Hydrodesulfurization Model Complexes: Nucleophilic Addition to π-Coordinated Benzo[*b*]thiophenes and Thiophene

Sara C. Huckett and Robert J. Angelici*

Ames Laboratory[1] and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received August 10, 1987

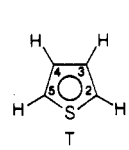
The π-bound thiophene (T) and benzo[*b*]thiophene (BT) complexes $[CpRu(BT)]^+$, $[Cp^*Ir(BT)]^{2+}$, and $[Cp^*Ir(T)]^{2+}$, models for the adsorption of thiophenic compounds to hydrodesulfurization (HDS) catalyst surfaces, react with a variety of nucleophiles (H^-, MeO^-, $(MeO_2C)_2CH^-$, EtS^-, and phosphines). The BT complexes yield the first isolable transition-metal cyclohexadienyl complexes derived from fused ring aromatic ligands; four isomers of each cyclohexadienyl complex are produced. The isomers result from addition at the four carbons on the benzene ring; for the nucleophiles studied, addition occurs preferentially at the carbon closest to the sulfur atom, C7. This isomer of CpRu(BT·H) has been characterized by an X-ray structure determination. The T complex reacts with phosphines to produce $[Cp^*Ir(\eta^4\text{-}T\cdot PR_3)]^{2+}$. Double nucleophilic addition reactions (H^- and MeO^-) of $[Cp^*Ir(BT)]^{2+}$ and $[Cp^*Ir(3\text{-}MeBT)]^{2+}$ are also discussed. Reaction of either $NaBEt_3H$ or Cp_2Co with $[Cp^*Ir(T)]^{2+}$ results in a 2e reduction of the Ir complex. On the basis of ^1H NMR data and by analogy to related complexes, this product is formulated as $Cp^*Ir(\eta^4\text{-}T)$.

Introduction

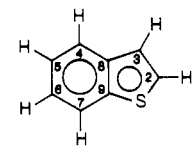
The process of catalytic hydrodesulfurization (HDS) is employed extensively in industry to remove sulfur, in the form of H_2S, from sulfur-containing hydrocarbons present in crude oils and coal liquids.[2] The desulfurization of these feeds is necessary because many of the catalysts used to process petroleum are poisoned by sulfur. In addition, the combustion of sulfur-containing fuels produces the air pollutant sulfur dioxide.[3]

Despite numerous investigations, the mechanism of HDS is not understood; therefore, elucidation of important reaction pathways on catalyst surfaces continues to be an active area of research. Mechanistic studies generally involve reaction of a representative sulfur-containing compound over an HDS catalyst; the compound most often used as a model is thiophene (T). The thiophenic compounds represent the largest class of organosulfur compounds found in crude oils and coal liquids[4] and are also the most difficult to desulfurize.[5] However, within this class, benzo[*b*]thiophene (BT) and its derivatives (BTs) are present in significantly greater quantities[6] and are less reactive under HDS conditions than Ts.[5,7] This suggests that BTs are also important compounds for the study of HDS.

Because heterogeneous reactor studies have yielded few details of the HDS mechanism for thiophenes,[8] our group has been investigating transition-metal complexes of



T



BT

thiophenes in order to learn more about the reactivity of coordinated sulfur-containing compounds. These model complexes incorporate π-bound thiophenic ligands; π-bonding of the aromatic system of thiophenes to the catalyst surface has been proposed to be an important mode of adsorption[7a,b,9] and for T is supported by spectroscopic data.[10] In the case of $[(CO)_3Mn(T)]^+$ and $[CpRu(T)]^+$, this approach has provided useful insights into reactions such as hydride addition, deuterium exchange, and carbon–sulfur bond cleavage, which occur over HDS catalysts.[11] An important extension of this work would include studying the reactivity of π-bound BTs in transition-metal complexes.

This paper describes the reactivity of π-bound T and BTs in cationic cyclopentadienyl Ru, Rh, and Ir complexes with respect to addition of a variety of nucleophiles (H^-, MeO^-, $(MeO_2C)_2CH^-$, EtS^-, and phosphines); nucleophilic species such as hydrides and sulfides have been proposed to be present on HDS catalyst surfaces.[12] The complexes are the first isolable transition-metal cyclohexadienyl complexes derived from fused-ring aromatic ligands.[13]

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

(2) (a) Schuman, S. C.; Shalit, H. In *Catalysis Reviews*; Heinemann, H., Ed.; Marcel Dekker: New York, 1971; p 246. (b) McCulloch, D. C. In *Applied Industrial Catalysis*; Leach, B. E., Ed.; Academic: New York, 1983; p 69.

(3) Satterfield, C. N. *Heterogeneous Catalysis in Practice*; McGraw-Hill: New York, 1980; p. 260.

(4) (a) Aksenov, V. S.; Kamyanov, V. F. In *Organic Sulfur Chemistry*; Freidina, R. Kh.; Skorova, A. E., Eds.; Pergamon: New York, 1981; p 201. (b) Thompson, C. J. In *Organic Sulfur Chemistry*; Freidina, R. Kh.; Skorova, A. E., Eds.; Pergamon: New York, 1981; p 9.

(5) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979; p. 392.

(6) (a) Lyapina, N. K. *Russ. Chemical Rev. (Engl. Transl.)* **1982**, *51*(2), 189. (b) Hoog, H.; Reman, G. H.; Smithuysen, W. C. B. *Proc. World Pet. Congr.* **1951**, *3rd*, 282.

(7) (a) Porkorny, D.; Zdrazil, M. *Collect. Czech. Chem. Commun.* **1981**, *46*, 2185. (b) Nag, N. K.; Sapre, A. V.; Broderick, D. H.; Gates, B. C. *J. Catal.* **1979**, *57*, 509. (c) Kilanowski, D. R.; Gates, B. C. *J. Catal.* **1980**, *62*, 70.

(8) Schuit, G. C. A.; Gates, B. C. *AIChE J.* **1973**, *19*, 177.

(9) (a) Cowley, S. W. Ph.D. Thesis, Southern Illinois University, Carbondale, 1975. (b) Sapre, A. V.; Broderick, D. H.; Fraenkel, D.; Gates, B. C.; Nag, N. K. *AIChE J.* **1980**, *26*, 690. (c) Singhal, G. H.; Espino, R. L.; Sobel, J. E. *J. Catal.* **1981**, *67*, 446. (d) Zdrazil, M. *Collect. Czech. Chem. Commun.* **1975**, *40*, 3491. (e) Zdrazil, M. *Collect. Czech. Chem. Commun.* **1977**, *42*, 1484.

(10) (a) Schoofs, G. R.; Presont, R. E.; Benziger, J. B. *Langmuir* **1985**, *1*, 313. (b) Edwards, T.; McCarroll, J. J.; Pilkethly, R. C. *Ned. Tijdschr. Vacuumtech.* **1970**, *8*, 162. (c) Sexton, B. A. *Surf. Sci.* **1985**, *163*, 99. (d) Zaera, F.; Kollin, E. B.; Gland, J. L. *Surf. Sci.* **1987**, *184*, 75.

(11) (a) Lesch, D. A.; Richardson, J. W.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 2901. (b) Spies, G. H.; Angelici, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5569. (c) Hachgenei, J. W.; Angelici, R. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 909. (d) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897. (e) Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 1146. (f) Huckett, S. C.; Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 591. (g) Huckett, S. C.; Eckman, M. J.; Schrader, G. L.; Angelici, R. J. *J. Catal.*, accepted for publication.

(12) (a) Mitchell, P. C. H. *Catalysis* **1981**, *4*, 175. (b) Vasudevans, S.; Thomas, J. M.; Wright, C. J.; Sampson, C. *J. Chem. Soc., Chem. Commun.* **1982**, 418. (c) Givens, K. E.; Dillard, J. G. *J. Catal.* **1984**, *86*, 108. (d) Millman, W. S.; Segawa, K. L.; Smrz, D.; Hall, W. K. *Polyhedron* **1986**, *5*, 169.

0276-7333/88/2307-1491$01.50/0

Table I. Analytical Data for the Complexes

compd	anal. found (calcd) C	H
[Cp*Ir(2-MeBT)]$(BF_4)_2$ (1)	34.98 (35.15)	3.69 (3.57)
[Cp*Ir(BT·H)]BF_4 (2)	39.26 (39.35)	4.43 (4.04)
[Cp*Ir(3-MeBT·H)]BF_4 (3)	40.26 (40.50)	4.20 (4.29)
[Cp*Ir(2-MeBT·H)]BF_4 (4)	40.23 (40.50)	4.41 (4.29)
[Cp*Ir(2,3-Me_2BT·H)]BF_4 (5)	41.45 (41.60)	4.93 (4.54)
CpRu(BT·H) (6)	51.32 (51.81)	4.39 (4.01)
[Cp*Ir(BT·OMe)]BF_4 (7)	39.10 (39.38)	4.24 (4.17)
[Cp*Ir(3-MeBT·OMe)]BF_4 (8)	40.23 (40.48)	4.43 (4.42)
[Cp*Ir(BT·CH(CO_2Me)$_2$)]BF_4 (9)	40.89 (40.65)	4.03 (4.15)
[Cp*Ir(3-MeBT·CH(CO_2Me)$_2$)]BF_4 (10)	41.41 (41.56)	4.31 (4.36)
[Cp*Ir(BT·SEt)]BF_4 (11)	39.14 (39.41)	4.35 (4.30)
[Cp*Ir(3-MeBT·SEt)]BF_4 (12)	40.13 (40.45)	4.29 (4.53)

The X-ray structure determination of one of the complexes, CpRu(BT·H) (6), is also reported.

Experimental Section

General Procedures. All reactions were performed under N_2 in reagent grade solvents. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from Na/benzophenone and CH_2Cl_2 and hexanes from CaH_2, and MeOH was distilled from NaOMe and benzene from $LiAlH_4$. 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 benzo[*b*]thiophene, BT, was sublimed at room temperature onto a water-cooled probe prior to use. The 2-MeBT,[14] [Cp*$IrCl_2$]$_2$ (Cp* = η^5-C_5Me_5),[15] [Cp*Ir(L)]$(BF_4)_2$ (L = BT, 3-MeBT, 2,3-Me_2BT, T),[16] [CpRu(BT)]PF_6 (Cp = η-C_5H_5),[16] PPN[HFe(CO)$_4$],[17] NaSEt,[18] and NaCH(CO_2Me)$_2$[19] were prepared according to literature methods. However, the NaCH(CO_2Me)$_2$[19] was not used in situ but was precipitated by addition of CH_2Cl_2 and then hexanes; the white solid was filtered, washed with additional CH_2Cl_2, and then dried in vacuo. The NaSEt was stored in a dessicator, and the NaCH(CO_2Me)$_2$ was stored under N_2. Both compounds were weighed in a glovebag under a N_2 atmosphere.

The products **1–12** were characterized by elemental analysis (Galbraith Laboratories, Inc., Table I) and their ^1H NMR spectra (Table II). The ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Nicolet NT-300 spectrometer using deuteriated solvents as internal locks and referenced to $SiMe_4$. Fast atom bombardment (FAB) spectra were run on a Kratos MS-50 mass spectrometer. Electron-ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. Conductivity data were obtained on a Markson Electro Mark analyzer and calibrated with a standard KCl solution.

