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Lewis Acid Adducts (BH_3, Me^+, and Et^+) of the η^4 and η^2 Isomers of Cp* Ir(thiophene)

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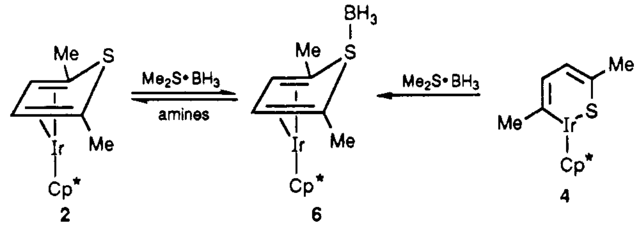
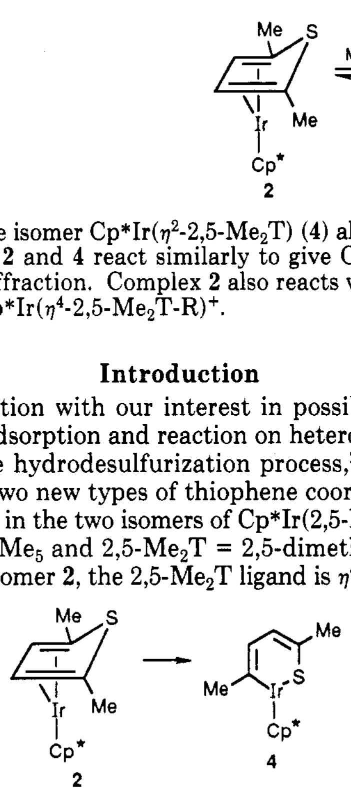
The η^4-thiophene complex Cp*Ir(η^4-2,5-Me_2T) (**2**), where 2,5-Me_2T is 2,5-dimethylthiophene, reacts with $Me_2S{\cdot}BH_3$ to give the BH_3 adduct Cp*Ir(η^4-2,5-$Me_2T{\cdot}BH_3$) (**6**), demonstrating the unusually high basicity of the sulfur in **2** as compared with that in Me_2S. Basic amines remove the BH_3 in **6** to give **2**. Surprisingly, the isomer Cp*Ir(η^2-2,5-Me_2T) (**4**) also reacts with $Me_2S{\cdot}BH_3$ to give **6**. The 2-methylthiophene analogues of **2** and **4** react similarly to give Cp*Ir(η^4-2-MeT$\cdot BH_3$) (**5**), whose structure was determined by X-ray diffraction. Complex **2** also reacts with R_3O^+ (R = Me, Et) to give the S-alkylated thiophene complexes Cp*Ir(η^4-2,5-Me_2T-R)$^+$.



Introduction

In connection with our interest in possible modes of thiophene adsorption and reaction on heterogeneous catalysts in the hydrodesulfurization process,[2] we recently reported[3,4] two new types of thiophene coordination to a metal center in the two isomers of Cp*Ir(2,5-Me_2T), where Cp* = η^5-C_5Me_5 and 2,5-Me_2T = 2,5-dimethylthiophene (eq 1). In isomer **2**, the 2,5-Me_2T ligand is η^4-coordinated via the four carbons, whereas in **4** the Ir has inserted into a C–S bond of the thiophene. The rearrangement of **2** to **4** means that **4** is the more stable isomer. In the communication,[3] we also noted that **2** reacts with THF$\cdot BH_3$ and $Me_2S{\cdot}BH_3$ to give the adduct Cp*Ir(η^4-2,5-$Me_2T{\cdot}BH_3$), in which the BH_3 is coordinated to the sulfur. In the present paper, we give details of not only the reaction of BH_3 with **2** but also the surprising reaction of **4** with BH_3. The 2-methylthiophene analogues Cp*Ir(η^4-2-MeT) (**1**) and Cp*Ir(η^2-2-MeT) (**3**) react similarly.



