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**Supplementary Material Available:** Tables of anisotropic thermal parameters for the non-hydrogen atoms, positional and

thermal parameters for the hydrogen atoms, and bond lengths, bond angles, and torsion angles involving non-hydrogen atoms for [Cp\*Mo(NO)(NCCH<sub>3</sub>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> (1), [CpMo(NO)Cl-(NCCH<sub>3</sub>)<sub>2</sub>BF<sub>4</sub>] (5), and [CpCr(NO)(NCCH<sub>3</sub>)<sub>2</sub>PF<sub>6</sub>] (9) and stereoviews of the packing diagrams (21 pages); listings of observed and calculated structure factors for all three complexes (56 pages). Ordering information is given on any current masthead page.

## Equilibrium Studies of the Displacement of $\eta^1(S)$ -Thiophenes (Th) from Cp(CO)(PPh<sub>3</sub>)Ru( $\eta^1(S)$ -Th)<sup>+</sup>

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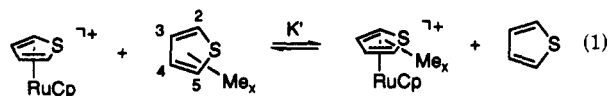
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The reactions of Cp(CO)(PPh<sub>3</sub>)RuCl (Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) with Ag<sup>+</sup> and thiophenes (Th) produce the stable sulfur-bound ( $\eta^1(S)$ ) thiophene complexes Cp(CO)(PPh<sub>3</sub>)Ru( $\eta^1(S)$ -Th)<sup>+</sup> (Th = T, 2-MeT, 3-MeT, 2,5-Me<sub>2</sub>T, Me<sub>4</sub>T, BT, and DBT). Equilibrium constants (*K'*) for the displacement of thiophene (T) by methyl-substituted thiophenes, benzo[*b*]thiophene (BT), and dibenzothiophene (DBT), Cp(CO)(PPh<sub>3</sub>)Ru( $\eta^1(S)$ -T)<sup>+</sup> + Th'  $\rightleftharpoons$  Cp(CO)(PPh<sub>3</sub>)Ru( $\eta^1(S)$ -Th')<sup>+</sup> + T, increase in the following order: T (1) < 2,5-Me<sub>2</sub>T (2.76) < 2-MeT (4.11) < 3-MeT (6.30) < BT (29.9) < Me<sub>4</sub>T (57.4) < DBT (74.1). In general, methyl groups on thiophene increase *K'*, but  $\alpha$ -methyl groups reduce the stabilities of complexes with 2-MeT, 2,5-Me<sub>2</sub>T, and Me<sub>4</sub>T ligands due to a steric interaction with the PPh<sub>3</sub> group. The ligands tetrahydrothiophene (THT) and MeCN have *K'* values (>7.1  $\times$  10<sup>6</sup>) which are much higher than any of the thiophenes, while MeI (*K'* = 2.0) is a slightly better ligand than T. An X-ray structure determination of [Cp(CO)(PPh<sub>3</sub>)Ru(2-MeT)]BF<sub>4</sub> is also reported.

### Introduction

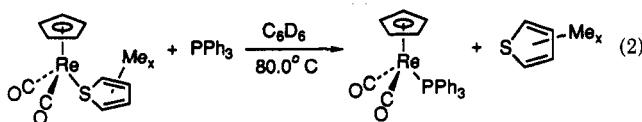
An important step in the mechanism(s) of thiophene (T) hydrodesulfurization (HDS) on heterogeneous catalysts is its adsorption to a metal site on the catalyst surface. Results of heterogeneous studies<sup>2</sup> indicate that methyl-substituted thiophenes bind more strongly to a Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst than thiophene itself; the adsorption equilibrium constants (in parentheses) decrease in the order 2,5-dimethylthiophene (2,5-Me<sub>2</sub>T) (2.5) > 3-methylthiophene (3-MeT) (1.7)  $\approx$  2-methylthiophene (2-MeT) (1.6) > T (1.0). The same trend is observed for  $\eta^5$ -thiophene binding in the complexes CpRu( $\eta^5$ -Th)<sup>+</sup>;<sup>3</sup> equilibrium constants (*K'*) for eq 1 decrease with different



methyl-substituted thiophenes Th' in the order Me<sub>4</sub>T > 2,5-Me<sub>2</sub>T > 3-MeT > 2-MeT > T (where Me<sub>4</sub>T is tetramethylthiophene). These similar trends are consistent with  $\eta^5$ -binding of thiophene on the catalyst surface. The well-known reactivity<sup>4</sup> of  $\eta^5$ -thiophene in its metal com-

plexes also supports such an adsorption mode on HDS catalysts.

The other common mode of thiophene coordination in transition-metal complexes is  $\eta^1(S)$  through the sulfur.<sup>5</sup> Complexes exhibiting this mode of thiophene binding are as follows: Ru(NH<sub>3</sub>)<sub>5</sub>(T)<sup>2+</sup>,<sup>6</sup> Cp(CO)<sub>2</sub>Fe(T)<sup>+</sup>,<sup>7</sup> CpFe(NCMe)<sub>2</sub>(2,5-Me<sub>2</sub>T)<sup>+</sup>,<sup>8</sup> W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>(T),<sup>9</sup> (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>4</sub>H<sub>3</sub>S)Ru(PPh<sub>3</sub>)<sub>2</sub><sup>+</sup>,<sup>10</sup> Cp\*(CO)<sub>2</sub>Re(T),<sup>11</sup> MX<sub>2</sub>(L') (M = Pd, X = Cl, Br, I, SCN; M = Pt, X = Cl),<sup>12a</sup> [CuCl<sub>2</sub>(L')]<sub>2</sub>,<sup>12b</sup> Pd( $\eta^3$ -allyl)(L')<sup>2+</sup> (L' = 2,5,8-trithia[9]-(2,5)thiophenophane), [RuClL<sub>2</sub>]BF<sub>4</sub><sup>+</sup> (L = 6-(2-thienyl)-2,2'-bipyridine), and Cp(CO)<sub>2</sub>Fe(2,5-Me<sub>2</sub>T)<sup>+</sup>.<sup>14</sup> Kinetic studies<sup>15</sup> of the replacement (eq 2) of methyl-sub-



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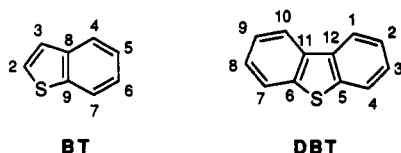
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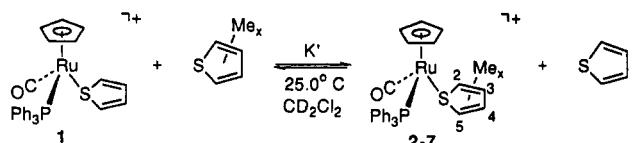
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stituted thiophenes in  $\text{CpRe}(\text{CO})_2(\eta^1(\text{S})\text{-Th})$  show that the rate of thiophene dissociation decreases in the order (rate constants,  $10^7 k_1 \text{ s}^{-1}$ , in parentheses) T (3000) > 3-MeT (1200) > 2-MeT (91) > 2,5-Me<sub>2</sub>T (13) > Me<sub>4</sub>T (2.7) > DBT (1.6). This trend suggests that Me groups on the thiophene strengthen its coordination to the Re, and there is no evidence of steric repulsion between the Me groups in the 2- and 5-positions with the other ligands around the Re; such a repulsion would be expected to weaken the M-S bond if the ligand were bound perpendicularly to the metal. However, structures of S-bound thiophenes indicate that the S is pyramidal,<sup>5,7b,16,17</sup> so that the Me groups in the 2- and 5-positions pose less of a steric problem. The above trend in rates of thiophene dissociation suggests that methyl substitution of thiophenes would strengthen bonding to metal sites on HDS catalysts. However, no studies of the relative equilibrium binding strengths of  $\eta^1(\text{S})$ -thiophenes have been reported.

