tions[40] of the Huzinaga (9s5p) and (4s) primitive Gaussian bases for carbon and hydrogen[41] (exponents for H scaled by 1.2). The VDZP basis added one set of unscaled 2p-polarization functions for the migrating hydrogen ($\zeta^p = 1.0$) to the VDZ basis. The VDZD basis added one set of carbon 3d-polarization functions ($\zeta^d = 0.64$) to the VDZ basis. The VDZDP basis added the two polarization functions above to the VDZ basis.

The geometries of 1a, 1b, and 6a were optimized at the GVB-RCI level [RCI(3/6) for 1a and 1b; RCI(1/2) for 6a, leaving the Ru–Cl bond at the HF level]. The RCI (restricted configuration interaction) starts from the GVB-PP wave function (generalized valence bond with perfect-pairing restriction) in which each correlated bond pair (Ru–H, Ru–C σ, Ru–C π) is described with two orbitals, so that each electron involved in the insertion process has its own orbital. All other electron pairs were left uncorrelated (but calculated self-consistently). The GVB-RCI wave function allows all configurations arising from the three possible occupations of two electrons in two orbitals for each GVB bond pair. [The rotational barrier in 1 was calculated at the GVB-RCI(3/6) level.] The geometries of 2, the $^1A'$ state of ClRuH, and the $^2A'$ state of RuCl were optimized by using Hartree–Fock (HF) gradient techniques.

The reaction pathway was followed at the HF, the GVB-PP(3/6), the GVB-RCI(3/6), the GVBCI(3/6), and

the GVBCI(3/6)-MCSCF levels. The GVBCI(3/6) allows a full CI within the six "active" orbitals (e.g., the Ru–C bond pairs and the Ru–H bond pair), while the GVBCI-(3/6)-MCSCF self-consistently optimizes the orbitals for the GVBCI(3/6) wave function.

The bond and excitation energies of the various species in Tables V–IX were calculated at the HF, GVB-PP, GVB-RCI, and higher order CI levels now described: (i) RCI*S_{val} allows all single excitations from all valence orbitals (except Cl) to all virtual (unoccupied) orbitals from the RCI reference configurations; (ii) RCI*[SD_{pair1} + SD_{pair2} + ...] allows all single and double excitations to all virtuals from pair 1, pair 2, etc. (but *not* simultaneously) from the RCI reference configurations; (iii) CCCI adds the configurations of (ii) to the configurations of (i), allowing for full correlation of the changing bonds (RCI*SD) along with orbital shape readjustments for the other valence orbitals (RCI*S_{val}).[10]

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Ruthenium, Rhodium, and Iridium Complexes of π-Bound Thiophene and Benzo[b]thiophenes: Models for Thiophene Binding to HDS Catalysts

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Ru, Rh, and Ir complexes of π-bound thiophene (T) and benzo[b]thiophenes (BTs), (η-C_5H_5)Ru(BT)$^+$, (η-C_5Me_5)M(BT)$^{2+}$, and (η-C_5Me_5)M(T)$^{2+}$ (M = Rh, Ir), which serve as models for the adsorption of thiophenes on hydrodesulfurization (HDS) catalysts, have been synthesized. The Rh and Ir compounds are the first dicationic transition metal complexes of either T or BTs. The BT ligands are bound to the transition metal centers via the benzene ring. The first X-ray structural characterization of a BT complex, [(η-C_5H_5)Ru(η^6-BT)]BF$_4$ (1), is reported.

The process of catalytic hydrodesulfurization (HDS) is performed industrially on a very large scale in order to remove sulfur from crude oils.[2] Typically, sulfided-cobalt-promoted molybdenum catalysts are used.[3] The mechanism of desulfurization has been investigated in-

tensively, but in spite of this effort key aspects of HDS such as binding of sulfur-containing hydrocarbons to the catalyst surface as well as important steps in the HDS process are not well-understood.[4]

Thiophene (T) has frequently been used as a representative sulfur-containing compound in mechanistic investigations involving heterogeneous reactor studies.[5] It

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T

BT
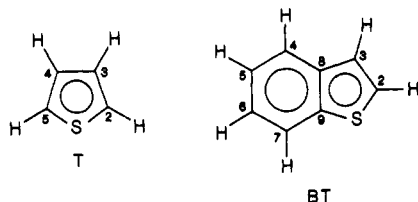
serves as a good model because it is difficult to desulfurize, presumably as a result of the aromatic stabilization provided by the delocalized π-system.[6] However, studies of other aromatic compounds, such as benzo[b]thiophenes (BTs: benzo[b]thiophene, BT; 3-methylbenzo[b]-thiophene, 3-MeBT; 2,3-dimethylbenzo[b]thiophene, 2,3-Me$_2$BT), have also been reported.[6,7] For both T and BTs, π-bonding of the aromatic system to a metal site on the surface of the catalyst, as opposed to the frequently proposed S-coordination, has been suggested.[8] The π-bonded proposal is supported by heterogeneous reactor studies.[2b,8d,9] In the case of T, results of recent spectroscopic[10] and discrete transition-metal model complex[11] studies also support the π-bound adsorption mode.