The electrochemical measurements were made by using a Bioanalytical Systems CV-1B cyclic voltammograph under an Ar atmosphere at room temperature. A three-electrode cell was used with a Ag/AgCl (NaCl, 3.0 M) reference electrode, a Pt wire counter electrode, and a stationary Pt disc working electrode (area = 3.1 mm^2). The supporting electrolyte Bu_4NPF_6 was prepared according to a literature method[20] and dried at 100 °C under vacuum for 30 h. A 0.1 M concentration of Bu_4NPF_6 was used for the cyclic voltammetric experiments. Analyte concentrations in the solvent CH_3NO_2 varied from 1.1 to 0.73 mM.

[Cp*Ir(2-MeBT)]$(BF_4)_2$ (1). To a stirred solution of [Cp*$IrCl_2$]$_2$ (0.236 g, 0.296 mmol) in 5 mL of acetone was added $AgBF_4$ (0.230 g, 1.18 mmol). The solution was stirred 5 min and filtered through Celite which was rinsed with additional acetone (~4 mL). The volume of the filtrate was reduced to ~4 mL in vacuo, and then 2-MeBT (0.701 g, 4.73 mmol) was added. The reaction mixture was refluxed for 2 min and then cooled to room temperature. Approximately 20 mL of CH_2Cl_2 was added to precipitate the product which was filtered, dried in vacuo, and then recrystallized from CH_3NO_2/CH_2Cl_2 to give a white solid: yield 0.260 g (67.8%); ^1H NMR (CD_3NO_2) δ 8.07 (m, H7), 7.86 (m, H4), 7.28 (m, H3, H5, H6), 2.98 (d, $J_{H3\text{-}C2CH_3}$ = 1.1 Hz, C2CH_3), 2.11 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 165.9 (C2), 120.3 (C9), 118.9 (C8), 118.3 (C3), 105.2 ($C_5(CH_3)_5$), 95.6 (C5), 93.8 (C6), 93.0 (C4), 92.0 (C7), 17.7 (C2CH_3), 9.1 ($C_5(CH_3)_5$).

[Cp*Ir(BT·H)]BF_4 (2). Approximately 5 mL of H_2O and 5 mL of CH_2Cl_2 were purged with N_2 for 5 min. To this stirred solution was added [Cp*Ir(BT)]$(BF_4)_2$ (43.0 mg, 0.0677 mmol) and then $NaBH_4$ (5.1 mg, 0.13 mmol). After 5 min the layers were separated, and the water layer was extracted with CH_2Cl_2 (3 × 5 mL). The CH_2Cl_2 extracts were combined, dried for ~30 min over Na_2SO_4, and filtered. The yellow product was precipitated from the filtrate by addition of Et_2O: yield, 29 mg (78%); FAB (2-nitrophenyl octyl ether–CH_2Cl_2), *m/e* 463 (M^+); Λ_M (0.98 × 10^{-3} M in CH_3NO_2) 79 Ω^{-1} cm^2 mol^{-1}.

[Cp*Ir(3-MeBT·H)]BF_4 (3). To a stirred solution of [Cp*Ir(3-MeBT)]$(BF_4)_2$ (40.0 mg, 0.0616 mmol) in 3 mL of H_2O and 3 mL of CH_2Cl_2 was added $NaBH_4$ (4.7 mg, 0.12 mmol). The layers were separated after 3 min, and the H_2O layer was extracted with additional CH_2Cl_2. The yellow CH_2Cl_2 solution was treated as for **2** resulting in the isolation of a pale yellow solid: yield, 27 mg (79%); Λ_M (1.0 × 10^{-3} M in CH_3NO_2) 81 Ω^{-1} cm^2 mol^{-1}.

[Cp*Ir(2-MeBT·H)]BF_4 (4). This complex was prepared analogously to **2** from **1** (52.0 mg, 0.0801 mmol) and $NaBH_4$ (6.1 mg, 0.16 mmol). The product was isolated as a bright yellow solid: yield, 35 mg (78%).

[Cp*Ir(2,3-Me_2BT·H)]BF_4 (5). This preparation was performed as for **2** from [Cp*Ir(2,3-Me_2BT)]$(BF_4)_2$ (55.0 mg, 0.0829 mmol) and $NaBH_4$ (6.3 mg, 0.17 mmol). A bright yellow solid was obtained: yield, 32.8 mg (68.5%).

CpRu(BT·H) (6). To a stirred solution of [CpRu(BT)]PF_6 (0.103 g, 0.231 mmol) in CH_2Cl_2 (5 mL) was added $NaBEt_3H$ (0.23 mL of a 1 M solution in THF, 0.23 mmol). The solution was stirred 5 min and evaporated to a yellow oil in vacuo. The oil was extracted with Et_2O, the Et_2O extract filtered, and the yellow filtrate passed through a short column (~4 cm) of alumina. The yellow Et_2O solution was then evaporated to dryness and the residue sublimed at room temperature onto a water-cooled probe in vacuo to give a bright yellow solid: yield, 49.5 mg (71.2%); EIMS (18 eV), *m/e* (base peak, M^+ – H), 167 (M^+ – BT·H), 134 (BT^+).

[Cp*Ir(BT·OMe)]BF_4 (7). To freshly distilled MeOH (5 mL) was added Na (1.8 mg, 0.078 mmol). The solution was stirred until all of the Na had dissolved. Then [Cp*Ir(BT)]$(BF_4)_2$ (51.3 mg, 0.0808 mmol) was added, and the mixture was stirred until none of the solid [Cp*Ir(BT)]$(BF_4)_2$ remained (~5 min). The yellow solution was evaporated to dryness, the residue extracted with CH_2Cl_2 (15 mL), and then the CH_2Cl_2 solution filtered. The volume of the yellow filtrate was reduced to 2 mL, and Et_2O (4 mL) was added to precipitate the product as a yellow solid that was then filtered, washed with Et_2O, and dried in vacuo: yield, 42.5 mg (93.7%); Λ_M (0.90 × 10^{-3} M in CH_3NO_2) 76 Ω^{-1} cm^2 mol^{-1}.

[Cp*Ir(3-MeBT·OMe)]BF_4 (8). The preparation of this complex from Na (1.8 mg, 0.078 mmol) and [Cp*Ir(3-MeBT)]$(BF_4)_2$ (51.9 mg, 0.0799 mmol) in freshly distilled MeOH proceeded analogously to that for **7**. A pale yellow product was isolated: yield, 36.7 mg (77.4%); Λ_M (1.0 × 10^{-3} in CH_3NO_2) 75 Ω^{-1} cm^2 mol^{-1}.

[Cp*Ir(BT·CH(CO_2Me)$_2$)]BF_4 (9). Under N_2, NaCH(CO_2Me)$_2$ (12.9 mg, 0.083 mmol) was weighed into a Schlenk flask. Acetone (4 mL) was vacuum distilled into the flask (cooled to −78 °C) which was stirred as it warmed to room temperature. Then, [Cp*Ir(BT)]$(BF_4)_2$ (53.6 mg, 0.0844 mmol) was added and the solution stirred for 2 min and then evaporated to dryness. The residue was extracted with CH_2Cl_2, and the yellow solution was filtered through a short alumina column (4 cm). The volume of the filtrate was reduced to ~0.5 mL in vacuo, and 25 mL of Et_2O was added. The mixture was frozen in N_2(l) and then slowly warmed to room temperature. This freezing process was repeated,

(13) (a) Henry, W. P.; Rieke, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 6314. (b) Semmelhack, M. F.; Wulff, W.; Garcia, J. L. *J. Organomet. Chem.* **1982**, *240*, C5.
(14) Shirley, D. A.; Cameron, M. D. *J. Am. Chem. Soc.* **1952**, *74*, 664.
(15) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.
(16) Huckett, S. C.; Miller, L. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1988**, *7*, 686.
(17) Darensbourg, M. Y.; Darensbourg, D. J.; Barros, H. C. C. *Inorg. Chem.* **1978**, *17*, 297.
(18) Kim, H. P.; Angelici, R. J. *Organometallics* **1986**, *5*, 2489.
(19) Hegedus, L. S.; Inoue, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4917.
(20) Lind, J. E., Jr.; Abdel-Rahim, H. A. A.; Rudich, S. W. *J. Phys. Chem.* **1966**, *70*, 3610.

Table II. ^{1}H NMR Data (δ) for Isomers of Complexes 2–13[a]

