Reactions of 2-Benzo[*b*]thienyl (2-BTyl) Complexes with Acid To Give $Cp(PMe_3)_2Ru(\eta^1(S)\text{-}BT)^+$ and $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}BT)^+$: A Model for Benzo[*b*]thiophene (BT) Deuterium Exchange on Hydrodesulfurization Catalysts

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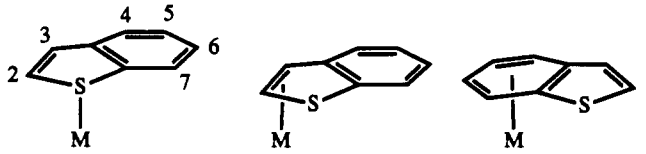
Hydrodesulfurization[2] (HDS) of benzo[*b*]thiophene (BT) over $Co\text{–}Mo/Al_2O_3$ catalysts to give ethylbenzene and H_2S is proposed to occur by two mechanistic pathways:[3] either by initial hydrogenation to give 2,3-dihydrobenzothiophene followed by desulfurization to form the final products or by initial desulfurization to give vinylbenzene followed by hydrogenation to ethylbenzene. Regardless of the pathway, the reaction involves only the thiophenic part of BT as the benzene ring is not hydrogenated. Also, deuterium exchange of BT, when passed with D_2 over HDS catalysts, occurs predominantly in the 2- and 3-positions[4,5] of the thiophene rather than in the benzene ring. A mechanism which accounts for this deuterium exchange has been proposed by Cowley[4] (Figure 1). He postulates that BT binds to a metal atom on the catalyst surface through either C2 or C3, forming 2-benzothienyl (2-BTyl) or 3-benzothienyl (3-BTyl) intermediates; these intermediates then incorporate deuterium from the surface to give deuterated BT. Only the mechanism for deuteration at C2 is shown in Figure 1.

Recent investigations of BT binding in organometallic complexes have indicated some possible modes for its binding to the catalyst surface:



(η^1(S)-BT) (2,3-η^2-BT) (η^6-BT)

Benzothiophene binds more strongly through the S atom than thiophene yet more weakly than dibenzothiophene as determined by equilibrium and kinetic studies[6] of these and other η^1(S)-thiophenes (Th) in $Cp(CO)_2Ru(\eta^1(S)\text{-}Th)^+$ and $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-}Th)^+$. Of the other known η^1(S)-BT complexes, $Cp(CO)_2Fe(\eta^1(S)\text{-}BT)^+$ [7] and $Cp'(CO)_2Re(\eta^1(S)\text{-}BT)$[8] (Cp' = η^5-C_5H_5, η^5-C_5Me_5), $Cp'(CO)_2Re(\eta^1(S)\text{-}BT)$ is in equilibrium with its 2,3-η^2-bound isomer. At present, there is no evidence that η^1(S)-coordination promotes deuterium exchange in these complexes; so, this adsorption mode does not account for deuterium exchange of the 2- and 3-hydrogens in BT on HDS catalysts.[4,5] Deuterium exchange of 2,3-η^2-bound BT by cis-dideuteration followed by H_2 elimination would lead to equal deuteration in the 2- and 3-positions. However, results of Cowley[4] and our group[5] show that exchange occurs faster in the 2- than in the 3-position, which suggests that 2,3-η^2 adsorption of BT is not involved in deuterium exchange on the catalysts. The third known mode of coordination, η^6, is observed in $CpM(\eta^6\text{-}BT)^{2+}$ (M = Rh, Ir),[9] $CpRu(\eta^6\text{-}BT)^+$,[9,10] and $(CO)_3Cr(\eta^6\text{-}BT)$.[11] However, since base-catalyzed deuterium exchange[5] in $Cp(Ru)(\eta^6\text{-}BT)^+$ occurs primarily at the 2- and 7-positions rather than at the 2- and 3-positions, η^6-coordination of BT does not account for the observed 2- and 3-exchange observed on HDS catalysts.

In order to probe the possibility that σ-coordination of 2-benzothienyl (2-BTyl) to a metal accounts for deuterium exchange at the 2-position as proposed by Cowley (Figure 1),[4] we describe herein the synthesis of 2-BTyl complexes of Ru and examine their reactions with CF_3SO_3H.