Therefore, in order to learn more about the process of HDS our group has chosen to explore the reactivity of π-bound T and BTs in model complexes. BTs are of particular interest because they are present in crude oils in significantly greater quantities than T[7d,12] and have been reported to be more difficult to desulfurize.[13] Since BTs are made up of two fused aromatic rings, they offer the possibility of forming π-complexes with transition metals by coordination of either one or both of these rings.

Several π-thiophene complexes have been reported,[14] but only two of BT are known. In Cr(CO)$_3$(η^6-BT)[15] the BT was proposed, on the basis of ^{1}H NMR data, to be coordinated through the benzene ring. King and Stone[15b] re-

ported the preparation of Fe$_2$(CO)$_5$(BT) in 1960. They proposed that Fe(CO)$_2$ and Fe(CO)$_3$ groups are coordinated to both rings of the BT ligand.

Sulfur-coordinated complexes of T[16] and very recently BT[16c] have also been reported. However, the S-bound T and BT ligands are easily displaced by coordinating solvents or CO and have not been reported to undergo any reactions.

In this publication we describe the synthesis and characterization of Ru, Rh, and Ir complexes containing π-bound T and BTs. The [Cp*ML](A)$_2$ (M = Rh, Ir; L = T, BTs; Cp* = η-C$_5$Me$_5$; A = PF$_6$, BF$_4$) complexes are the first dicationic of either T or BTs. Previously reported attempts to prepare Rh and Ir compounds of unsubstituted T were unsuccessful.[14d] The first X-ray structure determination of a BT complex is also discussed.

Experimental Section

General Procedures. All reactions were performed under N$_2$ in reagent grade solvents. Methylene chloride (CH$_2$Cl$_2$) was dried over CaH$_2$ and distilled. Diethyl ether (Et$_2$O) was distilled from Na/benzophenone, and dichloroethane (DCE) was distilled from P$_2$O$_5$. The solvents were stored over 4-Å molecular sieves, except for acetone which was stored over MgSO$_4$, and purged with N$_2$ prior to use. Commercial T and 3-MeBT were stirred with AgNO$_3$ (0.01 g/mL) for 24 h, decanted, and then distilled. Commercial BT was sublimed prior to use. The 2,3-Me$_2$BT,[17] [Cp*IrCl$_2$]$_2$ (Cp* = η-C$_5$Me$_5$),[18] [Cp*RhCl$_2$]$_2$,[18] CpRu(PPh$_3$)$_2$Cl (Cp = η-C$_5$H$_5$),[19] and [CpRu(NCCH$_3$)$_3$]PF$_6$[20] can be prepared by literature methods. The products were all characterized by elemental analysis (Table V) and ^{1}H and ^{13}C NMR (Tables VI and VII). ^{1}H, ^{13}C, and ^{1}H–^{13}C 2D NMR spectra were obtained on a Nicolet NT-300 spectrometer using deuteriated solvents as internal locks and referenced to Si(CH$_3$)$_4$. Conductivity data were obtained by using a Markson Electromark analyzer and calibrated with a standard potassium chloride solution. Fast atom bombardment (FAB) spectra were run on a Kratos MS-50 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc.

[CpRu(BT)]A (A = PF$_6$ or BF$_4$) (1). This complex was prepared by using either CpRu(PPh$_3$)$_2$Cl or [CpRu(NCCH$_3$)$_3$]PF$_6$ as described in methods A and B, respectively. **Method A.** To a solution of CpRu(PPh$_3$)$_2$Cl (0.52 g, 0.71 mmol) in CH$_3$OH (2 mL) was added BT (1.9 g, 14 mmol) and AgBF$_4$ (0.21 g, 1.1 mmol). The mixture was refluxed for 39 h. The solution was filtered and then evaporated to dryness. The residue was extracted with CH$_2$Cl$_2$ and the product precipitated by addition of Et$_2$O. Numerous recrystallizations from CH$_2$Cl$_2$/Et$_2$O were required to remove impurities resulting in a low yield (<15%) of the ivory-colored product 1 (A = BF$_4$). FAB (glycerol): m/e 301 (M$^+$). **Method B.** BT (1.89 g, 14.1 mmol) was added to a solution of [CpRu(NCCH$_3$)$_3$]PF$_6$ (0.400 g, 0.921 mmol) in DCE (20 mL). The solution was refluxed under N$_2$ for 21.5 h and then evaporated to dryness in vacuo. The brown residue was extracted with acetone. Addition of Et$_2$O resulted in precipitation of the tan-colored product, yield 0.318 g (77.5%). The product was purified by stirring in 10 mL of a 0.95 M solution of KOH in CH$_3$OH for 12 h. A stream of CO$_2$ was passed through the solution for 1.5 h and the resulting suspension evaporated to dryness in vacuo. The residue was extracted with acetone (4 × 10 mL) and filtered. The volume of the filtrate was reduced to approximately 5 mL followed by addition of Et$_2$O to precipitate the ivory-colored product 1 (A = PF$_6$). The purification step generally decreases

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the yield by approximately 15–20%.