In this study, we present the synthesis and characterization of a new series of stable  $\eta^1(\text{S})$ -thiophene complexes  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{Th})^+$ , where Th = T, 2-MeT, 3-MeT, 2,5-Me<sub>2</sub>T, Me<sub>4</sub>T, BT, and DBT; structures and numbering systems of benzo[b]thiophene (BT) and dibenzothiophene (DBT) are as follows:



Also, the X-ray-determined structure of  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(2\text{-MeT})^+$  and equilibrium constants ( $K'$ ) for the thiophene displacement reactions shown in eq 3 are reported.



Th: 2-MeT (2), 3-MeT (3), 2,5-Me<sub>2</sub>T (4), Me<sub>4</sub>T (5), BT (6), DBT (7)

## Experimental Section

**General Procedures.** All reactions were performed under a nitrogen atmosphere in reagent grade solvents using standard Schlenk techniques.<sup>18</sup> Diethyl ether was distilled under nitrogen from Na/benzophenone;  $\text{CH}_2\text{Cl}_2$  was distilled from  $\text{CaH}_2$ . Solvents were stored over 4-Å molecular sieves under nitrogen. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were obtained on Nicolet NT-300 or Varian VXR-300 spectrometers using  $\text{CD}_2\text{Cl}_2$  as the solvent and the internal lock. Fast atom bombardment (FAB) spectra were obtained in a  $\text{CH}_2\text{Cl}_2$ -3-nitrobenzyl alcohol matrix with a Kratos MS-50 mass spectrometer; infrared spectra of the compounds were taken in  $\text{CH}_2\text{Cl}_2$  solvent with a Nicolet 710 FT-IR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

The starting material,  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuCl}$ , was prepared according to a literature procedure.<sup>19</sup> Thiophene was purified as

previously described.<sup>20</sup> 2-MeT, 3-MeT, 2,5-Me<sub>2</sub>T, BT, DBT, and  $\text{AgBF}_4$  were purchased from Aldrich and used without further purification. Me<sub>4</sub>T was prepared by a literature method.<sup>21</sup>

**General Procedure for the Preparation of the  $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{Th})]\text{BF}_4$  Complexes (1-7).** To a solution of 0.103 g (0.209 mmol) of  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuCl}$  and 1.04 mmol of the thiophene (Th) in 25 mL of  $\text{CH}_2\text{Cl}_2$  was added 0.056 g (0.288 mmol) of solid  $\text{AgBF}_4$ . The mixture was stirred at room temperature for 1 h, during which time the solution turned cloudy and the color changed from orange to yellow. The solution was filtered through Celite, and the volatiles were removed under vacuum. The residue was dissolved in a minimum amount of  $\text{CH}_2\text{Cl}_2$  (the BT and DBT reaction residues were first washed with two 5-mL portions of  $\text{Et}_2\text{O}$  to remove the excess thiophene), and the solution was layered with  $\text{Et}_2\text{O}$ . The products (1-7) crystallized overnight at  $-20^\circ\text{C}$  as yellow powders or pale orange crystals in 65-85% yields.

**Characterization of 1-7.  $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{T})]\text{BF}_4$  (1).**  $^1\text{H}$  NMR:  $\delta$  7.21 (m, 2 H), 7.12 (m, 2 H), T; 4.98 (s, Cp); 7.60-7.30 (m, PPh<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  137.95 (d,  $^3J_{\text{CP}} = 2.11$  Hz, C2, C5) and 132.12 (s, C3, C4), T; 88.14 (d,  $^2J_{\text{CP}} = 1.5$  Hz, Cp); 200.17 (d,  $^2J_{\text{CP}} = 18.3$  Hz, CO); 133.41-129.67 (PPh<sub>3</sub>) [a typical pattern for the PPh<sub>3</sub> resonances in all of the complexes 1-7 is 133.41 (d,  $^3J_{\text{CP}} = 11.23$  Hz), 132.64 (d,  $^3J_{\text{CP}} = 51.6$  Hz), 132.09 (d,  $^3J_{\text{CP}} = 2.79$  Hz), and 129.67 (d,  $^3J_{\text{CP}} = 10.71$  Hz)]. IR:  $\nu(\text{CO})$  1999  $\text{cm}^{-1}$  (s).

**$[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(2\text{-MeT})]\text{BF}_4$  (2).**  $^1\text{H}$  NMR:  $\delta$  6.98 (m, H4), 6.92 (m, H3), 6.52 (d,  $J = 1.1$  Hz, H5), and 2.42 (d,  $J = 1.2$  Hz, Me), 2-MeT; 4.95 (s, Cp); 7.62-7.22 (m, PPh<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  152.02 (d,  $^3J_{\text{CP}} = 3.7$  Hz), 134.44 (s), 132.36 (s), 129.35 (s), and 14.43 (s, Me), 2-MeT; 88.35 (d,  $^2J_{\text{CP}} = 1.5$  Hz, Cp); 200.74 (d,  $^2J_{\text{CP}} = 18.6$  Hz, CO); 133.38-129.71 (PPh<sub>3</sub>). IR:  $\nu(\text{CO})$  1996  $\text{cm}^{-1}$  (s). Anal. Calcd for  $\text{C}_{29}\text{H}_{28}\text{BF}_4\text{OPRuS}$ : C, 54.30; H, 4.09. Found: C, 54.00; H, 4.24.

**$[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(3\text{-MeT})]\text{BF}_4$  (3).**  $^1\text{H}$  NMR:  $\delta$  7.02 (m, H2, H5), 6.60 (m, H4), and 2.22 (d,  $J = 1.2$  Hz, Me), 3-MeT; 4.99 (s, Cp); 7.60-7.28 (m, PPh<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  143.70 (s), 137.84 (d,  $^3J_{\text{CP}} = 2.2$  Hz), 135.22 (s), 130.99 (d,  $^3J_{\text{CP}} = 2.1$  Hz), and 16.38 (s, Me), 3-MeT; 88.14 (d,  $^2J_{\text{CP}} = 1.5$  Hz, Cp); 200.35 (d,  $^2J_{\text{CP}} = 18.6$  Hz, CO); 133.4-129.6 (PPh<sub>3</sub>). IR:  $\nu(\text{CO})$  1997  $\text{cm}^{-1}$  (s).