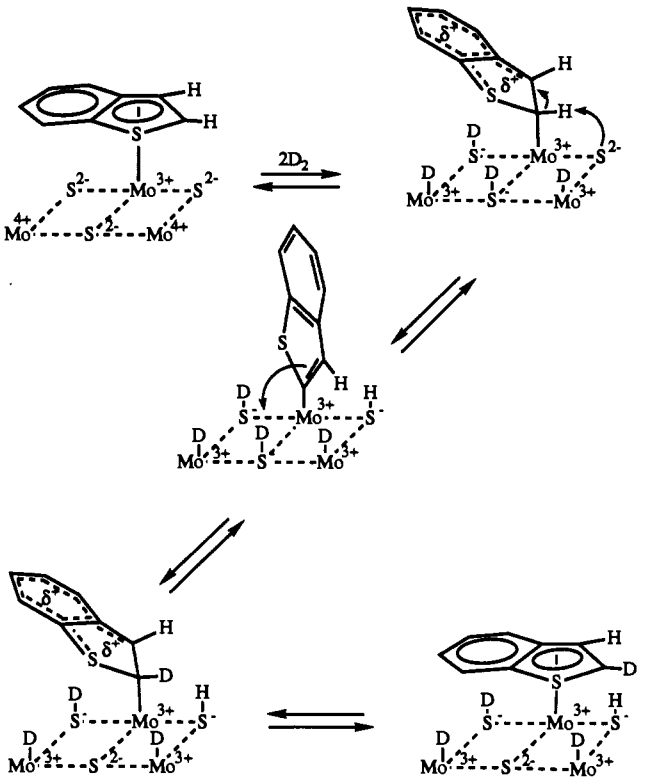


Figure 1. Cowley's proposed mechanism[4] for deuterium exchange of H at the 2-position.

(1) Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.

(2) (a) *Geochemistry of Sulfur in Fossil Fuels*; Orr, W. L., White, C. M., Eds. *ACS Symposium Series 429*; American Chemical Society: Washington, DC, 1990. (b) Prins, R.; deBeer, V. H. J.; Somorjai, G. A. *Catal. Rev.—Sci. Eng.* **1989**, *31*, 1. (c) McCulloch, D. C. In *Applied Industrial Catalysis*; Leach, B. E., Ed.; Academic: New York, 1983; Vol. 1, p 69. (d) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979; Chapter 5.

(3) (a) López, R.; Peter, R.; Zdrazil, M. *J. Catal.* **1982**, *73*, 406. (b) Obedunmi, E. O.; Ollis, D. F. *J. Catal.* **1983**, *80*, 65. (c) Pokorny, P.; Zdrazil, M. *Collect. Czech. Chem. Commun.* **1981**, *46*, 2185. (d) Bartsch, R.; Tanielian, C. *J. Catal.* **1974**, *35*, 353. (e) deBeer, V. H. J.; Dahlmans, J. G. J.; Smeets, J. G. M. *J. Catal.* **1976**, *42*, 467. (f) Furinsky, E.; Amberg, C. H. *Can. J. Chem.* **1976**, *54*, 1507. (g) Bartsch, R.; Tanielian, C. *J. Catal.* **1977**, *50*, 35. (h) Givens, E. N.; Venuto, P. B. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1970**, *14* (part 2), 135. (i) Geneste, P.; Amblard, P.; Bonnet, M.; Graffin, P. *J. Catal.* **1980**, *61*, 115. (j) Daly, F. P. *J. Catal.* **1978**, *51*, 221. (k) Girgis, M. J.; Gates, B. C. *Ind. Eng. Chem. Res.* **1991**, *30*, 2021. (l) Levaché, D.; Guida, A.; Geneste, P. *Bull. Soc. Chim. Belg.* **1981**, *90*, 1285. (m) Sánchez-Delgado, R. A.; González, E. *Polyhedron* **1989**, *8*, 1431.

(4) Cowley, S. W. Ph.D. Thesis, Southern Illinois University, 1975.

(5) Huckett, S. C.; Angelici, R. J.; Ekman, M. E.; Schrader, G. L. *J. Catal.* **1988**, *113*, 36.

(6) (a) Benson, J. W.; Angelici, R. J. *Organometallics* **1992**, *11*, 922. (b) Benson, J. W.; Angelici, R. J. *Organometallics* **1993**, *12*, 680.

(7) Goodrich, J. D.; Nickias, P. N.; Selegue, J. P. *Inorg. Chem.* **1987**, *26*, 3424.

(8) (a) Choi, M.-G.; Robertson, M. J.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 4005. (b) Choi, M.-G.; Angelici, R. J. *Organometallics* **1992**, *11*, 3328.

