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Synthesis and Reactivity of Ruthenium Complexes with Dibenzothiophene and Hexahydrodibenzothiophene Ligands: Models for Catalytic Hydrodesulfurization

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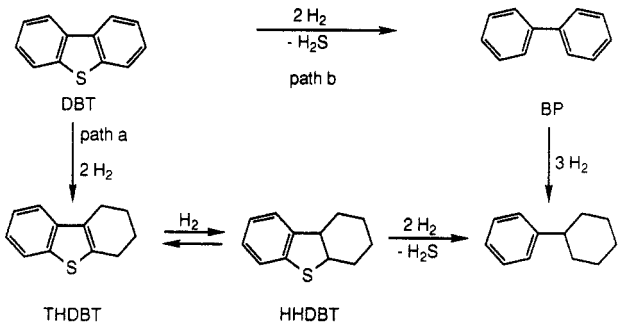
As models for the adsorption of dibenzothiophene (DBT) and hexahydrodibenzothiophene (HHDBT) on hydrodesulfurization (HDS) catalysts, the complexes $CpRu(DBT)^+$, $CpRu(HHDBT)^+$, and $[(CpRu)_2(DBT)]^{2+}$ were prepared. In all cases, the metal is bonded to the benzene portion of the ligand in an η^6 fashion. The reactions of $CpRu(DBT)^+$ and $CpRu(HHDBT)^+$ with a variety of nucleophiles (H^-, CH_3^-, MeO^-) give two or four isomers resulting from nucleophilic addition at different carbon atoms of the coordinated benzene ring. These isomers are oxidized back to $CpRu(DBT)^+$, $CpRu(HHDBT)^+$, or their methyl-substituted derivatives upon reaction with electrophiles or oxidizing agents (Ph_3C^+, H^+, Me_3O^+, Cp_2Fe^+). The reaction of $M(BEt_3H)$ (M = Na, Li) with $[(CpRu)_2(DBT)]^{2+}$ results in the formation of the reduced 38-electron dinuclear complex $(CpRu)_2(DBT)$ and the dihydride adduct $(CpRu)_2(DBT{\cdot}2H)$. An X-ray structure determination of $(CpRu)_2(DBT)$ shows it to consist of a planar DBT ligand bonded on opposite sides by the two CpRu units.

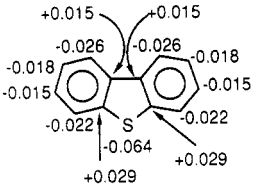
Introduction

Catalytic hydrodesulfurization (HDS) of petroleum is widely practiced on an industrial scale to produce clean-burning, low-sulfur fuels. There is also a need for extending the technology to other fuels, including coal. Dibenzothiophene (DBT), which is present in high concentrations in heavy oils and in coal-derived liquids,[2] is one of the most representative compounds of the least reactive sulfur-containing constituents of these feedstocks and is 1–2 orders of magnitude less reactive than thiophene.[3] Studies[4] of the mechanism of DBT hydrodesulfurization suggest two general pathways (Scheme I): one involves direct sulfur extrusion to give biphenyl (BP) and H_2S, while the other begins with hydrogenation of a benzene ring to give tetrahydrodibenzothiophene (THDBT) and hexahydrodibenzothiophene (HHDBT), which then undergo desulfurization. Beyond these general mechanistic outlines, little is known about the adsorption of DBT or intermediates in the reaction on the catalyst or the nature of their activation by the catalyst.

Since ruthenium is one of the best catalysts of DBT hydrodesulfurization,[5] we sought to understand how Ru might bind to DBT and how the coordinated DBT might react. If one considers a MO calculation on DBT[6]

Scheme I. Proposed Scheme for the HDS of DBT





the highest electron densities are on the outer benzene carbons and the sulfur. Hence, one might expect DBT to coordinate to metals either through the sulfur or as a π complex via one of the benzene rings. Sulfur coordination is known in $[Cp(CO)_2Fe(DBT)]BF_4$[7] and $Cl_2Ru[4\text{-}R_2P\text{-}(DBT)]_2$;[8] the structures of both complexes have been established by X-ray diffraction. Coordination via a π-benzene ring is known in $Cr(CO)_3(\eta^6\text{-}DBT)$,[9] $[CpFe(\eta^6\text{-}DBT)]PF_6$,[10] and $[(CpFe)_2(\mu\text{-}DBT)](PF_6)_2$.[10]

In this paper, we describe the synthesis of Ru complexes coordinated via the π-benzene ring of DBT or HHDBT

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and the reactions of these complexes with nucleophiles. Also, the X-ray-determined structure of the unusual 38-electron dinuclear complex $(CpRu)_2(DBT)$ is reported.

Experimental Section

General Procedure. All manipulations were carried out under an N_2 atmosphere with use of standard Schlenk techniques in reagent grade solvents. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from Na/benzophenone, CH_2Cl_2, hexane, and acetonitrile were distilled from CaH_2, methanol was distilled from MgO, and 1,2-dichloroethane (DCE) was distilled from P_2O_5. The solvents were stored over 4-Å molecular sieves, except for acetone, which was stored over $MgSO_4$, and degassed with N_2 before use. The neutral alumina (Brockmann, activity I) used for chromatography was deoxygenated under high vacuum for 16 h at room temperature, deactivated with 5% (w/w) N_2-saturated water, and stored under N_2. $[CpRu(NCCH_3)_3]PF_6$,[11] dibenzothiophene-4-carboxylic acid (4-COOH·DBT),[12] and hexahydrodibenzothiophene (HHDBT)[13] were prepared according to literature methods. Commercial DBT (Aldrich Chemical) was used without further purification.

The products 1–8 were characterized by their elemental analyses (Table I) and ^1H NMR (Table II) and mass spectra. ^1H NMR data were obtained on a Nicolet NT-300 spectrometer using deuteriated solvents as internal locks and standards (CD_3COCD_3, δ 2.04; CD_2Cl_2, δ 5.34; $CDCl_3$, δ 7.22). Mass spectral data (electron-impact MS) were collected on a Finnigan 4000 spectrometer; fast atom bombardment (FAB) MS data were collected on a Kratos MS-50 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc.

$[CpRu(DBT)]PF_6$ (1). A solution of DBT (2.43 g, 13.2 mmol) and $[CpRu(NCCH_3)_3]PF_6$ (0.573 g, 1.32 mmol) in DCE (50 mL) was refluxed under N_2 for 24 h and then evaporated to dryness in vacuo. The brown residue was extracted with 20 mL of acetone. Addition of about 150 mL of Et_2O resulted in the precipitation of the tan-colored product 1, yield 0.446 g (68%). The product was purified by recrystallization from hot benzene, from which white needlelike crystals of 1 were obtained. The recrystallization step generally decreased the yield by approximately 15–20%. FAB MS (3-nitrobenzyl alcohol–CH_2Cl_2): m/e 351 (M^+).

$[CpRu(4\text{-}COOH\cdot DBT)]PF_6$ (2). This complex was prepared analogously to 1. 4-COOH·DBT (0.730 g, 3.20 mmol) was added to $[CpRu(NCCH_3)_3]PF_6$ (0.279 g, 0.643 mmol) in DCE (20 mL), and the solution was refluxed for 24 h. The solution was evaporated to dryness in vacuo, and the residue was washed with cold ethyl acetate. The remaining tan-colored powder can be recrystallized by dissolving in hot ethyl acetate, adding hexane until cloudy, and cooling to −20 °C to yield 0.125 g (36%) of the ivory-colored crystalline product 2. FAB MS (3-nitrobenzyl alcohol–CH_2Cl_2): m/e 395 (M^+).

