The Benzo[*b*]thiophene (BT) Complexes $Cp'(CO)_2Re(BT)$: Models for BT Adsorption on Hydrodesulfurization Catalysts

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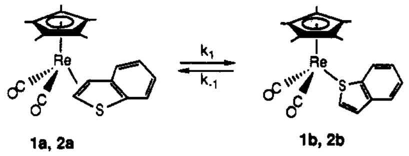
Benzo[*b*]thiophene (BT) coordinates in $Cp(CO)_2Re(BT)$ as an equilibrium mixture of $\eta^1(S)$ and 2,3-η^2 isomers. When the electron density on the Re is increased by replacing Cp (η^5–C_5H_5) with Cp* (η^5-C_5Me_5), the amount of η^2 isomer increases. This shift in equilibrium can be readily explained by assuming that the sulfur in BT is an electron donor toward Re, while bonding of the C(2)–C(3) olefinic bond to Re involves an important component of π back-bonding. The intramolecular nature of the isomerization between **1a** and **1b** was established by the observation that neither 2-MeBT nor PPh_3 was incorporated into the complexes during the time of isomerization. The observed isomerization and the novel (2,3-η^2)-BT coordination mode in **1a** and **2a** provide for the first time a basis for understanding the hydrogenation and initial steps in the hydrodesulfurization of BT on HDS catalysts. 2- and 3-Methylbenzo[*b*]thiophenes, 2-MeBT and 3-MeBT, are stronger sulfur-donor ligands than BT and therefore form only the $\eta^1(S)$ isomer of the complexes $Cp^*(CO)_2Re(MeBT)$. The reactions of $Cp^*(CO)_2Re(BT)$ (**1**) with Me_3O^+ and $W(CO)_5(THF)$ give the sulfur adducts $Cp^*(CO)_2Re((2,3\text{-}\eta^2)\text{-}BT\cdot CH_3)^+$ (**5**) and $Cp^*(CO)_2Re(\eta^2{:}\eta(S)\text{-}\mu_2\text{-}BT)W(CO)_5$ (**6**). An X-ray structural characterization of the $\eta^1(S)$-bound 3-MeBT complex $Cp^*(CO)_2Re(\eta^1(S)\text{-}3\text{-}MeBT)$ (**4**) is also reported.



1a, 2a **1b, 2b**

for **1**, the Cp' ligand = C_5Me_5
for **2**, the Cp' ligand = C_5H_5

Scheme I

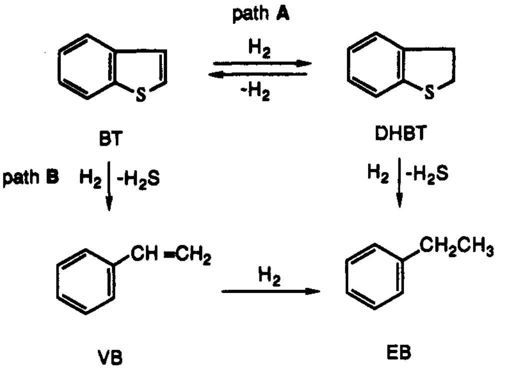
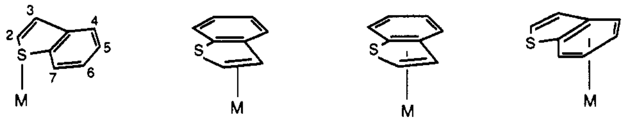


Chart I



S-BT 2,3-η^2-BT η^5-BT η^6-BT

Introduction

Heterogeneous catalytic hydrodesulfurization (HDS) is a very large scale industrial process for the removal of sulfur from petroleum.[2] Environmental and industrial considerations require that petroleum feedstocks and fuels contain lesser amounts of sulfur. Thiophenes, among the organosulfur compounds in petroleum, are the most difficult to desulfurize in the HDS process. Although recent studies of thiophene coordination and reaction in transition-metal complexes have suggested new modes of thiophene adsorption and activation on HDS catalysts,[3,4] much less is known about benzo[*b*]thiophene (BT) coordination in transition-metal complexes. It is especially important to understand mechanisms of benzo[*b*]thiophene HDS because these organosulfur compounds are present in heavy oils and coal-derived liquids[5] in significantly greater quantities than thiophenes[2a,5] and are more difficult to desulfurize.[6] Reactor studies of BT HDS[7] suggest two general pathways (Scheme I): one (pathway

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(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.

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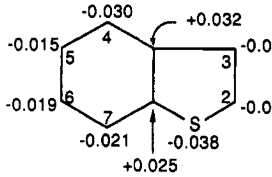
A) begins with initial hydrogenation of the thiophene double bond to give 2,3-dihydrobenzo[*b*]thiophene (DH-BT), which then undergoes desulfurization to give ethylbenzene (EB). The other pathway (**B**) involves hydrogenolysis of a C–S bond to give vinylbenzene (VB), which is subsequently hydrogenated to EB. Beyond these general mechanistic outlines, little is known about the adsorption of BT on the catalyst or the nature of its activation by the catalyst.

Some possible modes of BT coordination at a metal site on an HDS catalyst (Chart I) are $\eta^1(S)$ coordination through the sulfur, 2,3-η^2-π coordination through a carbon–carbon double bond, η^5 bonding through the thiophene ring, or η^6 coordination through the benzene ring. There are no reported examples of η^5-BT complexes. Before our preliminary report[8] of an equilibrium mixture of $\eta^1(S)$ and 2,3-η^2 isomers in Cp′Re(CO)$_2$(BT) (Cp′ = C_5H_5 or C_5Me_5), there was only one example of an S-bound BT complex, Cp(CO)$_2$Fe($\eta^1(S)$-BT)$^+$.[9] All other characterized complexes contain an η^6-BT ligand coordinated via the π-system of the benzene ring: CpRu(η^6-BT)$^+$,[10,11] Cp*Rh(η^6-BT)$^{2+}$,[10] Cp*Ir(η^6-BT)$^{2+}$,[10] and Cr(CO)$_3$(η^6-BT).[12] While η^6 coordination is a very favorable mode of binding to a metal site, it does not account for deuterium exchange of BT on HDS catalysts,[13] since the sites of deuterium exchange in BT are different over the catalyst and in CpRu(η^6-BT)$^+$. Likewise, reactions of CpRu(η^6-BT)$^+$ with hydride or other nucleophiles do not lead to products in which the C–S bond is cleaved.[14] Thus, η^6 adsorption on a metal site appears to be an unlikely mode of activating BT toward desulfurization.

