

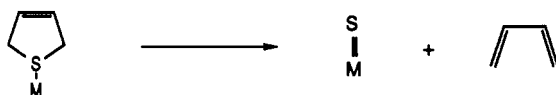
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## Synthesis and Desulfurization of 2,5-Dihydrothiophene Transition-Metal Complexes: Models for the Hydrodesulfurization (HDS) of Thiophene

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Several S-coordinated 2,5-dihydrothiophene (2,5-DHT) transition-metal complexes were synthesized in order to determine whether or not this type of coordination promotes butadiene elimination from the 2,5-DHT ligand, a step proposed in a mechanism for the hydrodesulfurization (HDS) of thiophene. Thermal decomposition of  $W(CO)_5(2,5-DHT)$  and  $Re_2(CO)_9(2,5-DHT)$  at 110



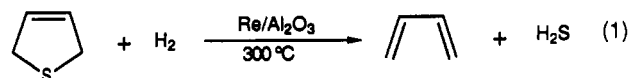
°C liberates butadiene and free 2,5-DHT (relative ratio 1:4). Uncoordinated 2,5-DHT itself does not decompose at 120 °C after 3 days. Thus, S-coordination of 2,5-DHT to these metal centers does promote the liberation of butadiene. Upon being heated at 180 °C,  $MCl_2(2,5-DHT)_2$  ( $M = Pd, Pt$ ) gives off mainly thiophene and free 2,5-DHT (1:1) with only a small amount of butadiene. Thus, depending on the complex either butadiene or thiophene may be evolved. The reaction of  $Ru_3(CO)_{12}$  with 2,5-DHT forms the trinuclear  $(\mu_2-H)Ru_3(CO)_9(\mu_3-1-4-\eta^4-DHT)$ , whose X-ray structure determination shows that the sulfur and olefin of the 2,5-DHT coordinate to two different ruthenium atoms but also C-H cleavage occurs at C(2) forming a C-Ru bond. The structure of an S-coordinated DHT complex  $[Cp(PMe_3)_2Ru(2,5-DHT)](PF_6)$  is also reported.

### Introduction

Hydrodesulfurization is an important catalytic process<sup>2,3</sup> in which sulfur is removed from sulfur-containing organic compounds in petroleum feedstocks by hydrogen treatment over Co- or Ni-promoted Mo or W catalysts supported on  $Al_2O_3$ . A mechanism (Scheme I) for thiophene HDS proposed and supported by results from these laboratories<sup>2,4</sup> involves initial partial hydrogenation of thiophene (steps 1 and 2 in Scheme I) to the dihydrothiophene isomers, 2,5-DHT and 2,3-DHT. The participation of these

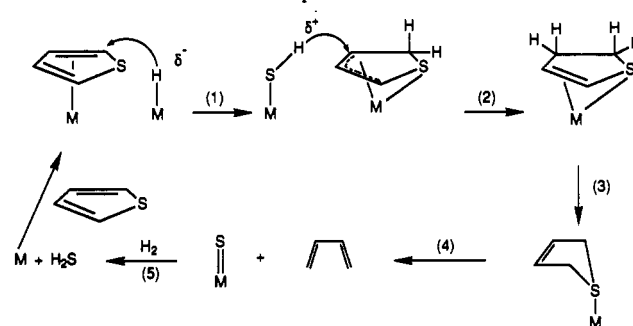


isomers as intermediates is supported by HDS reactor studies<sup>4c,d</sup> of 2,5-DHT and 2,3-DHT over  $Mo/\gamma-Al_2O_3$  and  $Re/\gamma-Al_2O_3$  heterogeneous catalysts. Over both catalysts, both 2,5-DHT and 2,3-DHT are much more reactive than thiophene and at 400 °C give the same distribution of desulfurized  $C_4$  products as thiophene. Over  $Re/\gamma-Al_2O_3$ , 2,3-DHT and 2,5-DHT interconvert and both are desulfurized to butadiene. The mechanism in Scheme I suggests that the actual desulfurization step in thiophene HDS is step 4 in which S-coordinated 2,5-DHT eliminates butadiene leaving an S atom coordinated on the catalyst surface. That this is a reasonable step is supported by HDS reactor studies,<sup>4d</sup> which show that the major product of 2,5-DHT hydrodesulfurization is butadiene (eq 1). We had shown previously that butadiene



is released when the unstable  $Fe(CO)_4(2,5-DHT)$  with an S-coordinated 2,5-DHT ligand decomposes.<sup>4c</sup> In this paper, we describe the synthesis of several S-coordinated 2,5-DHT transition-metal complexes and explore their tendencies to eliminate butadiene upon heating, thereby determining whether or not S-coordination of 2,5-DHT to various metal centers promotes butadiene liberation as proposed in the thiophene HDS mechanism in Scheme I. We also examine the reaction of 2,5-DHT with the trinuclear cluster  $Ru_3(CO)_{12}$ , which leads to a quite different type of product.

### Scheme I. Mechanism for Thiophene HDS



### Experimental Section

**General Procedures.** All reactions were carried out under an atmosphere of prepurified  $N_2$  at room temperature by using standard Schlenk techniques<sup>5</sup> unless otherwise stated. All solvents were reagent grade and dried by following standard methods.<sup>6</sup> Tetrahydrofuran (THF) and  $Et_2O$  were distilled from Na/benzophenone,  $CH_2Cl_2$  and hexanes were distilled from  $CaH_2$ , and benzene was distilled from  $LiAlH_4$ . Acetone was dried with  $K_2CO_3$ .

The  $^1H$  and  $^{13}C$  NMR spectra were obtained on a Nicolet NT-300 spectrometer with deuterated solvents used as internal locks. All  $^1H$

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NMR chemical shifts ( $\delta$ ) were referenced to  $(\text{CH}_3)_4\text{Si}$ . Electron-ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. Fast atom bombardment (FAB) spectra were obtained by using a Kratos MS-50 mass spectrometer. Infrared spectra were obtained on either a Perkin-Elmer 681 or Digilab FTS-7 FT-IR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

The following compounds were prepared by literature methods: 2,5-DHT,<sup>7</sup> 3,4-dimethylhydrothiophene,<sup>8</sup>  $\text{Cp}^*\text{Re}(\text{CO})_3$ ,<sup>9</sup>  $\text{Re}_2(\text{CO})_9$ ,<sup>10</sup>  $\text{Ru}_3(\text{CO})_{12}$ ,<sup>11</sup>  $\text{CpRu}(\text{PMe}_3)_2\text{Cl}$ ,<sup>12</sup>  $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ ,<sup>13</sup>  $\text{PdCl}_2(\text{MeCN})_2$  was prepared from MeCN by the method used for the synthesis of  $\text{PdCl}_2(\text{PhCN})_2$ .<sup>14</sup>