(1)

Experimental Section

General Procedure. All operations were performed under a N_2 atmosphere in reagent grade solvents. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from Na/benzophenone and CH_2Cl_2 and hexane from CaH_2; benzene was distilled from $LiAlH_4$. The solvents were stored over 4-Å molecular sieves under N_2. The neutral Al_2O_3 (Brockmann, activity I) and basic Al_2O_3 (Brockmann, activity I) used for chromatography were deoxygenated at room temperature under high vacuum for 16 h, and the neutral Al_2O_3 was deactivated with 5% (w/w) N_2-saturated water; both were stored under N_2. The borane–tetrahydrofuran complex (THF$\cdot BH_3$, 1.0 M solution in THF), borane–methyl sulfide complex ($Me_2S{\cdot}BH_3$, 2.0 M solution in THF), triethylamine, morpholine, propargyldimethylamine, $(Me_3O)BF_4$, and $(Et_3O)BF_4$ were purchased from Aldrich Chemical Co. Cp*Ir(η^4-2-MeT) (**1**), Cp*Ir(η^4-2,5-Me_2T) (**2**), Cp*Ir(η^2-2-MeT) (**3**), and Cp*Ir(η^2-2,5-Me_2T) (**4**) were prepared as previously reported.[4]

Elemental analyses were performed by Galbraith Laboratories, Inc. The ^1H NMR spectra were recorded on a Nicolet NT-300 spectrometer using deuteriated solvents as internal locks and referenced to tetramethylsilane (TMS). Electron ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. Fast atom bombardment (FAB) spectra were run on a Kratos MS-50 mass spectrometer using a 2-nitrophenyl octyl ether/CH_2Cl_2 matrix.

Reaction of 1 with THF·BH_3 To Give Cp*Ir(η^4-2-MeT·BH_3) (5). A 0.040-g (0.094-mmol) amount of **1** was dissolved in 20 mL of THF at 0 °C. To this solution was added 0.20 mL (0.20 mmol) of THF$\cdot BH_3$ solution with stirring. The solution changed gradually from light yellow to colorless. After the mixture was stirred for 3-5 h at 0-15 °C, the solvent and excess THF$\cdot BH_3$ were removed under vacuum. The residue was washed with a small amount (~1 mL) of hexane at -20 °C and then recrystallized from hexane/CH_2Cl_2 (20:1) at -80 °C to give 0.032 g (78%, based on **1**) of **5** as white crystals (mp 95–96 °C dec). ^1H NMR ($CDCl_3$): δ 4.77 (m, 1 H), 4.60 (d, 1 H), 2.98 (d, 1 H), 1.99 (s, 15 H), 1.31 (s, 3 H), 0.92 (m, 3 H). EIMS: *m/e* 440 (M^+), 426 ($M^+ - BH_3$). Anal. Calcd for $C_{15}H_{24}BSIr$: C, 41.00; H, 5.51. Found: C, 40.78; H, 5.43.

Reaction of 2 with THF·BH_3 To Give Cp*Ir(η^4-2,5-Me_2T·BH_3) (6). A 0.040-g (0.091-mmol) amount of **2** and 0.20 mL (0.20 mmol) of the THF$\cdot BH_3$ were allowed to react in a similar manner as described for **1**. The solvent was removed in vacuo, and the residue was recrystallized from hexane/CH_2Cl_2 (20:1) at -80 °C to give 0.035 g (85%, based on **2**) of white crystals (**6**; mp 106–108 °C dec). ^1H NMR ($CDCl_3$): δ 4.46 (s, 2 H), 1.96 (s, 15 H), 1.28 (s, 6 H), 0.91 (m, 3 H). EIMS: *m/e* 454 (M^+), 440 ($M^+ - BH_3$). Anal. Calcd for $C_{16}H_{26}BSIr$: C, 42.38; H, 5.78. Found: C, 42.50; H, 5.91.

Reaction of 3 with THF·BH_3 To Give 5. To a solution of **3** (0.040 g, 0.094 mmol) in 20 mL of THF was added 0.20 mL (0.20 mmol) of THF$\cdot BH_3$ solution at 0 °C. The reaction mixture was stirred for 3–5 h at 0–15 °C. The solution changed gradually from red to light yellow. After evaporation of the solvent under vacuum,

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[1] Ames Laboratory is operated by the U.S. Department of Energy by Iowa State University under Contract W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.

[2] Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387.

[3] Chen, J.; Angelici, R. J. *Oganometallics* **1989**, *8*, 2277.

[4] Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199.

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the residue was washed with hexane two times (2 × 1 mL) at −20 °C and then recrystallized from hexane/CH_2Cl_2 (20:1) at −80 °C to yield 0.030 g (73%, based on **3**) of **5** as white crystals, which were identified by melting point, elemental analyses, and ^1H NMR and mass spectra.