compd	H2	H3	H4	H5	H6	H7	BT-CH_3	C_5H_5 or $C_5(CH_3)_5$	nucleophile	selected coupling consts (Hz)
[Cp*Ir(BT·H)]BF_4 (2)										
A[b]	7.76 d	7.09 d	7.23 d	5.58 t	4.07 t	4.00–3.93[c]		1.87 s	5.03 d (H_{exo})	$J_{H7-Hexo}$ = 13.0
B[b]	8.00 d	6.64 d	4.00–3.93[c]	3.86 t	5.60 t	7.44 d		1.91 s	5.23 d (H_{exo})	$J_{H4-Hexo}$ = 13.4
C[b]	8.26 d	7.28 d	6.09 d	4.11–3.92[c]	3.23 p	4.28 d		d	4.30 d (H_{exo})	$J_{H6-Hexo}$ = 12.7
D[b]	8.17 d	6.87 d	4.11–3.93[c]	3.14 p	4.11–3.39[c]	6.28 d		d	4.19 d (H_{exo})	$J_{H5-Hexo}$ = 12.3
[Cp*Ir(3-MeBT·H)]BF_4 (3)										
A[b]	7.36 q		7.13 d	5.58 t	4.08 t	3.95–3.91[c]	2.19 d	1.88 s	5.02 d (H_{exo})	$J_{H7-Hexo}$ = 13.1 $J_{H2-C3-CH_3}$ = 1.2
B[b]	7.59 q		3.85–3.95[c]	3.87 t	5.61 t	7.40 d	2.27 d	d	5.15 d (H_{exo})	$J_{H4-Hexo}$ = 12.6 $H_{H2-C3-CH_3}$ = 1.1
C[b]	7.85 q		6.02 d	4.00–3.93[c]	3.23 p	4.25 d	2.40 d	d	4.28 d (H_{exo})	$J_{H6-Hexo}$ = 13.5 $H_{H2-C3-CH_3}$ = 1.2
D[b]	7.78 q		3.87–3.83[c]	3.16 p	3.80–3.95[c]	6.24 d	2.08 d	d	4.20 d (H_{exo})	$H_{H5-Hexo}$ = 13.2 $H_{H2-C3-CH_3}$ = 1.2
[Cp*Ir(2-MeBT·H)]BF_4 (4)										
A[b]		6.79 br s	7.10 d	5.52 t	4.03 t	3.95–3.75[c]	2.60 br s	1.92 s	4.94 d (H_{exo})	$J_{H7-Hexo}$ = 12.9
B[b]		6.34 br s	3.95–3.75[c]	4.10–3.75[c]	5.34 t	7.33 d	2.39 br s	1.90 s	5.19 d (H_{exo})	$J_{H4-Hexo}$ = 13.2
C[b]		7.00 br s	5.97 d	4.05–3.76[c]	3.18 p	4.20 d	2.73 br s	1.95 s	4.28 d (H_{exo})	$J_{H6-Hexo}$ = 12.7
D[b]		6.59 br s	4.05–3.76[c]	3.10 p	4.05–3.76[c]	6.19 d	2.71 br s	1.94 s	4.21 d (H_{exo})	$J_{H5-Hexo}$ = 12.6
[Cp*Ir(2,3-Me_2BT·H)]BF_4 (5)										
A[b]			7.06 d	5.53 t	4.04 t	3.95–3.75[c]	2.11 br s[e] 2.50 d[f]	1.90 s	4.90 d (H_{exo})	$J_{H7-Hexo}$ = 12.8
B[b]			3.95–3.75[c]	3.78 t	5.55 t	7.30 d	2.17 d[e] 2.30 br s[f]	1.89 s	5.13 d (H_{exo})	$J_{H4-Hexo}$ = 13.4
C[b]			5.96 d	4.10–3.95[c]	3.19 p	4.17 d	2.07 d[e] 2.60 d[f]	1.94 s	4.26 d (H_{exo})	$J_{H6-Hexo}$ = 12.7
D[b]			4.10–3.75[c]	3.12 p	4.10–3.75[c]	6.15 d	2.31 d[e] 2.63 d[f]	1.93 s	4.19 d (H_{exo})	$J_{H5-Hexo}$ = 12.2
CpRu(BT·H) (6)										
A[g]	6.44 d	6.34 d	6.13 d	4.27 t	2.96 t	3.44 dd		4.31 s	3.19 d (H_{exo})	$J_{H7-Hexo}$ = 11.6
B[g]	6.37 d	6.27 d	3.26 dd	2.69 t	4.33 t	6.38–6.33[c]		4.29 s	3.15 d (H_{exo})	$J_{H4-Hexo}$ = 11.3
C[g]	6.77 d	6.86 d	5.20 d	2.48–2.55[c]	2.73–2.54[c]	2.73–2.54[c]		d	2.73–2.54[c](H_{exo})	
D[g]	6.72 d	6.35 d	2.73–2.54[c]	2.73–2.54[c]	2.48–2.55[c]	5.50 d		d	2.73–2.54[c](H_{exo})	
[Cp*Ir(BT·OMe)]BF_4 (7)										
A[b]	7.94 d	7.10 d	7.15 d	5.69 t	4.71 t	4.83 d		1.90 s	3.02 s (OCH_3)	
[Cp*Ir(3-MeBT·OMe)]BF_4 (8)										
A[b]	7.56 q		7.05 d	5.70 d	4.71 t	4.78 d	2.24 d	1.92 s	3.03 s (OCH_3)	
[(Cp*Ir(BT·CH($CO_2Me)_2$)]BF_4 (9)										
A[b]	7.79 d	7.09 d	7.28 d	5.53 t	4.27 t	4.54 dd		1.89 s	2.87 d (C*H*) 3.52 s (CH_3) 3.61 s (CH_3)	J_{H7-CH} = 8.2
[Cp*Ir(3-MeBT·CH($CO_2Me)_2$)]-BF_4 (10)										
A[b]	7.40 q		7.19 d	5.56 t	4.27 t	4.50 dd	2.21 d	1.90 s	2.87 d (C*H*) 3.53 s (CH_3) 3.61 s (CH_3)	J_{H7-CH} = 8.4
[Cp*Ir(BT·SEt)]BF_4 (11)										
A[b]	7.88 d	7.07 d	7.23 d	5.67 t	4.54 t	5.25 d		1.90 s	1.06 m (CH_3) 2.36 m (CH_2)	
[Cp*Ir(3-MeBT·SEt)]BF_4 (12)										
A[b]	7.48 q		7.14 d	5.67 t	4.54 t	5.19 d	2.22 d	1.90 s	1.10 m (CH_3) 2.37 m (CH_2)	
[Cp*Ir(BT·PMe_3)]$(BF_4)_2$ (13)										
A[h]	7.81 d	7.15 d	7.28 d	5.71 t	4.28 t	5.42 dd		1.89 s	1.61 d (PMe_3)	J_{H7-P} = 3.3 J_{P-CH_3} = 13.4

[a] Abbreviations: d, doublet; t, virtual triplet; q, quartet; p, virtual pentet; br, broad. [b] Acetone-d_6. [c] Exact position of peak within the complex multiplet not determined. [d] Peak either not observed or could not be definitively assigned. [e] C3-CH_3. [f] C2-CH_3. [g] Benzene-d_6. [h] CD_3NO_2.

and the resulting yellow solid was filtered from the solution while it was still cold and then washed with cold Et_2O and dried in vacuo: yield, 22.6 mg (40.0%); Λ_M (1.0×10^{-3} M in CH_3NO_2) 75 Ω^{-1} cm^2 mol^{-1}.

[Cp*Ir(3-MeBT·CH($CO_2Me)_2$)]BF_4 (10). This preparation was performed analogously to that for **9**, from NaCH($CO_2Me)_2$ (12.0 mg, 0.0774 mmol) and [Cp*Ir(3-MeBT)]$(BF_4)_2$ (50.8 mg, 0.0782 mmol). The bright yellow oily product was crystallized by dissolving in CH_2Cl_2 (0.5 mL), adding Et_2O (80 mL), and storing at −20 °C for 58 h: yield, 31.9 mg (58.8%); Λ_M (1.2×10^{-3} M in CH_3NO_2) 65 Ω^{-1} cm^2 mol^{-1}.

[Cp*Ir(BT·SEt)]BF_4 (11). Under N_2, NaSEt (8.2 mg, 0.098 mmol) was weighed into a Schlenk flask. Then HSEt (1 mL) was added followed by acetone (5 mL, vacuum distilled into the flask cooled to −78 °C). After the solution had warmed to 25 °C additional HSEt (1 mL) was added, followed by [Cp*Ir(BT)]$(BF_4)_2$ (62.5 mg, 0.0984 mmol). The reaction mixture was stirred for 2 min and then evaporated to dryness in vacuo. The residue was extracted with CH_2Cl_2, and the solution was chromatographed on an alumina column (4 cm). The yellow product was eluted with acetone, and this solution was evaporated to a yellow oil in vacuo. The product was crystallized by dissolving in CH_2Cl_2 (0.5 mL), adding Et_2O (30 mL), and storing at −20 °C for 48 h. The green-yellow solid was filtered from the CH_2Cl_2/Et_2O solution and dried in vacuo: yield, 37.5 mg (62.5%).

[Cp*Ir(3-MeBT·SEt)]BF_4 (12). This compound was prepared from NaSEt (8.0 mg, 0.095 mmol) and [Cp*Ir(3-MeBT)]$(BF_4)_2$ (64.9 mg, 0.100 mmol) by using a method analogous to that for 11 to give a green solid: yield, 22.1 mg (37.2%).

[Cp*Ir(BT·PMe_3)]$(BF_4)_2$ (13). To an NMR tube containing CD_3NO_2 (0.25 mL) was added first [Cp*Ir(BT)]$(BF_4)_2$ (45.1 mg, 0.0710 mmol) and then PMe_3 (11 μL, 0.11 mmol). The clear solution turned bright yellow upon addition of the PMe_3; none of the [Cp*Ir(BT)]$(BF_4)_2$ was observed by ^{1}H NMR. The solution was evaporated to a yellow oil in vacuo: FAB (dithioerythritol/dithiothreitol), *m/e* 481 (base peak, $M^{2+} - PMe_3 + F^-$).

[Cp*Ir(BT-d_2)]$(BF_4)_2$. To a solution of KOH (2.1 g, 37 mmol) in MeOD (40 mL) was added [CpRu(BT)]PF_6 (1.776 g, 3.988 mmol); the mixture was stirred at room temperature for 19 h.[11g] Then, CO_2 was bubbled through the solution for 1.75 h. After

Table III. Crystal and Data Collection Parameters for the X-ray Diffraction Study of CpRu(BT•H) (6, Isomer A)

formula	$RuSC_{13}H_{12}$
fw	301.37
space group	$P2_1/n$
a, Å	5.914 (2)
b, Å	14.234 (2)
c, Å	12.800 (2)
β, deg	91.36 (2)
V, Å^3	1077.2
Z	4
d_{calcd}, g/cm^3	1.86
cryst size, mm^3	0.3 × 0.3 × 0.5
μ(Mo Kα), cm^{-1}	15.7
diffractometer	Enraf-Nonius CAD4
radiatn (monochromated in incident beam)	Mo Kα(λ_2 = 0.71073 Å)
temp, °C	21
scan method	ω–2θ
max 2θ, deg	55.0
std reflns	3, measd every hour of exposure (no obsd decay)
total unique reflns	2469
unique reflns obsd ($F_o^2 > 3\sigma(F_o^2)$)	2198
no. of parameters refined	156
T_{min}/T_{max}	0.996/0.793
R^a	0.029
R_w^b	0.043
quality of fit indicator^c	1.47
largest shift/esd, final cycle	0.01
largest peak, e/Å^3	0.73

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

evaporation of the reaction mixture to dryness in vacuo, the residue was extracted with CH_2Cl_2 and then acetone. The extracts were filtered, and Et_2O was added to precipitate out [CpRu(BT-d_2)]PF_6 which was dried in vacuo: yield, 1.354 g (76.24%). The compound was dissolved in CH_3CN (250 mL) and photolyzed (450-W Canrad-Hanovia medium-pressure, quartz, mercury-vapor lamp) for 7 days to give $CpRu(NCMe)_3PF_6$ and BT-d_2. The solvent was removed from the resulting orange solution by rotoevaporation giving a brownish oil which was extracted with pentane (100 mL). The bulk of the pentane was removed by rotoevaporation, and then the last 0.5 mL was removed in vacuo. The BT-d_2 remaining was purified by sublimation in vacuo at 25 °C onto a water-cooled probe: yield 0.325 g (79.7% from [CpRu(BT)]PF_6). The BT-d_2, with deuterium at the 2- and 7-positions (as determined by ^{1}H NMR), was then used in the preparation of [Cp*Ir(BT-d_2)]$(BF_4)_2$ from $[Cp^*IrCl_2]_2$ by the method which has been previously described.[16]

X-ray Structure Determination of CpRu(BT·H) (6). Gold-colored crystals of **6** were grown by slow evaporation of a concentrated hexanes solution at −1 °C. The crystal,[21] of approximate dimensions 0.3 × 0.3 × 0.5 mm, was mounted on the end of a glass fiber and coated with a thin layer of epoxy cement. A least-squares fit of 25 reflections found in the range 20° < 2θ < 30° by an automated search routine indicated a monoclinic crystal system. The intensities from ϕ scans of eight reflections were used to apply an empirical absorption correction to the data. Lorentz and polarization corrections were applied to the data, and the intensities of equivalent reflections were averaged.

The position of the Ru atom was determined by direct methods. The remaining non-hydrogen atoms were then located from a difference Fourier synthesis. Following full-matrix refinement[22] of all parameters for the non-hydrogen atoms, a difference Fourier map revealed peaks corresponding to all of the hydrogen atoms. Attempted full-matrix refinement using isotropic hydrogen atoms was unsuccessful. Therefore, only the hydrogen atoms on the

(21) X-ray data collection and structure solution were carried out at Iowa State Molecular Structural Laboratory. All calculations were performed on a Digital Equipment Corp. Micro VAX II computer using the CAD4-SDP package. (Enraf-Nonius Structure Determination Package; Enraf-Nonius, 1976: Delft, Holland.)