**$[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(2,5\text{-Me}_2\text{T})]\text{BF}_4$  (4).**  $^1\text{H}$  NMR:  $\delta$  6.62 (s, 2 H) and 2.07 (s, Me), 2,5-Me<sub>2</sub>T; 4.96 (s, Cp); 7.59-7.32 (m, PPh<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  148.71 (d,  $^3J_{\text{CP}} = 0.9$  Hz), 129.33 (s), and 14.81 (s, Me), 2,5-Me<sub>2</sub>T; 88.14 (d,  $^2J_{\text{CP}} = 1.5$  Hz, Cp); 200.17 (d,  $^2J_{\text{CP}} = 19.5$  Hz, CO); 133.4-129.7 (PPh<sub>3</sub>). IR:  $\nu(\text{CO})$  1996  $\text{cm}^{-1}$  (s). FAB:  $m/e$  569.0 ( $\text{M}^+$ ), 456.9 ( $\text{M}^+ - 2,5\text{-Me}_2\text{T}$ ). Anal. Calcd for  $\text{C}_{30}\text{H}_{28}\text{BF}_4\text{OPRuS}$ : C, 54.97; H, 4.31. Found: C, 55.00; H, 4.23.

**$[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{Me}_4\text{T})]\text{BF}_4$  (5).**  $^1\text{H}$  NMR:  $\delta$  1.97 (s, Me) and 1.93 (s, Me), Me<sub>4</sub>T; 4.93 (s, Cp); 7.56-7.30 (m, PPh<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  139.28 (s), 137.45 (d,  $^3J_{\text{CP}} = 1.5$  Hz), 13.78 (s, Me), and 12.60 (s, Me), Me<sub>4</sub>T; 88.13 (d,  $^2J_{\text{CP}} = 1.5$  Hz, Cp); 201.60 (d,  $^2J_{\text{CP}} = 20.1$  Hz, CO); 133.4-129.6 (PPh<sub>3</sub>). IR:  $\nu(\text{CO})$  1992  $\text{cm}^{-1}$  (s).

**$[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{BT})]\text{BF}_4$  (6).**  $^1\text{H}$  NMR:  $\delta$  7.86 (m, 1 H), 7.73 (m, 1 H), 7.41 (d,  $J = 5.7$  Hz, 1 H), and 6.40 (d,  $J = 5.7$  Hz, 1 H), BT; 7.61-7.34 (m, PPh<sub>3</sub>); 4.84 (s, Cp).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  146.10 (d,  $^3J_{\text{CP}} = 3.4$  Hz), 139.53 (s), 132.45 (d,  $^3J_{\text{CP}} = 1.0$  Hz), 131.15 (s), 128.88 (s), 127.81 (s), 126.48 (s), and 124.05 (s), BT; 88.68 (d,  $^2J_{\text{CP}} = 1.5$  Hz, Cp); 200.76 (d,  $^2J_{\text{CP}} = 18.6$  Hz, CO); 133.4-129.7 (PPh<sub>3</sub>). IR:  $\nu(\text{CO})$  1994  $\text{cm}^{-1}$  (s). Anal. Calcd for  $\text{C}_{32}\text{H}_{26}\text{BF}_4\text{OPRuS}$ : C, 56.73; H, 3.87. Found: C, 57.14; H, 3.91.

**$[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{DBT})]\text{BF}_4$  (7).**  $^1\text{H}$  NMR:  $\delta$  8.11 (d,  $J = 7.5$  Hz, 1 H) and 7.67-7.28 (m, 22 H), DBT and PPh<sub>3</sub>; 4.76 (s, Cp).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  142.15 (d,  $^3J_{\text{CP}} = 2.19$  Hz), 136.61 (s), 129.47 (s), 129.39 (s), 124.77 (s), and 123.44 (s), DBT; 88.96 (d,  $^2J_{\text{CP}} = 1.5$  Hz, Cp); 200.95 (d,  $^2J_{\text{CP}} = 19.23$  Hz, CO); 133.38-129.76 (PPh<sub>3</sub>). IR:  $\nu(\text{CO})$  1993  $\text{cm}^{-1}$  (s). FAB:  $m/e$  641.0 ( $\text{M}^+$ ), 457.0 ( $\text{M}^+ - \text{DBT}$ ). Anal. Calcd for  $\text{C}_{36}\text{H}_{28}\text{BF}_4\text{OPRuS} \cdot 0.8\text{CH}_2\text{Cl}_2$ : C, 55.56; H, 3.75. Found: C, 55.82; H, 3.91. The solvating  $\text{CH}_2\text{Cl}_2$  was identified in the  $^1\text{H}$  NMR spectra of 7 in  $\text{CD}_2\text{Cl}_2$  solvent.

**Preparation of  $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{THT})]\text{BF}_4$  (8).** Solid  $\text{AgBF}_4$  (40.1 mg, 0.206 mmol) was added to a solution of  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuCl}$  (59.2 mg, 0.120 mmol) in 20 mL of  $\text{CH}_2\text{Cl}_2$ . The

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**Table I. Crystal and Data Collection Parameters for [Cp(CO)(PPh<sub>3</sub>)Ru(2-MeT)]BF<sub>4</sub> (2)**

formula	[RuPSOC <sub>25</sub> H <sub>26</sub> ] <sup>+</sup> [BF <sub>4</sub> ] <sup>-</sup>
formula weight	646.47
space group	P $\bar{1}$
a, Å	9.441 (1)
b, Å	10.4858 (6)
c, Å	14.281 (2)
$\alpha$ , deg	87.690 (8)
$\beta$ , deg	82.14 (1)
$\gamma$ , deg	89.01 (1)
V, Å <sup>3</sup>	1399 (3)
Z	2
$d_{\text{calc}}$ , g/cm <sup>3</sup>	1.534
crystal size, mm	0.12 × 0.10 × 0.10
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	7.2
data collection instrument	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo K $\alpha$ ( $\lambda$ = 0.710 73 Å)
orientation reflns: no., range (2 $\theta$ )	25, 18.2 < $\theta$ < 35.2
temp, °C	22.0 (10)
scan method	$\theta$ - $2\theta$
data col range, 2 $\theta$ , deg	4.0-55.0
no. data collected	6427
no. unique data	5065
no. data with $F_o^2 > 3\sigma(F_o^2)$	4218
no. of parameters refined	343
transmission factors: max, min ( $\psi$ -scans)	0.999, 0.949
$R^a$	0.038
$R_w^b$	0.045
quality-of-fit indicator <sup>c</sup>	1.11
largest shift/esd. final cycle	0.00
largest peak, e/Å <sup>3</sup>	0.70 (5)

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ ;  $w = 1/\sigma^2(|F_o|)$ . <sup>c</sup> Quality-of-fit =  $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$ .

resulting solution was stirred for 5 min during which time the solution turned cloudy. Tetrahydrothiophene (THT) (55  $\mu$ L, 0.62 mmol) was added, and the mixture was stirred for 30 min. The reaction was worked up as for complexes 1-7 to give 8 as a light green powder (40.1 mg, 52.8% yield). <sup>1</sup>H NMR:  $\delta$  2.73 (m) and 2.00 (m), THT; 5.18 (s, Cp); 7.54-7.30 (m, PPh<sub>3</sub>). IR:  $\nu$ (CO) 1984 cm<sup>-1</sup> (s). Anal. Calcd for C<sub>25</sub>H<sub>26</sub>BF<sub>4</sub>OPRuS-0.54 CH<sub>2</sub>Cl<sub>2</sub>: C, 50.60; H, 4.33. Found: C, 50.98; H, 4.58. The solvating CH<sub>2</sub>Cl<sub>2</sub> was identified in the <sup>1</sup>H NMR spectra of 8 in CD<sub>2</sub>Cl<sub>2</sub> solvent.