Reaction of 4 with THF·BH$_3$ To Give 6. **4** (0.026 g, 0.060 mmol) in 20 mL of THF reacted with 0.14 mL (0.14 mmol) of THF·BH_3 solution in a manner similar to that described in the reaction of **3** to give 0.020 g (74%, based on **4**) of **6** as white crystals, which were identified by melting point and ^1H NMR and mass spectra.

Reaction of 2 with Me$_2$S·BH$_3$ To Give 6. A 0.027-g (0.061-mmol) amount of **2** was dissolved in 20 mL of THF at 0 °C. To this solution was added 0.10 mL (0.20 mmol) of $Me_2S·BH_3$ solution with stirring. The light yellow solution turned colorless gradually. After the mixture was stirred for 3 h at 0–15 °C, the solvent was removed in vacuo. The white residue was washed with hexane two times (2 × 1 mL) at −20 °C and then recrystallized from hexane/CH_2Cl_2 (20:1) at −80 °C to give 0.025 g (89%, based on **2**) of white crystals (**6**), which were identified by melting point and ^1H NMR and mass spectra.

Reaction of 4 with Me$_2$S·BH$_3$ To Give 6. To a solution of **4** (0.026 g, 0.060 mmol) in 20 mL of THF was added 0.10 mL (0.20 mmol) of $Me_2S·BH_3$ solution at 0 °C. The solution changed gradually from red to colorless. Workup of the reaction mixture as described for **2** gave 0.022 g (82%, based on **4**) of **6** as white crystals, which were identified by melting point and ^1H NMR and mass spectra.

Reaction of 6 with Et$_3$N To Give 4. A 0.035-g (0.077-mmol) amount of **6** was dissolved in 20 mL of hexane at room temperature. To this solution was added 0.50 mL (0.36 g, 3.6 mmol) of Et_3N with stirring. The mixture was stirred for 4 h at room temperature. The colorless solution turned red gradually. After removal of the solvent under vacuum, the residue was chromatographed (1.2 × 8 cm) on Al_2O_3 (neutral) with hexane as the eluant. The red eluate was collected. After evaporation of the solvent under vacuum, the crude product was recrystallized from hexane at −80 °C to give 0.024 g (71%, based on **6**) of dark red crystals (**4**; mp 146–147 °C dec). ^1H NMR ($CDCl_3$): δ 7.47 (d, 1 H), 7.34 (d, 1 H), 3.10 (s, 3 H), 2.78 (s, 3 H), 1.93 (s, 15 H). EIMS: *m/e* 440 (M^+).

Reaction of 6 with Morpholine To Give 2. A 0.015-g (0.033-mmol) amount of **6** reacted with 0.20 mL (0.20 g, 2.3 mmol) of morpholine for 6 h in a manner similar to that described for the reaction of **6** with Et_3N. The colorless solution gradually turned light yellow. After chromatography on Al_2O_3 (neutral), the crude product was recrystallized from hexane at −80 °C to give 0.011 g (75%, based on **6**) of **2** as light yellow crystals (mp 117–118 °C dec). ^1H NMR ($CDCl_3$): δ 4.53 (s, 2 H), 1.92 (s, 15 H), 1.11 (s, 6 H). EIMS: *m/e* 440 (M^+).

Reaction of 6 with (CH$_3$)$_2$NCH$_2$C≡CH To Give 2. **6** (0.015 g, 0.033 mmol) was reacted with $(CH_3)_2NCH_2C{\equiv}CH$ (0.20 g, 2.4 mmol) in a manner similar to that described for the reaction of **6** with morpholine to give 0.008 g (55%, based on **6**) of **2**, which was identified by melting point and ^1H NMR and mass spectra.

Conversion of 6 into 4 with Basic Al$_2$O$_3$. A solution of **6** (0.040 g) in 10 mL of benzene was chromatographed on a basic Al_2O_3 column (1.5 × 10 cm) at room temperature with benzene as the eluant. The light yellow band turned red gradually within 4 h. The red band was eluted and collected. After evaporation of the solvent, the red residue was recrystallized from hexane at −80 °C to give 0.033 g (85%) of dark red crystals (**4**; mp 147–148 °C dec). ^1H NMR ($CDCl_3$): δ 7.46 (d, 1 H), 7.34 (d, 1 H), 3.10 (s, 3 H), 2.78 (s, 3 H), 1.93 (s, 15 H). EIMS: *m/e* 440 (M^+). Anal. Calcd for $C_{16}H_{23}SIr$: C, 43.71; H, 5.27. Found: C, 43.70; H, 5.43.