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

Table IV. Positional and Thermal Parameters for CpRu(BT•H) (6, Isomer A)

atom	x	y	z	B(av),^{a} Å^2
Ru	0.07475 (3)	0.68578 (1)	0.19505 (1)	1.909 (4)
S	0.0256 (1)	0.92682 (5)	0.11371 (7)	3.26 (1)
C2	0.2929 (6)	0.9116 (2)	0.0658 (3)	3.59 (6)
C3	0.4243 (5)	0.8499 (2)	0.1181 (2)	2.79 (5)
C4	0.3738 (5)	0.7379 (2)	0.2788 (3)	3.06 (5)
C5	0.2130 (6)	0.7052 (2)	0.3509 (2)	3.08 (5)
C6	−0.0472 (5)	0.7427 (2)	0.3487 (2)	2.83 (5)
C7	−0.0472 (5)	0.8425 (2)	0.3127 (2)	2.74 (5)
C8	0.3007 (5)	0.8087 (2)	0.2067 (2)	2.32 (5)
C9	0.0738 (4)	0.8415 (2)	0.2117 (2)	2.22 (4)
C10	−0.1885 (5)	0.6390 (2)	0.0831 (3)	3.67 (6)
C11	0.1714 (6)	0.5742 (2)	0.1636 (3)	3.95 (7)
C12	0.0481 (7)	0.5347 (2)	0.1648 (3)	4.01 (7)
C13	0.1657 (6)	0.5762 (2)	0.0815 (3)	3.72 (6)
C14	0.0207 (6)	0.6407 (3)	0.0322 (2)	3.71 (6)
H10	−0.311 (6)	0.676 (2)	0.060 (3)	1.7 (8)
H11	−0.262 (7)	0.566 (3)	0.196 (4)	3 (1)
H12	0.096 (6)	0.496 (4)	0.205 (3)	4 (1)
H13	0.288 (7)	0.561 (3)	0.054 (4)	3 (1)
H14	0.071 (6)	0.674 (2)	−0.029 (3)	1.9 (8)

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

Table V. Bond Distances and Angles for CpRu(BT•H) (6, Isomer A)

Bond Distances (Å)			
Ru–C4	2.176 (3)	C3–C8	1.485 (4)
Ru–C5	2.155 (3)	C4–C8	1.427 (4)
Ru–C6	2.195 (3)	C4–C5	1.419 (4)
Ru–C8	2.204 (3)	C5–C6	1.416 (4)
Ru–C9	2.227 (3)	C6–C7	1.509 (4)
Ru–C10	2.194 (3)	C7–C9	1.493 (4)
Ru–C11	2.185 (3)	C8–C9	1.424 (4)
Ru–C12	2.191 (3)	C10–C11	1.385 (5)
Ru–C13	2.207 (3)	C11–C12	1.415 (5)
Ru–C14	2.198 (3)	C12–C13	1.415 (5)
S–C2	1.723 (4)	C13–C14	1.397 (5)
S–C9	1.764 (3)	C14–C10	1.412 (5)
C2–C3	1.341 (4)		
Bond Angles (deg)			
S–C2–C3	115.5 (3)	C7–C9–C8	120.9 (2)
C2–C3–C8	110.5 (3)	C9–C8–C4	118.3 (3)
C3–C8–C9	112.7 (2)	C8–C4–C5	117.0 (3)
C8–C9–S	109.3 (2)	C10–C11–C12	108.9 (3)
C9–S–C2	91.9 (1)	C11–C12–C13	107.0 (3)
C4–C5–C6	119.9 (3)	C12–C13–C14	107.9 (3)
C5–C6–C7	119.6 (3)	C13–C14–C10	108.4 (3)
C6–C7–C9	100.6 (2)	C14–C10–C11	107.8 (3)

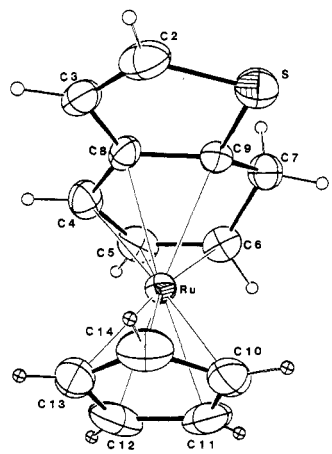


Figure 1. ORTEP drawing of CpRu(BT·H) (6, isomer A).

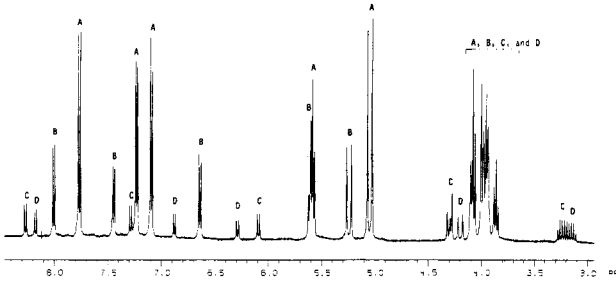


Figure 2. ^1H NMR spectrum of $[Cp^*Ir(BT{\cdot}H)]^+$ (**2**) in acetone-d_6.

cyclopentadienyl ring were refined. The positions of the hydrogen atoms in the BT·H ligand were calculated (C–H bond length = 0.95 Å, isotropic temperature factor = $1.3B_{eqv}$ for the attached carbon atom) and used in the structure factor calculations. Final refinement resulted in convergence to $R = 0.029$ and $R_w = 0.043$.

The crystal and data collection parameters for **6** are given in Table III. The final positional and thermal parameters are listed in Table IV. Bond lengths and angles are presented in Table V, and an ORTEP[23] drawing of **6** is given in Figure 1.

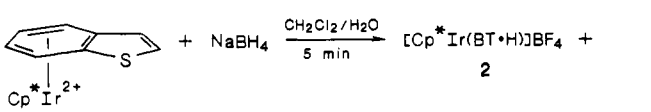
Results and Discussion

Preparation of $[Cp^*Ir(2\text{-MeBT})](BF_4)_2$ (1). The reaction of $[Cp^*IrCl_2]_2$, $AgBF_4$, and 2-MeBT produces **1**, as shown in eq 1. This method has previously been used to synthesize other iridium T and BT compounds.[16] Complex **1** is air-stable in the solid state.

$$[Cp^*IrCl_2]_2 + 4AgBF_4 \xrightarrow[\text{excess 2-MeBT}]{\text{acetone}} \underset{\mathbf{1}}{2[Cp^*Ir(2\text{-MeBT})](BF_4)_2} + 4AgCl \quad (1)$$

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** were assigned by comparison with spectra for the analogous complexes, $[Cp^*IrL]^{2+}$ (L = BT, 3-MeBT, 2,3-Me_2BT),[16] as well as by comparison with spectra for uncoordinated 2-MeBT.[24] The H3, H4, H7, and C2-CH_3 ^1H NMR resonances in **1** are downfield of those for free 2-MeBT, while the chemical shifts for H5 and H6 show very little change. The larger downfield shifts in **1** for H3 and C2-CH_3 relative to those for H4 and H7 suggest that the ligand is bound through the benzene ring. A similar trend was observed for the π-benzene-bound BT and 3-MeBT in $[CpRuL]^+$ (L = BT, 3-MeBT). The ruthenium BT complex was structurally characterized by X-ray crystallography.[16]

Reactions of $[Cp^*Ir(BTs)]^{2+}$ and $[CpRu(BT)]^+$ with Hydrides. Complex **2** was prepared by reaction of $NaBH_4$ and $[Cp^*Ir(BT)](BF_4)_2$ in CH_2Cl_2/H_2O as shown in eq 2. The bright yellow solid **2** is air stable and was characterized by its elemental analyses (Table I), FAB mass spectrum, molar conductivity, and ^1H NMR spectrum (Table II).



The ^1H NMR spectrum (a portion of which is shown in Figure 2) is much more complex than that which might be expected from a single compound. The complexity

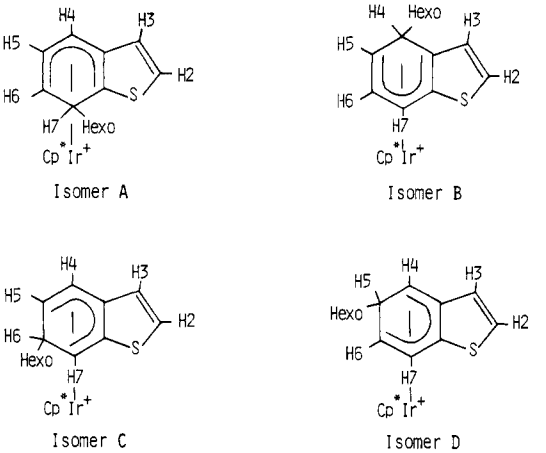


Figure 3. Isomers A–D of $[Cp^*Ir(BT{\cdot}H)]^+$ (**2**).

arises from the presence of four isomers of **2** which are shown in Figure 3. The ^1H NMR resonances corresponding to these isomers were assigned by selective decoupling experiments and by the use of $[Cp^*Ir(BT\text{-}d_2)]^{2+}$ to synthesize $[Cp^*Ir(BT{\cdot}H\text{-}d_2)]^+$. The $[Cp^*Ir(BT\text{-}d_2)]^{2+}$ had deuterium-substituted for hydrogen at the 2- (93%) and 7- (75%) positions.[11g] For isomer A of **2**, the resonance corresponding to H2 was no longer present, and the doublet for H3 ($J_{H2\text{-}H3} = 5.4$ Hz) had collapsed to a singlet ($J_{H\text{-}H}/J_{H\text{-}D} \simeq 6.51$).[25] The H4 (d, $J_{H4\text{-}H5} = 4.9$ Hz) and H5 (virtual t, $J_{H5\text{-}H6} \simeq 5.8$ Hz) resonances were unchanged. Due to the presence of deuterium at the 7-position the virtual triplet corresponding to H6 ($J_{H6\text{-}H7} = 6.3$ Hz) collapsed to a doublet and the H_{exo} resonance collapsed to a singlet $J_{H7\text{-}Hexo} = 13.0$ Hz).

The magnitude of the coupling constant between H7 (the endo hydrogen at C7) and H6 is expected to be greater than that between H6 and H_{exo} based on the Karplus relationship.[26] This trend in coupling constants has been observed in analogous organometallic systems.[27] A resonance for H7, which should be a doublet of doublets due to H6 and H_{exo} coupling, was not observed. With undeuteriated **2**, the approximate position of the H7 resonance was assigned by observing that H6, a virtual triplet, collapsed to a doublet upon irradiation of the multiplet in the 4.00–3.93 ppm region. The downfield shift of the H_{exo} resonance relative to that for the endo proton, H7, is unusual[28] but has previously been observed for $[Cp^*Ir(C_6H_6{\cdot}H)]^+$.[29] A reaction performed using $NaBD_4$ and $[Cp^*Ir(BT)]^{2+}$ showed that D^- addition occurs only at the exo face of the BT ligand. The integral of the H_{exo} doublet was small (but was observed, due to $NaBH_4$ impurities in the $NaBD_4$) relative to the other resonances for A, and the singlet at this position that would have resulted from an endo D was not observed.

The chemical shifts for isomers B, C, and D were assigned analogously to those for A. The virtual pentets corresponding to H6 in isomer C and H5 in isomer D result from coupling to H_{exo} and further splitting of the reso-

(23) Johnson, C. K. U.S. Atomic Energy Commission Report ORNL-3794 (Second Revision with Supplemental Instructions); Oak Ridge National Laboratory: Oak Ridge, TN, 1970. Thermal ellipsoids are drawn at a 50% probability level.