$[CpRu(HHDBT)]PF_6$ (3). This complex was synthesized in the same manner as that for 1. A solution of $[CpRu(NCCH_3)_3]PF_6$ (0.558 g, 1.29 mmol) in DCE (50 mL) was refluxed with HHDBT (2.40 g, 12.6 mmol) for 24 h. The solution was evaporated to dryness in vacuo and the residue chromatographed over untreated neutral alumina (1 × 5 cm) with CH_2Cl_2–CH_3CN (2:1) as eluant. The brown eluate was evaporated to dryness, and the residue was recrystallized from CH_2Cl_2–Et_2O at −20 °C to give a light brown powder, yield 0.420 g (65%). White powdery product (3) was obtained by further recrystallization from hot benzene; yield 40%. FAB MS (3-nitrobenzyl alcohol–CH_2Cl_2): m/e 357 (M^+).

$[(CpRu)_2(DBT)](PF_6)_2$ (4). The synthesis proceeded as for 1 by using $[CpRu(NCCH_3)_3]PF_6$ (0.223 g, 0.514 mmol) and DBT (0.0470 g, 0.257 mmol) in DCE (50 mL). After being refluxed for 24 h, the solution was cooled to room temperature. The resulting deep brown precipitate was filtered from the solution and then dissolved in CH_3CN. The CH_3CN solution was filtered through Celite to remove a black insoluble impurity. Addition of THF to the filtrate gave the product 4 as an ivory-colored solid that was separated by filtration and dried in vacuo; yield 0.112 g (54%).

CpRu(DBT·H) (5). To a stirred solution of 1 (0.030 g, 0.061 mmol) in CH_2Cl_2 (5 mL) was added $Na(BEt_3H)$ (0.06 mL of a 1 M solution in THF, 0.06 mmol). After 5 min at room temperature, the solution was evaporated to a yellow oil in vacuo. The oil was extracted with 6 mL (2 × 3 mL) of Et_2O, and the yellow Et_2O solution was evaporated to dryness. A bright yellow solid (5) was obtained by recrystallization of the residue from hexane at −78 °C; yield 0.017 g (80%). EI MS (18 eV): m/e 351 (base peak, $M^+ - H$), 167 (M^+ – DBT·H), 184 (DBT^+).

$CpRu(DBT\cdot CH_3)$ (6). To a solution of 1 (0.100 g, 0.202 mmol) in THF (20 mL) was added LiMe (0.15 mL of a 1.5 M solution in Et_2O, 0.23 mmol). The solution turned yellow immediately and was stirred 5 min. The yellow solution was then evaporated to dryness in vacuo and the residue chromatographed over neutral alumina (1 × 5 cm) with hexane as eluant. The bright yellow solid product (6) was obtained by recrystallization from hexane at −78 °C; yield 0.030 g (40%). EI MS (17 eV): m/e 365 ($M^+ - H$), 351 ($M^+ - CH_3$), 184 (base peak, DBT^+).

CpRu(HHDBT·H) (7). This preparation was performed analogously to that for 5. To a stirred solution of 3 (0.100 g, 0.200 mmol) in THF (20 mL) was added $Na(BEt_3H)$ (0.20 mL of a 1.0 M solution in THF, 0.21 mmol). After 40 min at room temperature, the solution was evaporated to dryness in vacuo. The residue was chromatographed on neutral alumina (1 × 5 cm) with hexane as eluant to give a light yellow oily solid. A white solid of 7 was obtained by recrystallization from hexane at −78 °C; yield 0.0621 g (87%). EI MS (14 eV): m/e 357 ($M^+ - H$), 276 (base peak, $M^+ - C_6H_{10}$), 190 ($HHDBT^+$).

$CpRu(HHDBT\cdot CH_3)$ (8). The preparation of this compound from 3 (0.100 g, 0.200 mmol) and LiMe (1.5 mL of a 1.5 M solution in Et_2O, 0.23 mmol) in THF (25 mL) proceeded analogously to that for 6. The white product (8) was isolated in 60% yield (0.0445 g). EI MS (15 eV): m/e 371 ($M^+ - H$), 357 (base peak, $M^+ - CH_3$), 190 ($HHDBT^+$).

H^- Abstraction from 5–8. To a stirred solution of 5 (0.018 g, 0.050 mmol) in CH_2Cl_2 (10 mL) was added $(Ph_3C)BF_4$ (0.017 g, 0.050 mmol), $(Me_3O)BF_4$ (0.0074 g, 0.050 mmol), $HBF_4\cdot Et_2O$ (7.0 μL, 0.050 mmol), or $(FeCp_2)BF_4$ (0.027 g, 0.050 mmol). After 10 min at room temperature, the solution was evaporated to dryness in vacuo. ^1H NMR spectra of the reaction residues in acetone-d_6 showed that complex 1 was formed quantitatively in all four reactions.

In similar experiments, compound 6 (0.020 g, 0.055 mmol) in CH_2Cl_2 (10 mL) was treated with 1 equiv of the above reagents for 10 min at room temperature. The solution was then evaporated to dryness in vacuo. The ^1H NMR spectrum of the resulting residues in $CDCl_3$ showed a very complex pattern for the four isomers of $[CpRu(DBT\cdot CH_3)]BF_4$ (9); however, four methyl singlets were observed in the range δ 2.4–2.6. There was no evidence for the formation of 1. White powdery $[CpRu(DBT\cdot CH_3)]BF_4$ was obtained by recrystallization from CH_2Cl_2–Et_2O; yield 0.024 g (95%). FAB MS (3-nitrobenzyl alcohol–CH_2Cl_2): m/e 365 (M^+).

The reaction of 7 (0.020 g, 0.056 mmol) with the above four reagents (1 equiv) proceeded analogously to that for 5. The ^1H NMR spectra showed that all of the starting complex 7 was converted to 3 in all reactions.

The reaction of 8 (0.020 g, 0.054 mmol) with the above reagents (1 equiv) proceeded analogously to that for 6. ^1H NMR spectra of the reaction residues showed that four isomers of $[CpRu(HHDBT\cdot CH_3)]BF_4$ (10) had formed, as indicated by the four new methyl singlets appearing in the range δ 2.2–2.5. The white powdery product, $[CpRu(HHDBT\cdot CH_3)]BF_4$, was obtained by recrystallization from CH_2Cl_2–Et_2O; yield 0.024 g (98%). FAB MS (3-nitrobenzyl alcohol–CH_2Cl_2): m/e 371 (M^+).

