.5 (s) and 16.3 (s), 3-MeT; 200.3 (d, $^2J_{CP}$ = 18.3 Hz, CO); 135.0 (d, $^1J_{CP}$ = 51.8 Hz), 134.2 (d, $^1J_{CP}$ = 51.7 Hz), 132.2 (d, J_{CP} = 11.2 Hz), 131.9 (d, J_{CP} = 2.6 Hz), 131.5 (d, J_{CP} = 10.8 Hz), 131.2 (d, J_{CP} = 2.3 Hz), 129.6 (d, J_{CP} = 10.6 Hz) and 129.5 (d, J_{CP} = 10.5 Hz), PPh; 87.5 (d, $^2J_{CP}$ = 1.7 Hz, Cp); 19.6 (d, $^1J_{CP}$ = 34.9 Hz, PMe). These spectral features are very similar to those of $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-3-MeT})^+$.[10]

Equilibrium Studies. Equilibrium constants, *K*, were determined for the thiophene substitution reactions in eq 3 by ^1H NMR spectrometry. Approximately 0.020 mmol (8.2–9.4 mg) of

$$Cp(CO)_2Ru(\eta^1(S)\text{-Th})^+ + Th' \underset{25.0\,°C}{\overset{K}{\rightleftharpoons}} Cp(CO)_2Ru(\eta^1(S)\text{-Th}')^+ + Th \quad (3)$$

a $[Cp(CO)_2Ru(\eta^1(S)\text{-Th})]BF_4$ complex was placed in a 5-mm NMR tube, dissolved in 0.50 mL of CD_2Cl_2 under nitrogen, and mixed with an equimolar amount of another thiophene (Th′). The tube was placed in liquid nitrogen and flame-sealed under vacuum. The solution was allowed to thaw, and the tube was placed in a 25.0 ± 0.1 °C temperature bath. The ^1H NMR spectrum of the sample was recorded on a Varian VXR-300 spectrometer with the probe thermostated at 25.0 ± 0.1 °C using CD_2Cl_2 as the solvent, internal lock, and reference (δ 5.32 ppm). Equilibrium constants, *K*, for eq 3 were calculated from integrations of the proton signals of each species in the ^1H NMR spectrum using eq 4, where I_{Cp} and $I_{Cp'}$ are the integrals of the Cp peaks of each

$$K = \frac{[Cp(CO)_2Ru(Th')^+][Th]}{[Cp(CO)_2Ru(Th)^+][Th']} = \frac{\left(\frac{I_{Cp'}}{5}\right)\left(\frac{I_{Th}}{x}\right)}{\left(\frac{I_{Cp}}{5}\right)\left(\frac{I_{Th'}}{y}\right)} \quad (4)$$

complex, I_{Th} and $I_{Th'}$ are integrals of the free thiophenes, and x and y are the numbers of protons for the particular thiophene peaks being integrated. The Me peaks were integrated on 2-MeT, 3-MeT, and Me_4T. The signal for H3 and H4 on 2,5-Me_2T and T and the H2 peak on BT were integrated. For example, if Th = 2-MeT and Th′ = T, then x = 3 and y = 2. A long delay time of 38 s between scans was used so that all the protons were fully relaxed. The reactions were followed by NMR to make sure that they reached equilibrium. This occurred within 24 h for most reactions. The reaction of $Cp(CO)_2Ru(\eta^1(S)\text{-}Me_4T)^+$ with BT (reaction G, Table I) took 52 h to reach equilibrium. Each equilibrium constant is the average of at least three different spectra taken during a 2–49-day period. Solutions containing complexes of 2-MeT, 3-MeT, and T showed some signs of decomposition; the solution color turned from yellow to orange, and new Cp peaks appeared in the NMR spectra at δ 5.58 (most intense), 5.55, and 5.51 (ppm). Over a period of 3 weeks, however, this decomposition was less than 5% of the Ru complex; the equilibrium constants were not affected by this decomposition because they are based on integrals of all reactants and products in eq 3. The *K* values resulting from these studies are shown in Table I.

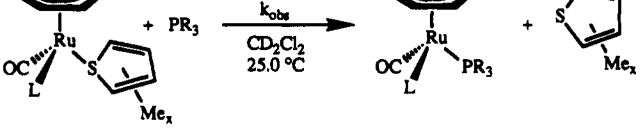
Table I. Equilibrium Constants, *K*, for Reactions (Eq 3) of $Cp(CO)_2Ru(\eta^1(S)\text{-Th})^+$ with Th′ at 25.0 °C in CD_2Cl_2

reacn	Th	Th′	*K*
A	2-MeT	T	0.303 (1)
B	2-MeT	3-MeT	1.52 (5)
C	2-MeT	2,5-Me_2T	6.26
D	BT	2,5-Me_2T	0.435 (11)
E	3-MeT	T	0.210 (12)
F	3-MeT	2-MeT	0.660
G	Me_4T	BT	0.0526
H	BT	Me_4T	19.2
I	2,5-Me_2T	Me_4T	40.7

Table II. Rate Constants, k_{obs} (s^{-1}), for Reactions of 0.010 M $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-Th})^+$ with PR_3 at 25.0 °C in CD_2Cl_2 According to Eq 5