(24) (a) ^1H NMR (CD_3NO_2): δ 7.79 (d, H7), 7.69 (d, H4), 7.32 (m, H6), 7.26 (m, H5), 7.04 (s, H3), 2.59 (d, C2-CH_3). (b) $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 140.8 (C2), 140.5 (C8), 139.7 (C9), 124.0 (C5), 123.3 (C6), 122.5 (C4), 122.0 (C7), 121.6 (C3), 16.0 (C2-CH_3). Clark, P. D.; Ewing, D. F.; Scrowston, R. M. *Org. Magn. Reson.* **1976**, *8*, 252.

(25) Brevard, C.; Kintzinger, J. P. In *NMR and the Periodic Table*; (Harris, R. K., Mann, B. E., Eds.); Academic: New York, 1978; p 110.

(26) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrophotometric Identification of Organic Compounds*; Wiley: New York, 1981; p210.

(27) (a) Honig, E. D.; Quin-Jin, M.; Robinson, W. T.; Willard, P. G.; Sweigart, D. A. *Organometallics* **1985**, *4*, 871. (b) Faller, J. W. *Inorg. Chem.* **1980**, *19*, 2857. (c) Herberich, G. E.; Schwarzer, J. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 143.

(28) Khand, I. V.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1969**, 2024.

(29) Grundy, S. L.; Smith, A. J.; Adams, H.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1747.

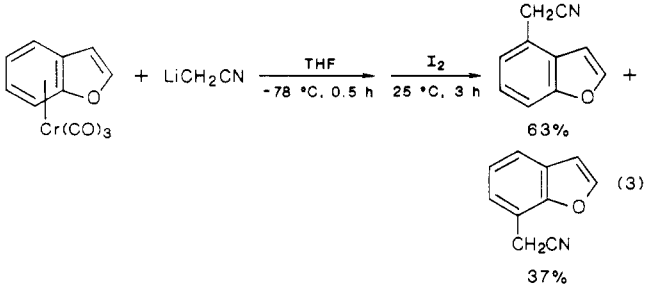
Table VI. Percentages of Isomers A–D of Complexes 2–13

compound	% isomer A	B	C	D
[Cp*Ir(BT·H)]BF_4 (2)	61	25	8	6
[Cp*Ir(3-MeBT·H)]BF_4 (3)	58	27	8	7
[Cp*Ir(2-MeBT·H)]BF_4 (4)	60	23	9	8
[Cp*Ir(2,3-Me_2BT·H)]BF_4 (5)	60	25	8	7
CpRu(BT·H) (6)	78	15	5	2
[Cp*Ir(BT·OMe)]BF_4 (7)	70	18	10	2
[Cp*Ir(3-MeBT·OMe)]BF_4 (8)	80	15	3	2
[Cp*Ir(BT·CH(CO_2Me)$_2$)]BF_4 (9)	61	26	8	5
[Cp*Ir(3-MeBT·CH(CO_2Me)$_2$)]BF_4 (10)	53	25	11	11
[Cp*Ir(BT·SEt)]BF_4 (11)	87	9	3	1
[Cp*Ir(3-MeBT·SEt)]BF_4 (12)	70	23	4	3
[Cp*Ir(BT·PMe_3)]$(BF_4)_2$ (13)	75	14	8	3

nances by the two vicinal protons (C, J_{H6-H5} = 6.3 Hz, J_{H6-H7} = 6.0 Hz; D, $J_{H5-H4} \simeq J_{H5-H6} \simeq$ 6.6 Hz). The Cp* resonances of isomers C and D were not resolved from the peaks for A and B. The $^{13}C\{^1H\}$ NMR spectrum of **2** was obtained, but assignments of the numerous resonances were not made.

The percentages of the isomers A–D present were determined by integration of the respective ^1H NMR signals and are given in Table VI. During 3 days at 25 °C in acetone-d_6 these percentages remained unchanged. The relative amounts of A–D were also the same when **2** was dissolved in $CDCl_3$ and CD_3NO_2 at 25 °C. Therefore, there is no isomer interconversion under these conditions. The distribution of isomers does change slightly with different preparations. As compared to the percentages given in Table VI, the amounts of A, B, C, and D formed in three other preparations of **2**, performed analogously to that described in the Experimental Section, were (56, 23, 11, 10%), (60, 25, 8, 7%), and (63, 24, 7, 6%). When PPN[$HFe(CO)_4$] was used as a H^- source, the relative amounts of A and B in **2** were 77% and 23%, respectively. The amounts of C and D were not determined due to the relatively poor quality of the spectrum. The relative amounts of A and B in the $NaBH_4$ reaction were 71% and 29%. Therefore, the H^- source has little effect on the isomeric distribution in **2**. The isomers could not be separated by either chromatography or fractional crystallization.

The only other reports of nucleophilic attack on transition-metal-bound fused ring aromatic ligands are for $Cr(CO)_3L$ (L = naphthalene,[30] benzofuran,[13b] and indole[13b,31]). The reaction of carbon nucleophiles with the chromium complexes to generate anionic cyclohexadienyl intermediates was followed by oxidation to produce the uncoordinated substituted ligand as shown in eq 3 for benzofuran.[13b,30a] The nucleophilic addition reactions



(3)

occurred preferentially at C4 except for 3 of the 17 reactions studied (in these cases, C7 addition was preferred).[13b] Attack at C6 was reported to give rise to a minor product in only a few of the reactions. Semmelhack[13b,30a] found that the selectivity correlated with the magnitude of the LUMO coefficients for uncoordinated naphthalene and indole.

The preference for H^- attack at C7 in $[Cp^*Ir(BT)]^{2+}$ and the significant amounts of isomers resulting from attack at C5 and C6 contrasts with the results reported for the chromium complexes. At this time the LUMO coefficients for BT (either coordinated to a transition metal or unbound) have not been reported, and, therefore, conclusions regarding the controlling factors in this reaction cannot be drawn.

The preparations of **3**, **4**, and **5** proceed analogously to that of **2** and result in the isolation of yellow air-stable solids. These complexes were characterized by their elemental analyses (Table I) and ^1H NMR spectra (Table II). The ^1H NMR spectra of **3** and **5** showed weak peaks due to **4**, which was formed from $[Cp^*Ir(2\text{-MeBT})]^{2+}$ impurities in $[Cp^*Ir(3\text{-MeBT})]^{2+}$ and $[Cp^*Ir(2,3\text{-}Me_2BT)]^{2+}$ starting materials. The 2-MeBT impurities were present in the commercial 3-MeBT which was used to synthesize 2,3-Me_2BT and the iridium complexes. The ^1H NMR spectra were assigned by analogy with **2**. As shown in Table VI, the distribution of isomers was not significantly affected by the presence or position of the methyl substituents.

Complex **6** is prepared from $NaBEt_3H$ and [CpRu(BT)]PF_6 as shown in eq 4. The resulting air-sensitive

$$[CpRu(BT)]PF_6 + NaBEt_3H \xrightarrow[5\ min]{CH_2Cl_2} \underset{\mathbf{6}}{CpRu(BT\cdot H)} + NaPF_6 + BEt_3 \quad (4)$$

yellow solid was identified by its elemental analyses (Table I), EIMS, and ^1H NMR spectrum (Table II). As for compounds **2–5**, four isomers of **6** are produced. The ^1H NMR resonances for these isomers were assigned by selective decoupling experiments and by analogy with the assignments for **2**. The assignments were confirmed by synthesis of CpRu(BT-d_2·H) and comparison of its ^1H NMR spectrum with the spectrum for **6**. The intensities and splittings of the resonances in the spectrum of CpRu(BT-d_2·H) also established that H^- addition occurs in an exo fashion.

Integration of the resonances in the ^1H NMR spectrum provided the isomeric distribution given in Table VI. In contrast to **2** the isomeric distribution of **6** changes significantly with different preparations. When a slight excess of $NaBEt_3H$ was used, the percentages of A–D in **6** were 51, 26, 14, and 9%, respectively, as compared to 78, 15, 5, and 2% given in Table VI. There is no interconversion of isomers in benzene-d_6 after 24 h at 25 °C.

Structural Characterization of CpRu(BT·H) (6). Complexes **2–12** represent the first isolable cyclohexadienyl complexes derived from fused-ring aromatic systems. The $[Cr(CO)_3(\eta^5\text{-naphthalene·H})]^-$ resulting from protonation of $[Cr(CO)_3(naphthalene)]^{2-}$ has only been observed spectroscopically.[13a,32] We were, therefore, interested in elucidating the structural characteristics of this type of complex by an X-ray diffraction study of **6**.

The crystal structure of **6** (which turned out to be the major isomer, A), Figure 1, clearly shows the cyclohexadienyl nature of the BT·H ligand. The C7 atom is displaced 0.645 (3) Å from the least-squares plane defined by C4, C5, C6, C8, and C9 (Table S-I, supplementary material). None of these five atoms deviates from the least-squares plane by more than 0.001 (3) Å. The C6–C7

(30) (a) Semmelhack, M. F.; Clark, G. R.; Farina, R.; Saeman, M. *J. Am. Chem. Soc.* **1979**, *101*, 217. (b) Oprunenko, Y. F.; Malyvgina, S. G.; Ustynyuk, Y. A.; Ustynyuk, N. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, *33*, 2405; *Chem. Abstr.* **1985**, *102*, 132198e.

(31) Kozikowski, A. P.; Isobe, K. *J. Chem. Soc., Chem. Commun.* **1978**, 1076.

(32) Rieke, R. D.; Henry, W. P.; Arney, J. S. *Inorg. Chem.* **1987**, *26*, 420.

and C9–C7 bond lengths, 1.509 (4) and 1.493 (4) Å, respectively, are slightly shorter than expected for a C(sp^3)–C(sp^2) bond (1.51 Å)[33] but are within the range observed for other η^5-cyclohexadienyl complexes (1.49–1.55 Å).[33,34] The C6–C7–C9 angle, 100.6 (2)°, is smaller than the ideal tetrahedral value of 109.46° but again near the range reported for analogous compounds (101–104°).[33,34b,35] The C–C bond lengths in the cyclohexadienyl ring (excluding C6–C7 and C9–C7) have an average value of 1.42 Å. This value is only slightly longer than the average C–C bond length of 1.41 Å in the benzene ring of [CpRu(BT)]BF_4[16] and within the range of analogous bond distances in other cyclohexadienyl complexes (1.40-1.44 Å).[33,34]

The average Ru–C distance for C4, C5, C6, C8, and C9 is 2.19 Å. The average value for the six carbons of the benzene ring bonded to Ru in [CpRu(BT)]BF_4 is 2.22 Å.[16] The BT ligand in [CpRu(BT)]BF_4 showed evidence of ring slippage[36] (the average Ru–C_5C_6 distance minus the average Ru–C8C9 distance = 0.07 Å). This slippage is also apparent in **6** but is of a much smaller magnitude (= 0.04 Å). The planes of the cyclohexadienyl and Cp rings are essentially parallel (dihedral angle = 2.8° ± 1.9°).