Reaction of 4 with $Na(BEt_3H)$. To a stirred solution of 4 (0.12 g, 0.15 mmol) in THF (25 mL) was added $Na(BEt_3H)$ (0.3 mL of a 1 M solution in THF, 0.3 mmol). After 40 min at room temperature, the solution was evaporated to dryness in vacuo. The residue was chromatographed over neutral alumina (1 × 5 cm) with CH_2Cl_2–hexane (1:1) as eluant. The eluate was evaporated to dryness and yielded 0.063 g (82%) of a yellow solid. Recrystallization from CH_2Cl_2–hexane at −78 °C gave a mixture of yellow platelike crystals, yellow needlelike crystals, and an unidentified yellow solid. The yellow platelike crystals (25% yield) separated by hand were identified as $(CpRu)_2DBT$ (11) on the

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Table I. Analytical Data for the Complexes

compd	anal. found (calcd), % C	H	compd	anal. found (calcd), % C	H
$[CpRu(DBT)]PF_6$ (1)	41.01 (41.22)	2.77 (2.65)	CpRu(DBT·H) (5)	57.31 (57.94)	4.68 (4.29)
$[CpRu(4\text{-}COOH\cdot DBT)]PF_6$ (2)	40.50 (40.08)	2.51 (2.43)	$CpRu(DBT\cdot CH_3)$ (6)	59.12 (59.16)	4.47 (4.41)
$[CpRu(HHDBT)]PF_6$ (3)	41.22 (40.72)	3.97 (3.82)	CpRu(HHDBT·H) (7)	57.61 (57.12)	5.79 (5.64)
$[(CpRu)_2DBT](PF_6)_2$ (4)	32.71 (32.76)	2.19 (2.25)	$CpRu(HHDBT\cdot CH_3)$ (8)	58.43 (58.20)	5.86 (5.97)

Table II. ^1H NMR Data (δ) for the Complexes[a]

compd	H1	H2	H3	H4	H6	H7	H8	H9	Cp	other
$[CpRu(DBT)]PF_6$ (1)[b]	8.41 dd[c]	7.64 ps t[c]	7.73 ps t[c]	8.05 d[c]	7.50 d[d]	6.45 ps t[d]	6.47 ps t[d]	7.61 d[d]	5.23 s	
$[CpRu(4\text{-}COOH\cdot DBT)]PF_6$ (2)[b]	8.60 d[c]	7.78 ps t[c]	8.40 d[c]	...	7.53 d[d]	6.49 ps t[d]	6.54 ps t[d]	7.68 d[d]	5.25 s	
$[CpRu(HHDBT)]PF_6$ (3)[b,f]		(1.20–2.00 m)[e]			6.42 d[d]	6.12 ps t[d]	6.25 ps t[d]	6.67 d[d]	5.53 s	
$[(CpRu)_2DBT](PF_6)_2$ (4)[b]	7.69 d[d]	6.71 ps t[d]	6.64 ps t[d]	7.59 d[d]	7.59 d[d]	6.64 ps t[d]	6.71 ps t[d]	7.69 d[d]	5.49 s	
CpRu(DBT·H) (5)										
A[b]		(7.13–7.95 m)[e]			3.37 dd[g]	3.10 dd[g]	4.62 ps t[g]	6.84 d[g]	4.35 s	3.08 d[g] (H_{exo})
B[b]		(7.13–7.95 m)[e]			6.68 d[g]	4.72 ps t[g]	2.97 ps t[g]	3.62 dd[g]	4.32 s	3.00 d[g] (H_{exo})
$CpRu(DBT\cdot CH_3)$ (6)										
A[h]		(7.08–8.15 m)[e]			3.38 ps p[i]	3.25 ps t[i]	4.43 ps t[i]	6.58 d[g]	4.32 s	0.28 d[i] (CH_3)
B[h]		(7.08–8.15 m)[e]			6.45 d[g]	4.54 ps t[i]	3.17 ps t[i]	3.53 ps p[i]	4.28 s	0.17 d[i] (CH_3)
C[h]		(7.08–8.15 m)[e]			3.82 d[i]	2.55 ps p[i]	2.97 ps t[i]	5.51 d[g]	4.43 s	0.17 d[i] (CH_3)
D[h]		(7.08–8.15 m)[e]			5.41 d[g]	2.95 ps t[i]	2.47 ps p[i]	3.84 d[i]	4.41 s	0.14 d[i] (CH_3)
CpRu(HHDBT·H) (7)										
A[j,f]		(0.80–2.10 m)[e]			(2.20–3.00 m)[e]		4.43 ps t[i]	6.02 d[g]		
B[j,f]		(0.80–2.10 m)[e]			5.74 d[g]	4.34 ps t[i]	(2.20–3.00 m)[e]			
C[j,f]		(0.80–2.10 m)[e]			(2.20–3.00 m)[e]			4.92 d[g]	(4.69–4.71 4 s)[e]	
D[j,f]		(0.80–2.10 m)[e]			4.59 d[g]		(2.00–3.00 m)[e]			
$CpRu(HHDBT\cdot CH_3)$ (8)										
A[h,f]		(0.80–2.10 m)[e]			(2.20–3.30 m)[e]		4.26 ps t[i]	5.94 d[g]	(4.64–4.67 4 s)[e]	0.29 d[i] (CH_3)
B[h,f]		(0.80–2.10 m)[e]			5.62 d[g]	4.16 ps t[i]	(2.20–3.30 m)[e]			0.30 d[i] (CH_3)
C[h,f]		(0.80–2.10 m)[e]			(2.20–3.30 m)[e]				4.78 d[g]	0.19 d[i] (CH_3)
D[h,f]		(0.80–2.10 m)[e]			4.42 d[g]		(2.20–3.30 m)[e]			0.14 d[i] (CH_3)
$(CpRu)_2(DBT\text{-}2H)$ (12)[b]	7.34 d[k]	6.26 t[k]	6.30 t[k]	7.01 d[k]	(2.95–3.35 m)[e]		4.76 t[k]	7.05 d[k]	5.32 s (Cp1) 4.61 s (Cp2)	(2.95–3.35 m)[e]
$CpRu(DBT\cdot OCH_3)$ (13)										
A[h]		(7.00–7.75 m)[e]			4.00 d[i]	3.32 ps t[i]	4.48 ps t[i]	6.60 d[g]	4.35 s	1.98 s (OCH_3)
B[h]		(7.00–7.75 m)[e]			6.49 d[g]	4.57 ps t[i]	3.24 ps t[i]	3.89 d[i]	4.30 s	1.77 s (OCH_3)
DBT[b,l]	8.30 m	7.49 m	7.50 m	7.95 m	7.95 m	7.50 m	7.49 m	8.30 m		
4-COOH·DBT[b]	8.60 dd[c]	7.67 ps t[c]	8.37 dd[c]	...	8.02 dd[m]	(7.54 m)[e]		8.27 dd[m]		
HHDBT[b,f]		(1.30–2.10 m)[e]				(6.95–7.25 m)[e]				

[a] Abbreviations: dd, doublet of doublets; d, doublet; s, singlet; ps t, pseudotriplet; dt, doublet of triplets; m, multiplet; ps p, pseudo pentet; ps q, pseudo quartet; br, broad. [b] Acetone-d_6. [c] $J_{H1\text{-}H2}$ = 7.7 Hz; $J_{H1\text{-}H3}$ = 1.1 Hz; $J_{H2\text{-}H3}$ = 7.7 Hz; $J_{H3\text{-}H4}$ = 8.0 Hz. [d] $J_{H6\text{-}H7} = J_{H7\text{-}H8} = J_{H8\text{-}H9}$ = 5.8 Hz. [e] Exact position of peak within the complex multiplet not determined. [f] Compound 3: δ 4.36 br (H4a), 3.20 dt (H9b), $J_{H9b\text{-}H4a}$ = 11.9 Hz, $J_{H9b\text{-}H1}$ = 5.8 Hz. Compound 7: δ 3.38, 3.41, 3.89, 4.12 (4 br).[n] Compound 8: δ 3.37, 3.43, 3.85, 4.86 (4 br).[n] HHDBT: δ 3.85 ps q (H4a), 3.28 ps q (H9b). [g] $^{A,C}J_{H9\text{-}H8} = {}^{B,D}J_{H6\text{-}H7}$ = 4.7 Hz; $^{A,B}J_{H8\text{-}H7}$ = 5.0 Hz; $^{A}J_{H7\text{-}H6} = {}^{B}J_{H8\text{-}H9}$ = 6.5 Hz; $^{A}J_{H6\text{-}H_{exo}} = {}^{B}J_{H9\text{-}H_{exo}}$ = 12.0 Hz. [h] $CDCl_3$. [i] $^{A,B}J_{H8\text{-}H7}$ = 5.4 Hz; $^{C,D}J_{H8\text{-}H7}$ = 6.0 Hz; $^{A}J_{H6\text{-}H7} = {}^{B}J_{H8\text{-}H9}$ = 6.0 Hz; $^{C}J_{H6\text{-}H7} = {}^{D}J_{H8\text{-}H9}$ = 6.6 Hz; $^{A}J_{H6\text{-}CH_3} = {}^{B}J_{H9\text{-}CH_3} = {}^{C}J_{H7\text{-}CH_3} = {}^{D}J_{H8\text{-}CH_3}$ = 6.3 Hz. [j] CD_2Cl_2. [k] $J_{H1\text{-}H2}$ = 5.7 Hz; $J_{H3\text{-}H4}$ = 5.4 Hz; $J_{H2\text{-}H3}$ = 5.6 Hz; $J_{H8\text{-}H9}$ = 4.8 Hz. [l] Reference 14. [m] $J_{H6\text{-}H7}$ = 7.8 Hz; $J_{H9\text{-}H8}$ = 7.4 Hz. [n] Signals for H4a in the four isomers.

