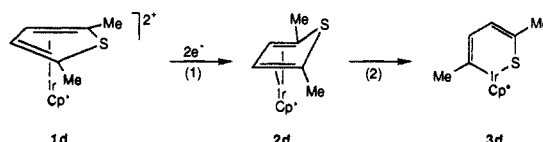


New Modes of Thiophene Coordination and Reactivity: Structures of Cp*Ir(η^2 -thiophene), an Iridathiabenzene, and Cp*Ir(η^4 -thiophene·BH₃)

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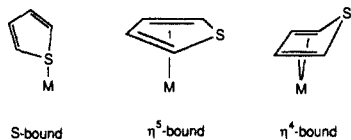
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Abstract: The [Cp*Ir(η^5 -2,5-Me₂T)](BF₄)₂ complex (**1d**), where Cp* is η^5 -C₅Me₅ and 2,5-Me₂T is 2,5-dimethylthiophene (other thiophenes react similarly), undergoes a two-electron reduction using Na[H₂Al(OCH₂CH₂OMe)]₂ to give Cp*Ir(η^4 -2,5-Me₂T) (**2d**). Basic Al₂O₃ catalyzes the isomerization of **2d** to the more stable and novel **3d**. X-ray and NMR studies

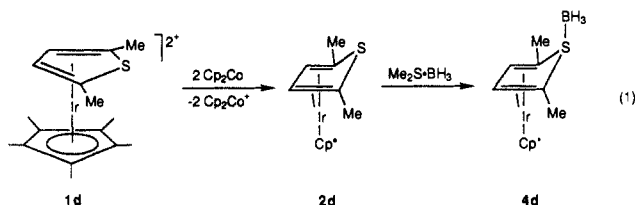


support a structure for **3d** in which the π -system of the six-membered ring is delocalized and may best be described as an iridathiabenzene. Oxidation of both **2d** and **3d** (surprisingly) yield **1d**. In addition to **2d** and small amounts of **3d**, the BH₃ adduct Cp*Ir(η^4 -2,5-Me₂T·BH₃) (**4d**) in which the BH₃ is coordinated to the sulfur of **2d** was isolated in trace amounts from the reduction of **1d**; the structure of **4d** was established by an X-ray diffraction investigation.

As part of an effort² to understand the mechanism(s) of the heterogeneously catalyzed hydrodesulfurization (HDS) of thiophenes, we have explored possible modes of thiophene coordination and subsequent reaction at metal centers. Three types of thiophene coordination to metals in their complexes are known:^{2,3} S-bound,⁴ where thiophene is a two-electron donor; η^5 -bound, where thiophene is a six-electron donor; and η^4 -bound, where it is a four-electron donor.⁵ The η^4 -thiophene complex (**2d**) was



recently prepared⁵ (eq 1) by a two-electron reduction of the 18-electron η^5 -thiophene complex, Cp*Ir(η^5 -2,5-Me₂T)²⁺,^{6,7} where Cp* = η^5 -C₅Me₅ and 2,5-Me₂T = 2,5-dimethylthiophene. The



X-ray-determined structure of **2d** shows a lengthening of the C-S bonds as compared with free or η^5 -coordinated thiophene. As a result of the change in thiophene structure, the sulfur atom in **2d** is an unusually strong donor, displacing Me₂S from Me₂S·BH₃ to form the BH₃ adduct (eq 1).⁵

In the present paper, we describe the reduction of Cp*Ir(η^5 -thiophenes)²⁺ with Na[H₂Al(OCH₂CH₂OMe)]₂, which gives not only complexes of type **2d** and **4d** but also a novel isomeric ring-opened thiophene complex which has an unusual structure and properties of an aromatic ring.

Experimental Section

General Procedures. All reactions were performed under an N₂ atmosphere in reagent grade solvents. Diethyl ether (Et₂O) and tetrahydrofuran (THF) were distilled from Na/benzophenone. CH₂Cl₂ and hexane from CaH₂, and benzene from LiAlH₄. The solvents were stored

over 4-Å molecular sieves under N₂, except for acetone which was stored over MgSO₄, and purged with N₂ prior to use. The neutral alumina (Brockmann, Activity I) and basic alumina (Brockmann, Activity I) used for chromatography were deoxygenated at room temperature in a high vacuum for 16 h, deactivated with 5% w/w N₂-saturated water for neutral alumina, and stored under N₂. Sodium bis(2-methoxyethoxy)aluminum hydride Na[H₂Al(OCH₂CH₂OMe)]₂ (Red-Al, 3.4 M solution in toluene) and triethylamine (Et₃N) were purchased from Aldrich Chemical Co. [Cp*IrCl₂]₂,⁸ [Cp*Ir(T)](BF₄)₂ (**1a**),⁶ [Cp*Ir(Me₄T)](PF₆)₂ (**1e**),⁷ and Cp₂Fe(PF₆)₂⁹ were prepared by literature methods. Thiophene (Aldrich, 99%) was purified as described previously.¹⁰ The thiophenes, 2-MeT, 3-MeT, and 2,5-Me₂T were used without further purification; Me₂T was prepared earlier.¹¹ Elemental analyses were performed by Galbraith Laboratories, Inc. The ¹H and ¹³C NMR spectra were recorded on a Nicolet NT-300 spectrometer by using deuterated solvents as internal locks and referenced to TMS. Electron ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer.