[CpRu(3-MeBT)]PF$_6$ (2). This complex was prepared analogously to 1 by using method B. The 3-MeBT (2.74 g, 18.5 mmol) was added to [CpRu(NCCH$_3$)$_3$]PF$_6$ (0.532 g, 1.22 mmol) in DCE (30 mL) and the solution refluxed for 24 h. The solution was evaporated to dryness in vacuo and extracted with acetone (2 × 10 mL). The resulting solution was filtered, the volume reduced in vacuo, and the tan product precipitated by addition of Et$_2$O; yield 0.501 g (89.4%). The purified pale yellow product was isolated after stirring in KOH/CH$_3$OH as for 1.

[Cp*Rh(T)](PF$_6$)$_2$ (3). To a stirred solution of [Cp*RhCl$_2$]$_2$ (70.4 mg, 0.114 mmol) in acetone (4 mL) was added AgPF$_6$ (121 mg, 0.480 mmol). The solution was stirred 5 min and filtered through Celite into a flask containing T (3.0 mL, 3.2 g, 38 mmol). The volume of the solution was reduced to 4 mL in vacuo. After the solution was stirred for 2 min, CH$_2$Cl$_2$ (20 mL) was added, and the resulting cream-colored solid was filtered, washed with additional CH$_2$Cl$_2$, and dried in vacuo; yield 79.3 mg (56.8%).

[Cp*Rh(BT)](PF$_6$)$_2$ (4). This complex was synthesized in the same manner as that for 3 by using [Cp*RhCl$_2$]$_2$ (0.15 g, 0.24 mmol), AgPF$_6$ (0.24 g, 0.96 mmol), and BT (0.33 g, 2.4 mmol). The product 4 was isolated as a pale yellow solid, yield 0.21 g (65%).

[Cp*Ir(T)](BF$_4$)$_2$ (5). To a solution of [Cp*IrCl$_2$]$_2$ (0.440 g, 0.552 mmol) in acetone (5 mL) was added AgBF$_4$ (0.430 g, 2.21 mmol), and the resulting mixture was filtered through Celite. The volume of the filtrate was reduced to 3 mL, and T (1.6 mL, 1.7 g, 20 mmol) was added. The solution was refluxed for 5 min and then cooled to room temperature. A slightly gray solid was produced by addition of CH$_2$Cl$_2$. The gray solid was filtered from the solution and then dissolved in CH$_3$NO$_2$. The CH$_3$NO$_2$ solution was filtered to remove a black insoluble impurity. Addition of CH$_2$Cl$_2$ to the filtrate gave the product 5 as a white solid that was separated by filtration and dried in vacuo, yield 0.453 g (70.1%). This complex is slightly moisture sensitive and should be stored in a sealed container in a dessicator. Λ$_m$ (Ω^{-1} cm^2 mol^{-1}, 1.02 × 10^{-3} M in CH$_3$NO$_2$): 165.

[Cp*Ir(BT)](BF$_4$)$_2$ (6). This complex was prepared in the same manner as that for 5. A solution of [Cp*IrCl$_2$]$_2$ (0.452 g, 0.568 mmol) in acetone (15 mL) was treated with AgBF$_4$ (0.446 g, 2.29 mmol), filtered, and refluxed with BT (3.09 g, 23.0 mmol) for 10 min. The white product 6 was isolated from the reaction mixture by addition of CH$_2$Cl$_2$; yield 0.591 g (81.9%). This reaction was also performed by using AgPF$_6$ and without refluxing, but the yields are lower (~50%). Λ$_m$ (Ω^{-1} cm^2 mol^{-1}, 1.01 × 10^{-3} M in CH$_3$NO$_2$): 179.

[Cp*Ir(3-MeBT)](BF$_4$)$_2$ (7). The synthesis proceeds as for 5 by using [Cp*IrCl$_2$]$_2$ (0.300 g, 0.377 mmol), AgBF$_4$ (0.294 g, 1.51 mmol), and 3-MeBT (1.47 g, 9.96 mmol). A pale yellow product, 7, was isolated; yield 0.394 g (80.6%). Λ (Ω^{-1} cm^2 mol^{-1}, 1.05 × 10^{-3} M in CH$_3$NO$_2$): 182.

[Cp*Ir(2,3-Me$_2$BT)](BF$_4$)$_2$ (8). This complex was prepared analogously to 5 from [Cp*IrCl$_2$]$_2$ (0.202 g, 0.254 mmol), AgBF$_4$ (0.198 g, 1.02 mmol), and 2,3-Me$_2$BT (1.01 g, 6.22 mmol) to give a pale yellow product; yield 0.229 g (68.0%).

