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Synthetic, Structural and Binding Studies of the 4,6-Dimethyldibenzothiophene Complex $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2(\eta^1(S)\text{-}4,6\text{-}Me_2DBT)]BF_4$: Toward an Understanding of Deep Hydrodesulfurization

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The removal of organosulfur compounds from automotive and diesel fuels is important for the reduction of atmospheric pollution by sulfur oxides that form acid rain in the atmosphere.[1] Sulfur compounds in these fuels also impair new vehicle emission control systems that lower the levels of nitrogen oxides (NO_x) and particulate matter released into the atmosphere during fuel combustion.[2] The EPA has mandated that sulfur in gasoline be reduced from the current average of 270 ppm to an average of 30 ppm by 2005[2a] and that sulfur in diesel fuel be reduced from the current limit of 500 ppm to 15 ppm by 2006.[2b] Sulfur is removed from gasoline and diesel fuels utilizing the industrial catalytic process known as hydrodesulfurization (HDS). The most difficult of the sulfur-containing compounds to be removed are the hindered dibenzothiophene derivatives (DBTh) that contain alkyl groups near the sulfur in the 4- and 6-positions.[1b,3−5] It is these hindered compounds that must be removed in order to meet the upcoming EPA requirements, and the process for removing these remaining sulfur compounds to obtain sulfur levels below 50 ppm has been termed "deep desulfurization".[6] Numerous studies[7] of the HDS of DBT and its 4- and 4,6-methyl substituted derivatives indicate that the rates of HDS decrease in the order: DBT > 4-MeDBT > 4,6-Me_2DBT. It has been proposed that the slow rates of 4-MeDBT and 4,6-Me_2DBT hydrodesulfurization are due to their weak coordination to metal sites on the catalyst surface because of steric repulsion by the 4- and 6- methyl groups. Indeed, there is only one report[8] of a sulfur-coordinated 4,6-Me_2DBT complex, Cp*Rh-(PMe_3)(4,6-Me_2DBT), which was characterized only by its ^{1}H NMR spectrum due to its instability. The purpose of the present work was to prepare stable complexes of 4-MeDBT and 4,6-Me_2DBT, to determine the effect of the 4- and 6-methyl groups on the coordinating abilities of these dibenzothiophenes to metal centers, and to relate their coordinating abilities to their rates of catalytic HDS.

The complexes $[Cp^*Ru(CO)_2(\eta^1(S)\text{-DBTh})]BF_4$, where Cp* = η^5-C_5Me_5 and DBTh = 4,6-Me_2DBT (**1**), 4-MeDBT (**2**), DBT (**3**), and 2,8-Me_2DBT (**4**), were prepared by reacting 0.30 mmol of $Cp^*Ru(CO)_2Cl$ with 0.35 mmol of DBTh and 0.35 mmol of $AgBF_4$ in 15 mL of CH_2Cl_2 for 30 min according to eq 1.

$$Cp^*Ru(CO)_2Cl + DBTh \xrightarrow[\text{rt, 30 min -AgCl}]{AgBF_4,\ CH_2Cl_2,} [Cp^*Ru(CO)_2(\eta^1(S)\text{-DBTh})]BF_4 \quad (1)$$

After filtration of the reaction mixture and precipitation with cold Et_2O, the solid products $[Cp^*Ru(CO)_2(\eta^1(S)\text{-DBTh})]BF_4$ were isolated in 80−90% yields and characterized by their elemental analyses, infrared, ^{1}H, and ^{13}C NMR spectra.[9] The pale-yellow powders are air and moisture stable and can easily be handled in the atmosphere. However, $[Cp^*Ru(CO)_2(\eta^1(S)\text{-}4,6\text{-}Me_2DBT)]^+$ must be handled below 0 °C for spectroscopic characterization, as it immediately begins to decompose at room temperature in solution (CD_2Cl_2, CD_3NO_2).

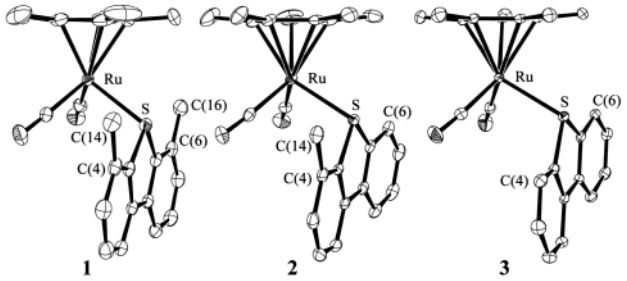

Figure 1. Thermal ellipsoid drawings of $[Cp^*Ru(CO)_2(\eta^1(S)\text{-}4,6\text{-}Me_2DBT)]BF_4$ (**1**), $[Cp^*Ru(CO)_2(\eta^1(S)\text{-}4\text{-}MeDBT)]BF_4$ (**2**), and $[Cp^*Ru(CO)_2(\eta^1(S)\text{-DBT})]BF_4$ (**3**). Ellipsoids are shown at the 30% probability level; hydrogens are omitted for clarity.