An interesting reaction is that of metal insertion into a C–S bond of BT. This is illustrated by the reaction of BT with $Fe_3(CO)_{12}$ to give a benzothiaferrole product in which a Fe(CO)$_3$ group inserts into a C–S bond.[15] Also, the Cp*Rh(PMe$_3$) fragment inserts into the C–S bond of BT.[4d,g] In the latter study, $\eta^1(S)$-BT was proposed as an intermediate prior to the insertion step.

On the basis of the results of an MO calculation on BT,[16] the highest electron densities are on the sulfur and the C2–C3 carbons:



Therefore, one might expect BT to coordinate to a metal either through the sulfur or in a 2,3-η^2 fashion via the olefinic C2–C3 π-bond. In our recent communication[8] we described the first example of a complex containing a (2,3-η^2)-BT ligand and isomerization between the 2,3-η^2 and $\eta^1(S)$ isomers. In the present paper, we report details and further studies of 2,3-η^2 and $\eta^1(S)$ complexes. Syntheses of Cp′(CO)$_2$Re(BTh) (BTh = BT, 2-MeBT, 3-MeBT) and an X-ray structural determination of Cp*(CO)$_2$Re(η^1-(S)-3-MeBT) are described.

Experimental Section

General Procedures. All reactions and reaction workups were carried out under an atmosphere of prepurified N_2 at room temperature using standard Schlenk techniques[17] unless otherwise stated. All solvents were reagent grade and dried under N_2 by following standard methods. Tetrahydrofuran (THF) was distilled from Na/benzophenone. Hexanes and CH_2Cl_2 were distilled from CaH_2. The solvents were used immediately after distillation or were stored over 4-Å molecular sieves under N_2. The neutral alumina (Brockman, activity I, ~150 mesh) used for chromatography was deoxygenated at room temperature under high vacuum for 16 h and then deactivated with 5% w/w N_2-saturated water, shaken, and stored under N_2.

The ^{1}H and ^{13}C NMR spectra were recorded on either a Nicolet NT-300 or a Varian VXR-300 spectrometer with $CDCl_3$ as the internal lock and internal reference (δ 7.25 for ^{1}H and δ 77.0 for ^{13}C). Electron impact mass spectra (EIMS) were obtained on a Finnigan 4000 spectrometer. Fast atom bombardment (FAB) spectra were obtained on a Kratos MS-50 mass spectrometer. Infrared spectra were recorded on a Digilab FTS-7 or a Nicolet 710 FT-IR spectrometer. Photochemical reactions (using a 450-W mercury UV lamp) were carried out in a quartz tube which was maintained at −20 °C using a Lauda RK 20 constant-temperature circulator. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Commercial benzo[*b*]thiophene (BT) was sublimed prior to use, and 3-methylbenzo[*b*]thiophene (3-MeBT) was used without further purification. 2-MeBT,[18] Cp*Re(CO)$_3$,[19] and CpRe(CO)$_3$[20] were prepared by literature methods.

Cp*(CO)$_2$Re((2,3-η^2)-BT) (1a) and Cp*(CO)$_2$Re(η^1(*S*)-BT) (1b). A solution of Cp*(CO)$_2$Re(THF) was prepared by a method similar to that previously reported in the literature.[21] A solution of Cp*Re(CO)$_3$ (0.20 g, 0.49 mmol) in freshly distilled THF (30 mL) in a quartz photolysis tube equipped with a N_2 bubbler was irradiated with a mercury UV lamp (450 W Canrad-Hanovia) for 3 h at −20 °C. An IR spectrum of the solution (ν(CO) 1890, 1820 cm^{-1}) showed a maximum conversion to the THF complex without too much subsequent decomposition.

This solution of Cp*(CO)$_2$Re(THF) was stirred with BT (0.30 g, 2.24 mmol) at room temperature for 10 h, the progress of the reaction being monitored by IR spectroscopy. After removal of the solvent in vacuo, the residue was extracted with hexanes/CH_2Cl_2 (20:1). The extract was chromatographed on a neutral alumina column (1 × 15 cm). After the unreacted Cp*Re(CO)$_3$ was eluted with hexanes, the yellow band containing the product was eluted with CH_2Cl_2/hexanes (1:4). The collected solution was concentrated under vacuum; slow cooling of the solution to −20 °C gave pale yellow, moderately air-stable crystals of 1 (0.053 g, 21%). EIMS (15 eV): *m/e* 512 (M$^+$ based on ^{187}Re), 456 (M$^+$ − 2CO), 378 (M$^+$ − BT), 350 (M$^+$ − (BT + CO)), 134 (BT$^+$). Anal. Calcd for $C_{20}H_{21}O_2ReS$: C, 46.95; H, 4.14. Found: C, 46.95; H, 4.13. IR (hexanes, ν(CO)): **1a**, 1970 (s), 1908 (s) cm^{-1}; **1b**, 1932 (s), 1871 (s) cm^{-1}.

Cp(CO)$_2$Re((2,3-η^2)-BT) (2a) and Cp(CO)$_2$Re(η^1(*S*)-BT) (2b). A THF solution (30 mL) of CpRe(CO)$_3$ (0.20 g, 0.60 mmol)

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was irradiated with the mercury UV lamp at −20 °C for 2 h until the concentration of $Cp(CO)_2Re(THF)$ was at a maximum, as indicated by intensities of the $\nu(CO)$ bands at 1910 and 1937 cm^{-1}. BT (0.40 g, 3.0 mmol) was added, and the solution was stirred at room temperature for 8–10 h. After chromatography and crystallization as described for 1, moderately air-stable pale yellow crystals of 2 (0.071 g, 27%) were obtained. EIMS (15 eV): *m/e* 442 (M^+ based on ^{187}Re), 386 (M^+ − 2CO), 308 (M^+ − BT), 280 (M^+ − (BT + CO)), 252 (M^+ − (BT + 2CO)), 134 (BT^+). Anal. Calcd for $C_{15}H_{11}ReO_2S$: C, 40.81; H, 2.51. Found: C, 40.63; H, 2.30. IR (hexanes, $\nu(CO)$): **2a**, 1977 (w), 1909 (w) cm^{-1}; **2b**, 1947 (s), 1885 (s) cm^{-1}.