**Preparation of  $\text{W}(\text{CO})_6(2,5\text{-DHT})$  (1).** Compound 1 was prepared by a modified literature method.<sup>15</sup> A solution of  $\text{W}(\text{CO})_6$  (0.15 g, 0.43 mmol) in freshly distilled THF (30 mL) in a quartz photolysis tube equipped with an  $\text{N}_2$  bubbler was irradiated with a 450-W mercury UV lamp for ~3 h. The progress of the reaction to give  $\text{W}(\text{CO})_5(\text{THF})$  was monitored by IR spectroscopy. To the yellow solution of  $\text{W}(\text{CO})_5(\text{THF})$  was added 2,5-DHT (50  $\mu\text{L}$ , 0.62 mmol) and the resulting mixture was stirred for 0.5 h. After removal of the solvent under vacuum, the yellow-brown residue was extracted with pentane ( $2 \times 20$  mL). The pale yellow solution was filtered through Celite. Slow evaporation of the solvent gave pale yellow crystals (0.14 g, 81%) of 1. IR and  $^1\text{H}$  NMR spectra agree with those reported<sup>15</sup> for this compound. IR (hexanes):  $\nu(\text{CO})$  2071 (w), 1980 (m), 1938 (vs)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (acetone- $d_6$ ):  $\delta$  6.04 (s, 2 H, H3,4), 4.20 (s, 4 H, H2,5).

**Preparation of  $\text{W}(\text{CO})_5(3,4\text{-Me}_2\text{DHT})$  (2).** Compound 2 was prepared by the same method as described above by using  $\text{W}(\text{CO})_6$  (0.10 g, 0.28 mmol) and 3,4-Me<sub>2</sub>DHT (35  $\mu\text{L}$ , 0.31 mmol). The product 2 was obtained as pale yellow crystals (0.10 g, 82%). IR (hexanes):  $\nu(\text{CO})$  2075 (w), 1988 (s), 1935 (vs, br)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.95 (s, 4 H, H2,5), 1.75 (s, 6 H, CH<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  201.1 (axial CO), 197.3 (equatorial CO), 128.6 (C3,4), 55.6 (C2,5), 14.0 (CH<sub>3</sub> of DHT). EIMS (16 eV):  $m/e$  438 ( $\text{M}^+$ ), 410 ( $\text{M}^+ - \text{CO}$ ), 382 ( $\text{M}^+ - 2\text{CO}$ ), 354 ( $\text{M}^+ - 3\text{CO}$ ), 326 ( $\text{M}^+ - 4\text{CO}$ ), 298 ( $\text{M}^+ - 5\text{CO}$ ), 114 ( $\text{Me}_2\text{DHT}^+$ ), 99 ( $\text{Me}_2\text{DHT}^+ - \text{Me}$ ), 82 ( $\text{Me}_2\text{DHT}^+ - \text{S}$ ). Anal. Calcd for  $\text{C}_{11}\text{H}_{10}\text{O}_5\text{W}$ : C, 30.16; H, 2.30. Found: C, 30.26; H, 2.28.

**Preparation of  $\text{Re}_2(\text{CO})_9(2,5\text{-DHT})$  (3).** To a benzene solution (15 mL) of  $\text{Re}_2(\text{CO})_9(\text{MeCN})$  (0.15 g, 0.23 mmol) was added 2,5-DHT (25  $\mu\text{L}$ , 0.31 mmol). The solution was refluxed for 3 h, and the solvent was evaporated under vacuum to yield an oily yellow residue. The residue was extracted with hexanes. The extract was filtered through Celite. After removal of the solvent under vacuum, the crude product was recrystallized from hexane at  $-70$  °C to give pale yellow crystals of 3 (0.098 g, 61%). IR (hexanes):  $\nu(\text{CO})$  2105 (w), 2075 (w), 2040 (s), 2018 (s), 1990 (vs), 1975 (s), 1930 (s), 1900 (w), 1835 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.97 (s, 2 H, H3,4), 4.08 (s, 4 H, H2,5).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  201.1, 199.9, 191.8, 187.8 (CO), 127.3 (C3,4), 52.3 (C2,5). EIMS (70 eV):  $m/e$  710 ( $\text{M}^+$ ), 682 ( $\text{M}^+ - \text{CO}$ ), 86 ( $\text{DHT}^+$ ), 54 ( $\text{DHT}^+ - \text{S}$ ). Anal. Calcd for  $\text{C}_{13}\text{H}_6\text{O}_9\text{Re}_2\text{S}$ : C, 21.97; H, 0.85. Found: C, 21.97; H, 0.79.

**Preparation of  $\text{Cp}^*(\text{CO})_2\text{Re}(2,5\text{-DHT})$  (4).** A solution of  $\text{Cp}^*(\text{CO})_2\text{Re}(\text{THF})$ , prepared by UV irradiation<sup>16</sup> of a THF solution (30 mL) of  $\text{Cp}^*\text{Re}(\text{CO})_3$  (0.10 g, 0.25 mmol) at  $-20$  °C, was stirred with 2,5-DHT (50  $\mu\text{L}$ , 0.61 mmol) at room temperature for 5 h. Following the removal of solvent in vacuo, the residue was chromatographed on a neutral alumina column (1  $\times$  15 cm). First, unreacted  $\text{Cp}^*\text{Re}(\text{CO})_3$  was eluted with hexanes, and then a yellow band containing the product was eluted with hexanes/ $\text{CH}_2\text{Cl}_2$  (4:1). The yellow eluent was concentrated and cooled to  $-70$  °C to give tan crystals (0.065 g, 57%) of 4. IR (hexanes):  $\nu(\text{CO})$  1919 (s), 1858 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.85 (s, 2 H, H3,4), 3.93 (s, br, 4 H, H2,5), 2.04 (s, 15 H, Cp\*).  $^{13}\text{C}$  NMR

**Table I.** Crystal and Data Collection Parameters for  $[\text{CpRu}(\text{PMe}_3)_2(2,5\text{-DHT})](\text{PF}_6)$  (5) and  $(\mu_2\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}1\text{-}4\text{-}7^{\text{a}}\text{-DHT})$  (7)