[Cp*Ir(2-MeT)](BF₄)₂ (**1b**). Following preparations of the analogous **1a** and **1e** complexes,^{6,7} a solution of [Cp*IrCl₂]₂ (0.570 g, 0.715 mmol) in acetone (10 mL) was treated with AgBF₄ (0.560 g, 2.87 mmol). After stirring for 5 min at room temperature, the resulting mixture was filtered. The volume of the filtrate was reduced to 3 mL under vacuum, and 2-MeT (1.8 mL, 1.83 g, 18.6 mmol) was added. The solution was refluxed for 5 min and then cooled to room temperature. A gray solid was produced by addition of CH₂Cl₂. The solid was filtered from the solution and then dissolved in CH₃NO₂. The CH₃NO₂ solution was filtered to remove a black insoluble impurity. Addition of CH₂Cl₂ (50 mL) to the filtrate gave the product **1b** as a white solid that was separated by filtration and dried in vacuo, yield 0.173 g (85%). This complex is slightly

(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.

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sensitive to moisture and should be stored under N_2 : 1H NMR (CD_3NO_2) δ 7.41 (d, 2 H), 7.36 (t, 1 H), 2.77 (s, 3 H), 2.46 (s, 15 H).

[Cp*Ir(3-MeT)](BF₄)₂ (1c). This complex was prepared in the same manner as **1b**. A solution of [Cp*IrCl₂]₂ (0.600 g, 0.753 mmol) in acetone (10 mL) was treated with AgBF₄ (0.580 g, 2.98 mmol), filtered, and refluxed with 3-MeT (1.8 mL, 1.83 g, 18.6 mmol) for 10 min. Further treatment as described for **1b** gave white, solid **1c**, yield 0.750 g (83%): 1H NMR (CD_3NO_2) δ 7.48 (m, 1 H), 7.43 (d, 1 H), 7.41 (s, 1 H), 2.64 (s, 3 H), 2.45 (s, 15 H).

[Cp*Ir(2,5-Me₂T)](BF₄)₂ (1d). This complex was prepared in a similar manner as [Cp*Ir(Me₄T)](PF₆)₂⁷ and **1b** by using [Cp*IrCl₂]₂ (0.370 g, 0.464 mmol), AgBF₄ (0.380 g, 1.95 mmol), and 2,5-Me₂T (1.5 mL, 1.48 g, 13.2 mmol). A white, solid product, **1d**, was obtained, yield 0.450 g (83%): 1H NMR (CD_3NO_2) δ 7.23 (s, 2 H), 2.74 (s, 6 H), 2.42 (s, 15 H).

Cp*Ir(η^4 -T) (2a). **1a** (0.170 g, 0.290 mmol) was dissolved in 30 mL of THF at room temperature. To this solution 0.17 mL (0.580 mmol) of Red-Al was added with stirring. The solution immediately turned yellow. After stirring for 5 h at room temperature, the solution was evaporated to dryness in vacuum. The orange-yellow residue was chromatographed on an alumina (neutral, 80–100 mesh) column (1.5 × 8 cm) at room temperature with hexane/CH₂Cl₂ (10:1) as the eluant. After vacuum evaporation of the solvent from the yellow band, the crude product was recrystallized from hexane/CH₂Cl₂ (10:1) at -80 °C to give 0.034 g (28.3%, based on **1a**) of **2a** as yellow needles (mp 116 °C, dec): MS *m/e* 412 (M⁺). Anal. Calcd for C₁₄H₁₉SiIr: C, 40.86; H, 4.65. Found: C, 40.78; H, 5.00.

Cp*Ir(η^4 -2-MeT) (2b), Cp*Ir(η^2 -2-MeT) (3b), and Cp*Ir(η^4 -2-MeT·BH₃) (4b). To a stirred solution of **1b** (0.420 g, 0.701 mmol) in 30 mL of THF was added 0.41 mL (1.40 mmol) of Red-Al at room temperature. The reaction solution immediately turned yellow but was stirred at room temperature for 6 h. After the solvent was removed under vacuum, the orange-red residue was chromatographed on Al₂O₃ (neutral) with hexane as the eluant. The yellow band which eluted first was collected, and then the red band was eluted with hexane/CH₂Cl₂ (10:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from hexane at -80 °C. From the first fraction, yellow crystals of **2b** and small amounts of white crystals of **4b** were obtained. The first fraction, a mixture of **2b** and **4b**, was again chromatographed in the same manner as described above to give yellow and light yellow fractions. The solvent was removed from each fraction under vacuum, and the residues were recrystallized from hexane at -80 °C. This gave yellow crystals of **2b** (0.063 g, 21% based on **1b**) and white crystals of **4b** (4%, based on **1b**). **2b**: mp 115 °C, dec; MS *m/e* 426 (M⁺). Anal. Calcd for C₁₅H₂₁SiIr: C, 42.33; H, 4.97. Found: C, 42.04; H, 5.17. **4b**: mp 95 °C dec; MS *m/e* 440 (M⁺). Anal. Calcd for C₁₅H₂₄BSiIr: C, 41.00; H, 5.51. Found: C, 41.04; H, 5.67. From the second fraction, 0.030 g (10%, based on **1b**) of **3b** as dark red crystals were obtained (mp 120–121 °C, dec): MS *m/e* 426 (M⁺). Anal. Calcd for C₁₅H₂₁SiIr: C, 42.33; H, 4.97. Found: C, 42.42; H, 5.24.