Table 1. Selected Distances (Å) and Twist Angles (deg) for Compounds **1**, **2**, and **3**

		d C_5Me_5 Plane (Å)				
ligand	Ru−S (Å)	C(4)	C(6)	C(14)	C(16)	twist angle
4,6-Me_2DBT (**1**)	2.4186(7)	4.436	4.477	3.076	3.111	0.4
4-MeDBT (**2**)[a]	2.3987(9)	4.694	3.793	3.417		11.3
	2.4038(9)	3.795	4.767		3.508	12.3
DBT (**3**)	2.3936(5)	4.946	3.416			20.2

[a] Values for the two enantiomers.

Crystals of both **1** and **3** for X-ray diffraction studies were obtained by layering a methylene chloride solution of each compound with diethyl ether and storing at −20 °C for 1 week.[10a,c] Crystals of **2** were obtained by slow diffusion of hexanes into an acetone solution of the compound and storing at −20 °C for 1 week.[10b] In all three structures (Figure 1), the DBTh ligands are oriented exo with respect to the Cp* ligand, as was previously observed in the related $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1(S)\text{-DBT})]^+$.[11] Selected distances and angles for compounds **1**, **2**, and **3** are listed in Table 1. The X-ray structures show that the Ru−S distance increases with the number of 4- and 6-methyl groups in the DBTh ligand: **3** (2.3936(5) Å) < **2** (2.4013(9) Å)[12] < **1** (2.4186(7) Å). To illustrate further the steric effects of the 4- and 6-methyl groups, one can examine the orientation of the DBTh ligand around the Ru−S bond by considering the dihedral angle defined by the Cp* centroid-Ru-S-midpoint between C(10) and C(11). For a symmetrical orientation of the DBTh ligand, this angle would be 180°; we define deviations from 180° as the twist angle. In **1**, the twist angle is only 0.4° because the 4,6-Me_2DBT ligand is prevented from rotating around the Ru−S bond by the close approach (3.076, 3.111 Å) of

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the methyl carbon atoms, C(14) and C(16), to a plane defined by the Cp* methyl carbon atoms. In **2**, the twist angle is 11.8° with the methyl carbon in the 4-MeDBT ligand at a distance (3.463 Å) from the Cp* methyl plane that is longer than that in **1**. In **3**, the twist angle (20.2°) is even larger, which indicates that there is even greater freedom of rotation around the Ru−S bond; the distance of closest approach of the DBT carbon atom C(6) to the Cp* methyl plane is 3.416 Å. This distance and the distance of closest approach (3.463 Å) in **2** are similar, which suggests that a distance of 3.42−3.51 Å between a DBTh carbon and the Cp* methyl carbon plane is sterically noncrowding. This means that the shorter distances (3.076 Å, 3.111 Å) in **1** indicate crowding of the 4,6-Me_2DBT methyl groups and the Cp* ligand.

To quantify the effect of hindering methyl groups on the coordinating abilities of the dibenzothiophenes, equilibrium constants (K) for the displacement of one dibenzothiophene by another (eq 2) were determined at 25.0 °C in CD_2Cl_2.[13] The relative

$$Cp^*Ru(CO)_2(DBTh)^+ + DBTh' \rightleftharpoons Cp^*Ru(CO)_2(DBTh')^+ + DBTh \quad (2)$$

equilibrium constants, K' (given in parentheses), for the displacement of DBT from $[Cp^*Ru(CO)_2(\eta^1(S)\text{-DBT})]^+$ by 4-MeDBT, 4,6-Me_2DBT, and 2,8-Me_2DBT increase in the order: 4,6-Me_2DBT (1.00) < 4-MeDBT (20.2(1)) < DBT (62.7(6)) < 2,8-Me_2DBT (223(3)). The larger K' value for 2,8-Me_2DBT (223) indicates that the electron-donating methyl groups increase the binding ability of DBT by a factor of 3.6. On the other hand, when the methyl groups are in the sterically hindering 4,6-positions, the 4,6-Me_2-DBT ligand is 62.7 times *less* strongly binding than DBT. Thus, the steric effect of the 4,6-methyl groups substantially reduces the binding ability of 4,6-Me_2DBT. The K' value (20.2) for 4-MeDBT is only 3.1 times less than that for DBT, which shows that the steric effect of one hindering methyl group is much less than that of two.