		10^4k_{obs}, s^{-1}		
Th	PR_3	0.10 M PR_3	0.20 M PR_3	0.40 M PR_3
T	PPh_3	11.1 (5)	15.0 (3)	17.1 (6)
2-MeT	PPh_3	2.3 (1)	2.1 (1)	2.2 (1)
3-MeT	PPh_3	1.7 (1)	1.7 (1)	1.8 (1)
2,5-Me_2T	PPh_3	1.2 (1)	1.3 (1)	1.3 (1)
BT	PPh_3	0.64 (3)	0.70 (1)	0.76 (1)
	$PPhMe_2$	0.66 (2)	0.71 (2)	0.75 (2)
DBT	PPh_3	0.16 (1)	0.16 (2)	0.18 (3)
Me_4T	PPh_3	0.055 (1)	0.056 (1)	0.063 (1)

Kinetic Studies. Reaction solutions of $Cp(CO)_2Ru(\eta^1(S)\text{-Th})[BF_4]$ (Th = 2-MeT, 3-MeT, BT, and 2,5-Me_2T), $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-Th})[BF_4]$ (Th = T, 2-MeT, 3-MeT, 2,5-Me_2T, and BT) and $Cp(CO)(PPh_2Me)Ru(\eta^1(S)\text{-3-MeT})[BF_4]$, whose reaction (eq 5) half-lives were less than 7 h, were prepared as follows.



L = CO, PPh₃, PPh₂Me (5)

A 0.0050-mmol sample of the complex was placed in an NMR tube with an excess, weighed amount of PPh_3. The tube was evacuated, flushed with nitrogen, and capped with a septum. A 0.50-mL aliquot of CD_2Cl_2 was added, and the tube was shaken to dissolve the reactants. The tube was immediately placed in the probe of a Varian VXR-300 NMR spectrometer thermostated at 25.0 ± 0.1 °C. The spectrometer was preprogrammed to take spectra at specific time intervals; the acquisition time for each spectrum was 60 s (16 scans at 3.744 s/scan). Rate constants, k_{obs}, were obtained from the least-squares slopes of plots of ln (1 + F) (where F = [product]/[reactant]) vs time; reactant and product concentrations were determined by integrating Cp peaks. Correlation coefficients of these plots were always greater than 0.995. Three samples were run at each concentration; the results (Tables II and III) are the average of the three runs at each concentration with the average deviation in the last digit given

Table III. Rate Constants, k_{obs} (s^{-1}), for Reactions of 0.010 M $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$ with PR_3 at 25.0 °C in CD_2Cl_2 According to Eq 5

Th	PR$_3$	[PR$_3$], M	10^4k_{obs}, s^{-1}
2-MeT	PPh$_3$	0.10	4.1 (2)
		0.20	4.1 (1)
		0.40	4.1 (1)
3-MeT	PPh$_3$	0.10	4.5 (1)
		0.20	4.4 (2)
		0.40	4.7 (1)
BT	PPh$_3$	0.10	0.99 (2)
		0.20	0.99 (2)
		0.40	1.1 (1)
2,5-Me$_2$T	PPh$_3$	0.10	0.27 (1)
		0.20	0.30 (3)
		0.30	0.35 (1)
		0.40	0.37 (1)
	PPh$_2$Me	0.10	0.45 (1)
		0.15	0.53 (7)
		0.20	0.64 (3)
		0.30	0.86 (9)
	PPhMe$_2$	0.10	3.7 (1)

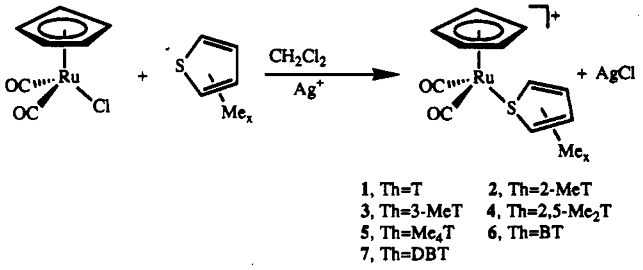
in parentheses. The products formed in these kinetic studies were $Cp(CO)_2(PPh_3)Ru^+$ or $Cp(CO)(PPh_3)_2Ru^+$, and the free thiophenes; they were identified by their NMR spectra, which were the same as those previously reported in the literature.[20-22] The product $Cp(CO)(PPh_3)Ru(PPh_2Me)^+$ (δ 5.02 ppm, Cp) was identified from its ^{1}H NMR spectrum, which was similar to that of $Cp(CO)(PPh_3)_2Ru^+$.[20,21]

Preparations of samples of $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)[BF_4]$ (Th = Me$_4$T and DBT), whose reaction half-lives were greater than 12 h, were slightly different. A sample (0.0050 mmol) of $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ was placed in an NMR tube with an excess, weighed amount of PPh$_3$. The tube was evacuated and flushed with nitrogen. A 0.50-mL aliquot of CD_2Cl_2 was added, and the tube was immediately immersed in liquid nitrogen. The tube was then flame-sealed under vacuum. After the solution thawed, the tube was placed in a constant-temperature bath thermostated at 25.0 ± 0.1 °C. Periodically the tube was removed from the bath and placed in the probe and a spectrum was recorded on a Nicolet NT-300 spectrometer at room temperature using CD_2Cl_2 as the internal lock and standard (δ 5.32). The tube was then returned to the bath within a 15-min period. The peaks of interest were integrated using a curve-fitting routine on NMRi[23] software. Rate constants were calculated as described above. Three samples were run at each phosphine concentration; the k_{obs} values given in Table III are the average of the three runs with the average deviation in the last digit given in parentheses.