Table III. Crystal and Data Collection Parameters for the X-ray Diffraction Study of $(CpRu)_2(DBT)$ (11)

formula	$Ru_2SC_{22}H_{18}$
fw	516.59
space group	*Pbca* (No. 61)
a, Å	11.650 (1)
b, Å	10.140 (2)
c, Å	15.238 (2)
V, Å^3	1800.1 (7)
Z	4
d_{calc}, g/cm^3	1.906
cryst size, mm	0.21 × 0.11 × 0.01
μ(MoKα), cm^{-1}	17.60
data collection instrument	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
orientation rflns: no.; range (2θ), deg	21; 13 < 2θ < 28
temp, °C	22 ± 1
scan method	ω scans
data collection range, 2θ, deg	4.0–45.0
no. of unique data: total no., no. with $F_o^2 > 3\sigma(F_o^2)$	1180, 456
no. of params refined	63
transmission factors: max, min (ψ scans)	0.997, 0.862
R^a	0.0489
R_w^b	0.0589
quality-of-fit indicator^c	1.18
largest shift/esd, final cycle	0.01
largest peak, e/Å^3	0.721

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

basis of its X-ray structure and mass spectrum. EI MS (17 eV): *m/e* 518 (base peak, M^+), 351 (M^+ – CpRu), 287 (MH^+ – Cp_2Ru), 184 (DBT^+). The ^1H NMR spectrum of **11** was much more complex than expected on the basis of its solid-state structure, suggesting that its structure may be different in solution: ^1H NMR ($CDCl_3$) δ 6.52 (d, J = 4.5 Hz), 6.35 (d, J = 4.5 Hz), 6.16 (d, J = 4.5 Hz), 6.03 (t, J = 4.5 Hz), 4.32–4.64 (m), 4.47 (s), 2.25–3.30 (m). Anal. Calcd for $C_{22}H_{18}Ru_2S$: C, 51.15; H, 3.51. Found: C, 50.17; H, 3.93. The yellow needlelike crystals (~5%) separated by hand were identified as $(CpRu)_2(DBT{\cdot}2H)$ (**12**) on the basis of their ^1H NMR (Table II) and mass spectra. CI MS (NH_3): *m/e* 520 (M^+), 353 (base peak, $CpRu(DBT{\cdot}2H)^+$), 184 (DBT^+).

X-ray Structure Determination of $(CpRu)_2(DBT)$ (11). A yellow platelike crystal of $(CpRu)_2(DBT)$ was mounted on a glass fiber with its long axis approximately parallel to the ϕ axis of the diffractometer. The cell constants were determined from a list of reflections found by an automated search routine. Pertinent data collection and reduction information are given in Table III.

A total of 2300 reflections were collected in the $+h,+k,+l$ quadrant, of which 1180 were unique. The average intensity of three intensity standards, measured every 1 h of exposure time, was constant within ±0.2% over the entire data collection period. An absorption correction was made, on the basis of a series of ϕ scans. Lorentz and polarization corrections were applied. The agreement factors for the averaging of 918 observed reflections were 4.0% based on intensity and 3.2% based on F_o.

The structure was solved by the Patterson method. Following placement of the Ru atom, all of the remaining non-hydrogen atoms were located in a difference Fourier map. Since the molecule lies on a crystallographic center of symmetry, it became obvious that the sulfur atom could not exist in both of its symmetry-related positions simultaneously, so its occupancy was fixed at 0.5. Only the Ru and S atoms were refined with anisotropic thermal parameters. Hydrogen atoms were not included in the calculations.[15]

X-ray data collection and structure solution were carried out at the Iowa State University Molecular Structure Laboratory. All calculations were performed on a Digital Equipment Corp. Micro VAX II computer using the CAD4-SDP package.[16] The final positional and thermal parameters for **11** are listed in Table IV. Bond lengths and angles are presented in Table V, and an ORTEP

Table IV. Positional and Thermal Parameters for $(CpRu)_2(DBT)$ (11)

atom	*x*	*y*	*z*	*B*,^{a} Å^2
Ru	0.0793 (2)	0.1515 (1)	0.3734 (1)	4.80 (3)
S	0.1601 (9)	0.026 (1)	0.5722 (7)	4.9 (3)
C(1)	–0.088 (2)	0.117 (2)	0.439 (2)	7.9 (6)*
C(2)	–0.099 (2)	0.252 (2)	0.417 (2)	8.3 (7)*
C(3)	–0.002 (2)	0.330 (2)	0.444 (2)	8.1 (7)*
C(4)	0.092 (2)	0.287 (2)	0.495 (2)	7.2 (6)*
C(5)	0.090 (2)	0.157 (2)	0.516 (1)	6.9 (5)*
C(6)	0.001 (2)	0.074 (2)	0.488 (2)	7.5 (6)*
C(7)	0.216 (2)	0.028 (2)	0.319 (1)	5.8 (5)*
C(8)	0.112 (2)	0.001 (2)	0.277 (1)	6.5 (6)*
C(9)	0.069 (2)	0.114 (2)	0.232 (1)	5.7 (5)*
C(10)	0.156 (2)	0.215 (2)	0.251 (1)	4.9 (4)*
C(11)	0.241 (2)	0.161 (2)	0.304 (1)	5.9 (5)*

^{a}Asterisks denote values for atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table V. Bond Distances and Angles for $(CpRu)_2(DBT)$ (11)

Bond Distances (Å)			
Ru–C(1)	2.21 (3)	C(1)–C(2)	1.42 (3)
Ru–C(2)	2.40 (3)	C(1)–C(6)	1.35 (3)
Ru–C(3)	2.30 (3)	C(2)–C(3)	1.44 (3)
Ru–C(4)	2.31 (2)	C(3)–C(4)	1.41 (3)
Ru–C(5)	2.18 (2)	C(4)–C(5)	1.35 (3)
Ru–C(6)	2.13 (3)	C(5)–C(6)	1.40 (3)
Ru–C(7)	2.19 (2)	C(6)–C(6)′	1.55 (5)
Ru–C(8)	2.16 (2)	C(7)–C(8)	1.39 (3)
Ru–C(9)	2.19 (2)	C(7)–C(11)	1.40 (2)
Ru–C(10)	2.17 (2)	C(8)–C(9)	1.42 (2)
Ru–C(11)	2.17 (2)	C(9)–C(10)	1.47 (3)
S–C(1)	1.68 (2)	C(10)–C(11)	1.39 (3)
S–C(5)	1.78 (3)		