X-ray Structure Determination of [CpRu(BT)]BF$_4$ (1). Gold-colored crystals of 1 were grown from CH$_2$Cl$_2$/Et$_2$O. A crystal of approximate dimensions 0.45 × 0.05 × 0.05 mm was mounted on the end of a glass fiber by using Duco cement and attached to a standard goniometer head. The crystal was aligned on a four-circle Datex X-ray diffractometer from which four preliminary ω-oscillation photographs were taken at various φ settings. The approximate positions of 20 reflections were selected from these photographs and used as input into an automatic indexing program.[21] The resulting reduced cell and reduced cell scalars indicated a monoclinic lattice. Observed layer spacings from three axial ω-oscillation photographs were within experimental error of those predicted for this cell.

Accurate unit cell parameters were obtained by a least-squares fit to ±2θ values of 25 independent high-angle reflections on a previously aligned four-circle diffractometer at room temperature using graphite-monochromated Mo Kα radiation. The data were collected by using a four-circle fully automated Datex diffrac-

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Table I. Crystal Parameters for the X-ray Diffraction Study of [CpRu(BT)]BF$_4$ (1)

formula	BC$_{13}$F$_4$H$_{11}$RuS
mol wt, g mol^{-1}	387.17
cryst system	monoclinic
space group	P2$_1$/c
a, Å	8.882 (2)
b, Å	11.034 (1)
c, Å	13.936 (2)
β, deg	94.60 (1)
V, Å^3	1361.5
Z	4
D(calcd), g cm^{-3}	1.85
μ(Mo Kα), cm^{-1}	12.80 (correction applied)
T$_{min}$/T$_{max}$	0.886/0.995
temp, °C	20
radiatn (graphite monochromated)	Mo Kα (λ = 0.710 32) Å)
reflctn measured	hkl, h̄kl, h̄kl̄, hkl̄ (4 octants)
scan type	ω-step scan
max 2θ, deg	50
std reflctns	1, measd every 50 reflctns (no obsd decay)
reflctns collected	4764
reflctions obsd (I ≥ 3σ(I))	3897
reflctns after averaging	1748
R(av)	0.028
R (conventional)	0.048
R (weighted)	0.062

Table II. Positional (×10^4) and Thermal Parameters (Å^2, ×10^3) for [CpRu(BT)]BF$_4$ (1)

atom	x	y	z	B(av)^a
Ru	2282.0 (6)	2208.4 (5)	395.0 (4)	49
S	3119 (3)	5153 (2)	−595 (2)	84
C2	1794 (16)	4767 (11)	−1516 (6)	103
C3	777 (6)	4097 (5)	−1400 (4)	38
C4	−57 (7)	2915 (7)	157 (6)	60
C5	306 (9)	2711 (7)	1153 (6)	70
C6	1606 (11)	3208 (8)	1634 (5)	71
C7	2572 (9)	3955 (7)	1168 (6)	65
C8	891 (7)	3707 (6)	−315 (4)	48
C9	2190 (7)	4239 (6)	175 (5)	54
C10	3742 (11)	1417 (8)	−601 (6)	80
C11	4549 (9)	1495 (8)	274 (7)	79
C12	3825 (11)	796 (8)	950 (7)	82
C13	2565 (13)	265 (7)	436 (8)	92
C14	2505 (11)	634 (8)	−519 (7)	81
B	6812 (13)	2311 (8)	2788 (7)	72
F1	7342 (8)	1510 (7)	2168 (5)	124
F2	5815 (7)	3123 (6)	2378 (5)	107
F3	8076 (10)	2972 (6)	3145 (6)	124
F4	6249 (17)	1751 (10)	3511 (9)	229

^{a} Given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$.

tometer which was interfaced to a VAX 730 computer in a real time mode. An empirical absorption correction was made[22] (μ = 12.80 cm^{-1}) where the maximum and minimum transmission factors were 0.995 and 0.886, respectively. Further details concerning the data collection are given in Table I.

The position of the Ru atom in 1 was obtained from an analysis of a standard sharpened three-dimensional Patterson map. The positions of the remaining non-hydrogen atoms were determined by successive structure factor[23] and electron density map calculations.[24] The positional and anisotropic thermal parameters for the non-hydrogen atoms were refined initially by block-matrix and finally by full-matrix least-squares procedures,[23] minimizing the function $\sum \omega(|F_o| - |F_c|)^2$ to a conventional residual index of

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Table III. Bond Distances and Angles for [CpRu(BT)]BF₄ (1)

Bond Distances (Å)			
Ru–C4	2.219 (7)	C2–C3	1.188 (14)
Ru–C5	2.191 (8)	C3–C8	1.568 (8)
Ru–C6	2.174 (8)	C4–C8	1.412 (9)
Ru–C7	2.213 (8)	C4–C5	1.418 (11)
Ru–C8	2.246 (6)	C5–C6	1.400 (12)
Ru–C9	2.262 (7)	C6–C7	1.389 (12)
Ru–C10	2.159 (9)	C7–C9	1.432 (10)
Ru–C11	2.182 (8)	C8–C9	1.420 (9)
Ru–C12	2.176 (9)	C10–C11	1.367 (13)
Ru–C13	2.159 (8)	C10–C14	1.410 (13)
Ru–C14	2.172 (9)	C11–C12	1.412 (13)
S–C2	1.724 (11)	C12–C13	1.407 (14)
S–C9	1.730 (7)	C12–C14	1.388 (15)