Reaction of 2 with (Me$_3$O)BF$_4$ To Give 7. To a solution of **2** (0.015 g, 0.034 mmol) in CH_2Cl_2 (5 mL) was added $(Me_3O)BF_4$ (0.005 g, 0.034 mmol). After 10 min of stirring at room temperature, the solvent was removed under vacuum to dryness. The residue was recrystallized from CH_2Cl_2/Et_2O (1:10) at −80 °C to yield 0.014 g (78%, based on **2**) of the white product **7**. ^1H NMR ($CDCl_3$): δ 4.92 (s, 2 H), 2.08 (s, 3 H), 2.01 (s, 15 H), 1.53 (s, 6 H). FABMS: *m/e* 455 (M^+). Anal. Calcd for $C_{17}H_{26}SBF_4Ir$: C, 37.71; H, 4.84. Found: C, 37.78; H, 4.86

Table I. Crystal and Data Collection Parameters for the X-ray Diffraction Study of Cp*Ir(η^4-2-MeT•BH$_3$) (5)

formula	$IrSC_{15}BH_{24}$
fw	439.43
space group	$P2_12_12_1$ (No. 19)
a, Å	11.247 (5)
b, Å	11.585 (5)
c, Å	12.218 (3)
V, Å^3	1592 (2)
Z	4
D_{calc}, g/cm^3	1.833
cryst size, mm	0.2 × 0.2 × 0.3
μ(Mo Kα), cm^{-1}	84.63
data collecn instrum	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
orientation rflns: no.; range (2θ), deg	24; $15 < 2\theta < 33$
temp, °C	−75
scan method	ω scans
data collecn range, 2θ, deg	4–50
unique data: total no., no. with $F_o^2 > 3\sigma(F_o^2)$	1611, 1380
no. of params refined	163
transmissn factors: max, min (ψ scans)	1.0, 0.857
R^a	0.0304
$R_w{}^b$	0.0376
quality-of-fit indicator^c	0.925
largest shift/esd, final cycle	0.01
largest peak, e/Å^3	1.31

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

Reaction of 2 with (Et$_3$O)BF$_4$ To Give 8. This preparation was performed analogously to that for **7** from **2** (0.016 g, 0.036 mmol) and $(Et_3O)BF_4$ (0.007 g, 0.037 mmol). The white product was obtained by recrystallization from CH_2Cl_2/Et_2O (1:10) at −80 °C; yield 0.015 g (75%, based on **2**). ^1H NMR ($CDCl_3$): δ 4.96 (s, 2 H), 2.40 (q, 2 H), 1.99 (s, 15 H), 1.54 (s, 6 H), 1.14 (t, 3 H). FABMS: *m/e* 469 (M^+). Anal. Calcd for $C_{18}H_{28}SBF_4Ir$: C, 38.92; H, 5.08. Found: C, 39.04; H, 5.44.

X-ray Structure Determination of 5. Single crystals of complex **5** were obtained by recrystallization from hexane at −80 °C. A single crystal of approximate dimensions 0.2 × 0.2 × 0.3 mm was mounted on the end of a glass fiber. The intensity data of 1611 independent reflections, of which 1380 with $F_o^2 > 3\sigma(F_o^2)$ were observable, were collected with an Enraf-Nonius CAD4 diffractometer at −75 °C using Mo Kα radiation with ω-scans within the range $4° < 2\theta < 50°$. **5** crystallized in the orthogonal crystal system. The cell constants of **5** were detd. from a list of reflections found by an automated search routine. The empirical absorption correction was made on the basis of a series of ψ scans.

The position of the Ir atom was determined from a Patterson map. Following refinement of the scale factor and the Ir position, a difference Fourier map indicated the position of the S atom and all of the carbon atoms. After full-matrix refinement of these atoms, one large peak, close to the S atom, remained in the difference map. A study of the reaction conditions and mass spectral results indicated the probability that the atom was boron. Successful refinement of the structure verified the identity of the boron atom. In the final cycles of refinement, all of the atoms were given anisotropic temperature factors; the refinement included 164 variable parameters and converged with unweighted and weighted agreement factors[5] of $R = 0.0304$ and $R_W = 0.0376$.

Details of the procedures used in data collection and reduction information are given in Table I. Final positional and thermal parameters are listed in Table II. Bond lengths and selected bond angles for **5** are presented in Tables III and IV, respectively. The ORTEP drawing of **5** is given in Figure 1.