Conversion of 2b into 3b. (a) On Basic Alumina. **2b** (0.050 g) was dissolved in 10 mL of benzene; the resulting solution was chromatographed on basic alumina (1.5 × 15 cm) at room temperature with benzene as the eluant. The yellow band turned red within 0.5 h. The red eluate was collected and evaporated in vacuum to dryness. The dark red residue was recrystallized from hexane at -80 °C to give 0.045 g (90%) of **3b** as dark red crystals.

(b) With Et₃N. To a stirred solution of **2b** (0.050 g, 0.120 mmol) in 20 mL of hexane was added 0.5 mL (0.36 g, 3.56 mmol) of Et₃N at room temperature. The color of the reaction mixture changed gradually from yellow to red. After being stirred for 10 h at room temperature, the solvent was removed under vacuum. Further treatment of the residue as described in the preparation of **2a** gave 0.038 g (76%) of **3b**.

Cp*Ir(η^4 -3-MeT) (2c). Following procedures described for the preparation of **2a**, the reaction of **1c** (0.265 g, 0.442 mmol) with Red-Al (0.26 mL, 0.885 mmol) and subsequent treatment of the resulting mixture as described for **2a** gave 0.060 g (32%, based on **1c**) of yellow needles, **2c** (mp 98 °C, dec): MS *m/e* 426 (M⁺). Anal. Calcd for C₁₅H₂₁SiIr: C, 42.33; H, 4.97. Found: C, 42.76; H, 5.19.

Cp*Ir(η^4 -2,5-Me₂T) (2d), Cp*Ir(η^2 -2,5-Me₂T) (3d), and Cp*Ir(η^4 -2,5-Me₂T·BH₃) (4d). Similar to the preparation of **2b**, 0.200 g (0.326 mmol) of **1d**, and 0.192 mL (0.654 mmol) of Red-Al were allowed to react with stirring at room temperature for 6 h. Further treatment as described in the preparation of **2b**, **3b**, and **4b** and repeated recrystallization from hexane gave 0.033 g (23%, based on **1d**) of yellow crystalline **2d**, 0.005 g (3.5%, based on **1d**) of white crystals of **4d**, and 0.016 g (11.2%, based on **1d**) of **3d** as dark red crystals. **2d**: mp 118 °C dec; MS *m/e* 440 (M⁺). Anal. Calcd for C₁₆H₂₃SiIr: C, 43.71; H, 5.27. Found: C, 43.40; H, 5.57. **4d**: mp 105 °C dec; MS *m/e* 454 (M⁺). Anal. Calcd for C₁₆H₂₆BSiIr: C, 42.38; H, 5.78. Found: C, 42.30; H,

Table I. 1H NMR Data (δ) for Complexes **2a–e**, **3b,d** and **4b,d** in CDCl₃

compd	H2	H3	H4	H5	CH ₃ on Th	Cp*
2a	3.08 d	4.89 d	4.89 d	3.08 d		2.04 s
2b		4.59 d	4.76 m	2.97 d	1.96 s ^a	2.00 s
2c	2.89 s		4.75 d	2.97 d	2.14 s ^b	1.99 s
2d		4.53 s	4.53 s		1.11 s ^c	1.92 s
2e					1.07 s ^c	1.79 s
					1.93 s ^d	
3b		7.64 d	7.83 d	9.35 d	3.24 s ^a	1.98 s
3d		7.34 d	7.47 d		3.10 s ^a	1.93 s
					2.79 s ^e	
4b ^f		4.59 d	4.77 m	2.98 d	1.31 s ^a	2.00 s
4d ^g		4.46 s	4.46 s		1.28 s ^c	1.95 s

^a2-Me. ^b3-Me. ^c2,5-Me₂. ^d3,4-Me₂. ^e5-Me. ^f0.92 m, BH₃. ^g0.90 m, BH₃.

Table II. $^{13}C\{H\}$ NMR Data for Complexes **2b,d** and **3b,d** in CDCl₃ (ppm)

compd	C2	C3	C4	C5	CH ₃ on Th	C ₅ (CH ₃) ₅	C ₅ (CH ₃) ₅
2b	14.19	67.12	65.89	30.06	19.03 ^a	91.07	10.33
2d	21.29	68.03	68.03	21.29	18.54 ^{a,b}	90.36	9.90
3b	137.24	126.20	128.08	182.83	43.41 ^a	95.70	10.09
3d	140.76	125.69	132.26	180.99	28.74 ^b	95.21	10.10
					42.86 ^a		

^a2-Me. ^b5-Me.

5.86. **3d**: mp 146–148 °C dec; MS *m/e* 440 (M⁺). Anal. Calcd for C₁₆H₂₃SiIr: C, 43.71; H, 5.27. Found: C, 44.09; H, 5.40.