H^- Abstraction from [Cp*Ir(BT·H)]$^+$ (2) and CpRu(BT·H) (6). To an NMR tube containing **2** (8.0 mg, 0.014 mmol) was added acetone-d_6 (0.3 mL) and cyclohexane (0.1 μL). The ^{1}H NMR spectrum was obtained, and then HBF_4·Et_2O (20 μL, 0.14 mmol) was added. The reaction, eq 5, was monitored by ^{1}H NMR over 43 h until all of **2** had reacted to form [Cp*Ir(BT)]$(BF_4)_2$. The

$$\underset{\mathbf{2}}{[Cp^*Ir(BT\cdot H)]BF_4} + HBF_4\cdot Et_2O \xrightarrow[43\ h]{\text{acetone-}d_6} [Cp^*Ir(BT)](BF_4)_2 + H_2 \quad (5)$$

integrals corresponding to the relative amounts of isomers A–D of **2** and [Cp*Ir(BT)]$^{2+}$, relative to an internal integration standard (cyclohexane), were determined from the ^{1}H NMR spectra obtained during the reaction. The percentages of A–D in **2** before addition of HBF_4·Et_2O were 63, 24, 7, and 6%, respectively. After 5.5 h isomer D was no longer observed and the percentages of A–C were 82, 14, and 4%, respectively. After 20 h only A and B were present (92 and 8%, respectively) and peaks due to uncoordinated BT were present in the spectrum. This is a result of acetone displacement of BT from [Cp*Ir(BT)]$^{2+}$. After 24 h only A, [Cp*Ir(BT)]$^{2+}$, and BT were present in the solution. When integrals for A–D and [Cp*Ir(BT)]$^{2+}$ are compared, it is clear that isomerization of B–D to A is not occurring under these conditions and that this reaction occurs by preferential H^- abstraction from isomers B–D relative to A. Reports of other selective H^- abstraction reactions have not been published, and it is not clear what factors determine the observed selectivity. Complex **2** does not react with $(Ph_3C)BF_4$.

The reaction of **6** with $(Ph_3C)BF_4$ is shown in eq 6. This reaction was also monitored by ^{1}H NMR. The spectrum of a solution of **6** (4 mg, 0.01 mmol) in CD_2Cl_2 (0.3 mL) was obtained, and then $(Ph_3C)BF_4$ (6.1 mg, 0.018 mmol) was added. A spectrum obtained after 1 h showed that

$$\underset{\mathbf{6}}{CpRu(BT\cdot H)} + (CPh_3)BF_4 \xrightarrow{CH_2Cl_2} [CpRu(BT)]BF_4 + HCPh_3 \quad (6)$$

all of **6** had reacted and that [CpRu(BT)]$^+$ was the only BT-containing product. When approximately half of **6** had reacted, the relative amounts of A and B were 85 and 15% (only trace amounts of C and D were observed at this time) compared to 66 and 34% of A and B in **6** before addition of $(CPh_3)BF_4$. Thus, this reaction also occurs selectively as observed for the reaction of **2** with HBF_4·Et_2O.

Preparation of [Cp*Ir(BT·Nuc)]$^+$ and [Cp*Ir(3-MeBT·Nuc)]$^+$ (Nuc = OMe, $CH(CO_2Me)_2$ and SEt) (7–12). These air-stable compounds were prepared by reaction of [Cp*Ir(BT)]$^{2+}$ or [Cp*Ir(3-MeBT)]$^{2+}$ with the nucleophiles as described in eq 2 and characterized by their elemental analyses (Table I), by ^{1}H NMR spectra (Table II), and in some cases by their molar conductivities. The ^{1}H NMR spectra were assigned by analogy to **2** and **3**. Selective decoupling experiments were used to confirm the assignments for **9** and **10**. The ^{1}H NMR spectra show that addition of MeO^-, $(MeO_2C)_2HC^-$, and EtS^- to either [Cp*Ir(BT)]$^{2+}$ or [Cp*Ir(3-MeBT)]$^{2+}$ results in the production of four isomers as was observed for the H^- addition reactions. The percentages of these isomers, A–D, were determined by integration of the ^{1}H NMR spectra of the compounds and are presented in Table VI. The methoxide and thioethoxide nucleophiles show a stronger preference for attack at C7 than H^-. The malonate anion shows approximately the same selectivity as H^-. The 3-Me group does not appear to cause major changes in the distributions of isomers.

The addition of an excess of $(Ph_3C)BF_4$ to an NMR tube solution of **7** in acetone-d_6 results in immediate reaction to regenerate the iridium BT dication as shown in eq 7. The only BT-containing product observed in the ^{1}H NMR spectrum was the iridium dicationic complex.

$$\underset{\mathbf{7}}{[Cp^*Ir(BT\cdot OMe)]^+} + Ph_3C^+ \xrightarrow[10\ min]{\text{acetone-}d_6} [Cp^*Ir(BT)]^{2+} + Ph_3COMe \quad (7)$$

The malonate adduct **9** also undergoes an abstraction reaction, eq 8. A solution of **9** (21 mg, 0.031 mmol) in

$$\underset{\mathbf{9}}{[Cp^*Ir(BT\cdot CH(CO_2Me)_2)]^+} + HBF_4\cdot Et_2O \xrightarrow[5.5\ h]{\text{acetone-}d_6} [Cp^*Ir(BT)]^{2+} + H_2C(CO_2Me)_2 \quad (8)$$

acetone-d_6 (0.3 mL) was prepared in an NMR tube. After the ^{1}H NMR spectrum was obtained, HBF_4·Et_2O (20 μL, 0.14 mmol) was added and the NMR spectrum was obtained periodically for 5.5 h at which time all of **9** had reacted. The BT iridium dication was the only BT-containing product. Cleavage of the C–C bond in **9** might seem surprising; however, abstractions of exo carbon groups by electrophiles have been reported. Semmelhack found that $[Cr(CO)_3(\eta^5\text{-}C_6H_6\text{-}R)]^-$ complexes (R = CN, CH_2CN, $C(CH_3)_2CN$, $CH(CO_2Et)_2$, and CH_2Ph, for example) react with electrophiles (CH_3I, benzophenone, Ph_3C^+, Et_3B, acetic acid, CF_3CO_2H, and H_2O) to produce Cr($CO)_3(\eta$-$C_6H_6)$ and the reacted carbanion.[34a,37]

Reactions of [Cp*Ir(BT)]$^{2+}$ with Phosphines. The immediate reaction of PMe_3 with [Cp*Ir(BT)]$^{2+}$ in CD_3NO_2 solution was observed by ^{1}H NMR. The resonances in the spectrum of the quantitatively produced yellow [Cp*Ir(BT·PMe_3)]$^{2+}$ (**13**) were assigned by analogy to **2**.

(33) (a) Mawby, A.; Walker, P. J. C.; Mawby, R. J. *J. Organomet. Chem.* **1973**, *55*, C39. (b) Mathew, M.; Palenik, G. J. *Inorg. Chem.* **1972**, *11*, 2809.

(34) (a) Semmelhack, M. F.; Hall, H. T., Jr.; Farina, R.; Yoshifuji, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 3535. (b) Werner, H.; Werner, R.; Burschka, C. *Chem. Ber.* **1984**, *117*, 152.

(35) (a) Churchill, M. R.; Scholer, F. E. *Inorg. Chem.* **1969**, *8*, 1950. (b) VanVurren, P. J.; Fletterick, R. J.; Meinwald, J.; Hughes, R. E. *J. Am. Chem. Soc.* **1971**, *93*, 4394.

(36) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

(37) Semmelhack, M. F.; Hall, H. T.; Jr.; Yoshifuji, M.; Clark, G. *J. Am. Chem. Soc.* **1975**, *97*, 1247.

The assignments were verified by selective decoupling experiments and also by synthesis of $[Cp^*Ir(BT\text{-}d_2\cdot PMe_3)]^{2+}$. The ^1H NMR spectrum of the deuteriated product exhibited changes in the splitting patterns and peak intensities expected for a compound with deuterium at the 2- and 7-positions. The four isomers A–D were produced in the relative amounts given in Table VI. The stronger preference for C7 addition in this reaction (relative to H^- and $(MeO_2C)_2HC^-$) is similar to that observed for the MeO^- and EtS^- addition reactions. Complex **13** can be isolated as a yellow oil by addition of Et_2O to the reaction mixture.

If only half an equivalent of PMe_3 is added, the relative amounts of A and B in **13** are the same as those observed when an excess of PMe_3 is added. Compound **13** does not undergo further addition of PMe_3 to form a bis(phosphine) complex even when a threefold excess of the phosphine is added to **13**. There is no reaction between PMe_3 and $[CpRu(BT)]^+$ under the same conditions.

Nucleophilic addition of PPh_2Me to $[Cp^*Ir(BT)]^{2+}$ also occurs. The broadness of the peaks in the ^1H NMR spectrum of $[Cp^*Ir(BT\cdot PPh_2Me)]^{2+}$ precluded the determination of the chemical shifts for the minor isomers and the percentages of isomers present. However, the positions of the resonances for the major isomers were quite similar to those observed for **13A** suggesting that an analogous complex had resulted from the reaction. In contrast to **13**, $[Cp^*Ir(BT\cdot PPh_2Me)]^{2+}$ could not be isolated. Addition of Et_2O to a CD_3NO_2 solution of the PPh_2Me adduct precipitates $[Cp^*Ir(BT)]^{2+}$ suggesting that PPh_2Me is bound less strongly than PMe_3 in **13**. The $[Cp^*Ir(BT)]^{2+}$ complex (1.7 mg, 2.3 μmol) does not react with PPh_3 (0.6 mg, 2.3 μmol) in CD_3NO_2 (0.25 mL).

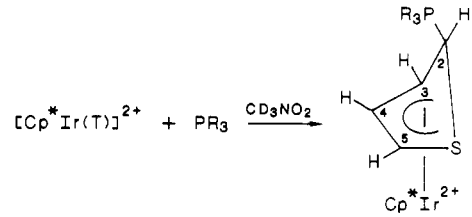
Double Nucleophilic Addition Reactions of $[Cp^*Ir(BT)]^{2+}$ and $[Cp^*Ir(3\text{-}MeBT)]^{2+}$. A compound tentatively identified as $Cp^*Ir(BT\cdot H_2)$ was produced by reaction of $[NaAlH_2(OCH_2CH_2OMe)_2]$ (0.20 mL of a 0.058 M solution in benzene, 0.012 mmol) and **2** (8.5 mg, 0.016 mmol) in benzene (3 mL) at 25 °C. Filtration of the reaction mixture followed by evaporation of the filtrate in vacuo produced an orange-yellow oil. The ^1H NMR spectrum of the complex ($CDCl_3$) was quite complex, and definitive assignments of the resonances were not made. However, the number and different intensities of the resonances suggested that more than one isomer of the product was present, which would seem reasonable for H^- addition to the four isomers of **2**. Peaks at *m/e* 464, 462, and 360 corresponding to M^+, $M^+ - H_2$, and $M^+ - C_8H_8$, respectively, were observed in the mass spectrum (EIMS) of the oil.

The addition of H^- to **4** (6.2 mg, 0.011 mmol) by reacting an excess of $Na[AlH_2(OCH_2CH_2OMe)_2]$ (0.1 mL of a 3.4 M solution in toluene, 0.34 mmol) in Et_2O produced a yellow solution. Filtration of the reaction mixture and evaporation of the solvent from the filtrate in vacuo yielded a tan oil. The ^1H NMR spectrum ($CDCl_3$) of the oil was complex and the resonances were not assigned, but the pattern and intensities of the peaks imply that more than one isomer of the product was produced in this reaction. The proposed product $Cp^*Ir(3\text{-}MeBT\cdot H_2)$ was characterized by its mass spectrum (EIMS, *m/e* 478 (M^+), 476 ($M^+ - H_2$, 360 ($M^+ - C_9H_{10}$)).