(9) Huckett, S. C.; Miller, L. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1988**, *7*, 686.

(10) Chaudret, B.; Jalón, F.; Pérez-Manrique, M.; Lahoz, F.; Plou, F. J.; Sánchez-Delgado, R. *New. J. Chem.* **1990**, *14*, 331.

(11) Fischer, E. O.; Goodwin, H. A.; Kreiter, C. G.; Simmons, H. D., Jr.; Sonogashira, K.; Wild, S. B. *J. Organomet. Chem.* **1968**, *14*, 359.

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Experimental Section

General Procedures. The IR spectra were taken in CH_2Cl_2 on a Nicolet 710 FT-IR spectrometer. The ^1H NMR spectra were recorded on either a Nicolet NT-300 or a Varian VXR-300 spectrometer using deuterated solvents as the internal lock. The $^{13}C\{^1H\}$ NMR spectra were taken on either a Bruker WM-200 or a Varian VXR-300 spectrometer using deuterated solvents as the internal lock and reference ($CDCl_3$, δ 77.0; CD_2Cl_2, δ 53.8; CD_3NO_2, δ 62.8). Fast atom bombardment (FAB) mass spectra were obtained in a CH_2Cl_2/3-nitrobenzyl alcohol matrix with a Kratos MS-50 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and Desert Analytics, Tucson, AZ.

Reactions were performed under nitrogen atmosphere using standard Schlenk techniques.[12] Solvents were dried under N_2 prior to use; hexanes and CH_2Cl_2 were distilled from CaH_2, and THF and diethyl ether were distilled from Na/benzophenone. Methanol was distilled from magnesium alkoxide, which was generated from magnesium turnings and iodine in absolute MeOH.[13] Starting materials $Cp(PMe_3)_2RuCl$,[14] $Cp(PMe_3)_2RuI$,[14] and $Cp(CO)(PPh_3)RuCl$[15] were prepared by literature methods. The synthesis of $[Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-BT})]BF_4$ was described previously.[6a] Benzo[*b*]thiophene (BT) was purchased from Aldrich and sublimed under vacuum at room temperature prior to use. A 2.1 M solution of *n*-BuLi in *n*-hexane was purchased from Johnson Matthey. Triflic acid, CF_3SO_3H (3M Co), was distilled at ambient pressure under N_2. Silver triflate ($AgCF_3SO_3$), $NH_4(PF_6)$, and $Me_3O(BF_4)$ were used as purchased from Aldrich. Neutral alumina, Brockman I (~150 mesh), was purchased from Aldrich and deactivated with 5% (w/w) deionized H_2O after 24 h under vacuum. CF_3SO_3D was prepared by stirring D_2O (99.8 atom %) (0.72 g, 0.036 mol) and $(CF_3SO_2)_2O$ (10.0 g, 0.0354 mol) for 3 h and then distilling the deuterio acid at ambient pressure and 162 °C. Subsequent reactions of **1** and **2** (see Results and Discussion) with CF_3SO_3D indicated the presence of 40% CF_3SO_3H. This may be due to exchange of CF_3SO_3D with small amounts of water in the solvent or adsorbed on the glassware.

Synthesis of $Cp(PMe_3)_2Ru(2\text{-BTyl})$ (1). Method A. A solution of 1.138 g (8.480 mmol) of BT in 30 mL of THF was cooled at 0 °C. To this solution was added 4.0 mL (8.4 mmol) of a 2.1 M solution of *n*-BuLi in *n*-hexane. After the solution was allowed to warm to room temperature with stirring for 30 min, it was refluxed for an additional 30 min, cooled to room temperature, and then cooled to 0 °C in an ice bath. To this solution was added 0.500 g (1.41 mmol) of $Cp(PMe_3)_2RuCl$ in 30 mL of THF. The resulting solution was refluxed for 2 h. The solution was cooled to room temperature, and the solvent was removed under vacuum. The residue was chromatographed on a neutral alumina column (2 cm × 20 cm) with a 1:5 mixture of CH_2Cl_2 and hexanes. Complex **1** eluted as the first yellow band. Removal of solvent gave 0.1675 g of **1** as a yellow powder (26.3% yield). ^1H NMR (CD_2Cl_2), δ: 7.48 (d, J = 7.7 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.00 (td, J = 6.9, 1.1 Hz, 1H), 6.82 (td, J = 7.5, 1.1 Hz, 1H), and 6.76 (s, 1H), BTyl; 4.70 (s, 5H), Cp; 1.45 (pst, 18H), PMe_3. $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ: 164.5 (t, $^2J_{CP}$ = 17.5 Hz), 146.6 (s), 144.1 (s), 130.2 (t, $^3J_{CP}$ = 4.2 Hz), 122.3 (s), 119.3 (s), 118.7 (s), and 118.1 (s), BTyl; 82.3 (t, J_{CP} = 2.1 Hz), Cp; 23.5 (t, J = 14.3 Hz), PMe_3. Anal. Calcd for $C_{19}H_{28}P_2RuS$: C, 50.54; H, 6.25. Found: C, 50.87; H, 6.16.