**X-ray Diffraction Study of [Cp(CO)(PPh<sub>3</sub>)Ru(2-MeT)]BF<sub>4</sub> (2).** A single crystal of 2 suitable for an X-ray diffraction study was obtained by slow evaporation of a CD<sub>2</sub>Cl<sub>2</sub> solution under nitrogen at room temperature and mounted on a glass fiber. Data collection and reduction information are given in Table I. The cell constants were determined from a list of reflections found by an automated search routine. Lorentz and polarization corrections were applied. A correction based on a decay in the standard reflections of 0.2% was applied to the data. An absorption correction based on a series of  $\psi$ -scans was applied. The agreement factor for the averaging of observed reflections was 1.7% based on  $F$ . The positions of the Ru, S, and P atoms were determined from a Patterson map.<sup>22</sup> All remaining non-hydrogen atoms were found in one successive Fourier map. All non-hydrogen atoms were refined with anisotropic thermal parameters. After the least-squares converged, all hydrogen atoms were placed at calculated positions, 0.95 Å from the attached atom with isotropic temperature factors set equal to 1.3 times the isotropic equivalent of that atom. The hydrogen atom positions were not refined in the final least-squares cycle. Bond distances, angles, and atomic positional parameters for 2 are given in Tables II and III. An ORTEP drawing of the cation in 2 is shown in Figure 1.

**Exchange Reactions.** Equilibrium constants ( $K$ ) for the displacement (eq 4) of one thiophene (Th) by another (Th') were

**Table II. Bond Distances (Å)<sup>a</sup> and Angles (deg)<sup>a</sup> for [Cp(CO)(PPh<sub>3</sub>)Ru(2-MeT)]BF<sub>4</sub> (2)**

Distances			
Ru-S	2.392 (1)	S-C(2)	1.753 (5)
Ru-C(6)	1.869 (4)	S-C(5)	1.756 (5)
Ru-P	2.332 (1)	C(1)-C(2)	1.489 (7)
Ru-C(41)	2.196 (4)	C(2)-C(3)	1.350 (7)
Ru-C(42)	2.204 (4)	C(3)-C(4)	1.417 (8)
Ru-C(43)	2.222 (4)	C(4)-C(5)	1.329 (7)
Ru-C(44)	2.241 (4)	C(6)-O(6)	1.143 (5)
Ru-C(45)	2.238 (4)		
Angles			
S-Ru-C(6)	95.2 (1)	C(2)-S-C(5)	92.3 (2)
S-Ru-P	91.67 (4)	S-C(2)-C(1)	120.6 (4)
C(6)-Ru-P	91.1 (1)	S-C(2)-C(3)	109.2 (4)
Ru-S-C(2)	108.8 (2)	S-C(5)-C(4)	109.4 (4)
Ru-S-C(5)	110.6 (2)	Ru-C(6)-O(6)	173.3 (4)
Ru-S-Midpt	119.11 (6)		

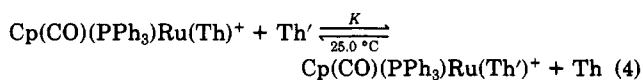
<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits.

**Table III. Positional Parameters and B Values for [Cp(CO)(PPh<sub>3</sub>)Ru(2-MeT)]BF<sub>4</sub> (2)**

atom	x	y	z	B (Å <sup>2</sup> ) <sup>a</sup>
Ru	0.19915 (3)	0.77508 (3)	0.15332 (2)	2.938 (6)
S	0.0757 (1)	0.6348 (1)	0.06499 (8)	3.86 (2)
C(1)	0.2897 (7)	0.6204 (6)	-0.0926 (4)	7.0 (2)
C(2)	0.1402 (6)	0.6574 (4)	-0.0555 (3)	4.7 (1)
C(3)	0.0343 (7)	0.7062 (5)	-0.1013 (4)	6.0 (1)
C(4)	-0.0961 (6)	0.7273 (5)	-0.0418 (4)	6.2 (1)
C(5)	-0.0932 (5)	0.6984 (5)	0.0494 (4)	5.1 (1)
C(6)	0.3735 (5)	0.6866 (4)	0.1339 (3)	4.2 (1)
O(6)	0.4863 (4)	0.6438 (4)	0.1198 (3)	6.9 (1)
P	0.1304 (1)	0.6567 (1)	0.29341 (7)	3.01 (2)
C(11)	0.2255 (4)	0.5066 (4)	0.3118 (3)	3.33 (8)
C(12)	0.2630 (5)	0.4271 (4)	0.2368 (3)	4.3 (1)
C(13)	0.3328 (6)	0.3115 (5)	0.2499 (4)	5.2 (1)
C(14)	0.3641 (6)	0.2741 (5)	0.3392 (4)	5.3 (1)
C(15)	0.3257 (5)	0.3514 (5)	0.4137 (4)	4.9 (1)
C(16)	0.2567 (5)	0.4668 (5)	0.4005 (3)	4.2 (1)
C(21)	0.1522 (5)	0.7465 (4)	0.3969 (3)	3.61 (9)
C(22)	0.0404 (6)	0.7689 (5)	0.4687 (3)	4.9 (1)
C(23)	0.0632 (8)	0.8403 (6)	0.5451 (4)	6.8 (2)
C(24)	0.1960 (8)	0.8899 (6)	0.5499 (4)	7.3 (2)
C(25)	0.3070 (7)	0.8680 (6)	0.4797 (4)	6.7 (1)
C(26)	0.2872 (5)	0.7961 (5)	0.4025 (4)	5.2 (1)
C(31)	-0.0571 (4)	0.6095 (4)	0.3114 (3)	3.33 (8)
C(32)	-0.1610 (5)	0.7022 (5)	0.2988 (4)	4.5 (1)
C(33)	-0.3049 (5)	0.6688 (5)	0.3086 (4)	5.3 (1)
C(34)	-0.3441 (5)	0.5458 (6)	0.3318 (4)	5.4 (1)
C(35)	-0.2432 (5)	0.4538 (5)	0.3445 (4)	5.1 (1)
C(36)	-0.0991 (5)	0.4852 (4)	0.3341 (3)	4.1 (1)
C(41)	0.2642 (5)	0.9623 (4)	0.1950 (4)	5.0 (1)
C(42)	0.3048 (5)	0.9529 (5)	0.0962 (4)	5.6 (1)
C(43)	0.1814 (6)	0.9417 (4)	0.0542 (4)	5.4 (1)
C(44)	0.0619 (5)	0.9456 (4)	0.1268 (4)	4.7 (1)
C(45)	0.1136 (5)	0.9603 (4)	0.2115 (4)	4.8 (1)
B	0.6466 (6)	1.0167 (6)	0.2117 (5)	5.4 (1)
F(1)	0.5622 (4)	0.9823 (4)	0.2933 (3)	7.7 (1)
F(2)	0.7737 (4)	1.0545 (6)	0.2271 (3)	12.4 (2)
F(3)	0.6729 (5)	0.9114 (4)	0.1568 (3)	10.4 (1)
F(4)	0.5774 (4)	1.1006 (4)	0.1588 (3)	8.8 (1)