Cp*(CO)$_2$Re(η^1(*S*)-2-MeBT) (3). This complex was prepared analogously to 1 from $Cp^*Re(CO)_3$ (0.20 g, 0.49 mmol) and 2-MeBT (0.50 g, 3.38 mmol). Moderately air-stable pale yellow crystals of 3 (0.060 g, 23%) were obtained. EIMS (70 eV): *m/e* 526 (M^+ based on ^{187}Re), 470 (M^+ − 2CO), 378 (M^+ − MeBT), 148 ($MeBT^+$). IR (hexanes, $\nu(CO)$): 1929 (s), 1870 (s) cm^{-1}.

Cp*(CO)$_2$Re(η^1(*S*)-3-MeBT) (4). Compound 4 was prepared in the same manner as for 1 using $Cp^*Re(CO)_3$ (0.20 g, 0.49 mmol) and 3-MeBT (1.0 mL, 1.17 g, 7.91 mmol). Moderately air-stable pale yellow crystals of 4 (0.10 g, 39%) were obtained. EIMS (70 eV): *m/e* 526 (M^+ based on ^{187}Re), 470 (M^+ − 2CO), 378 (M^+ − MeBT), 148 ($MeBT^+$). IR (hexanes, $\nu(CO)$): 1929 (s), 1868 (s) cm^{-1}. Anal. Calcd for $C_{21}H_{23}ReO_2S$: C, 47.98; H, 4.41. Found: C, 47.92; H, 4.24.

Reaction of 1 with (Me$_3$O)BF$_4$ To Give [Cp*(CO)$_2$Re((2,3-η^2)-BT·CH$_3$)](BF$_4$) (5). To a solution of 1 (80 mg, 0.16 mmol) in CH_2Cl_2 (10 mL) was added $(Me_3O)BF_4$ (32 mg, 0.22 mmol). After being stirred at room temperature for 1 h, the solution was filtered through Celite. The filtrate was concentrated to about 1 mL under vacuum. Adding Et_2O (10 mL) and cooling to −20 °C gave pale yellow crystals of 5 (71 mg, 74%). IR (CH_2Cl_2, $\nu(CO)$): 1992 (s), 1919 (s) cm^{-1}. FAB MS (CH_2Cl_2/3-nitrobenzyl alcohol matrix): *m/e* 527 (M^+, based on ^{187}Re). Anal. Calcd for $C_{21}H_{24}BF_4ReOS$: C, 41.11; H, 3.94. Found: C, 41.24; H, 3.97.

Reaction of 1 with W(CO)$_5$(THF) To Give Cp*(CO)$_2$Re(η^2:η(*S*)-μ_2-BT)W(CO)$_5$ (6). A solution of $W(CO)_5(THF)$ was generated by UV irradiation of a THF solution (25 mL) of $W(CO)_6$ (60 mg, 0.17 mmol). To this stirred solution of $W(CO)_5(THF)$ was added 1 (45 mg, 0.088 mmol) at room temperature. The resulting solution was stirred for 5 h. After evaporation of the solution to dryness in vacuo, the residue was chromatographed on neutral alumina (1 × 10 cm) with hexanes/CH_2Cl_2 (2:1) as the eluent. The yellow band was collected and reduced in volume under vacuum. Slow cooling of the concentrated solution to −70 °C gave air-stable, pale yellow crystals (31 mg, 42%). IR (hexanes, $\nu(CO)$): 2073 (w), 1983 (m), 1945 (s), 1935 (s), 1925 (s), 1923 (sh). EIMS (70 eV): *m/e* 512 (M^+ − $W(CO)_5$, based on ^{187}Re), 456 (M^+ − ($W(CO)_5$ + 2CO)), 378 (M^+ − ($W(CO)_5$ + BT)), 350 (M^+ − ($W(CO)_5$ + BT + CO)), 134 (BT^+). Anal. Calcd for $C_{25}H_{21}O_7ReSW$: C, 35.94; H, 2.53. Found: C, 36.09; H, 2.55.

Kinetic Measurements. The η^2 isomers (**1a** and **2a**) were separated from the $\eta^1(S)$ isomers (**1b** and **2b**) by hand-picking crystals on the basis of their morphology. Immediately after each of the η^2 isomers was dissolved in CH_2Cl_2, the rates of isomerization (eq 1) to the $\eta^1(S)$ isomers at room temperature (~22 °C) were

$$\eta^2\text{-BT} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \eta^1(S)\text{-BT} \tag{1}$$

followed by changes in intensities of the reactant (1959, 1886 cm^{-1} for **1a**; 1965, 1893 cm^{-1} for **2a**) and product (1914, 1844 cm^{-1} for **1b**; 1925, 1857 cm^{-1} for **2b**) $\nu(CO)$ bands at appropriate times until the reaction reached equilibrium. The rate constants, k_{obs}, were obtained from least-squares slopes of linear plots of ln $[[(\eta^2\text{-BT})_t - (\eta^2\text{-BT})_\infty]/[(\eta^2\text{-BT})_0 - (\eta^2\text{-BT})_\infty]]$ vs time,[22] where the parentheses represent the integrated areas of the $\nu(CO)$ band of the η^2-BT isomers. The plots were linear with correlation coefficients greater than 0.99. The negative of the slope (k_{obs}) is the sum $k_1 + k_{-1}$. The equilibrium constants *K* for 1 and 2 were determined to be 0.6 and 3, respectively, by integration of the ^{1}H NMR spectra of the reaction solutions at equilibrium. The forward and reverse rate constants k_1 and k_{-1} were calculated from values of k_{obs} and *K* using eqs 2 and 3.

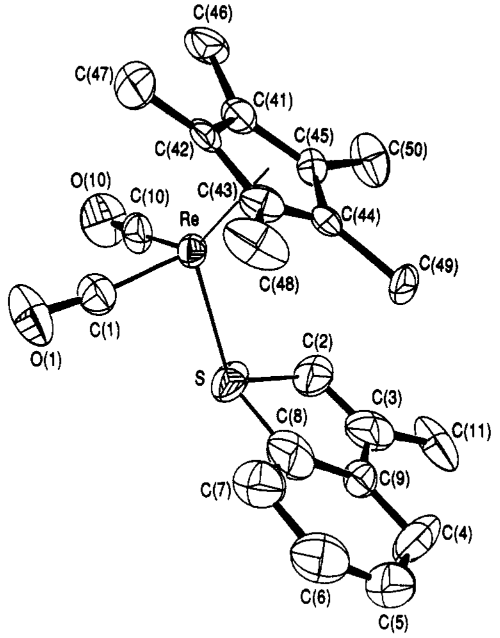
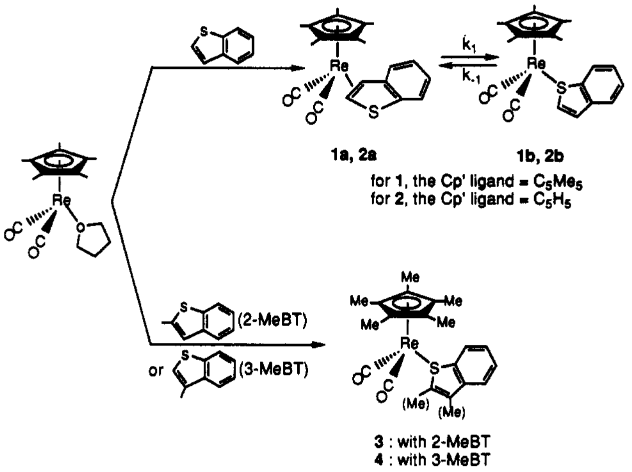


Figure 1. ORTEP drawing of Cp*(CO)$_2$Re(η^1(*S*)-3-MeBT) (4).