Method B. A solution of 0.1630 g (1.215 mmol) of BT in 20 mL of THF was cooled in an ice bath. To this solution was added 0.60 mL (1.3 mmol) of a 2.1 M *n*-BuLi solution in *n*-hexane. The resulting solution was allowed to warm to room temperature while being stirred for 30 min. The solution was then refluxed for 30 min, cooled to room temperature, and cooled again in the ice bath. In a separate flask, 0.1050 g (0.2358 mmol) of $Cp(PMe_3)_2RuI$ was dissolved in 20 mL of THF. Solid $AgCF_3SO_3$ (65.1 mg, 0.253 mmol) was added, and the resulting solution was stirred for 10 min. A precipitate formed immediately. The cloudy, orange solution was filtered and added to the LiBTyl solution. The resulting dark red solution was allowed to warm to room temperature while being stirred for 1 h. Solvent was removed under vacuum, and the residue was chromatographed on neutral alumina. Product **1** was isolated as above as a yellow powder (45.1 mg, 42% yield).

Synthesis of $Cp(CO)(PPh_3)Ru(2\text{-BTyl})$ (2). A solution of 0.1899 g (1.415 mmol) of BT in 30 mL of THF was cooled to 0 °C. To this solution was added 0.70 mL (1.5 mmol) of a 2.1 M *n*-BuLi solution in *n*-hexane. The flask was removed from the ice bath, and the mixture was stirred for 30 min at room temperature. The solution was then refluxed for 30 min, cooled to room temperature, and cooled again in the ice bath. To this solution was added 0.1065 g (0.2165 mmol) of $Cp(CO)(PPh_3)RuCl$ in 20 mL of THF. The resulting solution was stirred for 1 h, and the solvent was removed under vacuum. The residue was chromatographed on a neutral alumina column (2 cm × 20 cm). Complex **2** eluted from the column as the second yellow band with a 1:3 mixture of CH_2Cl_2 and hexanes. Solvent was removed under vacuum, and 48.1 mg of **2** was recovered as a yellow powder in 38.0% yield. IR: ν(CO) 1940 cm^{-1}. ^1H NMR ($CDCl_3$), δ: 7.55 (d, J = 7.8 Hz, 1H), 7.04 (t, J = 8.1 Hz, 1H), 6.90 (t, J = 7.0 Hz, 1H), and 6.48 (s, 1H), BTyl; 5.06 (s, 5H), Cp; 7.29 (m, 16H), PPh_3 + 1BTyl H. $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 147.1 (d, $^2J_{CP}$ = 16 Hz), 146.0 (s), 142.7 (s), 135.8 (s), 122.2 (s), 119.5 (s), 119.3 (s), and 119.0 (s), BTyl; 87.7 (s), Cp; 205.1 (d, $^2J_{CP}$ = 21 Hz), CO; 133.8 (d, $^1J_{CP}$ = 109 Hz), 133.4 (d, J_{CP} = 11.4 Hz), 129.9 (s), and 127.9 (d, J_{CP} = 10.4 Hz), PPh_3. Anal. Calcd for $C_{35}H_{25}OPRuS$: C, 65.18; H, 4.27. Found: C, 65.08; H, 4.44.