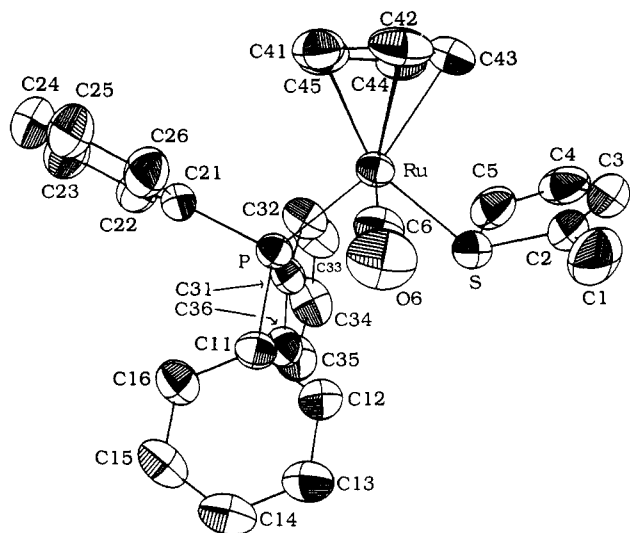
<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

determined by integration of <sup>1</sup>H NMR signals of the reactants and products. About 0.020 mmol of [Cp(CO)(PPh<sub>3</sub>)Ru(Th)]BF<sub>4</sub>



complex was placed in an NMR tube, dissolved in 0.5 mL of CD<sub>2</sub>Cl<sub>2</sub> under nitrogen and mixed with an equimolar amount of a different thiophene (Th'). The solution was frozen in liquid

(22) (a) SHELXS-86: G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Göttingen, FRG. (b) Enraf-Nonius Structure Determination Package: Enraf-Nonius, Delft, Holland. Neutral-atom scattering factors and anomalous scattering corrections were taken from: *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol IV.



**Figure 1.** ORTEP drawing of the cation in  $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(2\text{-MeT})]\text{BF}_4$  (2).

nitrogen, and the tube was flame sealed under vacuum. The solution was thawed, and the tube was kept in a 25.0 °C temperature bath. Spectra of the solution were recorded on a Varian VX-300 NMR spectrometer thermostated at 25.0 °C using  $\text{CD}_2\text{Cl}_2$  as the internal lock and reference ( $\delta$  5.32). A 38-s pulse delay between scans allowed all protons to relax.<sup>23</sup> The NMR spectra were followed with time to establish that all of the reactions reached equilibrium; this occurred within 24 h.

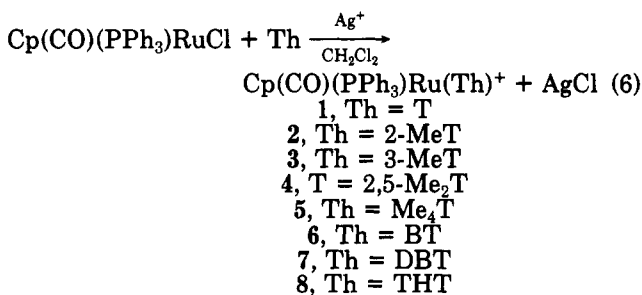
The equilibrium constants ( $K$ ) for eq 4 were calculated using eq 5 where  $I_{\text{Cp}'}$  and  $I_{\text{Cp}}$  are the Cp peak integrals of  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{Th}')^+$  and  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{Th})^+$ , respectively;  $I_{\text{Me}}$  is the integral of the Me peak of Th'; and  $x$  is 3 (for Th' = 2-MeT, 3-MeT, MeI) or 6 (for Th' = 2,5-Me<sub>2</sub>T, Me<sub>4</sub>T). The  $K$  values

$$K = \frac{(I_{\text{Cp}'}/5)^2}{(I_{\text{Cp}}/5)(I_{\text{Me}}/x)} = \frac{[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{Th}')^+][\text{Th}]}{[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{Th})^+][\text{Th}']} \quad (5)$$

in Table VI are averages of two independent determinations for most reactions. The error limits in Table VI are average deviations from the median value. The solutions were stable for at least 6 weeks.

## Results and Discussion

**Syntheses of the  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{Th})^+$  Complexes (1-7) and  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{THT})^+$  (8).** The  $\eta^1(\text{S})$ -coordinated thiophene complexes 1-7 are synthesized by  $\text{Ag}^+$  abstraction of  $\text{Cl}^-$  from  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuCl}$  in the presence of excess thiophene, benzothiophene, or dibenzothiophene, giving air-stable compounds in good yields (eq 6). The



air and thermal stability of these complexes in solution and as solids is quite remarkable since the corresponding bis(phosphine) complex  $\text{Cp}(\text{PPh}_3)_2\text{Ru}(\eta^1(\text{S})\text{-T})^+$ <sup>10</sup> loses its phosphine ligands and converts to the  $\eta^5\text{-T}$  complex

$\text{CpRu}(\eta^5\text{-T})^+$ . This stability is most likely due to the smaller CO ligand which reduces the steric bulk around the metal and makes the metal a better Lewis acid toward the electron-donor S atom of the thiophene. The alkyl and aryl iodide complexes  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{I-R})^+$  (where R = alkyl or aryl) also seem to be more stable than their bis(phosphine) and dicarbonyl counterparts.<sup>24</sup>