Results and Discussion

Reactions of Cp*Ir(η^4-thiophene) (1 and 2) with BH$_3$. Both THF·BH_3 and $Me_2S·BH_3$ react with complexes

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

Table II. Positional Parameters^a and Their Estimated Standard Deviations for Cp*Ir(η^4-2-MeT•BH$_3$) (5)

atom	*x*	*y*	*z*	*B*, Å^2
Ir	-0.20252 (4)	-0.17987 (3)	0.20956 (4)	1.983 (6)
S	-0.2626 (3)	0.0556 (2)	0.2814 (3)	2.92 (6)
C(2)	-0.198 (1)	-0.0048 (8)	0.160 (1)	3.4 (2)
C(3)	-0.290 (1)	-0.0668 (9)	0.0998 (9)	3.4 (2)
C(4)	-0.373 (1)	-0.114 (1)	0.174 (1)	3.0 (2)
C(5)	-0.339 (1)	-0.0796 (8)	0.285 (1)	2.6 (2)
C(6)	-0.409 (1)	-0.111 (1)	0.385 (1)	4.7 (3)
C(11)	-0.031 (1)	-0.260 (1)	0.172 (1)	3.4 (3)
C(12)	-0.120 (1)	-0.3363 (9)	0.137 (1)	3.0 (2)
C(13)	-0.191 (1)	-0.371 (1)	0.229 (1)	3.2 (2)
C(14)	-0.142 (1)	-0.318 (1)	0.3220 (9)	2.9 (2)
C(15)	-0.043 (1)	-0.244 (1)	0.287 (1)	3.2 (2)
C(21)	0.063 (1)	-0.202 (1)	0.103 (1)	4.0 (3)
C(22)	-0.134 (1)	-0.382 (1)	0.019 (1)	3.5 (3)
C(23)	-0.293 (1)	-0.457 (1)	0.230 (1)	4.2 (3)
C(24)	-0.187 (1)	-0.334 (1)	0.440 (1)	4.3 (3)
C(25)	0.041 (1)	-0.177 (1)	0.364 (1)	4.8 (3)
B	-0.377 (2)	0.172 (1)	0.246 (2)	4.5 (4)

^{a}Anisotropically refined atoms are 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 III. Bond Distances (Å)^a for Cp*Ir(η^4-2-MeT•BH$_3$) 5

Ir-C(2)	2.12 (1)	C(3)-C(4)	1.41 (2)
Ir-C(3)	2.12 (1)	C(4)-C(5)	1.47 (2)
Ir-C(4)	2.11 (1)	C(5)-C(6)	1.50 (2)
Ir-C(5)	2.14 (1)	C(11)-C(12)	1.41 (2)
Ir-C(11)	2.19 (1)	C(11)-C(15)	1.43 (2)
Ir-C(12)	2.22 (1)	C(11)-C(21)	1.50 (2)
Ir-C(13)	2.23 (1)	C(12)-C(13)	1.44 (2)
Ir-C(14)	2.21 (1)	C(12)-C(22)	1.54 (2)
Ir-C(15)	2.16 (1)	C(13)-C(14)	1.40 (2)
S-B	1.91 (2)	C(13)-C(23)	1.52 (2)
S-C(2)	1.79 (1)	C(14)-C(15)	1.47 (2)
S-C(5)	1.79 (1)	C(14)-C(24)	1.54 (2)
C(2)-C(3)	1.46 (2)	C(15)-C(25)	1.53 (2)

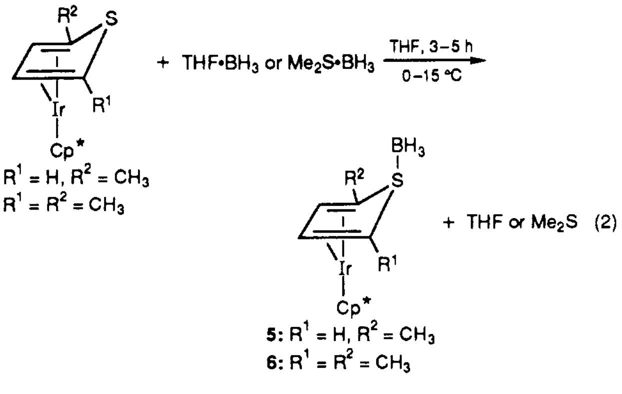
^{a}Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Selected Bond Angles (deg)^a for Cp*Ir(η^4-2-MeT•BH$_3$) (5)