For kinetic studies of reactions using the liquid phosphines PPh$_2$Me and PPhMe$_2$ 0.0050 mmol of $Cp(CO)_2Ru(\eta^1(S)\text{-}2,5\text{-}Me_2T)[BF_4]$ or $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}BT)[BF_4]$ was placed in an NMR tube. The tube was evacuated and flushed with nitrogen. Under a flow of nitrogen, 0.50 mL of CD_2Cl_2 was added, and the tube was capped with a septum. The phosphine was injected into the solution through the septum using a microsyringe, and the tube was immediately placed in the probe of a Varian VXR-300 spectrometer thermostated at 25.0 ± 0.1 °C. The spectrometer was programmed to acquire spectra at specific time intervals, and the data were worked up as described above. The products of these kinetic reactions were identified from their ^{1}H NMR spectra, which were similar to those of $Cp(CO)_2(PPh_3)Ru^+$ [20,21] or $Cp(CO)(PPh_3)_2Ru^+$,[22] reported in the literature: $Cp(CO)(PPh_3)Ru(PPhMe_2)^+$ (δ 5.02 ppm, Cp), $Cp(CO)_2Ru(PPh_2Me)^+$ (δ 5.63 ppm, Cp), and $Cp(CO)_2Ru(PPhMe_2)^+$ (δ 5.59 ppm, Cp).

Results

Synthesis of $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$ (1–7). The thiophene-containing complexes $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$ (1–7) were synthesized in a manner identical to that of the $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ complexes[10] using AgBF$_4$ to abstract the Cl$^-$ from $Cp(CO)_2RuCl$ in the presence of excess thiophene (eq 6). The structures of BT and DBT are shown as well. These complexes are thermally less stable and are more air-sensitive than the corresponding $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ complexes. The alkyl and aryl iodide complexes of $Cp(CO)(PPh_3)Ru(I\text{-}R)^+$ (R = alkyl, aryl)[24] were also more stable than their $Cp(CO)_2Ru(I\text{-}R)^+$ analogs. The thiophene complex 1 was not isolated as an analytically pure compound but was identified by its ^{1}H and ^{13}C NMR and IR spectra. Solid samples of the T (1), 2-MeT (2), and 3-MeT (3) complexes show noticeable decomposition at room temperature in air and under nitrogen after 24 h but may be kept under N$_2$ at −20 °C for over 1 month. In CD_2Cl_2 solution, complexes 1, 2, and 3 also show decomposition within 24 h, producing the free thiophenes and a number of species containing the Cp ligand (in all cases, the major product has a Cp peak at δ 5.58 ppm in the ^{1}H NMR) as seen in the ^{1}H NMR spectra. None of these products were identified. There was also no evidence for $CpRu(\eta^5\text{-}T)^+$, which exhibits a singlet at δ 5.40 ppm (Cp) and a pair of multiplets at δ 6.32 and 6.16 ppm (T).[25] The η^5-T complex was previously identified as a product of the decomposition of $Cp(PPh_3)_2Ru(\eta^1(S)\text{-}T)^+$ in CD_2Cl_2.[11] On the other hand, the $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}T)^+$ complex, which is stable at room temperature in solution, decomposes in refluxing CH_2Cl_2 to give the Cl bridging dimer $[Cp(CO)(PPh_3)Ru]_2Cl^+$ (IR ν(CO) 1973 cm^{-1}; ^{1}H NMR δ 4.82 (s, Cp), 7.54 (m), 7.45 (m) and 7.25 (m, PPh$_3$); FAB *m/e* 948.8 (M$^+$)). Similar halide bridging dimers,[26] e.g. $[Cp(CO)_2M]_2X^+$ (M = Fe, Ru; X = Cl, Br, I) are known. Complexes 4–7 are stable as solids and in solution at room temperature under N$_2$. The DBT complex 7 is only slightly soluble in CH_2Cl_2. Due to its low solubility, 7 was not used in either the kinetic or equilibrium experiments.



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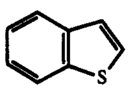
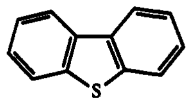


BT



DBT

Reactions of $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$ and $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ with PPh$_3$ produce the substituted

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products $Cp(CO)_2(PPh_3)Ru^+$ [20,21] and $Cp(CO)(PPh_3)_2Ru^+$,[22] respectively, and the free thiophenes (see Kinetic Studies in the Experimental Section). Likewise, reactions of $Cp(CO)_2Ru(\eta^1(S)\text{-BT})^+$ and $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-T})^+$ with $[(n\text{-Bu})_4N]Br$ give $Cp(CO)_2RuBr$[19] and $Cp(CO)(PPh_3)RuBr$[27] and free Th; $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-BT})^+$ reacts with MeCN to give $Cp(CO)(PPh_3)Ru(NCMe)^+$ [10,24] and BT. These reaction products were identified by comparison of their ^1H NMR spectra with those reported in the literature for these compounds.