Bond Angles (deg)			
C(1)′–S–C(5)	111 (1)	C(1)–C(6)–C(5)	123 (2)
S–C(1)′–C(2)′	139 (2)	C(1)–C(6)–C(6)′	115 (3)
C(2)–C(1)–C(6)	121 (2)	C(5)–C(6)–C(6)′	122 (3)
C(1)–C(2)–C(3)	113 (2)	C(8)–C(7)–C(11)	108 (2)
C(2)–C(3)–C(4)	126 (2)	C(7)–C(8)–C(9)	111 (2)
C(3)–C(4)–C(5)	115 (3)	C(8)–C(9)–C(10)	103 (2)
S–C(5)–C(4)	146 (2)	C(9)–C(10)–C(11)	109 (2)
S–C(5)–C(6)	92 (2)	C(7)–C(11)–C(10)	109 (2)
C(4)–C(5)–C(6)	122 (2)		

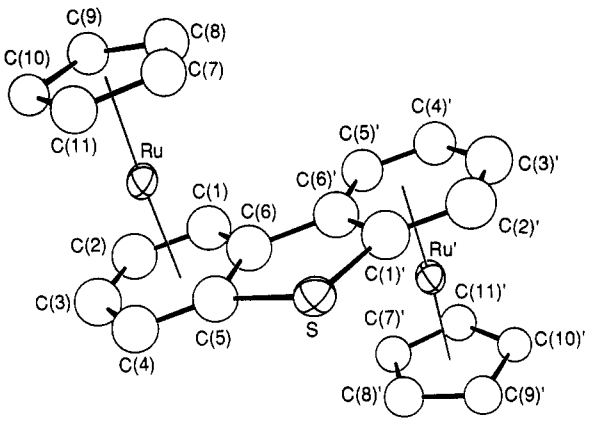


Figure 1. ORTEP drawing of $(CpRu)_2DBT$ (**11**).

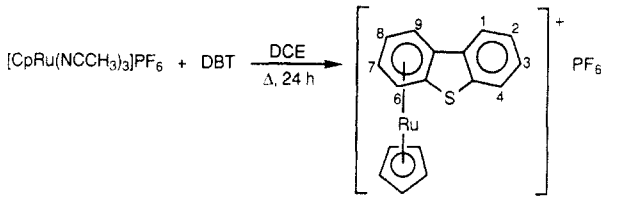
(15) Neutral-atom scattering factors and anomalous scattering corrections were taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(16) Enraf-Nonius Structure Determination Package; Enraf-Nonius: Delft, Holland.

drawing of 11 is given in Figure 1.

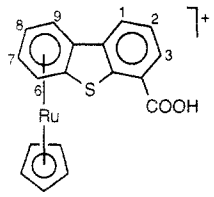
Results and Discussion

Preparation and Characterization of [CpRu(DBT)]PF_6 (1), [CpRu(4-COOH·DBT)]PF_6 (2), and [CpRu(HHDBT)]PF_6 (3). The acetonitrile complex $[CpRu(NCCH_3)_3]PF_6$ reacts with DBT in refluxing DCE to give the η^6-arene complex 1 (eq 1). Mann[11] used this

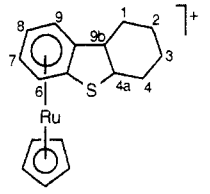


(1)

method to prepare a variety of other CpRu(η^6-arene)$^+$ complexes. The 4-COOH·DBT and HHDBT complexes 2 and 3 are synthesized analogously. Complexes 1–3 are



2



3

air-stable in the solid state, and the DBT, 4-COOH·DBT, and HHDBT ligands are not displaced by coordinating solvents such as acetone, THF, and water at room temperature over 24 h.

Complexes 1–3 are fully characterized by the mass spectral data mentioned previously, elemental analyses (Table I), and ^{1}H NMR spectra (Table II). The ^{1}H NMR spectrum of complex 1 was assigned by comparison to those of free DBT, 4-COOH·DBT, and complex 2 and with use of the results of selective decoupling. The ^{1}H NMR spectrum of free DBT has been assigned in the literature.[14] The chemical shifts of the H6–H9 resonances in 4-COOH·DBT do not shift much from those in DBT (Table II); however, the H1–H3 resonances are shifted downfield due to the electron-withdrawing –COOH group. Similar shifts are observed for benzoic acid as compared to benzene.[17] With a knowledge of these assignments for free 4-COOH·DBT, the protons in the coordinated ring of 2 are expected to be upfield, as is observed in arenes coordinated to neutral or cationic transition-metal centers.[10,18] Therefore, H6–H9 of complex 2 are assigned to the signals that are most upfield, while H1–H3 have almost the same chemical shifts as in 4-COOH·DBT. In a similar way, all of the protons in complex 1 are assigned by comparison with complex 2 and free DBT. The shifts of the coordinated ring protons in 1 are 0.5–1.2 ppm upfield of those in the uncoordinated ring. Moreover, the H7 and H8 resonances are identified by selective decoupling of H6 and H9, respectively. By irradiation of H1 and H4 in complex 1 the assignments of H2 and H3 are further confirmed. No evidence for complexation of the central thiophene ring, which contains the heteroatom, is observed in any of the complexes, as this would give rise to much simpler NMR spectra.

(17) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrophotometric Identification of Organic Compounds*; Wiley: New York, 1981; p 231.

(18) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

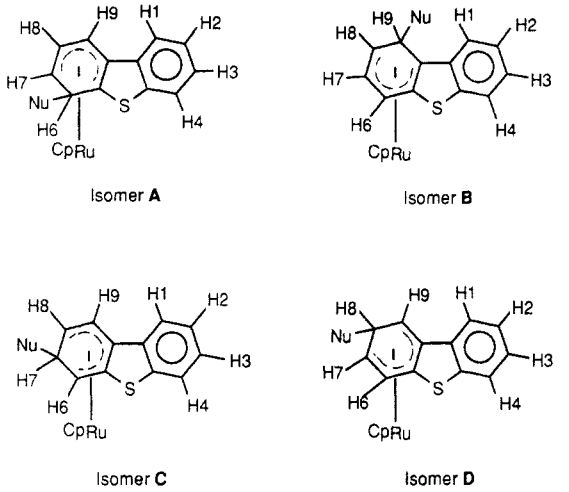


Figure 2. Isomers A–D of complexes 5 and 6.

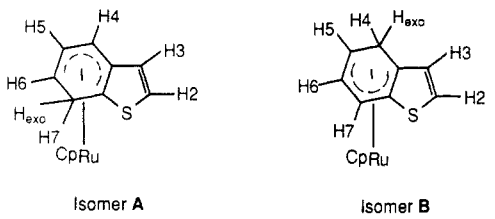
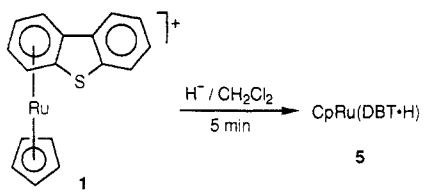


Figure 3. Isomers A and B of CpRu(BT·H).