B-S-C(2)	111.2 (7)	S-C(5)-C(6)	119.3 (9)
B-S-C(5)	107.7 (6)	C(4)-C(5)-C(6)	123 (1)
C(2)-S-C(5)	82.8 (5)	C(12)-C(11)-C(15)	108 (1)
S-C(2)-C(3)	109.0 (9)	C(11)-C(12)-C(13)	110 (1)
C(2)-C(3)-C(4)	110 (1)	C(12)-C(13)-C(14)	107 (1)
C(3)-C(4)-C(5)	108 (1)	C(13)-C(14)-C(15)	109 (1)
S-C(5)-C(4)	109.7 (8)	C(11)-C(15)-C(14)	106 (1)

^{a}Numbers in parentheses are estimated standard deviations in the least significant digits.

1 and **2** to give the white BH$_3$ adducts Cp*Ir(η^4-thiophene·BH$_3$) (**5** and **6**) in 78–89% yields (eq 2). The solid compounds are stable in air for a few hours but decompose quickly when their solutions are exposed to air.



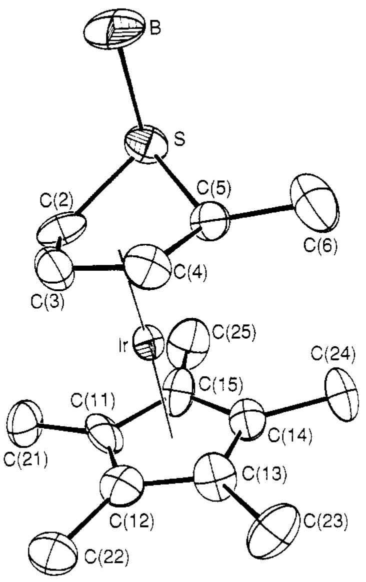


Figure 1. ORTEP drawing of Cp*Ir(η^4-2-MeT·BH$_3$) (**5**).

The elemental analyses and ^{1}H NMR and mass spectra of these complexes are consistent with the structure given in eq 2. X-ray diffraction studies of **5** (discussed later) and **6**[4] confirm the structures. Their formation via the displacement of THF or Me$_2$S from THF·BH$_3$ or Me$_2$S·BH$_3$ suggests that the sulfur in **1** and **2** is more basic than THF or Me$_2$S. The reverse reaction, the displacement of BH$_3$ from **6** with a large excess of Me$_2$S, does not occur in THF or hexane at room temperature during 15 h. To explore further the basicity of **2**, we compare it with other bases that are known[6] to increase in basicity toward BH$_3$ in the order Et$_2$O < THF < Me$_2$S < pyridine < Me$_3$N. Since **6** reacts with Et$_3$N in hexane at room temperature within 4 h to liberate **2**, Et$_3$N (pK_a = 10.7)[7] is more basic than **2**. Morpholine (pK_a = 8.36) and propargyldimethylamine (pK_a = 7.0) also displace **2** from **6** under the same conditions in 6 h. But pyridine (pK_a = 5.2) does not react with **6** under the same conditions even after 6 h; however, pyridine·BH$_3$ also does not react with **2**; the slowness of the pyridine reactions does not allow one to estimate the basicity of **2** relative to pyridine. However, one can state that the sulfur in **2** is unusually basic compared to Me$_2$S but is not as basic as the amines with pK_a's of 7.0 or greater.

In the reaction of **6** with Et$_3$N, complex **2** is formed initially as established by NMR studies, but Et$_3$N catalyzes[4] the rearrangement of **2** to **4**; thus, the final product of this reaction is **4**. Likewise, when basic Al$_2$O$_3$ reacts with **6**, **4** is the final product; in this case, basic Al$_2$O$_3$ catalyzes[4] the conversion of **2** to **4** so rapidly that **2** is not observed as an intermediate.