Scheme II



$$\frac{[\eta^1(S)\text{-BT}]_\infty}{[\eta^2\text{-BT}]_\infty} = K = \frac{k_1}{k_{-1}} \tag{2}$$

$$k_{obs} = k_1 + k_{-1} \tag{3}$$

X-ray Structure Determination of Cp*(CO)$_2$Re(η^1(*S*)-3-MeBT) (4). A single crystal of 4 suitable for X-ray diffraction study was obtained from recrystallization from hexane solution by slow cooling to −20 °C and mounted on the tip of a glass fiber.

Data for 4 were collected on a Rigaku AFC6 diffractomer at 22 °C, and the cell parameters were determined from a list of reflections found by an automated search routine. An empirical absorption correction was made on the basis of a series of ψ scans. No decay corrections were necessary. Relevant crystal data and parameters associated with data collection for 4 are given in Table III.

The positions of the Re and S atoms were obtained by direct methods.[23] The remainder of the non-hydrogen atoms were located in a difference Fourier map. In the final cycles of refinement, all of the non-hydrogen atoms were given anisotropic temperature factors. Hydrogen atoms were not included in the model. Refinement of structure 4 was carried out with TEX-

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Table I. ^{1}H NMR Data (δ) for the Complexes in $CDCl_3$

complex	BT	Cp* or Cp	Me on BT
$Cp^*(CO)_2Re((2,3\text{-}\eta^2)\text{-BT})$ (**1a**)	7.5–7.1 (3 m, 4 H), 4.25 (d, 1 H),[a] 3.96 (d, 1 H)[a]	2.02 (s, 15 H)	
$Cp^*(CO)_2Re(\eta^1(S)\text{-BT})$ (**1b**)	7.8–7.3 (4 m, 6 H)	1.81 (s, 15 H)	
$Cp(CO)_2Re((2,3\text{-}\eta^2)\text{-BT})$ (**2a**)	7.3–7.1 (3 m, 4 H), 5.31 (d, 1 H),[b] 5.11 (d, 1 H)[b]	4.95 (s, 5 H)	
$Cp(CO)_2Re(\eta^1(S)\text{-BT})$ (**2b**)	7.9–7.4 (3 m, 4 H), 7.20 (d, 1 H),[c] 7.14 (d, 1 H)[c]	4.81 (s, 5 H)	
$Cp^*(CO)_2Re(\eta^1(S)\text{-2-MeBT})$ (**3**)	7.6–7.0 (4 m, 5 H)	1.81 (s, 15 H)	2.34 (d, 3 H)[d]
$Cp^*(CO)_2Re(\eta^1(S)\text{-3-MeBT})$ (**4**)	7.8–6.7 (4 m, 5 H)	1.81 (s, 15 H)	2.40 (d, 3 H)[e]
$[Cp^*(CO)_2Re((2,3\text{-}\eta^2)\text{-BT}\cdot CH_3)]BF_4$ (**5**)	7.6–7.2 (4 m, 4 H), 4.57 (d, 1 H),[f] 3.65 (d, 1 H)[f]	2.12 (s, 15 H)	3.26 (s, 3 H)
$Cp^*(CO)_2Re(\eta^2{:}\eta(S)\text{-}\mu_2\text{-BT})W(CO)_5$ (**6**)	7.5–7.1 (4 m, 4 H), 4.02 (d, 1 H),[g] 3.71 (d, 1 H)[g]	2.04 (s, 15 H)	
BT	7.9–7.3 (4 m, 6 H)		
2-MeBT	7.8–7.2 (3 m, 5 H)		2.62 (d, 3 H)
3-MeBT	7.9–7.3 (3 m, 5 H)		2.48 (d, 3 H)

[a] $J_{H2\text{-}H3}$ = 6.0 Hz. [b] $J_{H2\text{-}H3}$ = 6.0 Hz. [c] $J_{H2\text{-}H3}$ = 6.0 Hz. [d] $J_{H3\text{-}CH_3}$ = 1.4 Hz. [e] $J_{H2\text{-}CH_3}$ = 1.5 Hz. [f] $J_{H2\text{-}H3}$ = 5.4 Hz. [g] $J_{H2\text{-}H3}$ = 6.3 Hz.

Table II. ^{13}C NMR Data (δ) for the Complexes in $CDCl_3$

complex	BT	Cp* or Cp	Me on Cp*	CO	Me on BT
1a	125.5, 123.7, 123.2, 122.6, 47.9, 46.6[a]	97.8	10.2	204.4, 204.3	
1b	145.6, 137.8, 128.1, 126.7, 124.6, 123.4[a]	95.9	10.4	205.5	
2a	126.2, 124.4, 124.0, 122.5, 45.5, 44.1[a]	88.6		202.5, 201.9	
2b	151.8, 140.7, 138.5, 127.2, 125.0, 123.9[a]	83.0		201.6	
3	148.9, 146.8, 140.7, 126.7, 124.7, 124.6, 123.4, 123.3	95.6	10.2	205.4	14.0
4	148.3, 141.1, 136.6, 132.1, 126.6, 125.5, 123.7, 122.4	95.9	10.4	205.8	14.1
5[b,c]	153.5, 132.8, 128.2, 127.6, 126.1, 125.6, 43.0, 35.6	101.4	10.0		
6	146.7, 127.0, 126.5, 125.6, 124.8, 124.3, 54.5, 40.7	98.9	10.1	204.5, 202.1, 201.1, 197.4	
BT	139.7, 139.6, 126.2, 124.2, 124.1, 123.8, 123.6, 122.4				
2-MeBT	140.8, 140.5, 139.7, 124.0, 123.3, 122.5, 122.0, 121.6				16.0
3-MeBT	140.2, 139.6, 132.0, 124.0, 123.7, 122.7, 121.6, 121.4				

[a] Bridging carbon C8, C9 signals are not observed due to low intensity. [b] In CD_2Cl_2 solvent. [c] 35.2 for $S\text{-}CH_3$; CO not observed.