	5	7
formula	$\text{C}_{15}\text{H}_{29}\text{F}_6\text{P}_3\text{RuS}$	$\text{C}_{13}\text{H}_6\text{O}_9\text{Ru}_3\text{S}$
fw	549.44	497.46
space group	$P2_1/c$	$P2_1$
$a$ , Å	8.687 (1)	8.703 (1)
$b$ , Å	10.428 (1)	11.733 (1)
$c$ , Å	24.747 (2)	8.919 (1)
$\beta$ , deg	95.092 (8)	92.39 (1)
$V$ , Å <sup>3</sup>	2232.8 (7)	913.0 (3)
$Z$	4	2
$d_{\text{calc}}$ , g/cm <sup>3</sup>	1.634	2.33
$\mu(\text{Mo K}\alpha)$ , $\text{cm}^{-1}$	10.365	25.57
radiation (monochromated in incident beam) ( $\lambda$ , Å)	Mo K $\alpha$ (0.71073)	Mo K $\alpha$ (0.71073)
$T$ , °C	22 (1)	22 (1)
max, min transm factors ( $\psi$ scans)	0.9999, 0.9391	0.998, 0.633
$R^a$	0.0408	0.0505
$R_w^b$	0.0644	0.0635

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|).$$

( $\text{CDCl}_3$ ):  $\delta$  207.1 (CO), 127.4 (C3,4), 56.5 (C2,5), 95.1 (C of Cp\*), 10.7 (Me of Cp\*). EIMS (70 eV):  $m/e$  464 ( $\text{M}^+$ , based on  $^{187}\text{Re}$ ), 408 ( $\text{M}^+ - 2\text{CO}$ ), 85 ( $\text{DHT}^+ - \text{H}$ ). Anal. Calcd for  $\text{C}_{16}\text{H}_{21}\text{O}_2\text{ReS}$ : C, 41.45; H, 4.57. Found: C, 41.72; H, 4.60.

**Preparation of  $[\text{CpRu}(\text{PMe}_3)_2(2,5\text{-DHT})](\text{PF}_6)$  (5).** To a MeOH (10 mL) solution of  $\text{CpRu}(\text{PMe}_3)_2\text{Cl}$  (0.10 g, 0.28 mmol) were added 2,5-DHT (100  $\mu\text{L}$ , 1.2 mmol) and  $\text{NH}_4\text{PF}_6$  (0.23 g, 1.4 mmol). The resulting reaction mixture was stirred for 12 h. After removal of the solvent under vacuum, the yellow residue was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10$  mL). The extract was filtered through Celite. The solution was reduced to about 5 mL, and  $\text{Et}_2\text{O}$  (20 mL) was added; the solution was kept at  $-20$  °C for 3 days to give yellow crystals (0.11 g, 71%) of 5.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.95 (s, 2 H, H3,4), 3.87 (s, br, 4 H, H2,5), 4.79 (s, 5 H, Cp), 1.55 (pseudo t, 18 H,  $\text{PMe}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  127.7 (C3,4), 55.6 (C2,5), 82.5 (Cp), 22.5 (pseudo t,  $\text{PMe}_3$ ). MS (FAB, 3-nitrobenzyl alcohol):  $m/e$  405 ( $\text{M}^+$ ), 319 ( $\text{M}^+ - \text{DHT}$ ). Anal. Calcd for  $\text{C}_{15}\text{H}_{29}\text{F}_6\text{P}_3\text{RuS}$ : C, 32.79; H, 5.24. Found: C, 32.58; H, 5.32.

**X-ray Structure Determination of  $[\text{CpRu}(\text{PMe}_3)_2(2,5\text{-DHT})](\text{PF}_6)$  (5).** A yellow crystal of  $[\text{CpRu}(\text{PMe}_3)_2(2,5\text{-DHT})](\text{PF}_6)$  (5), formed by vapor diffusion of  $\text{Et}_2\text{O}$  into a  $\text{CH}_2\text{Cl}_2$  solution at  $-20$  °C, was mounted on a glass fiber in a random orientation. A total of 8144 reflections were collected in the  $+h, \pm k, \pm l$  hemisphere, of which 3921 were unique. An absorption correction based on a series of  $\psi$  scans was applied, as were Lorentz and polarization corrections. Decay corrections were not applied, since the intensity standards indicated no change within the error of the measurements during data collection. The agreement factors for the averaging of 6994 observed reflections were 1.4% based on intensity and 1.2% based on  $F_o$ .

The position of the Ru atom was taken from a Patterson map.<sup>17a</sup> Following refinement of the scale factor, the remainder of the non-hydrogen atoms were located in subsequent difference Fourier maps. In the final stages of refinement, all 26 non-hydrogen atoms were given anisotropic temperature factors. Although the fluorine atoms exhibited large amplitudes of thermal motion, the positions and temperature factors refined smoothly. Hydrogen atoms were not considered in the model. Refinement of the structure was carried out by using the SHELX76 package.<sup>17b</sup> Important crystallographic data are summarized in Table I.

**Preparation of  $\text{RuCl}_2(\text{CO})_3(2,5\text{-DHT})$  (6).** To a solution of  $[\text{Ru}(\text{C}-\text{O})_3\text{Cl}_2]_2$  (0.15 g, 0.29 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) was added 2,5-DHT (80  $\mu\text{L}$ , 0.98 mmol) by micro syringe, and the mixture was stirred for 12 h. Removal of the solvent in vacuo gave a creamy white powder, which was recrystallized from  $\text{CH}_2\text{Cl}_2$  and hexanes at  $-20$  °C. White needle-shaped crystals of 6 were obtained (0.14 g, 70%). IR (hexanes):  $\nu(\text{CO})$  2130 (s), 2070 (s), 2041 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.99 (s, 2 H, H3,4), 4.51 and 4.00 (s, br, 4 H, H2,5). EIMS (16 eV):  $m/e$  306 ( $\text{M}^+ - \text{HCl}$ ), 270 ( $\text{M}^+ - 2\text{HCl}$ ), 242 ( $\text{M}^+ - (2\text{HCl} + \text{CO})$ ), 85 ( $\text{DHT}^+$

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-H). Anal. Calcd for  $C_7H_6Cl_2O_3RuS$ : C, 24.57; H, 1.77. Found: C, 24.65; H, 1.73.