Compounds **1**–**7** were characterized by IR and ^1H and $^{13}C\{^1H\}$ NMR, FAB mass spectroscopy, and elemental analysis (see Experimental Section). The $\nu(CO)$ absorptions in their IR spectra are 24–30 cm^{-1} higher than those of the neutral starting material, $Cp(CO)_2RuCl$ ($\nu(CO)$ = 2056, 2004 cm^{-1}). The Cp protons in their ^1H NMR spectra are slightly deshielded (0.15–0.29 ppm) as compared with $Cp(CO)_2RuCl$ (δ 5.45 ppm). The thiophene ring protons in **1**–**4** are downfield (0.11–0.27 ppm) from those of the free thiophene, as was found in the $Cp(CO)_2Fe(\eta^1(S)\text{-T})^+$ [4a] complex. These resonances are also slightly downfield of those in the $Cp(CO)_2Re(\eta^1(S)\text{-Th})$[9] and $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-Th})^+$ [10] complexes with more electron-rich metal centers. If the thiophene ligands were bound to the metal in an η^2 fashion through one of the C–C double bonds, the thiophene ring protons would be expected to shift significantly upfield, as reported for complexes of η^2-thiophene,[28] η^2-selenophenes,[29] η^2-benzo[*b*]thiophene,[3c,d] and olefins.[30] In the ^{13}C NMR spectra of complexes **1**–**7**, the thiophene carbons are slightly downfield (5.8–11.0 ppm) of those in the free thiophene, as was also observed for $Cp(CO)_2Fe(\eta^1(S)\text{-Th})^+$,[4a] $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-Th})^+$,[10] and $Cp(CO)_2Re(\eta^1(S)\text{-Th})$.[9] Again, an upfield shift in the ^{13}C resonances would have been expected[3c,29] for η^2-carbons if the thiophenes were η^2-bound through two carbons. Thus, the NMR spectra establish that the thiophenes are η^1(S)-bound. This type of coordination is confirmed by X-ray diffraction studies of $Cp(CO)_2Re(\eta^1(S)\text{-T})$[9] and $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-2-MeT})^+$.[10]

Only one CO resonance is observed in ^{13}C NMR spectra of complexes **2**, **3**, and **6** at room temperature in CD_2Cl_2. If the unsymmetric thiophenes in these complexes were nonfluxional, one would expect the diastereotopic CO groups to give two signals. Thus, there is a dynamic process which makes the two carbonyls equivalent on the NMR time scale. At temperatures below 198 K, the ^{13}C NMR spectrum of $Cp(CO)_2Ru(\eta^1(S)\text{-BT})^+$ in CD_2Cl_2 shows two peaks (δ 192.9 and 192.5 ppm) for the CO groups. At the coalescence temperature (205 K), the free energy of activation, $\Delta G^\ddagger$, is calculated[31] to be 43 kJ/mol. The fluxional process involved is likely to be inversion of the thiophene sulfur, as has been observed in other systems.[4a,10,32] Previously, $\Delta G^\ddagger$ values of 39 kJ/mol at 190 K[4a] for $Cp(CO)_2Fe(\eta^1(S)\text{-BT})^+$ and 40 kJ/mol at 213 K[10] for $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-Th})^+$ (Th = 2,5-Me_2T and Me_4T) were obtained. Since $Cp(CO)_2Ru(\eta^1(S)\text{-BT})^+$ has a higher inversion barrier at higher temperature than $Cp(CO)_2Fe(\eta^1(S)\text{-BT})^+$, the inversion is slower in the Ru complex.

Equilibrium Studies. Results of equilibrium studies of reaction 3 are shown in Table I. Numbers in parentheses are average deviations for at least three runs of the same reaction. Reactions B and F along with G and H approach equilibrium from opposite directions. The *K* value for reaction B (1.52) is identical to that of the reciprocal of F (1/0.660 = 1.52); likewise, the *K* value for H (19.2) is within experimental error of that of the reciprocal of G (1/0.0526 = 19.0). Similarly, adding reactions A and F together gives reaction E. Multiplying the experimental *K* values for A (0.303) and F (0.660) gives a calculated *K* value for reaction E of 0.200, which is within 5% of the experimental *K* value for reaction E (0.210). All other comparisons done in this manner result in calculated values that are within 6% of the directly measured value, ensuring the validity of the experimental *K* values.

Kinetic Studies. Results of kinetic studies of thiophene replacement in $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-Th})^+$ and $Cp(CO)_2Ru(\eta^1(S)\text{-Th})^+$ with PR_3 (PR_3 = PPh_3, PPh_2Me, $PPhMe_2$) according to eq 5 are shown in Tables II and III. The studies were done under pseudo first-order conditions, always with a greater than 10-fold excess of phosphine. Except for the reactions of $Cp(CO)_2Ru(\eta^1(S)\text{-2,5-Me}_2T)^+$ (**4**), the k_{obs} values are independent of phosphine concentration within experimental error (Tables II and III) and follow the rate law in eq 7, where $k_{obs} = k_1$. This rate

$$\frac{d[Cp(CO)(L)Ru(\eta^1(S)\text{-Th})^+]}{dt} = k_{obs}[Cp(CO)(L)Ru(\eta^1(S)\text{-Th})^+] \quad (7)$$

law indicates that the slow step in these reactions is the dissociation of Th from the Ru; this is followed by fast reaction of the 16 e$^-$ intermediate with PR_3 to form the product.