Table III. Crystal and Data Collection Parameters for $Cp^*(CO)_2Re(\eta^1(S)\text{-3-MeBT})$ (4)

formula	$C_{21}H_{23}O_2ReS$
fw	525.68
space group	$P2_1/n$
a, Å	8.710 (1)
b, Å	13.706 (2)
c, Å	16.603 (3)
β, deg	91.37 (1)
V, Å^3	1981 (1)
Z	4
d_{calc}, g/cm^3	1.762
crystal size, mm	0.2 × 0.1 × 0.1
μ(Mo Kα), cm^{-1}	63.268
data collecn instrument	Rigaku AFC 6R
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
orientation rflns: no.; range (2θ), deg	15; 25–32
temp, °C	22 (1)
scan method	2θ–ω
data collecn range, 2θ, deg	4.0–50.0
total no. of data measd	4037
no. of unique data	3695
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	2086
no. of params refined	227
transmissn factors: max, min (ψ scans)	0.999, 0.812
R[a]	0.045
R_w[b]	0.047
quality-of-fit indicator[c]	1.32
largest shift/esd, final cycle	0.73
largest peak, e/Å^3	1.0

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit = $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Table IV. Selected Bond Distances (Å) for $Cp^*(CO)_2Re(\eta^1(S)\text{-3-MeBT})$ (4)

Re–S	2.356 (4)[a]	O(1)–C(1)	1.15 (2)
Re–C(1)	1.88 (2)	O(10)–C(10)	1.18 (2)
Re–C(10)	1.85 (2)	C(2)–C(3)	1.33 (2)
Re–C(41)	2.26 (1)	C(3)–C(9)	1.51 (2)
Re–C(42)	2.25 (1)	C(3)–C(11)	1.48 (3)
Re–C(43)	2.31 (1)	C(4)–C(5)	1.64 (3)
Re–C(44)	2.33 (1)	C(4)–C(9)	1.34 (2)
Re–C(45)	2.32 (1)	C(5)–C(6)	1.31 (3)
S–C(2)	1.92 (2)	C(6)–C(7)	1.53 (3)
S–C(8)	1.74 (3)	C(7)–C(8)	1.34 (3)
		C(8)–C(9)	1.36 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table V. Selected Bond Angles (deg) for $Cp^*(CO)_2Re(\eta^1(S)\text{-3-MeBT})$ (4)

S–Re–C(1)	92.8 (5)[a]	C(2)–C(3)–C(9)	115 (2)
S–Re–C(10)	88.8 (5)	C(2)–C(3)–C(9)	122 (2)
C(1)–Re–C(10)	89.2 (7)	C(9)–C(3)–C(11)	122 (2)
Re–S–C(2)	115.1 (6)	C(5)–C(4)–C(9)	108 (2)
Re–S–C(8)	120.8 (8)	C(4)–C(5)–C(6)	121 (2)
C(2)–S–C(8)	90 (1)	C(5)–C(6)–C(7)	124 (2)
Re–C(1)–O(1)	175 (2)	C(6)–C(7)–C(8)	110 (2)
S–C(2)–C(3)	108 (2)	S–C(8)–C(7)	117 (2)
		S–C(8)–C(9)	114 (2)
		C(7)–C(8)–C(9)	128 (2)
		C(3)–C(9)–C(4)	120 (2)
		C(3)–C(9)–C(8)	112 (2)
		C(4)–C(9)–C(8)	128 (2)
		Re–C(10)–O(10)	178 (2)

[a] See footnote *a* in Table IV.

SAN.[24] Selected bond distances and angles are presented in Tables IV and V; an ORTEP drawing of **4** is given in Figure 1.

Results and Discussion

Syntheses of $Cp'(CO)_2Re(BT)$ Complexes and Interconversion of the η^2 and $\eta^1(S)$ Isomers. The reaction of $Cp^*(CO)_2Re(THF)$ with benzo[*b*]thiophene in THF solution results in the formation of $Cp^*(CO)_2Re(BT)$ (**1**) (Scheme II). Although elemental analyses and the mass spectrum (see Experimental Section) establish the composition of **1** as $Cp^*(CO)_2Re(BT)$, it is evident from the number of bands in the IR and ^{1}H and ^{13}C NMR spectra that it consists of two isomers, the 2,3-η^2 (**1a**) and $\eta^1(S)$

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[24] TEXSAN-Texray Structure Analysis Package; Molecular Structure Corp., 1985.

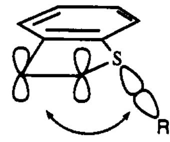
(**1b**) isomers, which are present at equilibrium in a 1.6:1 ratio in $CDCl_3$ solution at room temperature (Scheme II). The ^1H NMR spectrum of **1a** (Table I) shows that the H2 and H3 resonances (δ 4.25 (d), 3.96 (d)) of the BT are substantially upfield compared to those in free BT (δ 7.33 (H2) and 7.22 (H3)).[25] In the ^{13}C NMR spectrum of **1a** (Table II), two of the ^{13}C NMR resonances (δ 47.9 and 46.6), presumably those of C2 and C3, are substantially upfield of those (δ 126.2 (C2) and 123.8 (C3)) in free BT.[26] Such upfield ^1H and ^{13}C NMR shifts were observed previously in $Cp^*(CO)_2Re((2,3\text{-}\eta^2)\text{-selenophene})$,[27,28] $Cp^*(CO)_2Re(CH_3CH{=}CHCH_3)$,[29] and $[(NH_3)_5Os((2,3\text{-}\eta^2)\text{-thiophene})]^{2+}$ [30] and are characteristic of η^2-olefin[31,32] and η^2-arene[33] bonding. Crystals of **1a** that exhibited the upfield ^1H and ^{13}C signals were hand-picked from recrystallized **1** (from hexanes at −20 °C); they gave X-ray diffraction data of marginal quality that were refined to give a structure with the expected atom connectivity in which Re is coordinated to C(2) and C(3) above the BT plane. Although the bond distance and angle results were of low precision, the basic structure supports the 2,3-η^2 assignment made on the basis of the ^1H and ^{13}C NMR studies. Thus, the major isomer (**1a**, Scheme II) contains (2,3-η^2)-BT.