The complex $Cp^*Ir(BT\cdot(OMe)_2)$ was synthesized from NaOMe (from 2 mg of Na, 0.07 mmol) and **7** (9.8 mg, 0.017 mmol), stirring in MeOH (6 mL) at room temperature for 19 h. The solution was evaporated to dryness in vacuo and the resulting residue extracted with Et_2O. The Et_2O extract was filtered and the filtrate evaporated in vacuo to give a tan oil. The product was identified by its mass spectrum (EIMS, *m/e* 524 (M^+), 492 ($M^+ - OCH_3$), 462 ($M^+ - 2\ OCH_3$)).

These three complexes, $Cp^*Ir(BT\cdot H_2)$, $Cp^*Ir(3\text{-}MeBT\cdot H_2)$ and $Cp^*Ir(BT\cdot(OMe)_2)$, are very unstable; the initially yellow compounds slowly decompose under N_2 (within ~1–10 h). An η^4-coordination mode of the $BT\cdot H_2$ (or $BT\cdot(OMe)_2$) ligand would be the most reasonable for these neutral complexes. The analogous $Cp^*Ir(\eta^4\text{-}C_6H_6\cdot H_2)$[29] was characterized by mass spectrometry and ^1H and ^{13}C NMR spectra, but it was too unstable for elemental analysis.

Reactions of $[Cp^*Ir(T)]^{2+}$ with Phosphines and $NaBEt_3H$. The thiophene ring in $[Cp^*Ir(T)](BF_4)_2$ is even more reactive toward nucleophilic attack than the BT ligand in $[Cp^*Ir(BT)]^{2+}$. The reactions of $[Cp^*Ir(T)]^{2+}$ and phosphines were studied by NMR experiments; PMe_3, PPh_2Me, and PPh_3 were added to solutions of $[Cp^*Ir(T)]^{2+}$ in CD_3NO_2. The ^1H NMR spectra of the resulting NMR tube solutions showed signals[38] corresponding to an η^4-T complex, as shown in eq 9, as the only product. The



(9)

$PR_3 = PMe_3, PPh_2Me, PPh_3$

analogous $[Cp^*Rh(T)]^{2+}$ also reacted with PMe_3 to give an η^4-complex as the only product (in a CD_3NO_2 solution monitored by ^1H NMR).[39] Reaction of $P(OMe)_3$ with $[Cp^*Ir(T)]^{2+}$ in CD_3NO_2 resulted in the formation of $[Cp^*Ir(T\cdot P(O)(OMe)_2)]^+$ which was identified by its ^1H NMR spectrum (the $P(O)(OMe)_2$ resonance integrated to 6 H as opposed to 9 H which would be expected for the $P(OMe)_3$ adduct).[40] This reaction probably proceeds by initial addition of $P(OMe)_3$ to the T ring of $[Cp^*Ir(T)]^{2+}$ followed by a Michaelis–Arbuzov type rearrangement, as shown in eq 10. The proposed phosphonium intermediate

$$[Cp^*Ir(T)]^{2+} + P(OMe)_3 \xrightarrow{CD_3NO_2} [Cp^*Ir(T\cdot P(OMe)_3)]^{2+} \xrightarrow{H_2O} [Cp^*Ir(T\cdot P(O)(OMe)_2)]^+ + MeOH + H^+ \quad (10)$$

was not observed in the ^1H NMR spectrum of the reaction mixture, but an H_2O peak was. The reactions of $[(\eta\text{-}C_6H_6)_2Ru]^{2+}$[41] and $[(\eta\text{-}C_5Me_4Et)Rh(\eta\text{-}C_6H_6)]^{2+}$[42] with $P(OMe)_3$ also result in the formation of a phosphonate product. The $[Cp^*Ir(T)]^{2+}$ complex does not react with $P(OPh)_3$ in CD_3NO_2 at 25 °C.

The reaction of $[Cp^*Ir(T)]^{2+}$ (14 mg, 0.024 mmol) and $NaBEt_3H$ (40 μL of a 1 M solution in THF, 0.040 mmol)

(38) All spectra were obtained in CD_3NO_2 and were assigned by analogy to $[Mn(CO)_3(T\cdot PBu_3)]^+$.[10] (a) PMe_3: δ 6.47 (m, H5), 6.44 (m, H4), 6.06 (d, H2, J = 2.6 Hz), 4.54 (m, H3), 2.20 (s, Cp*), 1.85 (d, PMe_3, $J_{H\text{-}P}$ = 14.1 Hz). (b) PPh_2Me: δ 8.04–7.73 (m, PPh_2Me), 6.64 (m, H5), 6.12 (m, H4), 6.01 (d, H2, J = 1.1 Hz), 4.58 (m, H3), 2.16 (s, Cp*), 2.50 (d, PPh_2Me, $J_{H\text{-}P}$ = 13.3 Hz). (c) PPh_3: δ 8.04–7.79 (m, PPh_3), 7.08 (m, H5), 5.94 (m, H4), 5.89 (m, H2), 4.68 (m, H3), 2.16 (s, Cp*).

(39) The spectrum was obtained in CD_3NO_2 and assigned by analogy to $[Mn(CO)_3(T\cdot PBu_3)]^+$.[10a] NMR: δ 6.66 (m, H5), 6.20 (m, H4), 5.64 (d, H2, J = 2.4 Hz), 4.49 (m, H3), 2.08 (s, Cp*), 1.82 (d, PMe_3, $J_{H\text{-}P}$ = 14.2 Hz).

(40) (CD_3NO_2): δ 6.34 (br s, H5), 6.23 (m, H4), 5.40 (m, H2), 4.25 (m, H3), 3.74 (d, $PO(OMe)_2$, $J_{H\text{-}P}$ = 12.1 Hz), 2.18 (s, Cp*).

(41) Sweigart, D. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1159.

(42) Bailey, N. A.; Blunt, E. H.; Fairhurst, G.; White, C. *J. Chem. Soc., Dalton Trans.* **1980**, 829.

Table VII. Cyclic Voltammetric Data[a]

complex	cathodic peak potential(s),[b,c] V
$[Cp^*Rh(T)](PF_6)_2$	−0.56, −0.77, i
$[Cp^*Rh(BT)](PF_6)_2$	−0.43, −0.79, i
$[Cp^*Ir(T)](BF_4)_2$	−0.33, −0.53, i
$[Cp^*Ir(BT)](BF_4)_2$	−0.54, q

[a] All measurements made in CH_3NO_2, scan rate = 500 mV/s, with 0.1 M Bu_4NPF_6 as the supporting electrolyte. [b] Referenced to Ag/AgCl (3.0 M NaCl). [c] i = irreversible; q = quasi-reversible.

in benzene (5 mL) produced a gold-colored solution after 5 min at 25 °C. The solution was filtered and the solvent removed from the filtrate in vacuo which gave an orange residue. The ^1H NMR spectrum ($CDCl_3$) of the product showed signals at 4.78 (m, 2 H), 4.31 (m, 2 H), and 1.99 ppm (s, 15 H). The splitting patterns of the 4.78 and 4.31 ppm resonances are similar to those observed for T, but the chemical shifts occur at much higher field than those of T ($CDCl_3$: 7.35 (m, H2, H5), 7.14 ppm (m, H3, H4)).[43] The ^1H NMR spectrum suggests that the reaction which occurred was not H^- addition to the T ligand but rather a 2e reduction of the iridium complex as shown in eq 11.

$$[Cp^*Ir(T)](BF_4)_2 + 2NaBEt_3H \xrightarrow[5\ min]{benzene} Cp^*Ir(\eta^4\text{-}T) + 2NaBF_4 + 2BEt_3 + H_2 \quad (11)$$

Other reductions of transition-metal complexes by $NaBEt_3H$ have been reported.[44] The proposed identity of the product is supported by its mass spectrum (EIMS, m/e 412 (M^+), 360 ($M^+ - C_4H_4$), 84 (T^+)) and also by its preparation from $[Cp^*Ir(T)]^{2+}$ and an excess of Cp_2Co[45] in CH_2Cl_2 at 25 °C (eq 12). The η^4-T complex is relatively unstable and has not been characterized by elemental analysis.

$$[Cp^*Ir(T)]^{2+} + 2Cp_2Co \xrightarrow[5\ min]{CH_2Cl_2} Cp^*Ir(\eta^4\text{-}T) + 2Cp_2Co^+ \quad (12)$$

The η^4-bonding mode is proposed on the basis of the ^1H NMR chemical shifts for the T ligand and by analogy to the $Cp^*Ir(\eta^4\text{-}C_6Me_6)$ complex.[47] The T resonances in the ^1H NMR spectrum ($CDCl_3$) of $Cr(CO)_3(\eta\text{-}T)$ occur at 5.59 (m, H3, H4) and 5.37 ppm (m, H2, H5).[43] An η^4-coordination of T would make the ligand more dienelike and consequently shift the ^1H resonances to higher field. The $Cp^*Ir(\eta^4\text{-}C_6Me_6)$ complex can be synthesized by electrochemical or chemical reduction of $[Cp^*Ir(\eta^6\text{-}C_6Me_6)]^{2+}$, and the η^4-bonding of C_6Me_6 is clearly established by its ^1H NMR spectrum (2.19 (s, 6 H), 1.74 (s, 6 H), 1.66 (s, 6 H), 1.91 ppm (s, 15 H)), but neither mass spectral nor microanalytical data were reported for this compound.

A cyclic voltammogram of $[Cp^*Ir(T)]^{2+}$ shows irreversible cathodic peaks at −0.33 and −0.53 V (Table VII), possibly to produce Cp*Ir(T). The $[Cp^*Rh(T)]^{2+}$ complex also has two irreversible cathodic peaks in its cyclic voltammogram. The cyclic voltammogram of $[Cp^*Rh(BT)]^{2+}$ was similar to that observed for $[Cp^*Rh(T)]^{2+}$; however, the electrochemical reduction of $[Cp^*Ir(BT)]^{2+}$ was quasi-reversible. The chemically reversible reduction of $[Cp^*Ir(C_6Me_6)]^{2+}$ to $[Cp^*Ir(\eta^4\text{-}C_6Me_6)]$[41] suggests that η^4-C_6Me_6 bonding might be more stable than η^4-thiophene bonding in Cp*Ir(T).

Conclusions

Reactions of transition-metal model complexes of π-bound T with nucleophilic species such as hydride and sulfide, which are likely to be on HDS catalyst surfaces, have provided a basis for understanding the reactivity of T adsorbed on HDS catalysts.[11] Hydride addition to $[CpRu(T)]^+$ resulted in C–S bond cleavage[11c,d] and to $[Mn(CO)_3(T)]^+$ produced $Mn(CO)_3(T\text{-}H)$[11a] which could be protonated to give a 2,3-dihydrothiophene (2,3-DHT) complex. The intermediacy of 2,3-DHT in the HDS of T has been proposed,[50] and cleavage of the C-S bond of T is certainly an important step in the HDS process. Other types of reactions which occur over HDS catalysts, such as deuterium exchange, have been accounted for by studies of $[CpRu(\eta\text{-}T)]^+$ compounds. Thus, π-thiophene complexes serve as very useful models for reactions of T that might occur on HDS catalysts.