**Preparation of  $(\mu_2-H)Ru_3(CO)_9(\mu_3-1-4-\eta^4-DHT)$  (7).** To a stirred solution of  $Ru_3(CO)_{12}$  (0.20 g, 0.31 mmol) in THF (30 mL) was added 2,5-DHT (100  $\mu$ L, 1.22 mmol). (The 2,5-DHT must be very pure; otherwise, the yield of 7 decreases dramatically.) After 3 h of refluxing, the orange solution changed to dark brown. The solvent was evaporated under vacuum; the residue was extracted with hexanes ( $2 \times 15$  mL). The extract was chromatographed on neutral alumina by eluting with hexanes. The first orange-yellow band was unreacted  $Ru_3(CO)_{12}$  (0.036 mg). The second yellow-orange band was eluted with  $Et_2O$ /hexanes (1:4 mixture) and collected. After removal of the solvent under vacuum, the crude product was recrystallized from hexanes at  $-20^\circ C$  to give yellow-orange crystals (0.031 g, 24% yield based on consumed  $Ru_3(CO)_{12}$ ) of 7. IR (hexanes):  $\nu(CO)$  2082 (m), 2058 (s), 2036 (s), 2018 (s), 2000 (m), 1922 (w), 1975 (w), 1964 (w)  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  4.46 (d, 1 H, H2), 4.28 (m, 1 H, H5endo), 3.89 (m, 1 H, H3), 3.41 (d of d, 1 H, H4), 2.61 (m, 1 H, H5exo), -18.56 (d, 1 H, Ru-H), ( $J_{RuH,H5endo} = 2.9$  Hz,  $J_{H2,H3} = 3.2$  Hz,  $J_{H4,H5endo} = 2.8$  Hz,  $J_{H5endo,H5exo} = 12.3$  Hz,  $J_{H3,H4} = 5.1$  Hz,  $J_{H2,H5endo} = 0.9$  Hz,  $J_{H3,H5} = 0.7$  Hz).  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  199.8 (CO), 15.5 (C2), 36.5 (C3), 79.7 (C4), 59.8 (C5). EIMS (17 eV):  $m/e$  644 ( $M^+$ , based on  $^{102}Ru$ ), 616 ( $M^+ - CO$ ), 588 ( $M^+ - 2CO$ ), 560 ( $M^+ - 3CO$ ), 532 ( $M^+ - 4CO$ ), 504 ( $M^+ - 5CO$ ), 86 ( $DHT^+$ ), 84 ( $DHT^+ - 2H$ ), 54 ( $DHT^+ - S$ ). Anal. Calcd for  $C_{13}H_6O_9Ru_3S$ : C, 24.34; H, 0.97. Found: C, 24.39; H, 1.01.

**X-ray Structure Determination of  $(\mu_2-H)Ru_3(CO)_9(\mu_3-1-4-\eta^4-DHT)$  (7).** A yellow-orange crystal of  $(\mu_2-H)Ru_3(CO)_9(\mu_3-1-4-\eta^4-DHT)$  (7), formed by slow cooling from hexanes at  $-20^\circ C$ , was mounted on a glass fiber in a random orientation. The cell constants were determined from a list of reflections found by an automated search routine. A total of 3901 reflections were collected in the  $\pm h, \pm k, \pm l$  hemisphere, of which 2195 were unique. Intensity standards indicated no change within error of the measurements over the duration of the data collection. An absorption correction based on a series of  $\psi$  scans was applied, as were Lorentz and polarization corrections. The agreement factors for averaging of 3032 observed reflections were 3.6% based on intensity and 2.4% based on  $F_o$ .

The positions of the three Ru atoms were located by direct methods.<sup>17a</sup> Examination of a difference map produced after full-matrix least-squares refinement of the three metal atoms revealed most of the remainder of the non-hydrogen atoms, including the atoms of the major orientation of the capping ligand. Following further least-squares refinement and a subsequent difference map, the existence of a minor orientation of the capping ligand became evident. Two orientations of the five non-hydrogen atoms of the  $SC_4H_5$  ligand were thus modeled so that the sum of the occupancies of the two groups equaled 1. Due to a large amount of correlation between the two overlapping moieties, a loose restraint was applied to keep the S-C bond distances close to 1.8 Å. In the final refinement stages, the major orientation converged to an occupancy of 62% (indicated by the nonprimed atom labels). Only the Ru and S atoms were refined with anisotropic thermal parameters. The final cycle of refinement included 150 variable parameters and converged with unweighted and weighted agreement factors of  $R = 0.0505$  and  $R_w = 0.0635$ . The refinement calculations were carried out by using the SHELX76 package.<sup>17b</sup> Important crystallographic data are given in Table I.

**Preparation of  $PdCl_2(2,5-DHT)_2$  (8).** To a solution of  $PdCl_2(MeCN)_2$  (0.20 g, 0.77 mmol) in  $CH_2Cl_2$  (15 mL) was added 2,5-DHT (133  $\mu$ L, 1.62 mmol). The reaction mixture was stirred for 2 h, and then the solvent was removed under vacuum to give a golden powder. This crude product was redissolved in a minimum amount of hot acetone and the solution was slowly cooled at  $-20^\circ C$  to give tan needle crystals (0.19 g, 71%) of 8.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  5.90 (s, 2 H, H3,4), 4.43 and 3.84 (s, br, 4 H, H2,5). Anal. Calcd for  $C_8H_{12}Cl_2PdS_2$ : C, 27.48; H, 3.46. Found: C, 26.89; H, 3.54.

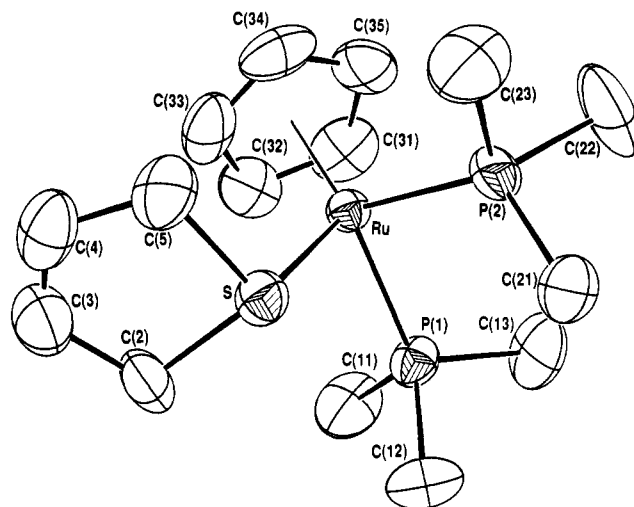
**Preparation of  $PtCl_2(2,5-DHT)_2$  (9).** To a solution of  $K_2PtCl_4$  (0.25 g, 0.60 mmol) in 10 mL of water was added 2,5-DHT (84  $\mu$ L, 0.95 mmol) in small portions. The mixture was stirred vigorously after each addition to ensure complete reaction. The bright yellow precipitate was immediately separated by suction filtration, washed with ice-cold ethanol ( $2 \times 5$  mL), and then washed with water ( $3 \times 5$  mL) to remove the potassium chloride. The product was dried in vacuo (0.19 g, 72%).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  5.92 (s, 2 H, H3,4), 4.55 and 3.68 (2 br m, 4 H, H2,5). Anal. Calcd for  $C_8H_{12}Cl_2PtS_2$ : C, 21.92; H, 2.76. Found: C, 22.01; H, 2.51.