The ^{1}H NMR assignment of complex 3 is made by comparison to that of complex 1. The resonances for H6 and H9 are doublets, while those of H7 and H8 are pseudotriplets. The H9 resonance in 3 is assigned to the doublet furthest downfield, and H8 is assigned to the triplet furthest downfield, because H9 and H8 are downfield of H6 and H7 in 1. The H4a resonance is assigned downfield of the H9b resonance, since C4a is closer to the sulfur atom than C9b.

Reactions of [CpRu(DBT)]PF_6 (1) and [CpRu(HHDBT)]PF_6 (3). Complex 1 reacts with Li(BEt_3H), Na(BEt_3H), or $NaBH_4$ to give the hydride addition product 5, as shown in eq 2. Because of the weaker hydride-



1 5 (2)

donating ability of $NaBH_4$, the yield of adduct in this case is only 23% as compared with 80% for the reactions with Li(BEt_3H) or Na(BEt_3H). The bright yellow, air-sensitive solid (5) is identified by the EI MS spectrum, elemental analyses (Table I), and the ^{1}H NMR spectrum (Table II). The ^{1}H NMR spectrum shows two isomers (A and B in Figure 2); the ratio of A to B is 1.8, 2.3, and 1.0 depending upon the hydride source ($NaBH_4$, Na(BEt_3H), and Li(BEt_3H), respectively).

The ^{1}H NMR resonances corresponding to these isomers are assigned by selective-decoupling experiments and by comparison with the resonances for the analogous benzothiophene (BT) CpRu(BT·H) isomers,[19] which are shown in Figure 3. For [CpRu(BT)]PF_6,[19] the H4 resonance is more upfield than H7. Assignments of the CpRu(BT·H) isomers were made by assuming the relative positions for

(19) Huckett, S. C.; Angelici, R. J. *Organometallics* **1988**, *7*, 1491.

Table VI. Percentages of Isomers A–D of Complexes 5–8 and 13

compd	amt of isomer, % A	B	C	D
CpRu(DBT·H) (5)[a]	70	30	0	0
CpRu(DBT·CH_3) (6)	30	48	12	10
CpRu(HHDBT·H) (7)[a]	20	40	20	20
CpRu(HHDBT·CH_3) (8)	10	40	25	25
CpRu(DBT·OMe) (13)	55	45	0	0

[a] The hydride source is $Na(BEt_3H)$.

H4 and H7 to remain the same. This assignment was confirmed by deuterium substitution at the 2- and 7-positions.[19] Likewise, the ^1H NMR spectrum of CpRu(DBT·H) (5) distinguishes isomers A and B. The magnitude of the coupling constant between H6 (the endo hydrogen in isomer A) and H7 (J_{H6-H7} = 6.5 Hz) is expected to be greater than that between H7 and H_{exo} ($J_{H7-H_{exo}} < 1$ Hz) on the basis of the Karplus relationship.[20] This has been observed in the $CpCo(C_6H_7)^+$,[21] $(C_7H_8)Mn(CO)_3^+$,[22] $(C_7H_8)Mo(CO)_3$,[23] and CpRu(BT·H)[19] complexes. Thus, the resonance for H7 is a doublet of doublets due to coupling to H8 and H6, and that for H_{exo} is a doublet ($J_{H6-H_{exo}}$ = 12.0 Hz). The H1–H4 resonances in **5A,B** (7.13–7.95 ppm) occur ~0.5 ppm upfield from those in 1 but could not be assigned due to the complexity of the multiplet. The reaction of $Li(BEt_3D)$ with complex 1 gives D^- addition at only the exo face of the DBT ligand, since the H_{exo} peaks in isomers A and B are not present in ^1H NMR spectra of these deuteriated products.

The percentages of isomers A and B obtained from the reaction of 1 with $Na(BEt_3H)$ are determined by integration of H9 on isomer A and H6 on isomer B and are given in Table VI. These percentages remained constant for more than 2 days when the samples were maintained at room temperature in acetone-d_6 or $CDCl_3$. Hence, there is no isomer interconversion under these conditions.

The reaction of 1 with LiMe gives CpRu(DBT·Me) (6) as four isomers, A–D (Figure 2). The resulting bright yellow, air-sensitive compound is characterized by its elemental analyses (Table I) and EI MS and ^1H NMR spectra (Table II). The ^1H NMR resonances for these isomers are assigned by analogy to those for 5, and their relative amounts are determined by integrating the Cp signals. As shown in Table VI, the trend for percentages of isomers is B > A ≫ C ≈ D. As indicated by the triplet corresponding to H7 in isomer A ($J_{H7-H6_{endo}}$ = 6.0 Hz, J_{H7-H8} = 5.4 Hz), the methyl anion addition also occurs at the exo position only.

Compounds CpRu(HHDBT·H) (7) and CpRu(HHDBT·Me) (8) are prepared similarly to 5 and 6, respectively, by using $[CpRu(HHDBT)]PF_6$ (3) instead of $[CpRu(DBT)]PF_6$ (eq 3). The resulting air-sensitive ad-

$$\underset{3}{CpRu(HHDBT)^+} + (LiBEt_3H \text{ or } LiMe) \xrightarrow{CH_2Cl_2} \underset{7,\ 8}{CpRu(HHDBT\cdot Nu)} \quad (3)$$

7, Nu = H; 8, Nu = Me

ducts are characterized by elemental analyses (Table I) and EI MS and ^1H NMR spectra (Table II). The ^1H NMR resonances of all four isomers are assigned analogously to those of compounds 5 and 6 mentioned above, and the relative amounts of these isomers as determined by Cp signal integrations are given in Table VI.

In order to investigate the reversibility of these nucleophilic addition reactions, the product adducts were reacted with electrophiles and oxidizing agents such as Ph_3C^+, $HBF_4{\cdot}Et_2O$, Me_3O^+, and Cp_2Fe^+. The addition of 1 equiv of the electrophile to the hydride compounds 5 and 7 in CH_2Cl_2 results in immediate reaction to generate the original 1 and 3 quantitatively as shown in eq 4. Cp_2Fe^+

$$\underset{5}{CpRu(DBT\cdot H)} \xrightarrow[10\text{ min}]{E^+/CH_2Cl_2} \underset{1}{CpRu(DBT)^+} \quad (4)$$

$$\underset{7}{CpRu(HHDBT\cdot H)} \xrightarrow[10\text{ min}]{E^+/CH_2Cl_2} \underset{3}{CpRu(HHDBT)^+}$$

$E^+ = Ph_3C^+, HBF_4{\cdot}Et_2O, Me_3O^+, Cp_2Fe^+$

presumably reacts by initially removing an electron from 5 and 7 to give Cp_2Fe as detected by ^1H NMR spectroscopy; the products, 1 and 3, presumably result from loss of a hydrogen atom from the radical-cation Ru complex intermediate. The reactions of Ph_3C^+, H^+, and Me_3O^+ may also proceed by oxidation followed by hydrogen atom transfer to give the products; however, they may also occur by direct H^- abstraction. When $^1/_2$ equiv of Ph_3C^+ is added to a solution of 5, the ratio of isomer A to B in the unreacted 5 increases from 1.0 to 1.8, which means that the hydrogen on isomer B is removed more easily than that on isomer A. The same preference for hydrogen abstraction from isomer B was also observed in CpRu(BT·H).[19]

In order to examine the site of hydrogen abstraction, the deuteriated CpRu(DBT·D) was prepared by reacting 1 (0.04 mmol) with $NaBD_4$ (0.05 mmol) in H_2O–CH_2Cl_2 (5 mL/5 mL). This gave a product that was a mixture of CpRu(DBT·D) (54%) and CpRu(DBT·H) (46%), due to $NaBH_4$ impurities in the $NaBD_4$. The percentages of the deuteride and hydride complexes were determined from EI MS data of the mixture. When 1 equiv of Ph_3C^+ was added to the mixture of CpRu(DBT·D) and CpRu(DBT·H) in acetone-d_6 solvent, only $CpRu(DBT)^+$ was observed in the ^1H NMR spectrum; none of the $CpRu(DBT)^+$ containing deuterium was formed. Thus, the hydride abstraction occurs from only the exo position of the DBT ligand.