In the IR spectra of complexes 1-7, the  $\nu(\text{CO})$  band is about 35  $\text{cm}^{-1}$  higher than that in  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuCl}$ . In the <sup>1</sup>H NMR spectra of these compounds, the thiophene resonances are shifted slightly (0.04-0.4 ppm) upfield from those of the free thiophene; this trend was also observed for  $\text{Cp}(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-Th})$ ,<sup>11b</sup> but it is opposite that for  $\text{Cp}(\text{CO})_2\text{Fe}(\eta^1(\text{S})\text{-Th})^+$ ,<sup>7b</sup> in which these resonances are shifted slightly downfield of the free thiophene. If the thiophene ligands were bound through one of the double bonds, one would expect the proton resonances of the coordinated carbons to shift much farther upfield, as in complexes with  $\eta^2$ -coordinated olefins,<sup>25b,c</sup>  $\eta^2$ -selenophene<sup>25a,d</sup> and  $\eta^2$ -thiophene.<sup>26</sup> In complexes 1, 4, and 5, the thiophene exhibits only two <sup>1</sup>H NMR absorptions at room temperature, indicating the existence of a dynamic process which equilibrates the 2- and 5-positions and the 3- and 4-positions. Low-temperature (198 K) spectra of 4 and 5 in  $\text{CD}_2\text{Cl}_2$  show two separate signals for the diastereotopic  $\alpha$ -methyl groups (in 4 at  $\delta$  2.39 and 1.52 and in 5 at  $\delta$  2.23 and 1.44) due to the slowing of the stereochemical inversion at the sulfur. The free energy of activation ( $\Delta G^\ddagger$ ) calculated<sup>27</sup> for this process at the coalescence temperature (213 K) in  $\text{CD}_2\text{Cl}_2$  is 40 kJ/mol. A similar  $\Delta G^\ddagger$  of inversion (39 kJ/mol at 190 K) was obtained by Goodrich et al.<sup>7b</sup> for  $\text{Cp}(\text{CO})_2\text{Fe}(\eta^1(\text{S})\text{-BT})^+$ .

In the <sup>13</sup>C NMR spectra of complexes 1-7, the thiophene signals are slightly downfield (5-12 ppm) from those of the free thiophene. Similar small shifts were observed in  $\text{Cp}(\text{CO})_2\text{Fe}(\eta^1(\text{S})\text{-Th})^+$  (where Th = T, BT, and DBT)<sup>7b</sup> and  $\text{Cp}(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-Th})$ .<sup>11b</sup> The  $\alpha$ -C signal, but not the  $\beta$ -C, of each compound is split into a doublet by coupling to the phosphorus (<sup>3</sup>J<sub>CP</sub> = 0.9-3.7 Hz); this supports the  $\eta^1(\text{S})$ -mode of thiophene coordination in these complexes, which is confirmed by an X-ray structure analysis of 2.

The synthesis of 8 is a slight modification of that for  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{Th})^+$ . For the more strongly binding tetrahydrothiophene (THT), the  $\text{Ag}^+$  is added to the  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuCl}$  solution prior to the addition of THT in order to prevent reaction between  $\text{Ag}^+$  and THT. The  $\nu(\text{CO})$  value (1984  $\text{cm}^{-1}$ ) of 8 is slightly lower than those (1999-1992  $\text{cm}^{-1}$ ) of compounds 1-7. The <sup>1</sup>H NMR spectrum shows two broadened multiplets ( $\delta$  2.73, 2.00) for THT that are shifted upfield from the free ligand ( $\delta$  3.23, 2.13).

**Structure of  $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(2\text{-MeT})]\text{BF}_4$  (2).** The cation of 2 is shown in Figure 1. It contains a planar thiophene ring ( $\pm 0.005$  Å for each C and  $\pm 0.001$  Å for S) bound to the Ru atom through a pyramidal S atom. The Ru-S distance (Table II) of 2.392 (1) Å is similar to that in the thienyl complex  $(\text{PPh}_3)_2\text{Ru}(\text{C}_5\text{H}_4\text{CH}_2\text{C}_4\text{H}_3\text{S})^+$  (2.408 (1) Å)<sup>10</sup> but is longer than the corresponding distances found in  $\text{Cp}(\text{PMe}_3)_2\text{Ru}(2,5\text{-DHT})^+$  (2.330 (1) Å)<sup>28</sup> (where

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(25) (a) Choi, M.-G.; Angelici, R. J. *J. Am. Chem. Soc.* 1990, 112, 7811. (b) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* 1987, 109, 915. (c) Harman, W. D.; Schaefer, W. P.; Taube, H. *J. Am. Chem. Soc.* 1990, 112, 2682. (d) Choi, M.-G.; Angelici, R. J. *J. Am. Chem. Soc.* 1991, 113, 5651.

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(27) Sandstrom, J. *Dynamic NMR Spectroscopy*, Academic Press: New York, 1982; p 96.

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(23)  $T_1$  values determined for  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{Me}_x\text{T})^+$  follow: Cp,  $T_1 = 5.0 \pm 0.2$  s; Ph,  $T_1 = 2.6 \pm 0.2$  s; 3,4 Me's,  $1.4 \pm 0.1$  s; 2,5 Me's,  $1.5 \pm 0.02$  s.

Table IV. Structural Data on  $\eta^1(S)$ -Thiophene Complexes

complex	M-S-Midpt angle, deg	sum of angles around S, deg
Cp(CO)(PPh <sub>3</sub> )Ru(T) <sup>+</sup>	119.11 (6)	311.7
Cp*(CO) <sub>2</sub> Re(T) <sup>a</sup>	140.4	333.6
Cp(CO) <sub>2</sub> Fe(DBT) <sup>ab</sup>	119.4 (2)	309.8
Cp(Cl) <sub>2</sub> Ir(DBT) <sup>c</sup>	128.0	317.9

<sup>a</sup>Reference 11b. <sup>b</sup>Reference 7b. <sup>c</sup>Reference 17.

Table V. Equilibrium Constants ( $K$ ) for the Exchange Reactions (Eq 4) of Cp(CO)(PPh<sub>3</sub>)Ru(Th)<sup>+</sup> with Th' in CD<sub>2</sub>Cl<sub>2</sub> at 25.0 °C

reactn no.	Th	Th'	$K$
1	T	3-MeT	6.30 (8)
2	T	2-MeT	4.11
3	T	2,5-Me <sub>2</sub> T	2.76 (3)
4	T	Me <sub>4</sub> T	57.4 (40)
5	2-MeT	2,5-Me <sub>2</sub> T	0.658 (8)
6	2-MeT	3-MeT	1.46 (2)
7	3-MeT	2,5-Me <sub>2</sub> T	0.461
8	Me <sub>4</sub> T	2,5-Me <sub>2</sub> T	0.0483
9	BT	2,5-Me <sub>2</sub> T	0.0918
10	BT	Me <sub>4</sub> T	1.85
11	DBT	2,5-Me <sub>2</sub> T	0.0375
12	DBT	Me <sub>4</sub> T	0.740 (2)
13	Me <sub>4</sub> T	THT	>1.3 × 10 <sup>6</sup>
14	BT	NCMe	>1.3 × 10 <sup>6</sup>
15	T	MeI	2.0