In summary, we have shown that the highly hindered 4,6-Me_2-DBT forms the air-stable $[Cp^*Ru(CO)_2(\eta^1(S)\text{-4,6-}Me_2DBT]^+$ complex, the first fully characterized complex containing a sulfur-bound 4,6-Me_2DBT ligand. Equilibrium studies show that 4,6-Me_2DBT is the most weakly coordinated dibenzothiophene in the series of $[Cp^*Ru(CO)_2(\eta^1(S)\text{-DBTh})]^+$ complexes, whose relative binding constants K' increase in the same order (4,6-Me_2DBT < 4-MeDBT < DBT < 2,8-Me_2DBT) as their rates of hydrodesulfurization on a variety of transition-metal sulfide catalysts.[7] This trend in HDS activity is consistent with a mechanism in which equilibrium coordination of the DBTh to an active metal site on the catalyst surface precedes hydrogenation that leads to desulfurization.

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Note Added after ASAP: The version published 2/4/2003 contained an error in the discussion of Ru−S distances. The final Web version published 2/6/2003 and the print version are correct.

Supporting Information Available: Crystallographic files for the structures of compounds **1**, **2**, and **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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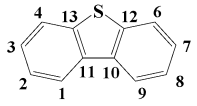

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(9) Characterization of $[Cp^*Ru(CO)_2(\eta^1(S)\text{-4,6-}Me_2DBT)]BF_4$ (**1**): ^{1}H NMR (δ, ppm in CD_2Cl_2) 8.03 (d, J = 7.6 Hz, 2H), 7.63 (t, J = 7.6 Hz, 2H), 7.44 (d, J = 7.6 Hz, 2H), 2.52 (s, 6H, CH_3), 2.00 (s, 15H, CH_3). ^{13}C NMR (δ, ppm in CD_2Cl_2) 195.92 (CO); 139.61, 137.90, 134.55, 130.75, 130.64, 121.77, 21.63 (4,6-Me_2DBT); 103.63, 10.57 (Cp*). IR (CH_2Cl_2, ν(CO) cm^{-1}) 2057(s), 2014(s). Anal. Calcd for $C_{26}H_{27}BF_4O_2RuS$: C, 52.80; H, 4.60; S, 5.42. Found: C, 52.49; H, 4.89; S, 5.13. Characterization of $[Cp^*Ru(CO)_2(\eta^1(S)\text{-4-MeDBT})]BF_4$ (**2**): ^{1}H NMR (δ, ppm in CD_2Cl_2) 8.18−8.16 (m, 1H), 8.09 (d, J = 7.6 Hz, 1H), 7.76−7.65 (m, 4H), 7.46 (d, J = 7.6 Hz, 1H), 2.51 (s, 3H, CH_3), 1.92 (s, 15H, CH_3). ^{13}C NMR (δ, ppm in CD_2Cl_2) 196.11 (CO); 140.67, 138.33, 137.55, 136.61, 135.03, 130.89, 130.87, 130.27, 130.19, 124.16, 123.83, 121.82, 21.07 (4-MeDBT); 103.83, 10.31 (Cp*). IR (CH_2Cl_2, ν(CO) cm^{-1}) 2057(s), 2013(s). Anal. Calcd for $C_{25}H_{25}BF_4O_2RuS$: C, 52.00; H, 4.36; S, 5.55. Found: C, 51.69; H, 4.10; S, 5.35. Characterization of $[Cp^*Ru(CO)_2(\eta^1\text{-}(S)\text{-DBT})]BF_4$ (**3**): ^{1}H NMR (δ, ppm in CD_2Cl_2) 8.22−8.20 (m, 2H), 7.76−7.68 (m, 6H), 1.92 (s, 15H, CH_3). ^{13}C NMR (δ, ppm in CD_2Cl_2) 196.11 (CO); 138.65, 137.94, 130.40, 130.09, 124.72, 123.92 (DBT); 104.02, 10.29 (Cp*). IR (CH_2Cl_2, ν(CO) cm^{-1}) 2058(s), 2014(s). Anal. Calcd for $C_{24}H_{23}BF_4O_2RuS$: C, 51.17; H, 4.11; S, 5.69. Found: C, 50.81; H, 4.49; S, 5.64. Characterization of $[Cp^*Ru(CO)_2(\eta^1(S)\text{-2,8-}Me_2DBT)]\text{-}BF_4$ (**4**): ^{1}H NMR (δ, ppm in CD_2Cl_2) 7.97 (s, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 2.57 (s, 6H, CH_3), 1.91 (s, 15H, CH_3). ^{13}C NMR (δ, ppm in CD_2Cl_2) 196.28 (CO); 141.23, 138.13, 135.66, 131.12, 124.37, 124.14, 21.93 (2,8-Me_2DBT); 103.91, 10.27 (Cp*). IR (CH_2Cl_2, ν(CO) cm^{-1}) 2057(s), 2012(s). Anal. Calcd for $C_{26}H_{27}BF_4O_2RuS$: C, 52.80; H, 4.60; S, 5.42. Found: C, 52.80; H, 4.82; S, 5.87.