The ^1H and ^{13}C NMR chemical shifts of the BT ligand in the minor isomer (**1b**) (Tables I and II) are similar to those in free BT (^1H NMR (CCl_4) δ 7.79, 7.72, 7.33, 7.26, 7.24, 7.22; ^{13}C NMR ($CDCl_3$) δ 139.7, 139.6, 126.2, 124.2, 124.1, 123.8, 123.6, 122.4),[25,26] which are also similar to those of the S-coordinated BT in $Cp(CO)_2Fe(\eta^1(S)\text{-BT})^+$.[9] These comparisons together with the similar positions of the ν(CO) bands (1932 and 1871 cm^{-1}) of **1b** and those (1934 and 1874 cm^{-1}) of the S-bound thiophene complex $Cp^*(CO)_2Re(T)$[34] strongly suggest that **1b** contains an S-coordinated BT.

It is also interesting to compare ν(CO) values of the η^2 and $\eta^1(S)$ isomers of complex **1**. An IR spectrum of **1** shows four ν(CO) bands at 1970, 1908 and 1932, 1871 cm^{-1} in hexanes. Two (1970, 1908 cm^{-1}) are similar to those of $Cp^*(CO)_2Re(\eta^2\text{-selenophene})$ (1962, 1898 cm^{-1}),[27,28] and the other two (1932, 1871 cm^{-1}) are similar to those of $Cp^*(CO)_2Re(\eta^1(Se)\text{-}2,5\text{-}Me_2Sel)$ (1925, 1866 cm^{-1})[27,28] and $Cp^*(CO)_2Re(T)$[34] (vide supra). Thus, η^2-BT coordination in **1** gives ν(CO) values that are about 35–40 cm^{-1} higher than those in the S-coordinated isomer, indicating that the S-coordinated BT donates more electron density to Re than the η^2-coordinated ligand.

The Cp analogs of **1** were prepared in the same manner as for **1** from the reaction of $Cp(CO)_2Re(THF)$ with BT (Scheme II). The spectroscopic data (Tables I and II and IR data in the Experimental Section) indicate that **2**, like **1**, exists in solution as an equilibrium mixture of η^2 (**2a**) and $\eta^1(S)$ (**2b**) isomers in a 1:3 ratio in $CDCl_3$ solution at room temperature. Thus, the S-bound isomer is the major form of **2**, but the η^2-isomer predominates in **1**. Comparisons of the IR spectra of the Cp* and Cp analogs show the ν(CO) bands in the Cp* complexes to be lower (~4 cm^{-1} for η^2-BT; ~15 cm^{-1} for $\eta^1(S)$-BT) than those of the Cp complexes. The methyl groups of the Cp* ligand provide more electron density to the metal, thereby increasing π back-bonding from the metal to the CO π^* orbitals and weakening the C≡O bond, thus accounting for the lower ν(CO) values in the Cp* complexes. The preference for the η^2 isomer in the Cp* analogue can also be rationalized by electronic effects. The additional electron density provided by the Cp* ligand in **1** presumably reduces the Lewis acid character of the Re, which weakens the bond with the electron-donating sulfur in the S-bonded isomer (**1b**); at the same time, the higher electron density on Re increases π back-bonding to the 2,3-η^2 olefinic bond of the BT ligand, which favors the η^2 isomer (**1a**).

In order to measure the isomerization rate, the η^2 isomers (**1a** and **2a**) were separated by hand from the $\eta^1(S)$ isomers (**1b** and **2b**) on the basis of the morphology of the crystals. After the η^2 isomers were dissolved in CH_2Cl_2, rates of isomerization to the $\eta^1(S)$ isomers at room temperature (~22 °C) were determined by following changes in intensity of the reactant and product ν(CO) bands until the reaction reached equilibrium. The isomerization of **1a** ($k_1 = 9 \times 10^{-4}$ s^{-1}, $k_{-1} = 15 \times 10^{-4}$ s^{-1}; $t_{1/2} = 13$ min for k_1) is approximately 8 times slower than that ($k_1 = 7 \times 10^{-3}$ s^{-1}, $k_{-1} = 2 \times 10^{-3}$ s^{-1}; $t_{1/2} = 1.7$ min for k_1) of **2a**. These isomerizations must occur intramolecularly, since BT does not dissociate from either the η^2 or $\eta^1(S)$ isomer during the time of the isomerization. This was shown by observing that no $Cp^*(CO)_2Re(2\text{-MeBT})$ formed, when a $CDCl_3$ solution of $Cp^*(CO)_2Re(BT)$ (**1**) and 2-methylbenzo[*b*]thiophene (2-MeBT, ~3-fold excess) was stirred at room temperature for 26 h. Also, there was no formation of $Cp^*(CO)_2Re(PPh_3)$ when **1** and PPh_3 (~10-fold excess) were stirred in CD_2Cl_2 at room temperature for 24 h; at longer times (2 weeks) $Cp^*(CO)_2Re(PPh_3)$ was observed. The intramolecular interconversion of the η^2 and $\eta^1(S)$ isomers presumably involves migration of the Re between sulfur and carbon orbitals on the same side of the BT ring:



A related migration of Re between the olefin and Se of the selenophene (Sel) ligand in $Cp'(CO)_2Re(Sel)$ has previously been described;[27,28] such a migration has also been proposed in $Cp^*(PMe_3)Rh(\text{thiophene})$.[4g]

Syntheses of $Cp^*(CO)_2Re(MeBT)$ Complexes. Reactions of the methyl-substituted benzo[*b*]thiophenes (2-MeBT and 3-MeBT) with $Cp^*(CO)_2Re(THF)$ give the $\eta^1(S)$-BTh complexes $Cp^*(CO)_2Re(2\text{-MeBT})$ (**3**, 23%) and $Cp^*(CO)_2Re(3\text{-MeBT})$ (**4**, 39%) (Scheme II). Unlike the case for **1**, the IR (see Experimental Section) and ^1H and ^{13}C NMR spectra (Tables I and II) for **3** and **4** indicate that only the S-coordinated BT complex is present in each case. An X-ray diffraction study (vide infra) of **4** confirms this bonding mode. The preference for S-bonding by 2-MeBT and 3-MeBT is probably caused by two factors; (1) a methyl group on C(2) or C(3) reduces the π-acceptor character of the olefin and also sterically hinders η^2-coordination; (2) the electron-donating Me groups enhance the donor ability of the sulfur, thereby favoring S-coordination.