Bond Angles (deg)			
S–C2–C3	122.3 (7)	C9–C8–C4	121.6 (6)
C2–C3–C8	108.1 (6)	C8–C4–C5	117.2 (6)
C3–C8–C9	109.7 (5)	C7–C9–S	129.7 (5)
C8–C9–S	110.6 (5)	C3–C8–C4	128.6 (6)
C9–S–C2	89.2 (4)	C10–C11–C12	109.1 (8)
C4–C5–C6	121.4 (7)	C11–C12–C13	105.9 (9)
C5–C6–C7	121.7 (7)	C12–C13–C14	109.5 (9)
C6–C7–C9	118.3 (7)	C13–C14–C15	106.7 (9)
C7–C9–C8	119.6 (6)	C14–C15–C10	108.8 (8)

Table IV. Interplanar Angles (deg) for [CpRu(BT)]BF₄ (1)[a]

rings	interplanar angles	rings	interplanar angles
1, 2	178.38	2, 3	1.47
1, 3	179.47	2, 4	0.60
1, 4	178.86	3, 4	0.88

[a] Ring 1, C10, C11, C12, C13, C14; ring 2, C4, C5, C6, C7, C8, C9; ring 3, S, C2, C3, C8, C9; ring 4, ring 2 + ring 3.

Table V. Elemental Analyses of the Complexes

	anal. found (calcd)	
	C	H
[CpRu(BT)]BF₄ (1)	40.44 (40.33)	2.86 (2.86)
[CpRu(3-MeBT)]PF₆ (2)	36.62 (36.61)	2.84 (2.85)
[Cp*Rh(T)](PF₆)₂ (3)	27.51 (27.41)	3.34 (3.13)
[Cp*Rh(BT)](PF₆)₂ (4)	32.72 (32.64)	3.51 (3.20)
[Cp*Ir(T)](BF₄)₂ (5)	28.47 (28.74)	3.22 (3.27)
[Cp*Ir(BT)](PF₆)₂ (6)	28.54 (28.77)	2.53 (2.82)
[Cp*Ir(3-MeBT)](BF₄)₂ (7)	34.82 (35.15)	3.57 (3.57)
[Cp*Ir(2,3-Me₂BT)](BF₄)₂ (8)	36.27 (36.22)	4.04 (3.80)

Figure 1. An ORTEP drawing of [CpRu(BT)]BF₄ (1).
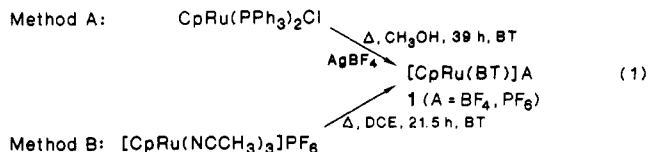
$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.048$ and a weighted residual index of $R_w = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega|F_o|^2]^{1/2} = 0.062$, $\omega = 1/\sigma_F^2$. The hydrogen positions were calculated and not refined. The final positional and thermal parameters for 1 are listed in Table II. The bond lengths and the bond angles are listed in Table III. An ORTEP[25] drawing of the molecule is given in Figure 1.

Residual electron density near C3 indicated a possible structural disorder. Attempts to model the disorder by introducing disorder partners of C2, C3, and S, constrained to either a two-fold axis or a mirror plane perpendicular to the C8–C9 bond, converged to an occupancy ratio of 80:20. However, the residual indices, the C2–C3 bond distance, and the C2 thermal ellipsoid did not improve. In an independent study[26] the occupancies of these three atoms and their disorder partners were allowed to refine without constraints. However, the pairs of atoms converged to their mean positions.

The data were, therefore, reweighted on the basis of $(\sin\theta)/\pi$ such that $\overline{\omega\Delta^2}$, $\Delta = |F_o| - |F_c|$, was approximately constant and further refined. The parameters listed in Tables I–III are for the structures refined without consideration of the disordering.

Results and Discussion

[CpRu(BT)]A (A = BF₄, PF₆) and [CpRu(3-MeBT)]PF₆ (1 and 2, Respectively). The reaction of either CpRu(PPh₃)₂Cl or [CpRu(NCCH₃)₃]PF₆ with BT results in the formation of [CpRu(BT)]⁺ as shown in eq 1. The 3-MeBT complex 2 is synthesized analogously by

Method A: CpRu(PPh₃)₂Cl

$\searrow$ Δ, CH₃OH, 39 h, BT

AgBF₄

[CpRu(BT)]A   (1)

1 (A = BF₄, PF₆)