(10) Crystal data for the following: (a) $[Cp^*Ru(CO)_2(\eta^1(S)\text{-4,6-}Me_2DBT)]\text{-}BF_4\cdot CH_2Cl_2$ (**1**), yellow crystal, $C_{26}H_{27}BF_4O_2RuS\cdot CH_2Cl_2$, M = 676.34, monoclinic, space group $P2(1)/c$, a = 15.467(3) Å, b = 11.661(2) Å, c = 17.591(3) Å, α = 90°, β = 115.373(3)°, γ = 90°, V = 2866.5(9) Å^3, Z = 4, D_c = 1.567 g cm^{-3}, λ = 0.71073 Å, μ(Mo Kα) 0.856 mm^{-1}. $R1$ = 0.0318, $wR2$ = 0.0859 for $I > 2\sigma(I)$. (b) $[Cp^*Ru(CO)_2(\eta^1(S)\text{-4-MeDBT})]BF_4$ (**2**), yellow crystal, $C_{25}H_{25}BF_4O_2RuS$, M = 577.39, monoclinic, space group $P2(1)/c$, a = 28.147(5) Å, b = 10.726(2) Å, c = 16.723(3) Å, γ = 90°, β = 106.583(4)°, γ = 90°, V = 4838.7(16) Å^3, Z = 8, D_c = 1.585 g cm^{-3}, λ = 0.71073 Å, μ(Mo Kα) 0.786 mm^{-1}. $R1$ = 0.0348, $wR2$ = 0.0794 for $I > 2\sigma(I)$. (c) $[Cp^*Ru(CO)_2(\eta^1(S)\text{-DBT})]\text{-}BF_4$ (**3**), yellow crystal, $C_{24}H_{23}BF_4O_2RuS$, M = 563.36, monoclinic, space group $P2(1)/n$, a = 10.8541(14) Å, b = 11.6452(15) Å, c = 19.156(3) Å, γ = 90°, β = 105.468(2)°, γ = 90°, V = 2333.6(5) Å^3, Z = 4, D_c = 1.603 g cm^{-3}, λ = 0.71073 Å, μ(Mo Kα) 0.812 mm^{-1}. $R1$ = 0.0261, $wR2$ = 0.0665 for $I > 2\sigma(I)$. For all X-ray data, $R1 = \sum||F_o| - ||F_c||/|F_o|$ and $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w\{F_o^2)^2]\}^{1/2}$.
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(12) The X-ray data show that $[Cp^*Ru(CO)_2(\eta^1(S)\text{-4-MeDBT})]BF_4$, (**2**), contains two structurally independent molecules (enantiomers of each other) in the asymmetric unit cell. Distances discussed within the text are averages of the parameters for the enantiomers.
(13) Approximately 0.02 mmol of each reactant, along with triphenylmethane as an internal standard, was introduced into an NMR tube and dissolved in 0.8 mL of CD_2Cl_2. After three freeze−pump−thaw cycles, the tube was flame-sealed under argon and thermostated in a bath at 25.0 °C. Relative concentrations of reactants and products were determined by integration of the DBTh and DBTh′ proton signals in the ^{1}H NMR spectra. Equilibria for all reactions were established within 48 h and were unchanged after 96 h. Experimentally determined equilibrium constants for reaction 2 expressed as K[DBTh; DBTh′] follow: 0.0159(2)[DBT; 4,6-Me_2DBT], 0.329(10)[DBT, 4-MeDBT], 3.55(2)[DBT; 2,8-Me_2DBT], 0.0496(2)[4-MeDBT; 4,6-Me_2DBT], where each K value is the K for the forward reaction and 1/K of the reverse reaction; the deviation from this average is given in parentheses.

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