Reactions of Cp*Ir(η^2-thiophene) (3 and 4) with BH$_3$. Not only do the complexes **1** and **2** form BH$_3$ adducts but the more stable, ring-opened isomers **3** and **4** also react with BH$_3$ under the same conditions to give the same BH$_3$ adducts **5** and **6** (eq 3) in high isolated yields (73–82%). The reaction in eq 3 is remarkable in that the carbon and sulfur atoms in **3** and **4** form a bond under mild

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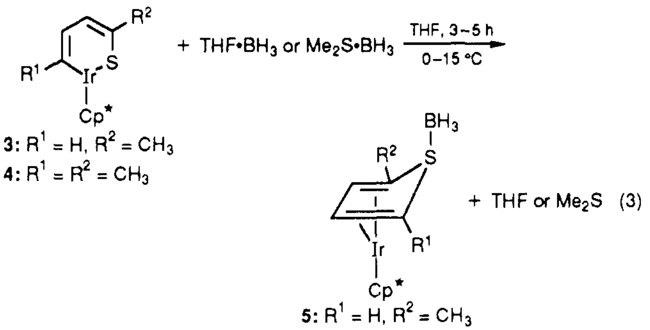
(6) (a) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984; p 188. (b) Shore, S. G. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975; p 127. (c) Stone, F. G. A. *Adv. Inorg. Chem. Radiochem.* **1960**, *2*, 279. (d) Stone, F. G. A. *Chem. Rev.* **1958**, *58*, 101.

(7) (a) Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworths: London, 1965. (b) Yukawa, Y. *Handbook of Organic Structural Analysis*; W. A. Benjamin: New York, 1965; p 584.



3: $R^1 = H, R^2 = CH_3$
4: $R^1 = R^2 = CH_3$

5: $R^1 = H, R^2 = CH_3$
6: $R^1 = R^2 = CH_3$

conditions to form η^4-thiophene complexes as the BH_3 adducts $Cp^*Ir(\eta^4\text{-thiophene}\cdot BH_3)$. Thus, the formation of the BH_3 adduct is a driving force for ring closure, since in the non-BH_3-adduct system Cp*Ir(thiophene) the open-ring forms **3** and **4** ($Cp^*Ir(\eta^2\text{-thiophene})$) are more stable than the closed-ring **1** and **2** ($Cp^*Ir(\eta^4\text{-thiophene})$) (eq 1).

The mechanism for ring closure in reaction 3 may involve **2** as an intermediate, which then forms the BH_3 adduct (eq 4 and 5). However, there is no ^1H NMR

$$\mathbf{4} \rightleftharpoons \mathbf{2} \tag{4}$$

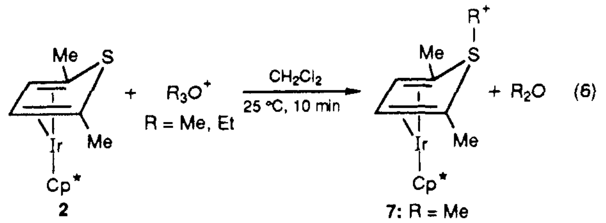
$$\mathbf{2} + BH_3 \rightarrow \mathbf{6} \tag{5}$$

evidence for **2** in solutions of **4** and, as established[4] in the conversion of **2** to **4**, the equilibrium (eq 4) must lie far toward **4**. Also, during the reactions (eq 3) of **3** and **4** with $THF\cdot BH_3$ in THF, there is no ^1H NMR evidence for **2** or any other intermediate. Thus, it seems likely that **2** is not an intermediate and reaction 3 occurs via BH_3 addition to either the Ir or S atom of **4**, which promotes ring closure to give the product **6**.

Structure of $Cp^*Ir(\eta^4\text{-2-MeT}\cdot BH_3)$ (5). The structure of **5** is very similar to that of **6**, which was reported earlier.[4] Both have structures which are essentially the same as that of **2**.[3] The plane of the four thiophene carbon atoms in **5** is nearly parallel (7.0 ± 3.0°) to the Cp* plane. The methyl group C(6) lies slightly (0.037 ± 0.016 Å) out of the four-carbon plane away from the Ir, which is 1.7237 ± 0.0004 Å below the plane. The sulfur is 0.855 ± 0.003 Å above the plane with an Ir–S distance of 2.944 ± 0.003 Å, indicating no bonding interaction. The thiophene ring is bent with a dihedral angle between the C(2)–C(3)–C(4)–C(5) and C(2)–S–C(5) planes of 39.6 (8)°.

Compared to the C–S distance in free thiophene (1.72 Å),[8] the C–S bonds (1.79 (1) Å) in **5** are significantly longer and presumably weaker. A similar lengthening is observed in both **2** and **6**.