$\nearrow$ Δ, DCE, 21.5 h, BT

Method B: [CpRu(NCCH₃)₃]PF₆

using method B. Method B is preferred due to the higher yield and purer product that result. Mann[20] has used this method to synthesize a variety of other CpRu(η⁶-arene)⁺ complexes. Complexes 1 and 2 are air-stable in the solid state. The BT and 3-MeBT ligands are not displaced by coordinating solvents such as acetone, methanol, or water at room temperature over 24 h.
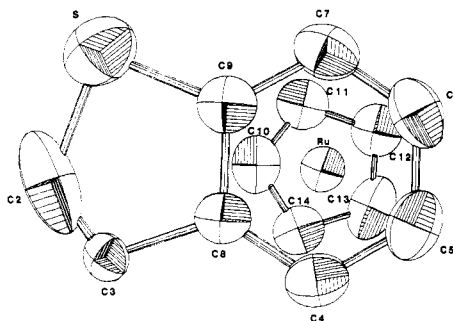
Complex 1 was identified by its elemental analysis and ¹H and ¹³C NMR spectra (Tables V–VII). The ¹H NMR spectrum was assigned by using the results of selective decoupling, ¹H–¹³C 2D, and gated-decoupled ¹³C NMR experiments. The initial step in assigning the ¹H NMR spectrum was obtaining the gated-decoupled ¹³C NMR spectrum (acetone-d₆) which showed only one resonance as a simple doublet of doublets. This could clearly be only the C2 peak because it is split only by H2 ($^1J_{C2-H2} = 189$ Hz) and H3 ($^3J_{C2-H3} = 7$ Hz). From the ¹H–¹³C 2D NMR spectrum the H2 peak could then be assigned. The H3 resonance was identified by selectively decoupling H2. The H7 peak was assigned by observation of long-range H3–H7 ($^5J_{H3-H7} = 0.7$ Hz) coupling[27] in a dilute solution (~1 mg/0.30 mL) of 1 in acetone-d₆. The use of a dilute solution resulted in enhanced resolution in the ¹H NMR spectrum; this H3–H7 coupling was not usually observed. The H4, H3, and H6 resonances were then assigned on the basis of further selective decoupling experiments.

For BT two coordination modes are possible; coordination of either the benzene or thiophene ring would result in 6e donation to Ru. A comparison of the ¹H NMR shifts for 1 with those for uncoordinated BT suggests that it is bound in an η⁶ fashion through the benzene ring as proposed for Cr(CO)₃(BT).[15] The H2 and H3 resonances for Cr(CO)₃BT shift downfield with respect to the free ligand while those of H4, H5, H6, and H7 shift upfield. This was also observed for 1. In general, upfield shifts are observed upon coordination of arenes to neutral or cationic transition metal centers.[18] However, to clearly identify the

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Table VI. ¹H NMR Data for the Complexes (ppm)

compd	H2	H3	H4	H5	H6	H7	Cp	Cp*	other
1[a]	8.16 d[c]	7.46 d[c]	7.26 d	6.32 t	6.37 t	7.55 d	5.22 s		
2[a]	7.75 q[d]		7.08 d	6.29 t	6.36 t	7.49 d	5.22 s		2.48 d[d,h]
3[b]	7.51 m	7.65 m	7.65 m	7.51 m				2.35 s	
4[b]	8.88 d[e]	7.71 d[e]	7.96 m	7.35 m	7.35 m	8.14 m		2.03 s	
5[b]	7.55 m	7.60 m	7.60 m	7.55 m				2.50 s	
6[b]	8.83 d[f]	7.61 d[f]	8.01 m	7.37 m	7.37 m	8.19 m		2.12 s	
7[b]	8.41 q[g]		7.94 m	7.37 m	7.37 m	8.16 m		2.12 s	2.58 d[g,h]
8[b]			7.82 d	7.28 m	7.28 m	8.04 d		2.17 s	2.88 s[i], 2.47 s[h]
T[b]	7.43 m	7.15 m	7.15 m	7.43 m					
BT[a,j]	7.61 d	7.41 d	7.87 m	7.37 m	7.35 m	7.95 m			
3-MeBT[b]	7.19 q		7.78 dd	7.38 td	7.45 td	7.90 dd			2.45 d
2,3-Me₂BT[b]			7.63 d	7.29 m	7.37 m	7.78 m			2.48 s, 2.30 s

[a] Acetone-d_6. [b] CD_3NO_2. [c] $^3J_{H2-H3} = 5.8$ Hz. [d] $^4J_{H2-CH_3} = 0.8$ Hz. [e] $^3J_{H2-H3} = 5.6$ Hz. [f] $J_{H2-H3} = 5.7$ Hz. [g] $J_{H2-CH_3} = 1.0$ Hz. [h] C3-CH₃. [i] C2-CH₃. [j] Reference 32.