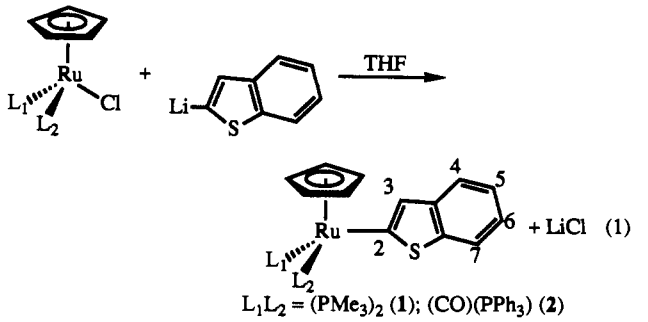
Synthesis of $[Cp(PMe_3)_2Ru(\eta^1(S)\text{-BT})]PF_6$ (3). A solution of 0.1010 g (0.2855 mmol) of $Cp(PMe_3)_2RuCl$ and 0.0882 g (0.657 mmol) of BT in 20 mL of MeOH was refluxed for 1.5 h. Solid $NH_4(PF_6)$ (0.2304 g, 1.414 mmol) was added, and the solution was cooled to room temperature. Solvent was removed under vacuum, 10 mL of CH_2Cl_2 was added to the residue, and the solution was filtered. The solution volume was reduced under vacuum, and complex **3** was precipitated (0.1211 g, 71.0% yield) by addition of 15 mL of Et_2O. ^1H NMR (CD_2Cl_2), δ: 7.87 (m, 1H), 7.74 (m, 1H), 7.53 (m, 2H), 7.46 (d, J = 5.6 Hz, 1H), and 7.20 (d, J = 5.6 Hz, 1H), BT; 4.47 (s), Cp; 1.68 (pst, 18H), PMe_3. $^{13}C\{^1H\}$ NMR (CD_3NO_2), δ: 150.3 (s), 141.3 (s), 136.9 (s), 129.6 (s), 128.7 (s), 127.6 (s), 127.1 (s), and 124.3 (s), BT; 83.4 (s), Cp; 22.9 (t, J_{CP} = 16.5 Hz), PMe_3. FAB: m/e 453.0 (M^+), 319.0 (M^+ – BT), and 243.0 (M^+ – BT – PMe_3). Anal. Calcd for $C_{19}H_{29}F_6P_3RuS{\cdot}0.5CH_2Cl_2$: C, 36.59; H, 4.72. Found: C, 36.86; H, 4.91. The solvating CH_2Cl_2 was identified in the ^1H NMR spectrum of **3** in CD_2Cl_2 solvent.

Reaction of 1 with CF_3SO_3H To Give 3. In a 5-mm NMR tube, 5.1 mg (0.011 mmol) of $Cp(PMe_3)_2Ru(2\text{-BTyl})$ was dissolved in 0.50 mL of CD_2Cl_2 under N_2, and the tube was capped with a septum. Using a microsyringe, 1.0 μL (0.011 mmol) of CF_3SO_3H was injected through the septum into the solution. The color changed immediately from yellow to orange. The ^1H NMR spectrum showed two Cp peaks at δ 5.28 and 4.47. The peak at δ 5.28 decreased in intensity as the peak at δ 4.47 increased; the peak at δ 4.47 was due to complex **3**, which was identified by its complete ^1H NMR spectrum; **3** was formed quantitatively after 1.5 h.

Reaction of 2 with CF_3SO_3H To Give 4. A solution of 6.8 mg (0.012 mmol) of **2** in 0.50 mL of CD_2Cl_2 was prepared under nitrogen in a 5-mm NMR tube. The tube was capped with a septum. Using a microsyringe, 1.0 μL (0.011 mmol) of CF_3SO_3H was injected into the solution. The solution color immediately turned from yellow to orange. Complex **4**, identified by its ^1H NMR spectrum,[6a] was formed quantitatively.

Results and Discussion

Lithiation of BT with *n*-BuLi to give 2-benzothienyllithium (LiBTyl) occurs exclusively at C2.[16] This LiBTyl reacts in situ with $Cp(PMe_3)_2RuX$ (X = Cl, O_3SCF_3) or $Cp(CO)(PPh_3)RuCl$ to give the 2-benzothienyl complexes $Cp(PMe_3)_2Ru(2\text{-BTyl})$ (**1**) and $Cp(CO)(PPh_3)Ru(2\text{-BTyl})$ (**2**) (eq 1). A better leaving group



L_1L_2 = $(PMe_3)_2$ (**1**); $(CO)(PPh_3)$ (**2**)

(12) (a) *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987. (b) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

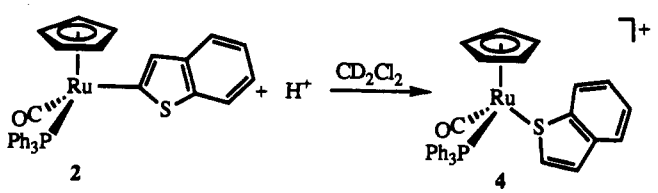
(13) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1987; p 249.