For the reaction of $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-BT})^+$ with PPh_3, the rate constants (Table II) appear to increase with increasing phosphine concentration; however, when the more basic, less sterically crowded phosphine PMe_2Ph is used as the incoming nucleophile, the reaction rate constants are the same within experimental error. So, the reactions of this complex also follow the first-order rate law (eq 7), but the errors are larger than in the other reactions.

Rate constants (k_{obs}) for the reactions of complex **4** increase slightly with increasing PPh_3 concentration. It is evident (Table III and Figure 1) that there is a phosphine dependence in this case, and the rate law contains both first- and second-order terms (eq 8). Linear correlations

$$k_{obs} = k_1 + k_2[PR_3] \quad (8)$$

(Figure 1) are obtained when the k_{obs} values (Table III) for the reactions of **4** with PPh_3 and PPh_2Me are plotted against phosphine concentration. The lines fit eq 9 (PPh_3) and eq 10 (PPh_2Me) as determined by linear least-squares

$$k_{obs} = 0.235 \times 10^{-4} + (0.350 \times 10^{-4})[PPh_3] \quad (9)$$

$$k_{obs} = 0.230 \times 10^{-4} + (2.08 \times 10^{-4})[PPh_2Me] \quad (10)$$

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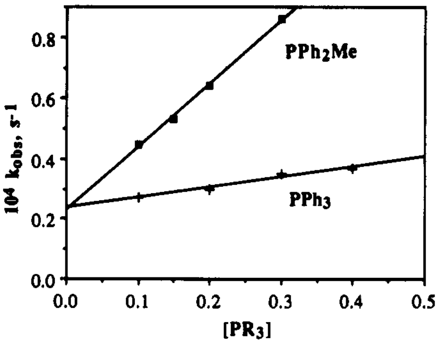


Figure 1. Plot of k_{obs} vs phosphine concentration for the reactions of $Cp(CO)_2Ru(\eta^1(S)\text{-}2,5\text{-}Me_2T)^+$ (4) with PPh_2Me and PPh_3 according to eq 5 at 25 °C.

regression analysis (the correlation coefficients $r = 0.988$ and 0.998, respectively). The y intercepts of both lines give the same value for k_1 within experimental error. The slope of the PPh_2Me line gives a second-order rate constant ($k_2 = 2.08 \times 10^{-4}\ M^{-1}\ s^{-1}$) that is larger than that of the PPh_3 line ($k_2 = 0.350 \times 10^{-4}\ M^{-1}\ s^{-1}$), which is consistent with PPh_2Me being the better nucleophile.

Due to its instability, 1 was not obtained as a pure compound and detailed kinetic studies of its reaction with PPh_3 were not performed. However, a reaction of 1 with a 10-fold excess of PPh_3 at room temperature is complete within 30 min; this is faster than reactions of 2 or 3 with PPh_3 under the same conditions.

The k_{obs} values (Table III) for the reactions of 4 with PPh_2Me show greater errors than for all of the other reactions. These errors may be due, in part, to light catalysis of the reaction. This was demonstrated by observing that the reaction was only 10% complete after 12 min when the NMR reaction tube was wrapped in aluminum foil prior to placing it in the spectrometer probe and taking the first spectrum. The same reaction, when allowed to stand in the light for the same amount of time, was more than 75% complete. Since tubes in the NMR probe are not completely shielded from light, this exposure probably affects the reproducibility of the reactions with PPh_2Me. The reaction of 5 with PPh_3 was so light-sensitive that it was impossible to obtain reproducible rate constants.

Reactions of $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}T)^+$ and $Cp(CO)_2Ru(\eta^1(S)\text{-}BT)^+$ with Br^- to give $Cp(CO)(PPh_3)RuBr$[27] and $Cp(CO)_2RuBr$[19] are very rapid compared to those with phosphines. In an NMR tube, reactions of 0.020 mol of both Ru complexes with 0.080 mol of $[(n\text{-}Bu)_4N]Br$ in 0.50 mL of CD_2Cl_2 were complete before the first spectrum was taken (less than 5 min). Under the same conditions, the reaction of $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}T)^+$ with PPh_3 requires 35 min to reach 95% completion. Thus, unlike PPh_3 reactions, those of Br^- presumably involve nucleophilic attack on the complex.

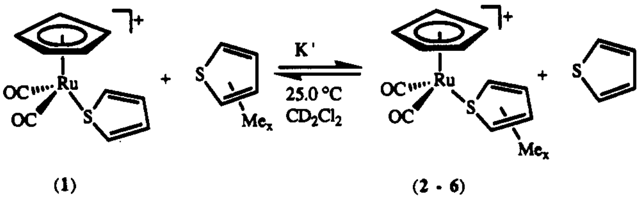
Discussion

Equilibrium Studies of Thiophene Substitution in $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$. Relative equilibrium constants, K', for the displacement of thiophene by methyl-substituted thiophenes and benzo[*b*]thiophene (eq 11) were calculated from the experimental K values in Table I. These values together with K' values for the analogous equilibrium (eq 2)[10] involving $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ are given in Table IV.