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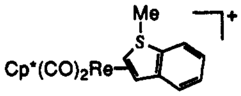
Reaction of Cp*(CO)$_2$Re(BT) (1) with (Me$_3$O)BF$_4$. Complex 1, the mixture of 2,3-η^2 and η^1(S) isomers, reacts with (Me$_3$O)BF$_4$ to give the S-methylated BT complex 5 in 74% yield (eq 4). In the ^{1}H NMR spectrum of 5 (Table I), there are two upfield protons (δ 4.57 and 3.65) that indicate the BT is η^2-coordinated. The S-CH$_3$ signal occurs at δ 3.26, which is slightly upfield of the methyl group (δ 3.37) in S-methylated benzo[b]thiophene.[35] Methylation of the sulfur in Cp*(CO)$_2$Re(BT) by (Me$_3$O)BF$_4$ appears to occur more rapidly than that of free BT, which is reported[35] to react with (Me$_3$O)(BF$_4$) in refluxing CH$_2$Cl$_2$ over 60 h. Thus, it is likely that η^2 coordination of BT in 1a enhances the nucleophilicity of the BT sulfur as compared with that of free BT. Similarly, we and others have observed that η^4 coordination of the thiophenes in Cp*Ir(η^4-2,5-Me$_2$T)[3,4b,f,36-38] and Cp*Rh(η^4-Me$_4$T)[4e] substantially increases the donor ability of the sulfur as compared with that of the free thiophenes.

$\mathrm{Cp^*(CO)_2Re(BT)} + \mathrm{(Me_3O)BF_4} \xrightarrow{-\mathrm{Me_2O}}$

1a and 1b

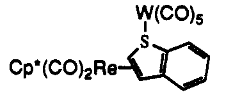


(4)

Reaction of Cp*(CO)$_2$Re(BT) (1) with W(CO)$_5$(THF). The uncoordinated sulfur atom in 1a reacts with W(CO$_5$(THF) to give the BT-bridged bimetallic complex 6 (eq 5) in 42% yield. In the ^{1}H and ^{13}C NMR spectra of 6 (Tables I and II), there are two upfield protons and two upfield carbon resonances that indicate the BT is η^2-coordinated. The structure of 6 is presumably similar to that[27,28] of Cp*(CO)$_2$Re(η^2:η(Se)-μ_2-Sel)W(CO)$_4$(L), in which the selenophene (Sel) is 2,3-η^2 coordinated to the Re and bonded to the W through a pyramidal Se.

$\mathrm{Cp^*(CO)_2Re(BT)} + \mathrm{W(CO)_5(THF)} \longrightarrow$

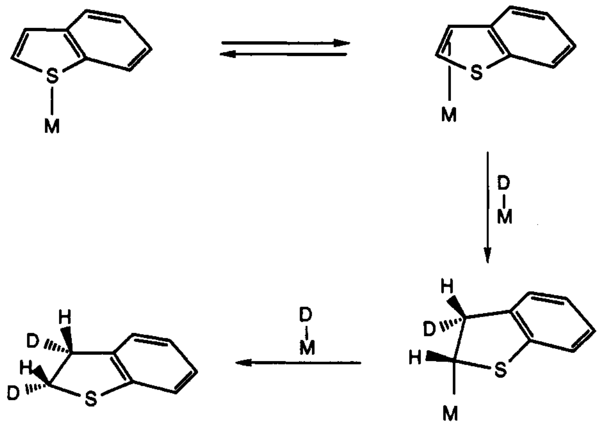
1a and 1b



(5)

Structure of Cp*(CO)$_2$Re(η^1(S)-3-MeBT) (4). In the structure of 4 (Figure 1), the coordinated BT sulfur has a trigonal-pyramidal geometry (i.e. is roughly sp^3 hybridized). The sum of the angles around S (326 (1)°) in 4 is somewhat smaller than that in the S-bound thiophene complex Cp*(CO)$_2$Re(η^1(S)-T) (333.6 (5)°).[34b] The Re–S distance of 2.356 (4) Å is similar to that (2.360 (3) Å) of Cp*(CO)$_2$Re(η^1(S)-T)[34] and is somewhat shorter than those (2.396 (4), 2.425 (5), 2.400 (5) Å) in ReBr$_3$(THT)$_3$ (THT = tetrahydrothiophene).[39] The Re lies out of the thiophene ring of BT such that the angle between the Re–S vector and the vector from S to the midpoint of the line between C(2) and C(8) is 131 (1)°. This angle is very similar to that in the S-coordinated DBT complex [RuCl$_2$\{P(4-MeC$_6$H$_4$)$_2$(SC$_{12}$H$_7$)\}$_2$] (131°),[40] smaller than that (140°) in Cp*(CO)$_2$Re(η^1(S)-T),[34] and somewhat larger than those in (PPh$_3$)$_2$Ru(C$_5$H$_4$CH$_2$C$_4$H$_3$S)$^+$ (126°),[41] Cp*IrCl$_2$[η^1(S)-DBT] (128°),[42] Cp(CO)(PPh$_3$)Ru(η^1(S)-2MeT)$^+$ (119.1°),[43] and Cp(CO)$_2$Fe(η^1(S)-DBT)$^+$ (119.4°).[9] One remarkable structural aspect of the S-coordinated BT in 4 is the lengthening (~0.2 Å) of the S–C(2) bond (1.92 (2) Å) as compared to the corresponding distances in 5-bromo-2,3-dimethylbenzo[b]thiophene (1.75 (1), 1.741 (9) Å),[44] 3-formylbenzo[b]thiophene (1.704 (5), 1.733 (5) Å),[45] [CpRu(η^6-BT)]$^+$ (1.72 (1), 1.730 (7) Å),[10] and CpRu(η^5-BT·H) (1.723 (4), 1.764 (3) Å).[14] Lengthening of the S–C bond is especially interesting because this bond must be cleaved during BT HDS. The other C–S bond (S–C(8) = 1.74 (3) Å) is not lengthened. Thus, only one of the C–S bonds is elongated upon S coordination. It is into this S–C(2) bond that Rh inserts to form Cp*Rh(PMe$_3$)(SC$_8$H$_6$).[4d] A Fe(CO)$_3$ unit also inserts into this bond of BT to give a benzothiaferrole, Fe$_2$(C$_8$H$_6$S)(CO)$_6$.[15] The BT ring is not exactly planar, since the sulfur is slightly out of the plane (0.14 Å) of C(2)–C(3)–C(8)–C(9) away from the Re. Other structural features of the BT ligand are similar to those in [CpRu(η^6-BT)]$^+$,[10] 5-bromo-2,3-dimethylbenzo[b]thiophene,[44] and 3-formylbenzo[b]thiophene.[45]