($CF_3SO_3^-$) on the metal expedites the reaction; thus, milder conditions are required and a higher yield is obtained when $AgCF_3SO_3$ is used to abstract I^- from $Cp(PMe_3)_2RuI$ (method B) prior to reaction with LiBTyl (eq 2). No reaction is observed when $Cp(PMe_3)_2RuI$ is refluxed with LiBTyl for 10 h.

$$Cp(PMe_3)_2RuI \xrightarrow[-AgI]{AgCF_3SO_3} \xrightarrow[-CF_3SO_3Li]{LiBTyl} \mathbf{1} \qquad (2)$$

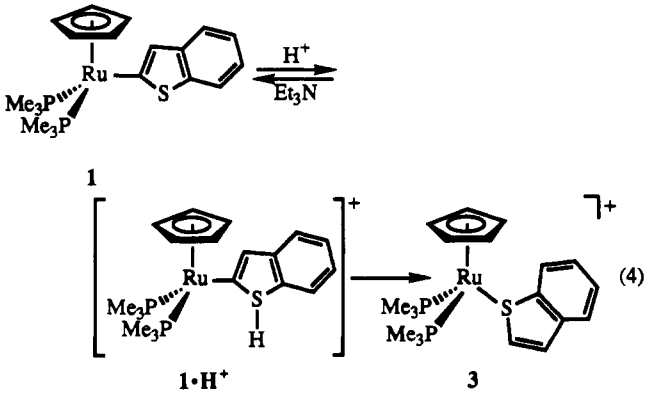
The 2-benzothienyl complexes, **1** and **2**, are characterized by ^1H and $^{13}C\{^1H\}$ NMR and elemental analyses (see Experimental Section). In their ^1H NMR spectra, the five BTyl protons are well resolved and exhibit a singlet (H3), two doublets (H4, H7), and two triplets (H5, H6) for both complexes (one of the doublets in the spectrum of **2** is obscured by Ph peaks). The ^{13}C NMR spectra of **1** and **2** show coupling of C2 to the phosphorus of the PR_3 ligands. For complex **2**, the two-bond coupling constant ($^2J_{CP}$ = 16 Hz) is similar to that of the CO (δ 205.1, $^2J_{CP}$ = 21 Hz) in this same complex. In the spectrum of **1**, C2 occurs as a triplet (δ 164.5, $^2J_{CP}$ = 17.5 Hz) as a result of coupling to the P atoms in the two PMe_3 ligands. Here, the signal for C3 in BTyl is also split by phosphorus (δ 130.2, $^3J_{CP}$ = 4.2 Hz). Thus, the NMR spectra of **1** and **2** are consistent with bonding of Ru to the C2 carbon of the benzothienyl ligand.

Protonation of **2** in CD_2Cl_2 with CF_3SO_3H gives the η^1(S)-BT complex **4** (eq 3) immediately and quantitatively as seen in the



2 **4** (3)

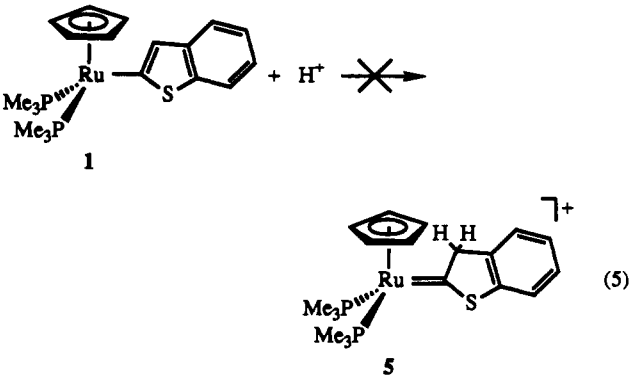
^1H NMR spectrum of the reaction mixture at room temperature. Complex **4** was identified by its ^1H NMR spectrum.[6a] Likewise, addition of 1 equiv of CF_3SO_3H to a CH_2Cl_2 solution of **1** at room temperature gives **3** (eq 4). Complex **3** is also prepared by a



1·H⁺ **3** (4)

second method[17] in which $Cp(PMe_3)_2RuCl$ is refluxed in MeOH with excess BT. Prepared by this route, **3** was characterized by ^1H and ^{13}C NMR and FAB mass spectroscopy and by elemental analysis. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **3** are similar to those of other η^1(S)-BT complexes.[6,7] In an NMR-tube reaction of **1** with CF_3SO_3H in CD_2Cl_2, an intermediate (**1·H⁺**) was detected (eq 4); it exhibits a singlet at δ 5.28 for Cp, a pseudotriplet at δ 1.54 for PMe_3, and two complex multiplets at δ 7.5 and 7.3 for the BTyl ligand (the BTyl peaks are partially obscured by the η^1(S)-BT peaks of **3**). At room temperature, these peaks rapidly disappear ($t_{1/2} \sim 11$ min) as **3** is formed.