Table IV. Relative Equilibrium Constants, K', for Reactions (Eqs 11 and 2) of $Cp(CO)(L)Ru(\eta^1(S)\text{-}Th)^+$ with Th′ at 25.0 °C

Th	$Cp(CO)_2Ru(Th)^+$	$Cp(CO)(PPh_3)Ru(Th)^{+\,a}$
T	1.00	1.00
2-MeT	3.30	4.11
3-MeT	4.76	6.30
2,5-Me_2T	20.7	2.76
BT	47.6	29.9
Me_4T	887	57.4
DBT		74.1

[a] Reference 10.



(1) (2 - 6) (11)

The K' values for reaction 11 increase in the following order: T (1.00) < 2-MeT (3.30) < 3-MeT (4.76) < 2,5-Me_2T (20.7) < BT (47.6) < Me_4T (887). Thiophene itself is the most weakly coordinating ligand studied. Adding a methyl group to thiophene in the 2-position increases K' to 3.30. Moving the methyl group to the 3-position increases the value slightly to 4.76. This increase in binding ability is most likely due to the electron-donating ability of the Me group, which makes the S atom a better donor to the Ru. With two methyl groups in the α-positions, as in 2,5-Me_2T, the K' value (20.7) increases by more than a factor of 6 as compared with 2-MeT. Finally, adding two more Me groups in the 3- and 4-positions on the thiophene ring makes Me_4T by far the most strongly coordinating thiophene. This trend of increasing K' values with increased Me substitution is slightly different than that (Table IV) determined in equilibrium studies of thiophene displacement from $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$[10] (eq 2); in this latter case, 2,5-Me_2T was found to be a weaker binding ligand than either 2-MeT or 3-MeT. On the basis of an X-ray-determined structure and computer modeling studies, we argued[10] that steric hindrance between an α-methyl group on thiophene and the phenyl groups on PPh_3 in $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}2,5\text{-}Me_2T)^+$ significantly reduced the K' value for 2,5-Me_2T as compared with the other thiophenes. This argument is reinforced in the present equilibrium study, since replacement of the PPh_3 in $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ with the less sterically crowding CO ligand dramatically increases the relative K' values for 2,5-Me_2T and Me_4T. Also, an X-ray structure determination of the structurally similar $Cp^*(CO)_2Re(\eta^1(S)\text{-}T)$[9] shows no indication of steric hindrance between the T and the two carbonyls. Thus, in $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$, the trend of increasing K' values with the number of methyl groups is due to the electron-donating ability of the methyl groups.

Kinetic Studies of Thiophene Dissociation from $Cp(CO)(L)Ru(\eta^1(S)\text{-}Th)^+$. First-order rate constants (k_1) for thiophene substitution by PR_3 in $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$ and $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ (eq 5) are listed in Table V. Since these constants are for a rate law which is independent of PR_3 concentration, they correspond to a mechanism (eq 12) which involves rate-determining dissociation of the thiophene followed by rapid reaction of the unsaturated ruthenium residue with PR_3 to give

Table V. First-Order Rate Constants, k_1 (s^{-1}), for the Dissociation of Th from $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$ and $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ in CD_2Cl_2 at 25.0 °C According to Eq 5

	$10^6 k_1$, s^{-1}	
Th	$Cp(CO)(PPh_3)Ru(Th)^+$	$Cp(CO)_2Ru(Th)^+$
T	1400	
2-MeT	220	410
3-MeT	170	450
2,5-Me_2T	130	23[a]
BT	70	100
DBT	17	
Me_4T	5.8	

[a] Second-order rate constants for reactions of $Cp(CO)_2Ru(\eta^1(S)\text{-}2,5\text{-}Me_2T)^+$ with PR_3: $k_2 = 35 \times 10^{-6}$ s^{-1} M^{-1} (PPh_3); $k_2 = 208 \times 10^{-6}$ s^{-1} M^{-1} (PPh_2Me).

$$Cp(CO)(L)Ru(\eta^1(S)\text{-}Th)^+ \xrightarrow[-Th]{k_1} Cp(CO)(L)Ru^+ \xrightarrow[PR_3]{fast} Cp(CO)(L)Ru(PR_3)^+ \quad (12)$$

the final product. For the $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$ complexes, the k_1 values decrease with the thiophene in the following order: 3-MeT ≥ 2-MeT > BT > 2,5-Me_2T. The dissociation rates of 3-MeT ($10^6 k_1 = 450$ s^{-1}) and 2-MeT ($10^6 k_1 = 410$ s^{-1}) are almost identical. Adding a second Me group to the thiophene to give 2,5-Me_2T decreases the rate of dissociation by a factor of 20 compared to 3-MeT and 18 compared to 2-MeT. The trend is similar to that of thiophene dissociation from $Cp(CO)_2Re(\eta^1(S)\text{-}Th)$ (eq 2): 3-MeT ($10^6 k_1 = 120$ s^{-1}) > 2-MeT ($10^6 k_1 = 9.1$ s^{-1}) > 2,5-Me_2T ($10^6 k_1 = 1.3$ s^{-1}) in C_6D_6 at 80 °C. These trends suggest that Me groups on the thiophene strengthen the Ru–S bond by making the sulfur a stronger donor. Methyl groups affect the equilibrium constants (eq 11, Table IV) for thiophene exchange in the same way, as discussed in the previous section.