**Thermal Decomposition of 2,5-DHT Complexes 1-4, 6, 8, and 9.** All decompositions were performed in the following manner. A solid sample of the complex was placed in a 50-mL flask, which was connected through a 3-way stopcock to an NMR tube and to a vacuum pump. After the entire system was evacuated, the stopcock was closed to the

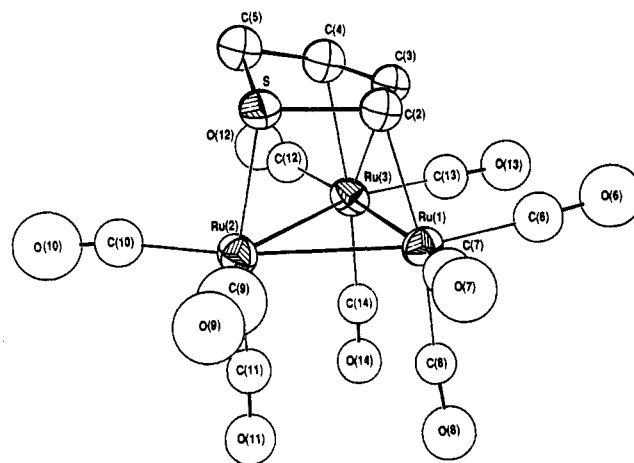
**Table II.** Selected Bond Distances (Å) and Angles (deg) for  $[CpRu(PMe_3)_2(2,5-DHT)](PF_6)$  (5)

Bond Distances <sup>a</sup>			
Ru-S	2.3295 (7)	S-C(5)	1.861 (3)
Ru-P(1)	2.2933 (7)	C(2)-C(3)	1.468 (5)
Ru-P(2)	2.2891 (7)	C(3)-C(4)	1.327 (6)
S-C(2)	1.855 (3)	C(4)-C(5)	1.493 (5)
Bond Angles <sup>a</sup>			
S-Ru-P(1)	91.43 (3)	C(2)-S-C(5)	93.8 (2)
S-Ru-P(2)	88.00 (3)	S-C(2)-C(3)	105.6 (3)
P(1)-Ru-P(2)	93.47 (3)	C(2)-C(3)-C(4)	117.8 (3)
Ru-S-C(2)	111.0 (1)	C(3)-C(4)-C(5)	118.0 (3)
Ru-S-C(5)	109.4 (1)	S-C(5)-C(4)	104.5 (3)

<sup>a</sup>The numbers in parentheses are estimated standard deviations.



**Figure 1.** ORTEP drawing of  $[CpRu(PMe_3)_2Ru(2,5-DHT)]^+$  (cation of 5).



**Figure 2.** ORTEP drawing of  $(\mu_2-H)Ru_3(CO)_9(\mu_3-1-4-\eta^4-DHT)$  (7).

vacuum pump and the flask was immersed in an oil bath at 110 or 180  $^\circ C$  while the NMR tube was cooled in liquid nitrogen ( $-196^\circ C$ ). After collection of the volatile products for 15-20 min,  $CDCl_3$  was added by syringe to the NMR tube; the volatile products in the tube were identified by the  $^1H$  NMR spectrum of this solution.

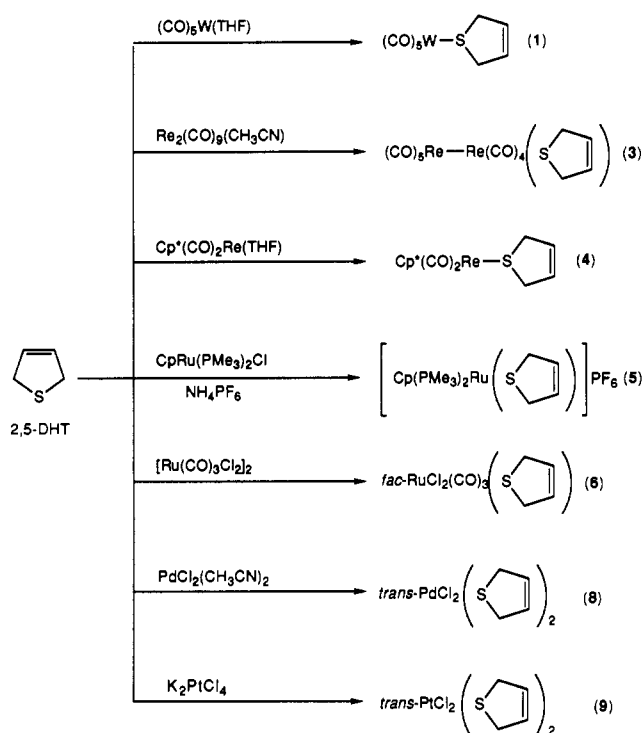
## Results

Reactions leading to the S-bound 2,5-DHT complexes are summarized in Scheme II. Selected bond lengths and angles for  $[CpRu(PMe_3)_2(2,5-DHT)](PF_6)$  (5) and  $(\mu_2-H)Ru_3(CO)_9(\mu_3-1-4-\eta^4-DHT)$  (7) are presented in Tables II and III, respectively. ORTEP drawings for 5 and 7 (showing the major orientation of the capping ligand) are illustrated in Figures 1 and 2, respectively.