As the intermediate, **1·H⁺**, in reaction 4 is rapidly isomerizing to **3**, its structure is difficult to establish from its ^1H NMR spectrum. Complex **1** contains three likely sites for H^+ addition: at Ru, at C3, or at S. An ^1H NMR spectrum of **1·H⁺** in CD_2Cl_2 shows no evidence of a metal hydride peak at high field (up to δ −25), which rules out H^+ addition at Ru. Addition of H^+ at C3 on BTyl (eq 5), in a reaction similar to protonation of a vinyl



(5)

group,[18] would likely give the carbene complex **5**. That **5** is unlikely to have the structure of **1·H⁺** is supported by the following experiments. When 1 equiv of CF_3SO_3D reacts with **1** and **2** in CD_2Cl_2, D is found exclusively in the 2-position of the η^1(S)-BT in the final products **3** and **4**. This was established by integrating the individual BT peaks in **3**. Since the PPh_3 peaks obscure the BT peaks in **4**, the CD_2Cl_2 solution of **4** resulting from CF_3SO_3D addition to **2** was treated with a 10-fold excess of MeCN to displace BT. After 12 h, the solution was passed through a small plug of Al_2O_3. The resulting solution contained only free BT and MeCN; after reduction of the solution volume, the free BT in acetone-d_6 was analyzed by ^1H NMR spectroscopy. For the BT ligand of both **3** and **4**, the integral of the H2 doublet was 40% of the H3 doublet, which integrated 1:1 with the H4 and H7 multiplets and 1:2 with the H5 and H6 multiplet; this establishes that deuterium is only in the H2 position and not in H3; some deuterium would be expected at H3 if **1·H⁺** had the carbene structure **5**. Also supporting the conclusion that **5** is not the **1·H⁺** intermediate is the result of an experiment in which 1 equiv of Et_3N was added immediately to **1·D⁺**, which was formed by the addition of CF_3SO_3D to a CD_2Cl_2 solution of **1**. The Et_3N regenerates **1** which does not contain deuterium in the 3-position or in any other position of the BTyl ligand. If the **1·D⁺** intermediate had structure **5**, deuterium would have had to be found in the 3-position of the regenerated **1**. Since the proton in **1·H⁺** is not on Ru or C3, it is most likely to be bound to the S atom in the benzothienyl ligand. This is supported by the reaction of BT with $Me_3O(PF_6)$ in CH_2Cl_2, which gives the S-methylated $BT{\cdot}CH_3^+$.[19] In reaction 4, the S-protonated intermediate **1·H⁺** apparently rearranges to **3** by proton migration to C2, which results in Ru–C bond cleavage. This rearrangement occurs more rapidly in the reaction of **2** than in the reaction of **1**, since a protonated intermediate is not detected in reaction 3.

Complexes **3** and **4** were not deprotonated to give **1** and **2** (the reverse of eqs 3 and 4) as shown by the reaction of **3** or **4** in CD_2Cl_2 with 1 equiv of NEt_3 at room temperature over a 12-h

(14) Treichel, P. M.; Komar, D. A. *Synth. React. Inorg. Met.-Org. Chem.* **1980**, *10*, 205.
(15) Davies, S. G.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1984**, 993.
(16) (a) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1. (b) Kellogg, R. M. *Compr. Heterocycl. Chem.* **1984**, *4*, 771.
(17) (a) Haines, R. J.; DuPreez, A. L. *J. Organomet. Chem.* **1975**, *84*, 357. (b) Treichel, P. M.; Komar, D. A.; Vincenti, P. J. *Inorg. Chim. Acta* **1984**, *88*, 151. (c) Treichel, P. M.; Vincenti, P. J. *Inorg. Chem.* **1985**, *24*, 228.
(18) (a) Bodner, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.
(19) (19) Acheson, R. M.; Harrison, D. R. *J. Chem. Soc. C* **1970**, 1764.