Conversion of 2d into 3d. (a) On Basic Alumina. A 0.100-g sample of **2d** was chromatographed on a basic Al₂O₃ column (1.5 × 20 cm) in a similar manner to that described in the conversion of **2b** into **3b** to give 0.092 g (92%) of **3d** as dark red crystals. **(b) With Et₃N.** Reaction of **2d** (0.050 g, 0.110 mmol) with 0.5 mL (0.36 g, 3.56 mmol) of Et₃N and subsequent treatment in a manner similar to that described in the conversion of **2b** into **3b** gave 0.040 g (80%) of **3d** as dark red crystals.

Cp*Ir(η^4 -Me₄T) (2e). Similar to the procedures described above for **2a**, **1e** (0.300 g, 0.468 mmol) was reacted with Red-Al (0.28 mL, 0.936 mmol) to yield 0.068 g (31%, based on **1e**) of yellow crystalline **2e** (mp 135–137 °C, dec): MS *m/e* 468 (M⁺). Anal. Calcd for C₁₈H₂₇SiIr: C, 46.23; H, 5.82. Found: C, 46.56; H, 5.92.

Reaction of 2d with Cp₂Fe*PF₆⁻. To a solution of **2d** (0.032 g, 0.0728 mmol) in 15 mL of CH₂Cl₂ was added Cp₂Fe*PF₆⁻ (0.050 g, 0.151 mmol) at 0 °C. The color of solution changed quickly from essentially black to green. After stirring for 2 h at 15–20 °C, the volume of the solution was reduced under vacuum to about 5 mL. White solid **1d** precipitated from the resulting solution. After decanting the solution, white **1d** was dried in vacuum: yield 0.042 g (98%); 1H NMR (CD_3NO_2) δ 7.22 (s, 2 H), 2.74 (s, 6 H), 2.42 (s, 15 H).

Reaction of 3d with Cp₂Fe*PF₆⁻. **3d** (0.020 g, 0.0455 mmol) was dissolved in 15 mL of CH₂Cl₂ at 0 °C. To this solution was added 0.030 g (0.0910 mmol) of Cp₂Fe*PF₆⁻. The color of the solution changed from red to green immediately. After 1 h stirring at 0–15 °C, the white product **1d** precipitated and was separated by decanting the solution and dried in vacuum: yield 0.026 g (98%); 1H NMR (CD_3NO_2) δ 7.23 (s, 2 H), 2.75 (s, 6 H), 2.43 (s, 15 H).

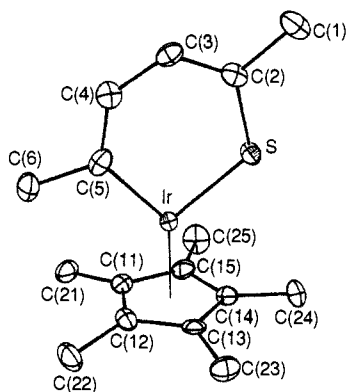
X-ray Structure Determinations of 3d and 4d. Single crystals of complexes **3d** and **4d** suitable for X-ray diffraction study were obtained by recrystallization from hexane solution at -80 °C. Single crystals of approximate dimensions 0.20 × 0.20 × 0.50 mm for **3d** and 0.10 × 0.12 × 0.15 mm for **4d** were mounted on the end of a glass fiber. The X-ray diffraction intensity data of 2744 and 2241 independent reflections, of which 2327 and 1530 with $F_o^2 > 3\sigma(F_o^2)$ were observable, were collected with an Enraf-Nonius CAD4 diffractometer at -100 °C and -90 °C by using Mo K α radiation with ω - 2θ and ω scans within the range $4^\circ < 2\theta < 50^\circ$ and $4^\circ < 2\theta < 45^\circ$ for **3d** and **4d**, respectively. Complexes **3d** and **4d** crystallized in the monoclinic crystal system. The cell constants of both complexes were determined from a list of reflections found by an automated search routine.

For **3d**, the position of the Ir atom was determined from a Patterson map. Following three cycles of full-matrix least-squares refinement, a difference Fourier map indicated the positions of all of the remaining non-hydrogen atoms, all of which were refined with anisotropic thermal parameters in the final cycles. A statistical analysis of the results indicated a secondary extinction effect, so a secondary extinction coefficient was included in the final refinement and refined to a value of 1.5×10^{-7} (in absolute units). Hydrogen atoms were not included in the calcula-

Table III. Crystal Data and Experimental Details for Structure Determinations of **3d** and **4d**