## Discussion

**Preparation of Transition-Metal Complexes with Sulfur-Bound 2,5-DHT Ligands.** Dihydrothiophene exists in two isomeric forms,

Scheme II

Table III. Selected Bond Distances (Å) and Angles (deg) for  $(\mu_2\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}1\text{-}4\text{-}\eta^4\text{-DHT})$  (7)

Bond Distances <sup>a</sup>			
Ru(1)-Ru(2)	2.803 (2)	S-C(2)	1.77 (3)
Ru(1)-Ru(3)	2.821 (2)	S-C(5)	1.72 (3)
Ru(2)-Ru(3)	3.032 (2)	S'-C(2')	1.80 (4)
Ru(1)-C(2)	2.18 (3)	S'-C(5')	1.83 (4)
Ru(1)-C(2')	2.18 (4)	C(2)-C(3)	1.50 (5)
Ru(2)-S	2.331 (6)	C(3)-C(4)	1.33 (5)
Ru(2)-C(3')	2.52 (3)	C(4)-C(5)	1.62 (5)
Ru(2)-C(4')	2.40 (6)	C(2')-C(3')	1.45 (6)
Ru(3)-S'	2.26 (1)	C(3')-C(4')	1.40 (9)
Ru(3)-C(3)	2.44 (3)	C(4')-C(5')	1.53 (9)
Ru(3)-C(4)	2.39 (3)		
Bond Angles <sup>a</sup>			
Ru(2)-Ru(1)-Ru(3)	65.25 (5)	C(2)-C(3)-C(4)	119 (3)
Ru(1)-Ru(2)-Ru(3)	57.65 (3)	Ru(3)-C(4)-C(3)	76 (2)
C(3')-Ru(2)-C(4')	33 (2)	Ru(3)-C(4)-C(5)	115 (2)
Ru(1)-Ru(3)-Ru(2)	57.10 (5)	C(3)-C(4)-C(5)	109 (3)
C(3)-Ru(3)-C(4)	32 (1)	S-C(5)-C(4)	105 (2)
Ru(2)-S-C(2)	97.3 (9)	Ru(1)-C(2')-S'	110 (2)
Ru(2)-S-C(5)	103 (1)	Ru(1)-C(2')-C(3')	97 (2)
C(2)-S-C(5)	97 (2)	S'-C(2')-C(3')	101 (3)
Ru(3)-S'-C(2')	96 (1)	Ru(2)-C(3')-C(2')	107 (3)
Ru(3)-S'-C(5')	101 (1)	Ru(2)-C(3')-C(4')	69 (3)
C(2')-S'-C(5')	95 (2)	C(2')-C(3')-C(4')	127 (4)
Ru(1)-C(2)-S	108 (1)	Ru(2)-C(4')-C(3')	78 (3)
Ru(1)-C(2)-C(3)	94 (2)	Ru(2)-C(4')-C(5')	115 (4)
S-C(2)-C(3)	104 (2)	C(3')-C(4')-C(5')	104 (4)
Ru(3)-C(3)-C(2)	109 (2)	S'-C(5')-C(4')	108 (4)
Ru(3)-C(3)-C(4)	72 (2)		

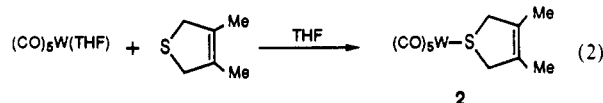
<sup>a</sup>See Table II for footnote.

2,3-DHT and 2,5-DHT. While 2,3-DHT is not very stable,<sup>18</sup> polymerizing upon heating and slowly decomposing on exposure to air, 2,5-DHT is relatively stable.<sup>19</sup> In principle, 2,5-DHT may coordinate to metals via either the S atom or the olefinic bond.

In all of the mononuclear complexes described in this paper the 2,5-DHT coordinates through the sulfur atom, as is typical

of simple thioethers<sup>20</sup> and also occurs in 2,3-DHT complexes.<sup>4a,b,e</sup> The complexes containing the S-bound 2,5-DHT described in this paper are air-stable.

Substitution of the labile THF ligand in  $\text{W}(\text{CO})_5(\text{THF})$  with 2,5-DHT leads to the S-coordinated DHT complex  $(\text{CO})_5\text{W}(2,5\text{-DHT})$  (1) (Scheme II). The analogous reaction with 3,4-Me<sub>2</sub>DHT gives  $(\text{CO})_5\text{W}(3,4\text{-Me}_2\text{DHT})$  (2) (eq 2). The reaction



of  $\text{Re}_2(\text{CO})_9(\text{MeCN})$  and 2,5-DHT in refluxing benzene leads to the formation of the S-coordinated complex 3. Complex 3 presumably has a structure in which the 2,5-DHT is in an equatorial position, since its  $\nu(\text{CO})$  pattern is very similar to that of  $\text{Re}_2(\text{CO})_9(\text{MeCN})$ <sup>10</sup> for which a structure with an equatorial MeCN has been assigned. Compound 4 was prepared by the substitution of the THF ligand in  $\text{Cp}^*(\text{CO})_2\text{Re}(\text{THF})$  with 2,5-DHT. The reaction of  $\text{CpRu}(\text{PMe}_3)_2\text{Cl}$  with excess 2,5-DHT and  $\text{NH}_4\text{PF}_6$  in  $\text{CH}_3\text{OH}$  yields  $[\text{Cp}(\text{PMe}_3)_2\text{Ru}(2,5\text{-DHT})]\text{PF}_6$ . Cleavage of the chloride bridges in  $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$  by 2,5-DHT gives *fac*- $\text{RuCl}_2(\text{CO})_3(2,5\text{-DHT})$  (6). The IR spectrum of 6 shows three CO bands (2130, 2070, 2041  $\text{cm}^{-1}$ ) of the same intensity. Its  $\nu(\text{CO})$  pattern is very similar to that of *fac*- $\text{RuCl}_2(\text{CO})_3(\text{L})$  (L = pyridine, EtCN, PhCN).<sup>21</sup> Displacement of MeCN from  $\text{PdCl}_2(\text{MeCN})_2$  by 2,5-DHT gives *trans*- $\text{PdCl}_2(2,5\text{-DHT})_2$  (8). When  $\text{K}_2\text{PtCl}_4$  is reacted with 2,5-DHT, it forms *trans*- $\text{PtCl}_2(2,5\text{-DHT})_2$  (9). The products 8 and 9 are presumed to have the *trans* structures as are typical of other bis(thioether)palladium<sup>4e</sup> and -platinum complexes.<sup>22,23</sup>