2,5-DHT is 2,5-dihydrothiophene) and Cp(PPh<sub>3</sub>)<sub>2</sub>Ru(*n*-PrSH)<sup>+</sup> (2.377 (2) Å);<sup>29</sup> this longer Ru-S bond in **2** perhaps reflects weaker bonding to thiophene than to DHT or *n*-PrSH. The coordinated thiophene in **2** is distorted from its uncoordinated geometry. The C(2)-S and C(5)-S bonds of 1.753 (5) and 1.756 (5) Å are slightly longer than the 1.714 (1) Å in free thiophene,<sup>30</sup> but very similar to those in (PPh<sub>3</sub>)<sub>2</sub>Ru(C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>4</sub>H<sub>3</sub>S)<sup>+</sup> (1.754 (6), 1.736 (6) Å); although the error limits are larger in Cp(CO)<sub>2</sub>Re( $\eta^1(S)$ -T),<sup>11b</sup> the C-S distances (1.72 (1), 1.73 (1) Å) are similar. The C(2)-C(3) (1.350 (7) Å), C(3)-C(4) (1.417 (8) Å), and C(4)-C(5) (1.329 (7) Å) distances in **2** are all slightly shorter than the corresponding distances in free thiophene (1.370 (2), 1.424 (2), 1.370 (2) Å), but the short-long-short pattern is the same. This same pattern (1.344 (8), 1.409 (8), 1.339 (8) Å)<sup>10</sup> was also observed in (PPh<sub>3</sub>)<sub>2</sub>Ru(C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>4</sub>H<sub>3</sub>S)<sup>+</sup>, another structure with small standard deviations for its bond distances. However, in structures where the standard deviations are larger, this pattern is not always observed.<sup>5</sup> The C(2)-S-C(5) angle of 92.3 (2)° is the same as in the free ligand (92.2 (1)°). The Ru-S-Midpt (where Midpt is the midpoint of the C(2)-C(5) vector) angle is 119.11 (6)°, indicating the pyramidal nature of the thiophene. The sum of the angles around the S is 311.7°, which is much less than the 360° required for a trigonal-planar S atom. The three other structurally characterized  $\eta^1(S)$ -thiophene complexes also contain a pyramidal S atom (Table IV); however, the geometry around the S as measured by the M-S-Midpt angle and sum of the angles around S does vary from one complex to another.

**Equilibrium Studies.** The equilibrium constants ( $K$ ) for the exchange reaction (eq 4) were calculated according to eq 5 and are shown in Table V. At least three NMR spectra of each reaction were taken over a period of 28 days. During this time, the solution color did not change nor did any new peaks appear in the NMR spectra to

Table VI. Relative Equilibrium Constants ( $K'$ ) for the Reactions of Cp(CO)(PPh<sub>3</sub>)Ru(T)<sup>+</sup> with Th' (Eq 3) in CD<sub>2</sub>Cl<sub>2</sub> at 25.0 °C

Th	$K'$	Th	$K'$
T	1.00	Me <sub>4</sub> T	57.4 (40)
MeI	2.0	BT	29.9 (1)
2,5-Me <sub>2</sub> T	2.76 (3)	DBT	74.1 (10)
2-MeT	4.11	THT	>7.1 × 10 <sup>6</sup>
3-MeT	6.30 (8)	NCMe	>7.1 × 10 <sup>6</sup>

indicate that the compounds were decomposing. Equilibrium constants were also obtained for reactions 1-3, 5, 6, 9, and 11 (Table V) at 15 and 35.0 °C, but the values were found to be within experimental error of those at 25 °C. Thus, the  $\Delta H$  values for these exchange reactions are small (less than 1 kcal/mol).

In order to put the  $K$  values in Table V on the same scale, equilibrium constants ( $K'$ , Table VI) for the displacement (eq 3) of T from Cp(CO)(PPh<sub>3</sub>)Ru(T)<sup>+</sup> by the methyl-substituted thiophenes, BT and DBT were calculated from the  $K$  values. The results in Table V allow the  $K'$  values to be calculated independently from different data sets. For example, the  $K$  (4.11) for reaction 2 multiplied by the  $K$  (0.658) for reaction 5 gives a  $K'$  value of 2.70 for the displacement of T with 2,5-Me<sub>2</sub>T. The  $K$  value for this reaction measured directly (reaction 3) is 2.76. All the values calculated in this manner are in extremely good agreement (within 5%), ensuring the validity of each experimental  $K$  value.

The  $K'$  values (Table VI) give the following trend in binding abilities of the thiophenes: T < 2,5-Me<sub>2</sub>T < 2-MeT < 3-MeT < BT < Me<sub>4</sub>T < DBT. This is the same trend as that obtained in a kinetic study<sup>15</sup> of thiophene substitution by PPh<sub>3</sub> (eq 2), with the exception that the 2,5-Me<sub>2</sub>T, 2-MeT, 3-MeT order is reversed; as discussed below, this reversal appears to be due to repulsion between 2-methyl groups in the thiophene and the bulky PPh<sub>3</sub> ligand in the Cp(CO)(PPh<sub>3</sub>)Ru(Th)<sup>+</sup> complexes. In both the equilibrium studies (eq 3) and the kinetic studies (eq 2), all of the methyl-substituted thiophenes bind more strongly than thiophene itself; presumably the electron-donating methyl groups make the thiophene sulfur a stronger donor ligand. In the Cp(CO)<sub>2</sub>Re( $\eta^1(S)$ -Th) kinetic studies, 2-MeT dissociates more slowly than 3-MeT; this is in contrast to the equilibrium studies where 3-MeT binds more strongly than the sterically involved 2-MeT. The addition of another  $\alpha$ -methyl group to 2-MeT to give 2,5-Me<sub>2</sub>T reduces the  $K'$  value still further, from 4.11 to 2.76; on the contrary, the dissociation of 2,5-Me<sub>2</sub>T is 7 times slower than that of 2-MeT in Cp(CO)<sub>2</sub>Re( $\eta^1(S)$ -Th).<sup>15</sup> This difference is also most likely due to a steric interaction between the thiophene Me's and the phenyl groups of the phosphine ligand in **4**. In the structure of **2** (Figure 1), the Me group of 2-MeT is oriented toward the carbonyl ligand and away from the bulky phosphine. A computer-generated model of Cp(CO)(PPh<sub>3</sub>)Ru( $\eta^1(S)$ -2,5-Me<sub>2</sub>T)<sup>+</sup> (**4**) using the structural data of **2** shows that it is impossible to add the 5-Me group because it interferes with a Ph group of the PPh<sub>3</sub>; therefore, the 2,5-Me<sub>2</sub>T ligand must adopt a different orientation in **4** than 2-MeT does in **2**. The addition of two more Me groups in the 3- and 4-positions to give Me<sub>4</sub>T strengthens the M-S bond ( $K' = 57.4$ ) as expected. Thus, except for specific steric interactions, the binding of thiophenes in Cp(CO)(PPh<sub>3</sub>)Ru(Th)<sup>+</sup> is enhanced by electron-donating methyl groups in the thiophene ring.

With a  $K'$  value of 29.9, BT is a weaker ligand than Me<sub>4</sub>T, but DBT is the most strongly bound ( $K' = 74.1$ ) of all of the thiophene ligands that were studied.