In attempts to model reactions of benzo[*b*]thiophene on HDS catalysts, we find that BT prefers to π-coordinate via the benzene, rather than the thiophene ring, in $[CpRu(BT)]^+$, $[Cp^*Ir(BT)]^{2+}$, and $[Cp^*Rh(BT)]^{2+}$ complexes.[16] This type of coordination activates C4–C7 toward reactions with H^- and other nucleophiles giving primarily C7 adducts. Products that might lead to or are similar to proposed intermediates in the HDS of BT such as 2,3-dihydrobenzothiophene[51] or thiophenols,[7a,52] were not observed. Thus, the π-arene-bonded complexes do not seem to account for the HDS reactivity of BT. Better model complexes might involve coordination of all or part of the thiophene ring of BT to the transition-metal center.

Acknowledgment. We thank Dr. Lee Daniels for the crystal structure determination of CpRu(BT·H) and Johnson Matthey, Inc., for a generous loan of $RuCl_3$.

Registry No. **1**, 114032-45-0; **2A**, 114057-28-2; **2B**, 114032-47-2; **2C**, 114032-49-4; **2D**, 114032-51-8; **3A**, 114032-53-0; **3B**, 114032-55-2; **3C**, 114032-57-4; **3D**, 114032-59-6; **4A**, 114032-61-0; **4B**, 114032-63-2; **4C**, 114057-30-6; **4D**, 114032-65-4; **5A**, 114032-67-6; **5B**, 114032-69-8; **5C**, 114032-71-2; **5D**, 114057-32-8; **6A**, 114032-72-3; **6B**, 114032-73-4; **6C**, 114032-74-5; **6D**, 114032-75-6; **7A**, 114032-77-8; **7B**, 114032-79-0; **7C**, 114032-81-4; **7D**, 114032-83-6; **8A**, 114032-85-8; **8B**, 114032-87-0; **8C**, 114032-89-2; **8D**, 114032-91-6; **9A**, 114032-93-8; **9B**, 114057-34-0; **9C**, 114032-95-0; **9D**, 114032-97-2; **10A**, 114032-99-4; **10B**, 114033-01-1; **10C**, 114057-36-2; **10D**, 114033-03-3; **11A**, 114033-05-5; **11B**, 114033-07-7; **11C**, 114033-09-9; **11D**, 114033-11-3; **12A**, 114033-13-5; **12B**, 114033-15-7; **12C**, 114057-38-4; **12D**, 114033-17-9; **13A**, 114033-19-1; **13B**, 114033-21-5; **13C**, 114033-23-7; **13D**, 114033-25-9; 2-MeBT, 1195-14-8; BT-d_2, 62338-39-0; $[Cp^*IrCl_2]_2$, 12354-84-6; $[Cp^*Ir(BT)](BF_4)_2$, 114033-27-1; $[Cp^*Ir(3\text{-}MeBT)](BF_4)_2$, 114033-29-3; $[Cp^*Ir(2,3\text{-}Me_2BT)](BF_4)_2$, 114033-31-7; $[CpRu(BT)]PF_6$,

(43) Guilard, R.; Tirouflet, J.; Fournari, P. *J. Organomet. Chem.* **1971**, *33*, 195.

(44) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553.

(45) The Cp_2Co was prepared by Na/K alloy reduction of $[Cp_2Co]PF_6$[46] dissolved in THF (45 min at room temperature). The THF solution was filtered and the filtrate evaporated in vacuo to give a pink-purple residue of Cp_2Co.

(46) Sheats, J. E.; Dierkes, J.; de Marco, L. *Organomet. Synth.* **1986**, *3*, 84.

(47) Bowyer, W. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 5657.

(48) (a) Kang, J. W.; Childs, R. F.; Maitlis, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 720. (b) Wakatsuki, Y., Yamazaki, H. *J. Organomet. Chem.* **1974**, *64*, 393. (c) Albright, J. O.; Datta, S.; Dezube, B.; Kouba, J. K.; Marynick, D. S.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1979**, *101*, 611. (d) Hull, J. W.; Gladfelter, W. L. *Organometallics* **1984**, *3*, 605.

(49) A benzonitrile-solvated complex, $[Pd(Me_4\text{-}T)Cl_2]$, was tentatively suggested to contain η^4-bonded Me_4T. Russell, M. J. H.; White, C.; Yates, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 857.

(50) (a) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1980**, *61*, 128. (b) Kieren, P.; Kemball, C. *J. Catal.* **1965**, *4*, 394.

(51) (a) Givens, E. N.; Venuto, P. B. *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **1970**, *15*, A183. (b) Geneste, P.; Bonnet, M.; Frouin, C.; Levaché, D. *J. Catal.* **1980**, *61*, 277.

(52) Landa, S.; Mrnkova, A. *Collect. Czech. Chem. Commun.* **1966**, *31*, 2202.

114033-33-9; $NaCH(CO_2Me)_2$, 18424-76-5; [CpRu(BT-d_2)]PF_6, 114033-35-1; $CpRu(NCMe)_3PF_6$, 84987-57-5; [Cp*Ir(BT-d_2)]$(BF_4)_2$, 114033-37-3; PPN[$HFe(CO)_4$], 56791-54-9; [Cp*Ir(BT·PPh_2Me)]$^{2+}$, 114057-39-5; [Cp*Ir(T)]$(BF_4)_2$, 112068-91-4; [Cp*Ir(T·PMe_3)]$^{2+}$, 114033-38-4; [Cp*Ir(T·PPh_2Me)]$^{2+}$, 114033-39-5; [Cp*Ir(T·PPh_3)]$^{2+}$, 114033-40-8; [Cp*Rh(T)]$(PF_6)_2$, 112068-87-8; [Cp*Ir(T·P(O)$(OMe)_2$)]BF_4, 114033-42-0; [Cp*Rh(T·PMe_3)]$(BF_4)_2$, 114033-44-2; Cp*Ir(η^4-T), 114057-40-8; Cp_2Co, 1277-43-6; [Cp*Rh(BT)]$(PF_6)_2$, 112068-89-0.

Supplementary Material Available: Tables of least-squares planes for **6** and ^1H NMR data for all isomers of complexes **2–13** (6 pages); a listing of structure factors for **6** (11 pages). Ordering information is given on any current masthead page.

EPR Studies of the 1,2-Diketone Chelate Paramagnetic Complexes Produced in the Photochemical Reactions of Hexacarbonylbis(η^5-2,4-cyclopentadien-1-yl)dimolybdenum, $[CpMo(CO)_3]_2$, and 1,2-Diketones

Minoru Hanaya,[1a] Shozo Tero-Kubota,[1b] and Masamoto Iwaizumi*,[1a]

Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira, Sendai 980, and Okazaki National Research Institutes, Institute for Molecular Science, Okazaki 444, Japan

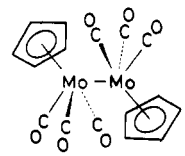
Received August 12, 1987

The paramagnetic products generated in the photochemical reaction of hexacarbonylbis(η^5-2,4-cyclopentadien-1-yl)dimolybdenum, $[CpMo(CO)_3]_2$, with a series of 1,2-diketones have been examined by the EPR spectroscopy. The observed paramagnetic products are shown to have a structure in which the 1,2-diketone chelates to Mo in $CpMo(CO)_2$, which is produced by photocleavage of the Mo–Mo bond and subsequent elimination of one of the carbonyl groups. The series of the complexes show marked changes of the spin distribution in the molecules with the 1,2-diketone ligands; i.e., in some cases most of the unpaired spin is distributed on the 1,2-diketone ligand, while in other cases the spin is distributed mainly on the fragment $Mo(CO)_2^{2+}$. The isotropic g values and Mo hyperfine (hf) coupling constants change with the spin distribution in the complexes, and a good correlation was observed between the g and Mo hf coupling values. The change of the spin densities on the 1,2-diketone ligands correlate well with the orbital energies of LUMO's of the 1,2-diketones.

Introduction

The chemical reactivity of metal carbonyl complexes containing a metal–metal bond has been the subject of extensive study. It has been shown that photolytic cleavage of the metal–metal bonds commonly occurs and the resulting paramagnetic species undergo various reactions.[2,3] Although the paramagnetic intermediates are too reactive to be detected directly by EPR, they are known to be trapped by quinones or 1,2-diketones to form moderately stable paramagnetic complexes.[4-15] The structure and electronic configuration of these complexes are interesting because both the central metal and the 1,2-diketone ligands can accept the unpaired electron.

Hexacarbonylbis(η^5-2,4-cyclopentadien-1-yl)dimolybdenum, $[CpMo(CO)_3]_2$, has a Mo–Mo bond,[16] and cleavage of the bond occurs by the near-UV and visible photoirradiation with a high quantum yield.[17,18] Though $[CpMo(CO)_3]_2$ has been shown to undergo photochemical reactions with di-*tert*-butyl-1,2-benzoquinones, *o*-chloranil, and fluorinated 1,2-diketones to yield paramagnetic products,[11,12] details of the structures of the products are not known. Few reports have appeared on paramagnetic products containing the cyclopentadienyl group. In the present work, we examine the photochemical reactions of $[CpMo(CO)_3]_2$



with a series of 1,2-diketones involving *o*-quinones and

(1) (a) Chemical Research Institute of Non-Aqueous Solutions, Tohoku University. (b) Okazaki National Research Institutes. Present address: Chemical Research Institute of Non-aqueous Solutions, Tohoku University.
(2) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979.
(3) Geoffroy, G. L. *J. Chem. Educ.* **1983**, *60*, 861.
(4) Alberti, A.; Camaggi, C. M. *J. Organomet. Chem.* **1978**, *161*, C63.
(5) Alberti, A.; Camaggi, C. M. *J. Organomet. Chem.* **1979**, *181*, 355.
(6) Bowmaker, G. A.; Campbell, G. K. *Aust. J. Chem.* **1979**, *32*, 1897.
(7) Foster, T.; Chen, K. S.; Wan, J. K. S. *J. Organomet. Chem.* **1980**, *184*, 113.
(8) Creber, K. A. M.; Wan, J. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 2101.
(9) Creber, K. A. M.; Ho, T.-I.; Depew, M. C.; Weir, D.; Wan, J. K. S. *Can. J. Chem.* **1982**, *60*, 1504.
(10) Tumanskii, R. L.; Sarbasov, K.; Solodovnikov, S. P.; Bubnov, N. N.; Prokof'ev, A. I.; Kabachnik, M. I. *Dokl. Akad. Nauk SSSR* **1981**, *259*, 611.
(11) Sarbasov, K.; Solodovnikov, S. P.; Tumanskii, B. L.; Bubnov, N. N.; Prokof'ev, A. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 1509.
(12) Sarbasov, K.; Tumanskii, B. L.; Solodovnikov, S. P.; Bubnov, N. N.; Prokof'ev, A. I.; Kurykin, M. A.; Kabachnik, M. I. *Khim. Fiz.* **1982**, 1570.
(13) Abakumov, G. A.; Cherkasov, V. K.; Shalnova, K. G.; Teplova, I. A.; Razuvaev, G. A. *J. Organomet. Chem.* **1982**, *236*, 333.
(14) Depew, M. C.; Adeleke, B. B.; Rutter, A.; Wan, J. K. S. *Can. J. Chem.* **1985**, *63*, 2281.
(15) Vlček, A., Jr. *J. Organomet. Chem.* **1986**, *306*, 63.
(16) (a) Wilson, F. C.; Shoemaker, D. P. *J. Chem. Phys.* **1957**, *27*, 809. (b) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086.
(17) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 4246.
(18) Hughey IV, J. L.; Bock, C. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 4440.

0276-7333/88/2307-1500$01.50/0