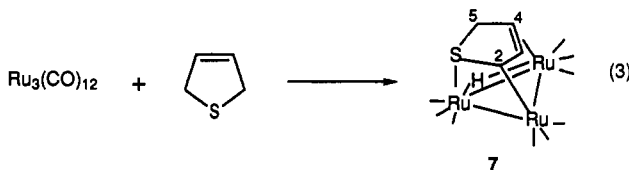
All of these S-coordinated 2,5-DHT complexes are characterized by their IR, <sup>1</sup>H and <sup>13</sup>C NMR, and mass spectra as well as elemental analyses (see Experimental Section). In the <sup>1</sup>H NMR spectra of the 2,5-DHT complexes both the H2, H5 and H3, H4 sets of resonances are downfield compared to those ( $\delta$  5.85, 3.76;  $\text{CDCl}_3$ ) in free 2,5-DHT; since they are closer to the coordinated sulfur, H2, H5 move further downfield than H3, H4. Similar small downfield shifts also have been observed in previously reported S-coordinated 2,3-DHT complexes:  $\text{W}(\text{CO})_5(2,3\text{-DHT})$ ,<sup>4c</sup>  $[\text{Re}(\text{CO})_5(2,3\text{-DHT})]^+$ ,<sup>4c</sup> *trans*- $\text{PdCl}_2(2,3\text{-DHT})_2$ ,<sup>4c</sup>  $\text{Ru}(\text{CO})_3\text{-Cl}_2(2,3\text{-DHT})$ ,<sup>4c</sup>  $\text{Cr}(\text{CO})_5(2,3\text{-DHT})$ ,<sup>15</sup> and  $[\text{HPT}(\text{PET}_3)_2(2,3\text{-DHT})]^+$ .<sup>4a</sup> If olefin coordination had occurred, H3 and H4 would be expected to shift upfield. In the <sup>13</sup>C NMR spectra, large upfield shifts of the olefinic carbons would also be expected upon coordination of the double bond. Such upfield shifts are observed in  $\eta^2$ -bound olefins<sup>24</sup> and arenes<sup>25</sup> in both the <sup>1</sup>H and <sup>13</sup>C NMR spectra. However, the C3 and C4 resonances for the complexes in Scheme II lie in the region typical of uncoordinated olefins. Therefore, both the <sup>1</sup>H and <sup>13</sup>C NMR spectra support S-coordination of 2,5-DHT in these complexes.

An X-ray diffraction study of  $[\text{Cp}(\text{PMe}_3)_2\text{Ru}(2,5\text{-DHT})]\text{PF}_6$  (5) confirms (Figure 1) the S-coordination of 2,5-DHT. The Ru-S distance (2.330 (1) Å) is similar to that (2.355 (1) Å) between Ru and the tetrahydrothiophene (THT) in *mer*-(BEPS)-*cis*- $\text{Br}_2(\text{THT})\text{Ru}$  (BEPS = bis(3-(ethylsulfanyl)propyl) sulfide)<sup>26</sup> and

(20) (a) Omae, I. *Coord. Chem. Rev.* **1979**, *28*, 97. (b) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365.(21) Benedetti, E.; Braca, G.; Sbrana, G.; Salvetti, F.; Grassi, B. *J. Organomet. Chem.* **1972**, *37*, 361.(22) Kaufman, G. B.; Cowan, D. O. *Inorg. Synth.* **1960**, *6*, 211.(23) Cross, R. J.; Green, T. H.; Keat, R. *J. Chem. Soc., Dalton Trans.* **1976**, 382.(24) (a) Choi, M.-G.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7811. (b) Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969. (c) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 915. (d) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.(25) (a) Harman, W. D.; Schaefer, S. P.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2682. (b) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1989**, *111*, 8722. (c) Benn, R.; Mynott, R.; Topalovič, I.; Scott, F. *Organometallics* **1989**, *8*, 2299. (d) van der Heijden, H.; Orpen, A. G.; Pasman, P. J. *Chem. Soc., Chem. Commun.* **1985**, 1576.(18) (a) Birch, S. F.; McAllan, D. T. *J. Chem. Soc.* **1951**, 2556. (b) Sauer, N. N.; Angelici, R. J.; Huang, Y. C. J.; Trahanovsky, W. S. *J. Org. Chem.* **1986**, *51*, 113.(19) Davies, J. V.; Sumner, S. *Acta Chem. Scand.* **1962**, *16*, 1870.

to the Ru-S distances in  $(\text{PPh}_3)_2\text{Ru}(\text{C}_5\text{H}_4\text{CH}_2\text{C}_4\text{H}_3\text{S})^+$  (2.408 (1) Å)<sup>27</sup> and in  $\text{CpRu}(\text{PPh}_2\text{Me})(\eta^3\text{-S}(\text{Me})\text{C}(\text{Me})=\text{CHCH}=\text{CH}(\text{Me}))^+$  (2.327 Å).<sup>28</sup> The C(3)-C(4) distance (1.327 (6) Å) of the DHT ring is very similar to that (1.32 Å)<sup>29</sup> of normal  $\text{C}(\text{sp}^2)=\text{C}(\text{sp}^2)$  bonds. The C-S distances (1.855 (3), 1.861 (3) Å) in **5** appear to be slightly longer than normal  $\text{C}(\text{sp}^2)$ -S distances (1.82 Å)<sup>29</sup> in thioethers. The dihedral angle between the planes defined by C(2), C(3), C(4), C(5) and C(2), S, C(5) is 26.2 (3)°.

**Reaction of  $\text{Ru}_3(\text{CO})_{12}$  with 2,5-DHT.** The reaction of  $\text{Ru}_3(\text{CO})_{12}$  with 2,5-DHT in refluxing THF yields the cluster compound  $(\mu_2\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}1\text{-}4\text{-}\eta^4\text{-DHT})$  (**7**) (eq 3). Compound