For the $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ complexes, the $10^6 k_1$ values (s^{-1}) decrease as follows: T (1400) > 2-MeT (220) > 3-MeT (170) > 2,5-Me_2T (130) > BT (70) > DBT (17) > Me_4T (5.8). As in the $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$ system, the rate of thiophene dissociation decreases as the number of Me groups in the thiophene increases. However, there is evidence that methyl groups in the 2- and 5-positions sterically accelerate the dissociation by interacting with the bulky PPh_3. For example, 2-MeT dissociates more rapidly than 3-MeT, but the reverse was true in the $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$ and $Cp(CO)_2Re(\eta^1(S)\text{-}Th)$ (eq 1). Also, the rate of 2,5-Me_2T dissociation in $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ is just slightly slower (less than a factor of 2) than 2-MeT. In the less sterically hindered systems $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$ and $Cp(CO)_2Re(\eta^1(S)\text{-}Th)$, where 2,5-$Me_2$T dissociation is not enhanced by crowding, 2,5-Me_2T dissociates *much* more slowly than 2-MeT. This steric interaction is supported by trends in equilibrium constants, K', for Th binding in $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ (eq 2) that showed 2,5-Me_2T to be less strongly bound than the 2-MeT, but in the less crowded $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$ (eq 11), 2,5-Me_2T binds more strongly than 2-MeT.

Rates of BT ($10^6 k_1 = 70$ s^{-1}) and DBT ($10^6 k_1 = 17$ s^{-1}) dissociation from $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ are substantially slower than those of T. Relative equilibrium constants, K', for these thiophenes (Table IV) also in the $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ system follow the same trend: T (1.00) < BT (29.9) < DBT (74.1).

Table VI. Equilibrium Constants for Binding of Methyl-Substituted Thiophenes on a Co–Mo/Al_2O_3 Catalyst, in $CpRu(\eta^5\text{-}Th)^+$, $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$, and $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ and Rates of Th Dissociation from $Cp(CO)_2Re(\eta^1(S)\text{-}Th)$, $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$, and $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$

Th	K_{rel}[a]	K'[b]	K'[c]	K'[d]	$10^7 k_1$[e]	$10^6 k_1$[f]	$10^6 k_1$[g]
T	1.0	1	1.0	1.0	3000		1400
2-MeT	1.6	6	4.1	3.3	91	410	220
3-MeT	1.7	7	6.3	4.8	1200	450	170
2,5-Me_2T	2.5	35	2.8	20	13	23	130
Me_4T		1300	74	887	2.7		5.8

[a] For adsorption on a sulfided Co–Mo/Al_2O_3 catalyst at 350 °C.[14] [b] For η^5-Th coordination in $CpRu(\eta^5\text{-}Th)^+$ at 50.0 °C in acetone-d_6, according to eq 13.[34] [c] For $\eta^1(S)$-Th coordination in $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ at 25.0 °C in CD_2Cl_2 according to eq 2.[10] [d] For $\eta^1(S)$-Th coordination in $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$ at 25.0 °C in CD_2Cl_2 according to eq 11 (this work). [e] Rate constants (k_1) for the dissociation of Th from $Cp(CO)_2Re(\eta^1(S)\text{-}Th)$ at 80.0 °C in C_6D_6 according to eq 1.[13] [f] Rate constants (k_1) for the dissociation of Th from $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$ at 25.0 °C in CD_2Cl_2 according to eq 5 (this work). [g] Rate constants (k_1) for the dissociation of Th from $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$ at 25.0 °C in CD_2Cl_2 according to eq 5 (this work).

The interaction between the thiophenes and the metal may be described as a donation of sulfur electron density to the metal center. This bonding picture suggests that an increase in electron density at the metal center should weaken the Ru–S bond. To test this effect, we compared the rates of dissociation of the sterically small 3-MeT from $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}3\text{-}MeT)^+$ and $Cp(CO)(PPh_2Me)Ru(\eta^1(S)\text{-}3\text{-}MeT)^+$. Reactions of $[Cp(CO)(PPh_2Me)Ru(\eta^1(S)\text{-}3\text{-}MeT)]BF_4$ (**9**) with PPh_3 to give $[Cp(CO)(PPh_2Me)Ru(PPh_3)]BF_4$ follow a first-order rate law (eq 7), giving the following k_1 values: $[4.2\ (1)] \times 10^{-4}$ s^{-1} (0.10 M PPh_3), $[4.1\ (2)] \times 10^{-4}$ s^{-1} (0.20 M PPh_3), and $[4.7\ (1)] \times 10^{-4}$ s^{-1} (0.40 M PPh_3). As expected, k_1 for this dissociation is faster for $Cp(CO)(PPh_2Me)Ru(\eta^1(S)\text{-}3\text{-}MeT)^+$ ($k_1 = 4.3 \times 10^{-4}$ s^{-1}) than for $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}3\text{-}MeT)^+$ ($k_1 = 1.7 \times 10^{-4}$ s^{-1}). This observation is consistent with the effect of the Cp′ ligand on the rate of 3-MeT dissociation from $Cp'(CO)_2Re(\eta^1(S)\text{-}3\text{-}MeT)$ (Cp′ = Cp, Cp*) complexes;[13] here the rate of 3-MeT dissociation from the more basic Re complex containing Cp* (Cp* = $\eta^5\text{-}C_5Me_5$) is 3.5 times faster than that from the analogous Cp complex.