	3d	4d
formula	IrSC ₁₆ H ₂₃	C ₁₆ H ₂₆ IrSB
formula wt	439.63	453.46
space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
<i>a</i> , Å	7.488 (1)	8.774 (2)
<i>b</i> , Å	13.320 (1)	11.461 (2)
<i>c</i> , Å	16.097 (3)	17.109 (3)
β , deg	102.47 (1)	94.92 (1)
<i>V</i> , Å ³	1567.6 (7)	1714 (1)
<i>Z</i>	4	4
<i>d</i> _{calcd} , g/cm ³	1.863	1.757
crystal size, mm	0.2 × 0.2 × 0.5	0.10 × 0.12 × 0.15
μ (Mo K α), cm ⁻¹	85.96	78.631
data collection instrument	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo K α (λ = 0.71073 Å)	Mo K α (λ = 0.71073 Å)
orientation reflns, number, range (2θ)	25, 20° < 2θ < 32°	25, 18° < 2θ < 32°
temp, °C	-100	-90
scan method	ω - 2θ	ω -scans
data col. range, 2θ , deg	4-50	4-45
no. unique data, total:	2744	2241
with $F_o^2 > 3\sigma(F_o^2)$:	2327	1530
no. of parameters refined	164	172
trans. factors, max, min (ψ -scans)	1.0, 0.603	0.997, 0.686
correction factors, max, min (numerical)	1.23, 0.805	
<i>R</i> ^a	0.0329	0.0252
<i>R</i> _w ^b	0.0465	0.0346
quality-to-fit indicator ^c	1.15	0.849
largest shift/esd, final cycle	<0.01	0.01
largest peak, e/Å ³	1.39	0.615

^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 = $[\sum w(|F_o| - |F_c|)^2 / (N_{obs} - N_{parameters})]^{1/2}$.

**Figure 1.** ORTEP drawing of Cp*Ir(η^2 -2,5-Me₂T) (**3d**).

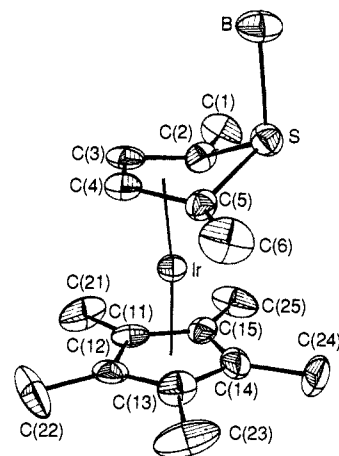
tions. The final cycle of refinement included 164 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.0329$ and $R_w = 0.0465$.

The structure of **4d** was solved by the Patterson method. All of the non-hydrogen atoms appeared in a difference map produced after the successful placement of the Ir atom. Hydrogen atoms were not included in the model. In the final cycles of refinement, all of the atoms were given anisotropic temperature factors; the refinement included 172 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.0252$ and $R_w = 0.0346$.^{12,13}

Pertinent data collection and reduction information for **3d** and **4d** are given in Table III. The final positional and thermal parameters are listed

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

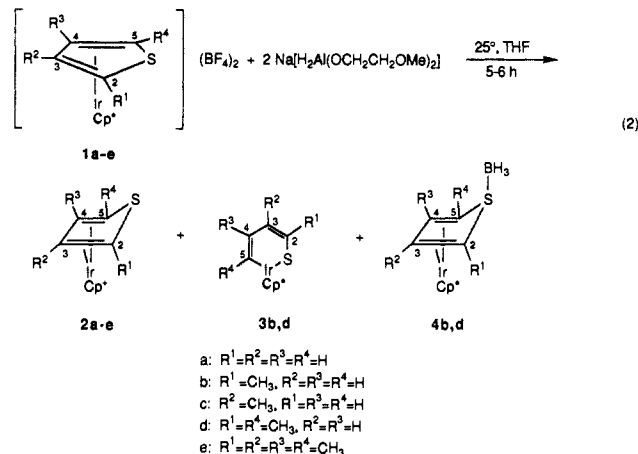
(13) All crystallographic calculations were carried out on a Digital Equipment Corporation Micro VAX II computer with the CAD4-SDP package; Enraf-Nonius: Delft, The Netherlands.

**Figure 2.** ORTEP drawing of Cp*Ir(η^4 -2,5-Me₂T·BH₃) (**4d**).

in Table IV. Bond lengths and selected bond angles are presented in Table V and VI, and ORTEP drawings of **3d** and **4d** given in Figures 1 and 2, respectively.

Results and Discussion

Preparations of the Complexes. The η^5 -bound thiophene and methyl-substituted thiophene complexes of iridium, [Cp*Ir(Th)]X₂ (Cp* = C₅Me₅, X = BF₄, Th = T (**1a**), 2-MeT (**1b**), 3-MeT (**1c**), 2,5-Me₂T (**1d**); X = PF₆, Th = Me₄T (**1e**)), react with 2 mol of Na[H₂Al(OCH₂CH₂OMe)₂] (Red-Al, 3.4 M solution in toluene) at room temperature for 5 to 6 h according to eq 2. Up to three



products could be isolated from the product mixtures. The complexes, [Cp*Ir(T)](BF₄)₂ (**1a**), [Cp*Ir(3-MeT)](BF₄)₂ (**1c**), and [Cp*Ir(Me₄T)](PF₆)₂ (**1e**), gave only one type of isolated product, Cp*Ir(η^4 -Th) (**2**) as yellow crystals in 28-32% yield. However, in the reactions of [Cp*Ir(2-MeT)](BF₄)₂ (**1b**) and [Cp*Ir(2,5-Me₂T)](BF₄)₂ (**1d**), not only were the yellow **2b** and **2d** complexes obtained (21, 23%) but also smaller amounts of dark red **3b** and **3d** (10, 11%) as well as still smaller yields of white **4b** and **4d** (4, 3.5%). All of the complexes are soluble in both polar and nonpolar organic solvents.