Table VII. ¹³C{¹H} NMR Data for the Complexes (ppm)

compd	C2	C3	C4	C5	C6	C7	C8	C9	C₅H₅	C₅(CH₃)₅	C₅(CH₃)₅	other
1[a]	137.7	123.7	81.6	84.4	83.9	81.3	106.2	110.2	81.6			
2[a]	132.3	131.4	81.6	84.1	83.8	79.9	105.8	110.9	81.3			13.3[i]
3[b]	107.1 d[c]	110.3 d[d]	110.3 d[d]	107.1 d[c]						114.3 d[e]	11.3	
4[b]	147.7	122.4	103.3	103.6 d[f]	102.4 d[g]	102.6	122.4	126.4		112.1 d[h]	9.7	
5[b]	95.0	101.3	101.3	95.0						107.7	10.7	
6[b]	148.6	121.8	93.8	95.9	94.7	93.4	117.3	121.2		105.7	9.2	
7[b]	141.8	131.6	94.0	95.5	94.6	91.8	116.7	121.3		105.4	9.3	13.7[i]
8[b]	157.9	125.9	93.1	95.2	93.8	90.8	118.9	125.9		105.2	9.3	15.6,[j] 11.5[i]
T[a,l]	125.6	127.3	127.3	125.6								
BT[k,m]	126.2	123.8	123.6	124.1	124.2	122.4	139.6	139.7				
3-MeBT[k,m]	121.4	132.0	121.6	123.7	124.0	122.6	139.6	140.2				13.8
2,3-Me₂BT[k,m]	133.6	127.9	121.0	123.7	123.3	121.9	140.0	138.0				13.6, 11.2

[a] Acetone-d_6. [b] CD_3NO_2. [c] $J_{Rh-C} = 4.0$ Hz. [d] $J_{Rh-C} = 2.7$ Hz. [e] $J_{Rh-C} = 9.1$ Hz. [f] $J_{Rh-C} = 3.6$ Hz. [g] $J_{Rh-C} = 3.1$ Hz. [h] $J_{Rh-C} = 8.4$ Hz. [i] C3-CH₃. [j] C2-CH₃. [k] CDCl₃. [l] Reference 33. [m] Reference 34.

coordination mode, in addition to learning more about the structural effects of coordination on the BT ligand, an X-ray diffraction study of 1 was undertaken.

The crystal structure of 1 (Figure 1) shows that the benzo portion of the ligand is coordinated to the metal. The Ru–C8C9, Ru–C4C7, and Ru–C5C6 distances show evidence of ring slippage that has been observed in other transition-metal complexes containing fused arene ring ligands (naphthalene, phenanthrene, anthracene, octa-methylnapthalene).[28] The slipped distance (the average Ru–C8C9 distance minus the average Ru–C5C6 distance) for 1 is 0.07 Å; in other complexes slippage from 0.03 to 0.12 Å has been observed. One explanation offered for this phenomenon is that slippage allows the uncoordinated ring to retain more of its aromatic character, but it has also been suggested that the junction carbons cannot interact as effectively with the metal because they are already π-bonded to three other atoms.[28a] CNDO molecular orbital calculations of the localized charges for each of the carbon atoms and sulfur have been reported.[29] These results, shown in I, suggest that there is less electron density

I
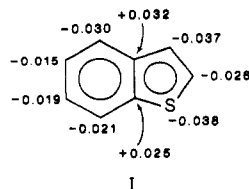
(28) (a) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499. (b) Kunz, V.; Nowack, W. *Helv. Chim. Acta* **1967**, *50*, 1052. (c) Hanic, F.; Mills, O. S. *J. Organomet. Chem.* **1968**, *11*, 151. (d) Muir, K. W.; Ferguson, G.; Sim, G. A. *J. Chem. Soc. B* **1968**, 467. (e) Cais, M.; Kaftory, M.; Kohn, D. H.; Tatarsky, D. *J. Organomet. Chem.* **1979**, *184*, 103. (f) Hull, J. W., Jr.; Gladfelter, W. L. *Organometallics* **1982**, *1*, 264.

(29) Geneste, P.; Guicla, A.; Levache, D. *Bull. Soc. Chim. Fr.* **1983**, 5–6, 136.

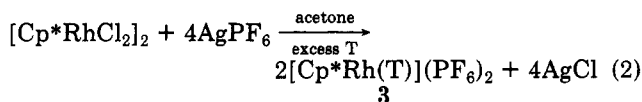**Table VIII. A Comparison of ¹H NMR Shifts for Uncoordinated and π-Bound T (ppm)**

compound	H2,5	H3,4
Cr(CO)₃(T)[b,d]	5.37	5.59
CpRu(T)⁺[c,e]	6.50	6.57
T[a]	7.43	7.15
Cp*Rh(T)²⁺[a]	7.51	7.65
Cp*Ir(T)²⁺[a]	7.55	7.60

[a] CD_3NO_2. [b] CDCl₃. [c] Acetone-d_6. [d] Reference 14g. [e] Reference 11b.

available at C8 and C9 for bonding to Ru. The BT and Cp rings are, within experimental error, parallel (Table IV). The atoms in the BT ligand show slight deviations (≤0.034 Å) from planarity.

Comparison of the ¹H NMR shifts of the 3-MeBT ligand of 2 to those for uncoordinated 3-MeBT and 1 (Table VI) suggests that the ligand is bound via the benzene ring. Thus, the H2 and C3–CH₃ resonances move downfield relative to free 3-MeBT while those for H4–H7 move up-field.