Scheme III



Comments on the Mechanism of Benzo[b]thiophene HDS on Heterogeneous and Homogeneous Catalysts. Much evidence[7a,g-j] indicates that the hydrogenation of BT to 2,3-dihydrobenzo[b]thiophene is the first step in an important pathway (A in Scheme I) for the catalytic HDS of BT. Our studies reported herein suggest that the initial stage of this hydrogenation is the coordination of BT to a metal site on the catalyst via either the sulfur or the C(2)–C(3) olefin, and these η^1(S) and 2,3-η^2 isomers are in equilibrium with each other as in Cp′(CO)$_2$Re(BT) (Scheme II). The 2,3-η^2 form would presumably be activated (Scheme III) to accept a migrating hydrogen to give an alkyl intermediate. Reductive elimination with another hydrogen would give the 2,3-dihydrobenzo[b]thiophene (DHBT) product. This familiar metal-catalyzed olefin hydrogenation mechanism reasonably accounts for the known hydrogenation of BT to DHBT under mild conditions (85–175 °C) with the following homogeneous catalysts: Ru(H)(Cl)(PPh$_3$)$_3$,[46] Rh(Cl)(PPh$_3$)$_3$,[47] RuCl$_2$(PPh$_3$)$_3$,[48] Ru(H)(Cl)(CO)(PPh$_3$)$_3$$^+$,[48]

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Os(H)(Cl)(CO)$(PPh_3)_3$,[48] Rh(COD)$(PPh_3)_2^+$,[48] Ir(COD)$(PPh_3)_2^+$,[48] and Cp*Rh$(NCMe)_3^{2+}$.[49] In fact, the Cp*Rh$(NCMe)_3^{2+}$-catalyzed deuteration (D_2) of BT gives specifically the *cis*-dideuteriobenzo[*b*]thiophene; this is the stereochemistry predicted by the mechanism in Scheme III. Thus, the mechanism that was proposed for this reaction by Fish and co-workers[49] is supported by the characterization of Cp′$(CO)_2$Re(2,3-η^2-BT).

This olefin hydrogenation mechanism is also likely to be involved in the conversion of BT to DHBT on heterogeneous catalysts. It allows one to account for the relative rates of hydrogenation and HDS of methyl-substituted benzo[*b*]thiophenes on Co–Mo/Al_2O_3 catalysts. These rates decrease with increasing methyl substitution in the order BT > 2-MeBT > 3-MeBT > 2,3-MeBT.[7a,i,j] This trend can be readily explained by the results of our rhenium studies reported herein, which show that 2,3-methyl substitution favors $\eta^1(S)$-BT coordination and decreases the amount of the 2,3-η^2 form. On an HDS catalyst, a lower concentration of methyl-substituted (2,3-η^2)-BT would reduce the overall rate of hydrogenation.

It is also interesting to note that the equilibrium between the 2,3-η^2 and $\eta^1(S)$ forms is affected by the electron density on the metal, which we reduced by replacing Cp* with Cp in the Cp′$(CO)_2$Re(BT) complexes (Scheme II). On a catalyst, the electron richness of a metal site would be affected by its oxidation state as well as the other groups attached to it. Since 2,3-η^2 coordination is favored by an electron-rich metal center, one would expect metal catalysts in low oxidation states to be the most effective catalysts for the hydrogenation of BT to DHBT.

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Supplementary Material Available: For **4**, full tables of bond distances, bond angles, and positional and thermal parameters (5 pages). Ordering information is given on any current masthead page.

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Incorporation of Trialkylsilyl and Trialkylstannyl Groups into Ruthenium Carbonyl Clusters. Carbonyl Substitution versus Trialkylsilane or Trialkylstannane Elimination in These Clusters

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The clusters $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(PPh_3)_n(CO)_{9-n}]$ (n = 0 (**1**), 1 (**2**), 2 (**3**); Hampy = 2-amino-6-methylpyridine) react with $HSiEt_3$ to give the oxidative substitution products $[Ru_3(\mu\text{-H})_2(\mu_3,\eta^2\text{-ampy})(SiEt_3)(PPh_3)_n(CO)_{8-n}]$ (n = 0 (**4a**), 1 (**5a**), 2 (**6a**)). Similar reactions of **1**–**3** with $HSnBu_3$ afford $[Ru_3(\mu\text{-H})_2(\mu_3,\eta^2\text{-ampy})(SnBu_3)(PPh_3)_n(CO)_{8-n}]$ (n = 0 (**4b**), 1 (**5b**), 2 (**6b**)). In all cases, (a) the added hydride spans a metal–metal edge adjacent to that supported by the bridging amido group, (b) the $SiEt_3$ or $SnBu_3$ ligands occupy an equatorial site on the Ru atom bound to the two hydrides, being trans to the hydride which spans the same edge as the amido group, and (c) in the compounds containing PPh_3 ligands, these ligands occupy equatorial positions, cis to hydrides, on the Ru atoms bound to only one hydride. The reactions of **4a** and **5a** with PPh_3 produce the elimination of $HSiEt_3$, rendering the complexes **2** and **3**, respectively; however, similar reactions of the tin-containing compounds **4b** and **5b** afford the substitution products **5b** and **6b**, respectively. The compounds have been characterized by infrared and ^1H, ^{13}C, and ^{31}P NMR spectroscopies and, in the case of **4a** by X-ray diffraction. Crystal data for **4a**: monoclinic, space group $P2_1/n$, a = 10.849 (8) Å, b = 20.809 (4) Å, c = 12.049 (8) Å, β = 98.21 (5)°, V = 2692 (2) Å^3, Z = 4, μ(Mo Kα) = 17.17 cm^{-1}, R = 0.048, R_w = 0.053 for 2036 reflections and 287 variables.

Introduction

Organosilanes and organostannanes are widely used in metal-catalyzed hydrosilylation[2] and hydrostannation[3] reactions. However, little attention has been paid to metal carbonyl clusters as catalyst precursors in such reactions.[2–4]

Concerning ruthenium, the trinuclear clusters $[Ru_3(CO)_{12}]$ and $[Ru_3(\mu\text{-H})(CO)_{11}]^-$ have been reported as catalyst precursors for the dehydrogenative silylation[4c] and hydrosilylation[4d] of olefins, respectively. In the latter process, the anionic cluster $[Ru_3(\mu\text{-H})(CO)_{11}]^-$ reacts with triethylsilane to give the trinuclear derivative $[Ru_3(\mu\text{-H})$-

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