Structures (eq 2) of representative examples of all three types of complexes have been determined by X-ray diffraction. The structure of **2d** was described previously.⁵ Structural results for complexes **3d** and **4d** are described later in this paper. The type **2** complexes, Cp*Ir(η^4 -Th), have structures in which the thiophene ligand is η^4 -coordinated to the metal through the four carbon atoms.⁵ Type **3** complexes, isomers of **2**, contain a thiophene in which the iridium has inserted into a C-S bond; these complexes are designated Cp*Ir(η^3 -Th); this is a new mode of thiophene binding to a metal. Type **4** complexes, Cp*Ir(η^4 -Th·BH₃), contain an η^4 -thiophene as in **2**, but the BH₃ Lewis acid is coordinated to the sulfur.

Complexes **2** presumably form by a two-electron reduction of **1**, as occurred in the reaction of **1d** with Cp₂Co as the reducing agent (eq 1).⁵ The high electron density on the **2** complexes is

Table IV. Positional Parameters^a and Their Estimated Standard Deviations for **3d** and **4d**

atom	3d				4d			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Ir	0.09458 (3)	0.02033 (2)	0.27816 (1)	1.113 (5)	0.23150 (4)	0.24189 (3)	0.11414 (2)	2.007 (7)
S	0.2443 (2)	-0.0472 (1)	0.3980 (1)	1.58 (3)	0.2409 (3)	-0.0133 (2)	0.1296 (1)	2.65 (5)
C(1)	0.4748 (9)	-0.1954 (5)	0.4728 (5)	2.5 (1)	0.251 (1)	0.0535 (9)	-0.0302 (5)	4.0 (2)
C(2)	0.3765 (8)	-0.1503 (5)	0.3903 (4)	1.6 (1)	0.293 (1)	0.0870 (8)	0.0543 (5)	2.5 (2)
C(3)	0.3908 (8)	-0.1908 (4)	0.3134 (4)	1.7 (1)	0.433 (1)	0.1492 (7)	0.0836 (5)	2.9 (2)
C(4)	0.3124 (8)	-0.1553 (5)	0.2308 (4)	1.8 (1)	0.432 (1)	0.1605 (7)	0.1659 (5)	2.7 (2)
C(5)	0.1964 (9)	-0.0741 (5)	0.2048 (4)	1.9 (1)	0.299 (1)	0.1062 (7)	0.1932 (5)	2.2 (2)
C(6)	0.148 (1)	-0.0591 (6)	0.1091 (5)	2.9 (2)	0.268 (1)	0.0992 (9)	0.2788 (5)	4.1 (2)
C(11)	-0.1615 (8)	0.0845 (4)	0.2031 (4)	1.5 (1)	0.183 (1)	0.4093 (7)	0.0499 (5)	2.6 (2)
C(12)	-0.0157 (8)	0.1506 (5)	0.1988 (4)	1.6 (1)	0.214 (1)	0.4354 (7)	0.1317 (5)	2.8 (2)
C(13)	0.0635 (8)	0.1846 (4)	0.2832 (4)	1.6 (1)	0.104 (1)	0.3729 (8)	0.1723 (5)	3.3 (2)
C(14)	-0.0388 (8)	0.1415 (4)	0.3401 (4)	1.5 (1)	-0.001 (1)	0.3132 (8)	0.1156 (5)	3.0 (2)
C(15)	-0.1711 (8)	0.0776 (4)	0.2924 (4)	1.7 (1)	0.053 (1)	0.3334 (8)	0.0397 (5)	2.5 (2)
C(21)	-0.296 (1)	0.0387 (5)	0.1295 (5)	2.4 (1)	0.270 (1)	0.459 (1)	-0.0153 (5)	4.9 (3)
C(22)	0.030 (1)	0.1929 (5)	0.1187 (4)	2.5 (1)	0.337 (1)	0.5149 (8)	0.1670 (7)	5.1 (3)
C(23)	0.2134 (9)	0.2588 (5)	0.3065 (5)	2.1 (1)	0.087 (1)	0.381 (1)	0.2604 (6)	5.5 (3)
C(24)	-0.0065 (9)	0.1600 (5)	0.4345 (4)	2.0 (1)	-0.141 (1)	0.2463 (9)	0.1343 (8)	5.6 (3)
C(25)	-0.314 (1)	0.0198 (5)	0.3256 (5)	2.6 (2)	-0.017 (1)	0.2898 (9)	-0.0369 (6)	4.8 (3)
B					0.390 (2)	-0.1412 (9)	0.1435 (7)	3.5 (3)

^aAnisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(\text{Å}^2)/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