The reactions of the compounds 6 and 8 with electrophiles give only the methyl-substituted arene complexes 9 and 10, resulting from quantitative removal of the endo hydrogen (eq 5). When 1 equiv of $(Ph_3C)BF_4$ is used, the

$$\underset{6}{CpRu(DBT\cdot CH_3)} \xrightarrow[10\text{ min}]{E^+/CH_2Cl_2} \underset{9}{CpRu(DBT\cdot CH_3)^+} \quad (5)$$

$$\underset{8}{CpRu(HHDBT\cdot CH_3)} \xrightarrow[10\text{ min}]{E^+/CH_2Cl_2} \underset{10}{CpRu(HHDBT\cdot CH_3)^+}$$

$E^+ = Ph_3C^+, HBF_4{\cdot}Et_2O, Me_3O^+, Cp_2Fe^+$

percentages of isomers A–D in $CpRu(DBT\cdot CH_3)^+$ (9) are 38, 41, 15, and 6%, respectively, as compared to 30, 48, 12, and 10% in the starting $CpRu(DBT\cdot CH_3)$ (6). Thus, the various isomers of 6 appear to be converted to the corresponding isomers of $CpRu(DBT\cdot CH_3)^+$ (9). When 0.67 equiv of $(Ph_3C)BF_4$ reacts with 6, the ratio of A to B in the unreacted 6 decreases from 0.67 to 0.23 (only small amounts of C and D are observed), which means that the endo hydrogen is removed more readily in isomer A than in isomer B. This is in contrast to the reaction of 5 with

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(21) Herberich, G. E.; Schwarzer, J. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 143.
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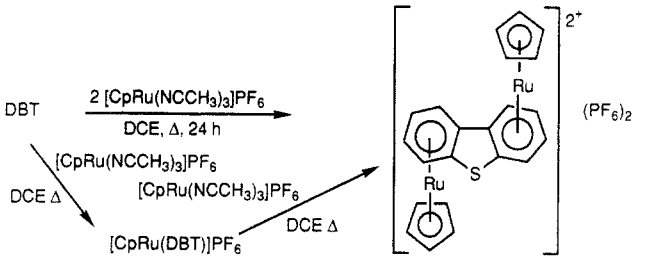
$^1/_2$ equiv of $(Ph_3C)BF_4$, where the exo hydrogen is removed more readily from isomer B than from A. It is not clear why the isomeric preference for the removal of exo and endo hydrogens is different for **5** and **6**. In a hydrothiophene complex, $(C_4H_5S)Mn(CO)_3$,[24] $(Ph_3C)BF_4$ also removes only the exo hydrogen.

In an attempt to explore more broadly the reactivity of $CpRu(DBT)^+$ (**1**), other nucleophiles such as NaOMe, $NaNMe_2$, and NaSEt were reacted with **1**. In dry MeOH, NaOMe reacts with **1** in 20 min to give a yellow solid, which was characterized by its ^1H NMR (Table II) and mass spectra (EI MS: m/e 381 (M^+ - H), 351 (M^+ - OCH_3), 184 (DBT^+), 167 ($CpRu^+$)) as a mixture of two isomers (A and B) of CpRu(DBT·OMe) (**13**). Although **13** was not successfully purified, it reacts with 1 equiv of $(Ph_3C)BF_4$ in acetone-d_6 to give **1** as the only DBT-containing product as established by ^1H NMR spectroscopy.

The reaction of $NaNMe_2$ and **1** in THF produced an unstable yellow-brown solid whose ^1H NMR spectrum in C_6D_6 indicated the presence of several isomers of a complex whose mass spectrum (EI MS: m/e 394 (M^+ - H), 351 (M^+ - NMe_2), 184 (DBT^+), 44 (NMe_2^+)) indicated its composition as $CpRu(DBT{\cdot}NMe_2)$. There was no reaction between **1** and NaSEt even in refluxing CH_2Cl_2–HSEt (20 mL/1 mL) overnight.

Preparation and Reactions of $[(CpRu)_2(DBT)](PF_6)_2$ (4). Complex **4** is prepared either directly from free DBT and $CpRu(NCCH_3)_3^+$ or stepwise via the monocation **1** as shown in eq 6. The overall yields from both routes



(6)

are about the same (54%). The Fe analogue $[(CpFe)_2(DBT)](PF_6)_2$[10] was previously synthesized by direct ligand exchange of ferrocene with DBT in the presence of $AlCl_3$–Al. The air-stable Ru dictation **4** was identified by its elemental analyses (Table I) and ^1H NMR spectrum (Table II). All of the proton chemical shifts of the complexed rings in **4** occur at higher field than those in free DBT, as expected; the ^1H NMR spectrum is assigned by selective decoupling and comparison with the ^1H NMR data of the monocation **1**. The simple pattern (two doublets and two triplets) for DBT clearly indicates that the two benzene rings are equivalent and are coordinated. A trans arrangement of the CpRu groups is assumed for steric reasons. The assignments of $(CpFe)_2(DBT)^{2+}$ and other related compounds reported by Sutherland[10,25] also support this assumption.

The reaction of $Na(BEt_3H)$ or $Li(BEt_3H)$ with **4** in THF produces **11**, **12**, and an unidentified yellow solid (eq 7).

$$\underset{4}{[(CpRu)_2(DBT)](PF_6)_2} + (2Na(BEt_3H) \text{ or } 2Li(BEt_3H)) \xrightarrow[40\ min]{THF} \underset{11}{(CpRu)_2(DBT)} + \underset{12}{(CpRu)_2(DBT{\cdot}2H)} \quad (7)$$

The formation of **11** must occur as a result of $Na(BEt_3H)$ and $Li(BEt_3H)$ acting as reducing agents; these borohydrides have also been used as reducing agents in other systems, e.g., $[Co(CO)_4]_2$, $[CpMo(CO)_3]_2$, and $[Mn(CO)_5]_2$,[26] to give the corresponding metal carbonyl anions. The yellow, platelike crystals of **11**, which are characterized by the EI MS spectrum and an X-ray diffraction study, are also prepared by the reduction of **4** with 2 equiv of Cp_2Co[27] in THF for 3 h at room temperature, but the yield is less than 10%. Complex **11** is air-stable in the solid state but not in solution. No EPR signal is observed for **11** in $CDCl_3$ solution at room temperature.

The crystal structure of the binuclear 38-electron complex **11** (Figure 1) shows a center of inversion at the midpoint of the C(6)–C(6)′ bond. The sulfur atom is shown in one of the two possible (equivalent) positions. The Ru is not equally bonded to all six benzene carbon atoms but appears to be slipped toward C(5) and C(6); the direction of slippage is opposite to that from $CpRu(BT)^+$[28] and other transition-metal complexes containing a fused arene ring[29] where the metal is further from the fused carbons than from the other side of the ring. The slipped distance (the average Ru–C(2)C(3) distance minus the average Ru–C(5)C(6) distance) for **11** is 0.04 Å, as compared with 0.07 Å for $CpRu(BT)^+$, which is slipped in the opposite direction. The average aromatic C–C distance (1.40 (3) Å) in the DBT ligand of **11** is about the same as that in free DBT (1.39 Å),[30] but the range is large, 1.35 (3)–1.44 (3) Å.