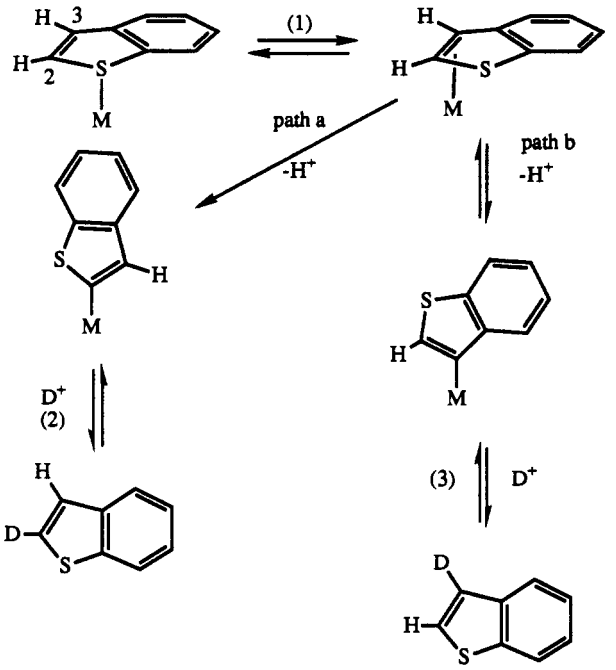
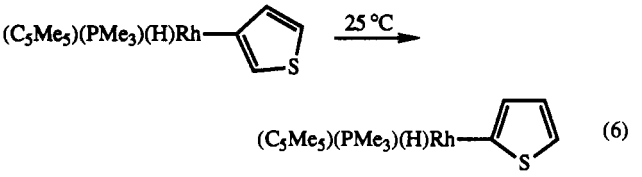


Figure 2. Mechanism for deuterium exchange on BT which accounts for D incorporation into the 2- and 3-positions.

period; only a small amount of free BT was observed in the ^1H NMR spectrum.

Relevance to Deuterium Exchange of Benzo[*b*]thiophene on HDS Catalysts. The reactions (eqs 3 and 4) of the 2-benzothienyl complexes **1** and **2** with CF_3SO_3D result in deuteration of the 2-position of the benzothiophene in the BT products **3** and **4**. This is a reaction that is very similar to that (Figure 1) proposed by Cowley[4] for deuterium exchange of BT with D_2 on an HDS catalyst surface. His mechanism involves a 2-BTyl intermediate which reacts with a D^+ on a surface sulfide to give the 2-deuteriobenzothiophene. To account for the lesser amount of deuterium incorporated into the 3-position of BT, he suggests the formation of a 3-BTyl surface group which reacts with D^+ to give deuterium at the 3-position. The studies presented in this paper are consistent with the idea that both 2- and 3-benzothienyl intermediates are necessary to account for the observed deuteration of BT at the 2- and 3-positions when BT exchanges with D_2 over HDS catalysts. Cowley's mechanism can be elaborated on the basis of results presented in this paper and other recent studies of BT complexes as shown in Figure 2. In step 1, BT adsorbs as an equilibrium mixture of the η^1(S) and η^2 forms, on the basis of the analogous equilibrium known[8] to exist in $Cp'(CO)_2Re(BT)$. The η^2 intermediate could convert to either the 2-BTyl (path a) or the 3-BTyl (path b) surface species. Deuterium transfer from the surface to the 2-BTyl group would give 2-deuterio-BT (step 2) and deuterium transfer to the 3-BTyl would give 3-deuterio-BT (step 3). Path a would be faster than path b since more deuteration occurs[4,5] in the 2- than in the 3-position. In fact, the 2-BTyl surface species may be thermodynamically favored over the 3-BTyl species. This is supported by the reported[20] rearrangment of the 3-thienyl complex $(C_5Me_5)(PMe_3)Rh$(3-thienyl)(H) to the more stable 2-thienyl analog (eq 6); this isomerization is proposed to



(6)

occur via reductive elimination of H and the 3-thienyl group to give a coordinated thiophene, which undergoes oxidative addition across the 2-position C–H bond to give the 2-thienyl product.

In summary, the mechanism shown in Figure 2, which is a modification of Cowley's original proposal (Figure 1), reasonably accounts for preferential deuteration of BT at the 2-position on the basis of reactions of organometallic benzothienyl and thienyl complexes.

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(20) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151.