Table V. Bond Distances (Å)^a for **3d** and **4d**

	3d		4d	
Ir-S	2.203 (2)	2.937 (3)	C(1)-C(2)	1.498 (9)
Ir-C(2)		2.14 (1)	C(2)-C(3)	1.375 (9)
Ir-C(3)		2.16 (1)	C(3)-C(4)	1.41 (1)
Ir-C(4)		2.12 (1)	C(4)-C(5)	1.394 (9)
Ir-C(5)	1.986 (6)	2.11 (1)	C(5)-C(6)	1.52 (1)
Ir-C(11)	2.206 (6)	2.23 (1)	C(11)-C(12)	1.416 (8)
Ir-C(12)	2.206 (6)	2.25 (1)	C(11)-C(15)	1.458 (8)
Ir-C(13)	2.203 (6)	2.16 (1)	C(11)-C(21)	1.508 (9)
Ir-C(14)	2.242 (6)	2.20 (1)	C(12)-C(13)	1.433 (9)
Ir-C(15)	2.188 (6)	2.20 (1)	C(12)-C(22)	1.514 (9)
S-C(2)	1.713 (6)	1.81 (1)	C(13)-C(14)	1.435 (8)
S-C(5)		1.80 (1)	C(13)-C(23)	1.482 (9)
S-B		1.97 (1)	C(14)-C(15)	1.402 (9)
			C(14)-C(24)	1.506 (8)
			C(15)-C(25)	1.507 (9)

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

Table VI. Selected Bond Angles (deg)^a for **3d** and **4d**

	3d	4d
S-Ir-C(5)	94.3 (2)	
Ir-S-C(2)	117.2 (2)	
B-S-C(5)		110.7 (5)
C(2)-S-C(5)		110.0 (6)
S-C(2)-C(1)	116.0 (5)	82.6 (5)
S-C(2)-C(3)	122.6 (5)	117.7 (8)
S-C(5)-C(4)		108.6 (7)
S-C(5)-C(6)		109.3 (7)
C(1)-C(2)-C(3)	121.4 (6)	118.6 (8)
C(2)-C(3)-C(4)	128.2 (6)	125. (1)
C(3)-C(4)-C(5)	130.2 (6)	128.2 (6)
Ir-C(5)-C(4)	127.4 (5)	108.0 (1)
Ir-C(5)-C(6)	118.8 (5)	111.0 (1)
C(4)-C(5)-C(6)	113.8 (6)	124. (1)
C(11)-C(12)-C(13)	108.4 (6)	107. (1)
C(12)-C(11)-C(15)	106.9 (6)	109.1 (9)
C(12)-C(13)-C(14)	108.1 (6)	109.0 (9)
C(13)-C(14)-C(15)	107.7 (5)	107.0 (9)
C(11)-C(15)-C(14)	108.8 (5)	107.8 (9)

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

evident in the substantial upfield shifts of the H, CH₃, and Cp* protons, e.g., from Cp*Ir(η⁵-2,5-Me₂T)²⁺ (**1d**) [δ 7.23 (H), 2.74 (CH₃), 2.42 (Cp*)] to Cp*Ir(η⁴-2,5-Me₂T) (**2d**) [δ 4.53 (H), 1.11 (CH₃), 1.92 (Cp*)]. The Cp* resonance in the series of Cp*Ir(η⁴-Th) complexes (**2**) moves upfield with an increase in

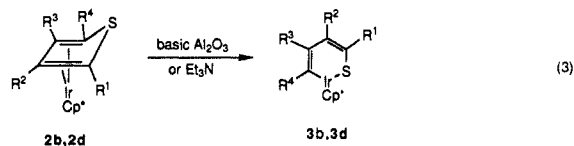
the number of Me groups in the Th from δ 2.04 in **2a** to δ 1.92 in **2e** (Table I).

The BH₃ adduct complexes **4b** and **4d**, obtained in low yields, presumably form as a result of the conversion of the BF₄⁻ anions of the **1** complexes to BH₃ upon reaction with Na[H₂Al(OCH₂CH₂OMe)₂]. The presence of the BH₃ group is indicated in the ¹H NMR spectra by signals at δ 0.92 for **4b** and 0.90 for **4d**, which are multiplets due to splitting by the boron. These values compare with δ 0.88 (CDCl₃) for THF·BH₃ and 0.85 (CDCl₃) for Me₂S·BH₃. The positions of the thiophene and Cp* resonances in **4b** and **4d** are very similar to those in **2b** and **2d** (Table I). Thus, the addition of BH₃ to the sulfur in **2** changes the Cp*Ir(η⁴-Th) chemical shifts very little.

Complexes of type **3** are formed only in the reactions (eq 2) of **1b** and **1d**. They appear not to form via complexes of type **2**, since complex **2d** is not converted to **3d** in the presence of Na-[H₂Al(OCH₂CH₂OMe)₂] under the conditions of reaction 2; it is not clear by what path complexes **3** form in these reactions (eq 2). The ¹H NMR and ¹³C NMR spectra of **3b** and **3d** (Tables I and II) are quite different than those of the corresponding complexes of types **2** and **4**. In complex **3d**, the two Me groups and 2 H atoms of the Th ring are no longer equivalent, and there are substantial downfield shifts of the Th protons in **3** as compared with **2**, e.g., Cp*Ir(η²-2,5-Me₂T) (**3d**) [δ 7.34, 7.47 (2 H), 3.10, 2.79 (2 CH₃)] vs Cp*Ir(η⁴-2,5-Me₂T) (**2d**) [δ 4.53 (2 H), 1.11 (2 CH₃)]. As discussed later, the downfield proton resonances in complexes of type **3** are associated with the aromatic character of the six-membered ring.