DBT in **11** is essentially planar, with individual atoms showing only small deviations (≤0.046 Å) from the average DBT plane. The planes of the DBT and both Cp rings are essentially parallel (dihedral angle 3.53 ± 6.91°). This is similar to the X-ray crystal structure of the 19e mononuclear $CpFe(C_6Me_6)$ complex.[31] In $CpFe(C_6Me_6)$, the Fe–Cp(ring centroid) distance is 0.1 Å longer than in the 18e complex $CpFe(C_6Et_6)^+$,[32] whereas the Fe–arene(ring centroid) distance in $CpFe(C_6Me_6)$ (1.58 (1) Å) is not greatly perturbed as compared to that in $CpFe(C_6Et_6)^+$ (1.55 (1) Å). The crystal structure of cobaltocene shows a lengthening (0.05 Å) of the metal–Cp(ring centroid) distances from those in the 18e cobaltocenium cation Cp_2Co^+;[33] the Fe–arene(ring centroid) distance of $(C_6Me_6)_2Fe^+$ is also 0.05 Å longer than that observed in the dication $(C_6Me_6)_2Fe^{2+}$.[34] The distance (1.811 (2) Å) between Ru and Cp in $(CpRu)_2(DBT)$ (**11**) is essentially the same as 1.815 (1) Å in $CpRu(BT)^+$[28] and 1.809 (1) Å in $CpRu[(\eta^6\text{-}C_6H_5)Ph_2PO]^+$;[35] the Ru–arene distance (1.769

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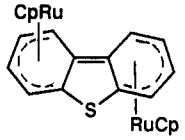
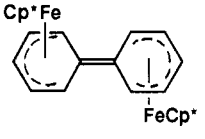
(2) Å) in **11** is 0.059 Å longer than in $CpRu(BT)^+$ (1.710 (1) Å) and 0.076 Å longer than in $CpRu[(\eta^6\text{-}C_6H_5)Ph_2PO]^+$ (1.693 (1) Å). This lengthening in **11** is presumably due to the occupation of an orbital that is antibonding with respect to the Ru atoms and DBT, as has been suggested for the iron–arene and –cyclopentadienyl complexes.[30,31,33,36] However, it is clear that the two added electrons in **11** are paired, since the complex is diamagnetic.

Another possible electronic structure (I) for **11** is one involving a double bond between C(6) and C(6)′ by analogy with the related $(Cp^*Fe)_2$(biphenyl) (II).[37] Although this



I



II

structure allows each Ru to achieve an 18-electron count, the C(6)–C(6)′ bond distance (1.55 (5) Å) in **11** is unreasonably long for a double bond even considering the large standard deviation. Also, the benzene rings in **11** are essentially planar, whereas the bridging carbon is significantly out of the benzene plane in II.[37] Finally, one would expect the Ru to slip away from C(6) in I; however, the Ru appears to slip toward C(6). For these reasons, it appears that structure I does not represent the bonding in **11**.

The yellow needlelike crystals of $(CpRu)_2(DBT{\cdot}2H)$ (**12**) obtained (eq 7) in low yield are air-stable, but its solutions decompose in air. The mass spectrum (CI MS) of **12** shows peaks corresponding to the parent ion, $(CpRu)_2(DBT{\cdot}2H)^+$, as well as to $CpRu(DBT{\cdot}2H)^+$. The tentative ^1H NMR assignments (Table II) are based on selective decoupling, integrations, and comparisons with the related compounds **1**, **4**, and **5A**. The presence of two Cp resonances and protons (H1–H4) that can be assigned to a coordinated arene ring (as in **1** and **4**) suggests that the two hydrogens in $(CpRu)_2(DBT{\cdot}2H)$ are on the same arene ring; however, further studies are necessary to make a definitive structural assignment.

Complexes **11** and **12** react with $(Ph_3C)BF_4$ to give **4** (eq 8). The ^1H NMR spectrum of a solution of **11** or **12** (0.01

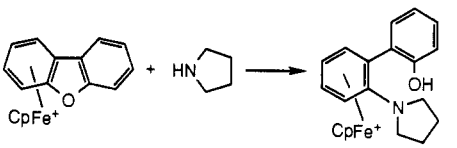
$$\underset{\mathbf{11}}{(CpRu)_2(DBT)}\ (\text{or}\ \underset{\mathbf{12}}{(CpRu)_2(DBT{\cdot}2H)})\ + \quad 2(Ph_3C)BF_4 \xrightarrow[5\ \text{min}]{CD_2Cl_2} \underset{\mathbf{4}}{[(CpRu)_2(DBT)](BF_4)_2} \quad (8)$$

mmol) in CD_2Cl_2 (0.4 mL) was obtained, and then $(Ph_3C)BF_4$ (0.028 mmol) was added. After 5 min, the spectrum showed that all of **11** or **12** reacted and that $[(CpRu)_2(DBT)](BF_4)_2$ was the only DBT-containing product.

Conclusions

These studies demonstrate that, in $CpRu(DBT)^+$ (**1**), DBT prefers to coordinate to the ruthenium via the π-benzene rather than the central thiophene ring. In this form, the benzene is activated to react with nucleophiles such as H^- sources (eq 2). This activation reasonably accounts for one of the major modes of DBT reactivity on HDS catalysts, namely, the hydrogenation of a benzene ring (Scheme I, path a). Others[4a,37] have suggested that DBT hydrogenation and desulfurization occur at different sites on the catalyst. While complex **1** offers a reasonable model for the hydrogenation site, it does not lead to desulfurization. Also, HHDBT, a proposed intermediate[4a,b,38] (Scheme I) in the HDS of DBT, coordinates in $CpRu(HHDBT)^+$ (**3**) via the π-benzene ring, and while its coordinated ring is activated to attack by H^- nucleophiles (eq 3), none of these reactions lead to C–S bond cleavage.

We had hoped that nucleophilic attack on $CpRu(DBT)^+$ would lead to C–S cleavage by analogy with the known reaction of the dibenzofuran (DBF) complex $CpFe(DBF)^+$[39] (eq 9). Unfortunately, the analogous reaction



(9)

does not occur with $CpFe(DBT)^+$, nor does it occur with $CpRu(DBT)^+$ by use of pyrrolidine or H^- and CH_3^- nucleophiles.

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Registry No. **1**, 126927-55-7; **2**, 126927-57-9; **3**, 126927-59-1; **4**, 126927-61-5; **5A**, 126927-62-6; **5B**, 126927-68-2; **6A**, 126948-81-0; **6B**, 126927-69-3; **6C**, 126948-85-4; **6D**, 126948-86-5; **7A**, 126927-63-7; **7B**, 126927-70-6; **7C**, 126927-71-7; **7D**, 126948-87-6; **8A**, 126927-64-8; **8B**, 126948-88-7; **8C**, 126948-89-8; **8D**, 126948-90-1; **9A**, 126948-83-2; **9B**, 126948-93-4; **9C**, 126927-73-9; **9D**, 126927-75-1; **10A**, 126927-66-0; **10B**, 126948-95-6; **10C**, 126927-77-3; **10D**, 126927-79-5; **11**, 126927-67-1; **13A**, 126948-84-3; **13B**, 126948-91-2; $[CpRu(NCCH_3)_3]PF_6$, 80049-61-2.

Supplementary Material Available: Tables of bond angles, displacement parameters, and least-squares planes (5 pages); a table of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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