Preparation of [Cp*Rh(T)](PF₆)₂ (3) and [Cp*Rh-(BT)](PF₆)₂ (4). Complexes 3 and 4 were parpared from [Cp*RhCl₂]₂, AgPF₆, and T or BT as shown in eq 2. The

$$[Cp^*RhCl_2]_2 + 4AgPF_6 \xrightarrow[\text{excess T}]{\text{acetone}}$$
$$\underset{\mathbf{3}}{2[Cp^*Rh(T)](PF_6)_2} + 4AgCl \quad (2)$$

[Cp*RhCl₂]₂ and AgPF₆ react to form [Cp*Rh(acetone)₃](PF₆)₂ which was previously reported by Maitlis and has been used to synthesize other Cp*Rh (arene) dica-tions.[30] The Rh complexes are air-stable as solids. However, the T and BT ligands are easily displaced by

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acetone (both in less than 15 min). They are relatively stable in nitromethane (3, at least 1 h; 4, 12 h).

The ¹H NMR of 3 shows a downfield shift of the thiophene protons relative to free T (Table VIII) as has been observed for other dicationic arene complexes.[30] The BT protons of 4 also shift downfield relative to the free ligand. However, the H2 and H3 resonances show large downfield shifts, H4 and H7 shift to slightly lower field, and H5 and H6 show little change relative to uncoordinated BT.

Cp*IrL²⁺ (L = T, BT, 3-MeBt, and 2,3-Me₂BT) (5–8). The preparation of 5 from [Cp*Ir(acetone)₃](BF₄)₂ proceeds analogously to that of 3 shown in eq 2. This method has been used by Maitlis and co-workers to synthesize other Ir arene dications.[30] For the Rh complexes refluxing had little effect on the yield, but for Ir the yield is increased approximately twofold when the reactions are refluxed. Complexes 6–8 are synthesized in a similar manner.

Compounds 5–8 have all been characterized by ¹H and ¹³C NMR as well as elemental analysis (Tables V–VII). The solids are all air-stable, but 5 is extremely moisture-sensitive. The Ir complexes are much more stable than the Rh analogues toward ligand displacement. Acetone displaces T from 5 in approximately 2 h at room temperature while 6 will not lose BT even after 12 h in acetone.

The ¹H NMR spectra of 6–8 suggest that coordination occurs through the benzene ring of BT, 3-MeBT, and 2,3-Me₂BT. Thus, the H2, H3, C2-CH₃, and C3-CH₃ resonances move further downfield relative to the free ligand upon coordination to Ir, than those of H4–H7 (Table VI).

Conclusion

In all of the Ru, Rh, and Ir complexes the BTs coordinate through the π-system of the benzene ring as in $Cr(CO)_3(BT)$.[15] Even in the case of 2,3-Me₂BT, where the presence of two electron-donating methyl groups might be expected to promote thiophene coordination, the benzene ring was bound.

All of the metals used in these complexes are active HDS catalysts.[31] We are exploring the reactivities of these complexes as possible models for reactions of π-bound T and BTs on catalysts in the HDS process.

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Manganese Tricarbonyl and Methylmolybdenum Tricarbonyl Derivatives of the *as*-Indacene Bridging Ligand

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Deprotonation of 1,6-dihydro-2,7-dimethyl-*as*-indacene (1) with *tert*-butyllithium yields the 2,7-dimethyl-*as*-indacene dianion (2). Reaction of 2 with molybdenum hexacarbonyl followed by methyl iodide yields (2,7-dimethyl-*as*-indacene)bis(methylmolybdenum tricarbonyl) (3). An X-ray structural study of 3 indicates it has a trans disposition of molybdenum groups with respect to the planar tricyclic ligand. Reaction of 2 with bis(pyridine)manganese tricarbonyl bromide at low temperature yields a mixture of cis and trans isomers of (2,7-dimethyl-*as*-indacene)bis(manganese tricarbonyl) that were chromatographically separated. An X-ray structural study of the cis isomer indicates considerable steric interaction between the manganese tricarbonyl groups and a bending of the *as*-indacene bridging ligand to accommodate this.

Introduction

The geometry, electronic structure, and reactivity of polynuclear transition-metal compounds with bridging carbocyclic ligands are areas of general interest.[2] As part of an effort to compare the structure and bonding of the flexible bicyclic fulvalene ligand to the rigid tricyclic *s*- and *as*-indacene ligands, we recently reported improved syntheses of these ligands and the preparation of manganese tricarbonyl complexes of *s*-indacene.[3] Here we report the synthesis of molybdenum and manganese carbonyl complexes of 2,7-dimethyl-*as*-indacene.

Earlier work by Katz and co-workers[4] used the *as*-indacene dianion to prepare bis(*as*-indacene)diiron as a mixture of isomers, with the centrosymmetric isomer

(1) (a) Solar Energy Research Institute. (b) Red Rocks Community College. (c) University of Colorado.
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