**7** was obtained as a yellow-orange crystalline solid and characterized by its IR, mass, and <sup>1</sup>H and <sup>13</sup>C NMR spectra, elemental analysis, and X-ray-determined structure. The <sup>1</sup>H NMR spectrum shows six different chemical resonances, compared to the simple spectra of S-coordinated 2,5-DHT complexes. The hydride resonance of **7** is observed at -18.56 ppm as a doublet with a coupling constant of  $J_{\text{RuH,H}^{\text{Sendo}}} = 2.9$  Hz; coupling of the hydride to H<sup>Sendo</sup> was established by a COSY 2-D NMR experiment. This experiment together with a computer simulation of the spectrum using observed coupling constants provides assignments of the other protons. The signals at 4.46 (d,  $J_{\text{H}2,3} = 3.2$  Hz), 4.28 (m,  $J_{\text{H}4,\text{H}^{\text{Sendo}}} = 2.8$  Hz,  $J_{\text{H}^{\text{Sendo}},\text{endo}} = 12.3$  Hz), and 2.61 (m,  $J_{\text{H}3,\text{H}^{\text{Sexo}}} = 0.7$  Hz) are assigned to H<sup>2</sup>, H<sup>Sendo</sup> and H<sup>Sexo</sup>, respectively. The H<sup>3</sup> and H<sup>4</sup> protons of the coordinated olefin are observed at 3.89 (m,  $J_{\text{H}3,4} = 5.1$  Hz) and 3.41 (d of d,  $J_{\text{H}3,4} = 5.1$  Hz,  $J_{\text{H}4,6} = 2.8$  Hz), which is 2–2.5 ppm upfield of the olefinic protons in free 2,5-DHT (5.85 ppm,  $\text{CDCl}_3$ ), as expected for a coordinated olefin. In the <sup>13</sup>C NMR spectrum, the coordinated carbon resonances (C(3), 79.9; C(4), 36.5) are also upfield by 40–80 ppm compared to free 2,5-DHT (C(3), C(4); 128.9 ppm).<sup>30</sup> The other two carbon resonances are at 59.8 ppm (C(5)) and 15.5 ppm (C(2)). These chemical shifts are unequivocally assigned on the basis of selective <sup>1</sup>H-coupled <sup>13</sup>C NMR experiments. The structural assignment based on spectroscopic data was established by an X-ray diffraction study of complex **7**. The structure shown in Figure 2 shows that the sulfur and the olefin coordinate to two different ruthenium atoms and C-H activation occurs at C(2) of 2,5-DHT forming a C-Ru bond at the third ruthenium atom of the cluster. Thus, the  $\text{C}_4\text{H}_5\text{S}$  ligand sits on the triangle of ruthenium atoms. Since there are two orientations of the 2,5-DHT ring in the crystal, the bond distances and angles of the 2,5-DHT ligand have relatively large errors. The longest Ru-Ru distance (3.032 (2) Å) is assigned to the hydride-bridged Ru(2)-Ru(3) bond, as it is known that metal-metal bonds are lengthened by a hydride bridge.<sup>31</sup> This hydride location is also supported by <sup>1</sup>H NMR spectroscopic data, which show that the metal-hydride is coupled with the proximate H<sup>Sendo</sup> proton.

**Relevance to Thiophene HDS.** As noted in the Introduction, 2,5-DHT undergoes HDS over  $\text{Re}/\gamma\text{-Al}_2\text{O}_3$  at 300 °C to give butadiene as the major desulfurized product (eq 1).<sup>4d</sup> Under the same conditions but with D<sub>2</sub> instead of H<sub>2</sub>, 65% of the butadiene

product contained no deuterium.<sup>4d</sup> This suggests that 2,5-DHT adsorbs to the catalyst in a manner that does not promote C-H cleavage and/or exchange with deuterium on the catalyst surface prior to or during butadiene formation. Since sulfur is the strongest donor in 2,5-DHT, as observed in its coordination to metal complexes in this paper, this coordination mode may also be involved on the catalyst. If such coordination were to also promote the liberation of butadiene from 2,5-DHT, it would reasonably account for the large amount of butadiene formed and the relatively low amount of deuterium incorporation into the butadiene product. Thus, we examined the decomposition of our S-coordinated 2,5-DHT complexes to determine whether or not this coordination promotes butadiene liberation; the metal-containing products of these reactions were not investigated; presumably they are metal sulfides. The solid complexes  $\text{W}(\text{CO})_5(2,5\text{-DHT})$  and  $\text{Re}_2(\text{CO})_9(2,5\text{-DHT})$  start to decompose at 110 °C. The volatile products were collected after 15–20 min at 110 °C in a liquid-nitrogen bath. The <sup>1</sup>H NMR spectra of these volatile materials from both complexes show the presence of butadiene (~20%) and free 2,5-DHT (~80%). The analogous  $\text{W}(\text{CO})_5(3,4\text{-Me}_2\text{DHT})$  also decomposes at 110–120 °C to give off 2,3-dimethyl-1,3-butadiene (~15%) and free 3,4-Me<sub>2</sub>DHT (~85%) under the same conditions. Uncoordinated 2,5-DHT itself does not decompose at all at 120 °C after 3 days. Therefore, S-coordination of 2,5-DHT to metal centers does promote the liberation of butadiene. Butadiene elimination is also a major decomposition pathway for 2,5-DHT adsorbed on Mo(110).<sup>32</sup>

Other S-coordinated 2,5-DHT complexes,  $\text{Cp}^*(\text{CO})_2\text{Re}(2,5\text{-DHT})$  and  $\text{RuCl}_2(\text{CO})_3(2,5\text{-DHT})$ , give only free 2,5-DHT upon heating at 110 °C. Also,  $\text{Cp}(\text{PPh}_3)_2\text{Ru}(2,5\text{-DHT})^+$  was reported<sup>33</sup> not to eliminate butadiene under mild conditions. The S-coordinated 2,5-DHT palladium and platinum complexes  $\text{MCl}_2(2,5\text{-DHT})_2$ , **8** and **9**, are more stable and require higher temperatures (180 °C) for decomposition. Upon being heated at 180 °C for 15–20 min, complexes **8** and **9** give off mainly thiophene and free 2,5-DHT (1:1) with only small amounts of butadiene. The formation of thiophene was not observed from the other 2,5-DHT complexes. Presumably, this occurs by elimination of two HCl molecules to give a very unstable intermediate,  $\text{M}(2,5\text{-DHT})$ - (thiophene) (M = Pd, Pt), which decomposes to 2,5-DHT, thiophene, and the metals. This dehydrogenation of 2,5-DHT to give thiophene accompanies the formation of butadiene in the reactor studies<sup>4d</sup> as well. Thus, butadiene and thiophene formation are competing reactions on  $\text{Re}/\gamma\text{-Al}_2\text{O}_3$ . In the Pd and Pt complexes **8** and **9**, thiophene is the primary product. However,  $\text{W}(\text{CO})_5(2,5\text{-DHT})$ ,  $\text{Re}_2(\text{CO})_9(2,5\text{-DHT})$ , and  $\text{Fe}(\text{CO})_4(2,5\text{-DHT})$ <sup>4c</sup> give butadiene but no thiophene. At this point, it is not clear what properties of the metal complex determine whether or not butadiene is formed. Although it is tempting to suggest that butadiene formation occurs by a concerted process, further studies are required before any mechanistic conclusions can be drawn. However, it is clear that S-coordination does promote butadiene release in certain complexes. Thus, it is possible, or perhaps even probable, that the formation of butadiene from 2,5-DHT over  $\text{Re}/\gamma\text{-Al}_2\text{O}_3$  (eq 1) occurs by such a reaction. These results also support step 4 in Scheme I as a viable desulfurization reaction in the HDS of thiophene.

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**Supplementary Material Available:** For **5** and **7**, full tables of crystal data, bond distances, bond angles, and positional and thermal parameters (11 pages); listings of calculated and observed structure factors (28 pages). Ordering information is given on any current masthead page.

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