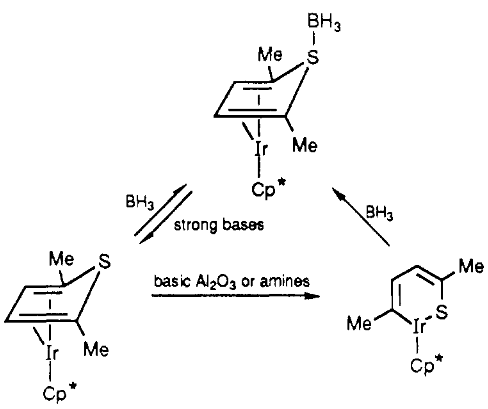
Reactions of $Cp^*Ir(\eta^4\text{-2,5-Me}_2T)$ (2) with $(Me_3O)BF_4$ and $(Et_3O)BF_4$. As in its reaction (eq 2) with BH_3, **2** also reacts rapidly with the alkylating agents $(R_3O)BF_4$ (R = Me, Et) to give the white *S*-alkyl sulfonium complexes **7** and **8** (eq 6) in 78 and 75% yields, respectively. In the ^1H NMR spectrum of **7**, the Me and H groups of the thiophene are at δ 1.53 and 4.92, respectively, which are downfield of the same groups (δ 1.11 and 4.53) in **2**. The $S\text{-}CH_3$ signal occurs at δ 2.08, which is upfield of that for typical sulfonium methyl groups, as in $CpRe(NO)(PPh_3)(CH_2SMe_2)^+$ at δ 2.60.[9] The somewhat higher field position in **7** may reflect the greater bacicity of the sulfur. There is a possibility that the Me or Et group in **7** or **8** is bonded to the Ir rather than the S. However, the CH_3 resonance in that case would be expected at still higher field as found in $IrCl_xMe_{3-x}(PMe_2Ph)_3$ (δ 0.0–1.0),[10] $CpRh[P(OMe)_3]_2(Me)^+$ (δ 0.9),[11] and $[\eta^5\text{-}C_5H_3(i\text{-}Pr)_2]Co(PMe_3)_2(Me)^+$ (δ 0.32).[12]



2

7: R = Me
8: R = Et

Scheme I



Unlike the BH_3 reaction (eq 3), the ring-opened complex **4** does not give **7** or **8** upon reaction with Me_3O^+ or Et_3O^+. Only decomposition to uncharacterized products occurs. In this reaction, perhaps R^+ adds at the metal, and the inertness of the Ir–C bond prevents rearrangement to the S-alkylated product **7** or **8**.

Conclusions. The sulfur of the η^4-thiophene in the $Cp^*Ir(\eta^4\text{-thiophene})$ complexes **1** and **2** is much more basic than the sulfur in free thiophene. This is a highly unusual situation where coordination of a ligand, a thiophene in this case, to a metal *enhances* the basicity of other donor atoms, the sulfur here, in the ligand. The sulfur in **1** and **2** is also more basic than in organic sulfides such as Me_2S and readily forms a BH_3 adduct (eq 2). Stronger amine bases will remove the BH_3 group. The ring-opened isomers $Cp^*Ir(\eta^2\text{-thiophene})$ (**3** and **4**) also react (eq 3) with BH_3 to give the closed-ring η^4-thiophene complexes $Cp^*Ir(\eta^4\text{-thiophene}\cdot BH_3)$. The remarkable ring-opening and ring-closing reactions that characterize this system are summarized in Scheme I. Such facile thiophene C–S bond cleavage and formation may be relevant to the mechanism of thiophene hydrodesulfurization (HDS); these aspects were discussed in another report.[4]

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Supplementary Material Available: Tables of additional bond angles, least-squares planes, and displacement parameters (5 pages); a table of calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

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(8) Bak, B.; Christensen, D.; Rastrup-Andersen, J.; Tannenbaum, E. *J. Chem. Phys.* **1956**, *25*, 892.

(9) McCormick, F. B.; Gleason, W. B.; Zhao, X.; Heah, P. C.; Gladysz, J. A. *Organometallics* **1986**, *5*, 1778.

(10) Shaw, B. L.; Smithies, A. C. *J. Chem. Soc. A* **1967**, 1047.

(11) Werner, H.; Neukomm, H.; Kläui, W. *Helv. Chim. Acta* **1977**, *60*, 326.

(12) Werner, H.; Hofmann, W. *Chem. Ber.* **1981**, *114*, 2681.