The reactions of $Cp(CO)_2Ru(\eta^1(S)\text{-}2,5\text{-}Me_2T)^+$ (**4**) with phosphines show a significant contribution from a second-order (k_2) pathway that is not observed with any of the other $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$ complexes. Complex **4** is also the slowest to undergo Th dissociation; it is perhaps this slow 2,5-Me_2T dissociation that allows the rate of PR_3 nucleophilic attack to become competitive with the dissociation. That nucleophilic attack is possible on these complexes is suggested by the fast reaction of Br^- with $Cp(CO)_2Ru(\eta^1(S)\text{-}BT)^+$ (**6**) (see Results).

Relevance to Thiophene Adsorption on HDS Catalysts. Relative adsorption coefficients (K_{rel}) for thiophenes (Table VI) on a sulfided Co–Mo/Al_2O_3 HDS catalyst at 350 °C increase[33] with the number of methyl groups in the thiophene: T (1.0) < 2-MeT (1.6) < 3-MeT (1.7) < 2,5-Me_2T (2.5).[14] The absence of a steric effect that reduces adsorption by thiophenes with 2- and 5-methyl groups was interpreted to mean that η^1(S) coordination to a metal site on the catalyst was unlikely; therefore, η^5 was suggested as the most probable mode of thiophene adsorption. This conclusion was supported by equilibrium

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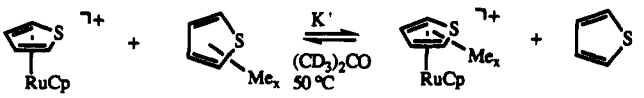
[33] It should be noted that the adsorption sites on the catalyst are not necessarily the sites at which thiophene HDS occurs.

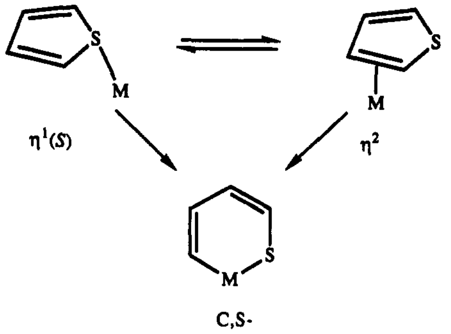
studies[34] (eq 13) that showed that K' also increases with



(13)

the number of methyl groups on the thiophene: T (1) < 2-MeT (6) ≤ 3-MeT (7) < 2,5-Me_2T (35). Moreover, there is much evidence to indicate that η^5-coordination[25,35] in organometallic complexes activates the thiophene to undergo a variety of reactions, some of which have been used as the basis of proposed thiophene HDS mechanisms.[36]

While η^5 coordination logically accounts for the trend in methylthiophene adsorption on the Co–Mo/Al_2O_3 catalyst, η^1(S) binding also accounts for this trend. Thus, equilibrium constants, K', for η^1(S) binding of thiophenes in Cp$(CO)_2$Ru(η^1(*S*)-Th)$^+$ increase in the same order: T (1.0) < 2-MeT (3.30) < 3-MeT (4.76) < 2,5-Me_2T (20.7). In these studies, there appears to be no steric effect caused by methyl groups in the 2- and 5-positions. Steric effects do become significant in the related Cp(CO)(PPh_3)-Ru(η^1(*S*)-Th)$^+$ (Tables IV and VI) which contains a bulky PPh_3 ligand. However, such bulky ligands are normally not present on the surface of an HDS catalyst. Thus, the η^1(S) coordination mode also accounts for the trend in thiophene adsorption on the Co–Mo/Al_2O_3 catalyst. There is also recent evidence to suggest that η^1(S) coordination can activate the thiophene by inserting into a C–S bond.[18,37] This could occur as the metal migrates between the sulfur (η^1(S)) and olefin (η^2) coordination modes (eq 14).[37] This



(14)

migration has been established in the selenophene (Sel) complexes Cp$(CO)_2$Re(Sel)[29] and in Cp$(CO)_2$Re(BT).[3c,d] The C,S-ring-opened structure has been observed in Cp*Ir(C,S-C_4R_4S)[38] and Cp*(PR_3)M(C,S-C_4R_4S),[18,37,38c] where M = Rh, Ir. Thus, it is possible that thiophene could adsorb in the η^1(S) form and be activated to undergo HDS by a pathway that begins with the insertion in eq 14.

A comparison of the η^1(S)-coordinating abilities of thiophene and the benzothiophenes (Tables IV and V) show that they increase in the order T < BT < DBT. If these thiophenes coordinate in the same way at a metal site on a catalyst surface, one would expect to find the same trend in their adsorption on the catalyst. However, at this time there are no data on the relative binding abilities of these thiophenes on HDS catalysts that would allow this comparison to be made.

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