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**Table VII. Equilibrium Constants for the Binding of Methyl-Substituted Thiophenes on a Co-Mo/Al<sub>2</sub>O<sub>3</sub> Catalyst, in CpRu( $\eta^5$ -Th)<sup>+</sup> and Cp(CO)(PPh<sub>3</sub>)Ru( $\eta^1$ (S)-Th)<sup>+</sup>, as Well as Rates of Dissociation from Cp(CO)<sub>2</sub>Re( $\eta^1$ (S)-Th)**

Th	$K_{rel}^a$	$K'^b$	$K'^c$	$10^7 k_1,^d \text{ s}^{-1}$
T	1.0	1	1.0	3000
2-MeT	1.6	6	4.1	91
3-MeT	1.7	7	6.3	1200
2,5-Me <sub>2</sub> T	2.5	35	2.8	13

<sup>a</sup> For adsorption on a sulfided Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst at 350 °C.<sup>2</sup>

<sup>b</sup> For  $\eta^5$ -Th coordination in CpRu( $\eta^5$ -Th)<sup>+</sup> at 50.0 °C in acetone-*d*<sub>6</sub> according to eq 1.<sup>3</sup> <sup>c</sup> For  $\eta^1$ (S)-Th coordination in Cp(CO)(PPh<sub>3</sub>)Ru( $\eta^1$ (S)-Th)<sup>+</sup> in CD<sub>2</sub>Cl<sub>2</sub> at 25.0 °C according to eq 3 (this work).

<sup>d</sup> Rate constant ( $k_1$ ) for the dissociation of Th from Cp(CO)<sub>2</sub>Re( $\eta^1$ (S)-Th) in C<sub>6</sub>D<sub>6</sub> at 80.0 °C according to eq 2.<sup>15</sup>

Despite the stability of complexes 1–7, the thiophenes are still very weakly bound. Other more strongly coordinating ligands, such as tetrahydrothiophene (THT) and NCMe, completely displace the thiophene ligands. The exchange equilibrium where Th = Me<sub>4</sub>T and Th' = THT was studied in both directions. There was no change in the NMR spectrum during 1 week when 8 was mixed with equimolar Me<sub>4</sub>T; on the other hand, there was complete displacement of Me<sub>4</sub>T by THT within 24 h when 5 was reacted with THT. Likewise, BT is completely displaced from 6 by equimolar NCMe within the same time period. Based on the sensitivity of the <sup>1</sup>H NMR instrument used in the equilibrium studies, we estimate that  $K$  is greater than  $1.3 \times 10^5$  for these reactions (reactions 13 and 14, Table V), which means that  $K'$  is greater than  $7.1 \times 10^6$ . Thus, THT and NCMe are much more strongly coordinating ligands than any of the thiophenes.

Methyl iodide, a weakly binding ligand, is known to form stable complexes with the Cp(CO)(PPh<sub>3</sub>)Ru<sup>+</sup> fragment.<sup>24</sup> A study of the reaction of 1 with equimolar MeI conducted under the same conditions as the thiophene reactions, after 24 h, gives an equilibrium constant of 2.0 according to eq 5. This value, however, is less accurate than the others since a small amount of decomposition of Cp(CO)(PPh<sub>3</sub>)Ru(MeI)<sup>+</sup> to other Cp-containing products occurs with the liberation of free MeI.<sup>24</sup> Thus, the equilibrium constant (Table VI) for MeI is between those of T and 2,5-Me<sub>2</sub>T. The weak  $\eta^1$ (S)-coordinating ability of thiophene is demonstrated by its  $K'$  value (1.00), which is even less than that (2.0) of MeI toward Cp(CO)(PPh<sub>3</sub>)Ru<sup>+</sup>.

**Relevance to Thiophene Adsorption on HDS Catalysts.** In an effort to gain insight into the nature of the adsorption of thiophene on HDS catalysts, we have measured equilibrium constants for the binding of methyl-substituted thiophenes as  $\eta^5$ -ligands<sup>3</sup> in CpRu( $\eta^5$ -Th)<sup>+</sup> (eq 1) and as  $\eta^1$ (S)-ligands in Cp(CO)(PPh<sub>3</sub>)Ru( $\eta^1$ (S)-Th)<sup>+</sup> in the present study (eq 3). Relative equilibrium constants ( $K'$ ) for  $\eta^5$ - and  $\eta^1$ (S)-coordination are compared in Table

VII with relative adsorption coefficients ( $K_{rel}$ ) for thiophenes<sup>2</sup> on a sulfided Co-Mo/Al<sub>2</sub>O<sub>3</sub> HDS catalyst at 350 °C.<sup>31</sup> It is clear from the table that the trend (T < 2-Me < 3-Me < 2,5-Me<sub>2</sub>T) in equilibrium constants for adsorption ( $K_{rel}$ ) and  $\eta^5$ -coordination ( $K'$ ) in CpRu( $\eta^5$ -Th)<sup>+</sup> is the same. It was this comparison and several reactivity studies<sup>4</sup> of  $\eta^5$ -Th complexes that led us to propose  $\eta^5$ -Th adsorption as a mode of thiophene activation that leads to thiophene HDS by two possible mechanisms.<sup>4a,32,33</sup> Taken together, these results offer the most complete explanation for thiophene adsorption and its HDS.

On the other hand, the data in Table VII also offer some support for  $\eta^1$ (S)-adsorption since  $K'$  for reaction 3 increases with the number of methyl groups in the thiophene. This trend in  $K'$  does not entirely parallel  $K_{rel}$  values (Table VII), but as noted above, the bulky PPh<sub>3</sub> group sterically weakens the bonding of thiophenes with Me groups in the 2- and 5-positions. Without the bulky PPh<sub>3</sub> group, the trend in  $K'$  values for eq 3 would probably be similar to that of  $K_{rel}$ . This statement is supported by the rate constants  $k_1$  in Table VII for the dissociation of thiophenes from Cp(CO)<sub>2</sub>Re( $\eta^1$ (S)-Th) according to eq 2.<sup>15</sup> Here there is no steric effect, and the 2,5-Me<sub>2</sub>T is the slowest to dissociate, indicating that it is likely to be the most strongly coordinated, as is observed ( $K_{rel}$ ) on the catalyst. Thus, the general increase in both  $K_{rel}$  and  $K'$  (for eq 3) with an increasing number of methyl groups is consistent with  $\eta^1$ (S)-binding on the catalyst. The observed slight lengthening (0.04 Å) of the C–S bond upon  $\eta^1$ (S)-coordination of thiophene in Cp(CO)(PPh<sub>3</sub>)Ru( $\eta^1$ (S)-2-MeT)<sup>+</sup> suggests that this mode of coordination could activate the thiophene to undergo C–S cleavage. Recent evidence<sup>34</sup> for such an activation is the insertion of Rh into a C–S bond in the proposed intermediate Cp\*(PMe<sub>3</sub>)Rh( $\eta^1$ (S)-Th). Thus,  $\eta^1$ (S)-thiophene adsorption and activation on HDS catalysts is a possibility. It is, of course, possible that the mode of coordination and activation depend on the catalyst and even on the reaction conditions.

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**Supplementary Material Available:** Tables of bond distances and angles, displacement parameters, and least-squares planes (8 pages); a table of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

(31) It should be noted that the adsorption sites on the catalyst are not necessarily the sites at which thiophene HDS occurs.

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