The Ir insertion into the C-S bond of the 2-MeT ring in **3b** could occur either at the carbon bearing the methyl group or at the carbon with the hydrogen. The ¹H NMR spectrum of **3b** shows a resonance at unusually low field, δ 9.35, which is attributed to the H at C(5) (see later discussion). This means that the Ir insertion occurs into the S-C(5) bond, i.e., at the carbon with the hydrogen, and there is no evidence for another isomer involving insertion into the S-C(2) bond.

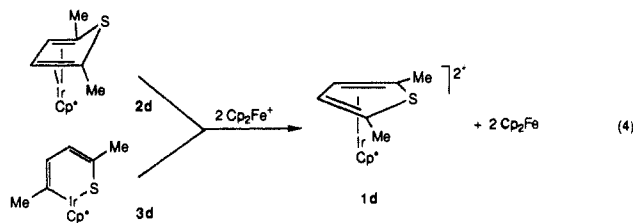
Conversion of Cp*Ir(η⁴-Th) (2**) into Cp*Ir(η²-Th) (**3**).** When the yellow complexes **2b** and **2d** in benzene solvent are passed through a column of basic alumina, the solution turns red on the column, and the red **3b** and **3d** are isolated in 90% yield (eq 3).



If neutral Al₂O₃ is used instead, there is no isomerization of **2b**

and **2d**; in fact, neutral Al_2O_3 is used to separate complexes **2** from **3** in the original preparation (eq 2), and there is no interconversion between **2** and **3** under those conditions. The conversion of **2b** and **2d** to **3b** and **3d** also occurs in the presence of the base Et_3N in hexane solvent, but 10 h are required at room temperature as compared with 30 min for basic Al_2O_3 . Other bases, NaOH , K_2CO_3 , EtONa , and pyridine, under the same conditions do not catalyze the conversion. One puzzling aspect of the conversions of **2** to **3** are the lack of conversion of **2a**, **2c**, and **2e** to their corresponding ring-opened complexes **3** in the presence of basic Al_2O_3 under the same conditions used for **2b** and **2d**. Although the mechanism of the catalyzed isomerization of **2b** and **2d** to **3b** and **3d** is not known, this is a thermodynamically very favorable reaction, since none of the complexes **2** remain after the isomerization.

Oxidation of $\text{Cp}^*\text{Ir}(\eta^4\text{-2,5-Me}_2\text{T})$ (2d**) and $\text{Cp}^*\text{Ir}(\eta^2\text{-2,5-Me}_2\text{T})$ (**3d**) by Cp_2Fe^+ .** When **2d** is oxidized by 2 equiv of Cp_2Fe^+ at 0°C , the cationic complex $\text{Cp}^*\text{Ir}(\eta^5\text{-2,5-Me}_2\text{T})^{2+}$ forms quickly and is isolated in 98% yield (eq 4). This is an expected reaction

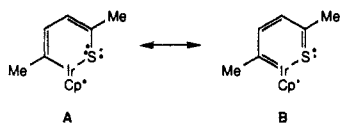


in the sense that a two-electron oxidation of the 18-electron **2d** would leave the metal two electrons short; coordination of the sulfur would allow it to return to 18 electrons.

In a surprising reaction, the $\eta^2\text{-2,5-Me}_2\text{T}$ complex, **3d**, is oxidized even more readily than **2d** to give the same product, **1d**, in 98% yield. The somewhat greater reactivity of **3d** means that **2d** cannot be an intermediate in the conversion of **3d** to **1d**. Thus, the oxidation of **3d** promotes the reformation of the C-S bond to regenerate the $\eta^5\text{-2,5-Me}_2\text{T}$ complex.

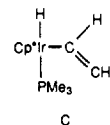
Structure of $\text{Cp}^*\text{Ir}(\eta^2\text{-2,5-Me}_2\text{T})$ (3d**).** The structure of **3d** (Figure 1) basically consists of two planar rings which are perpendicular ($89.7 \pm 0.2^\circ$) to each other. The cyclopentadienyl carbons (C(11) through C(15)) of the Cp^* ring lie in one plane ($\pm 0.02 \text{ \AA}$); the five methyl carbons are an average of 0.11 \AA out of this plane away from the Ir. The other plane is defined by Ir, S, and C(1) through C(6) in a six-membered ring; the largest deviations from this plane are Ir (0.040 \AA), C(3) (0.043 \AA), and C(6) (0.057 \AA). To further examine this ring for nonplanarity, we define a plane consisting of S, C(2), C(4), and C(5), all of whose atoms are within 0.004 \AA of the plane, and find that Ir and C(3) are 0.059 and 0.028 \AA , respectively, out of this plane on the same side. Thus, there is a very slight boat conformation to the basically planar six-membered ring; C(1) and C(6) are out of this plane 0.025 \AA and 0.080 \AA , respectively, on the side away from the Ir and C(3).

In the six-membered ring, the interior angle at Ir is $94.3 (2)^\circ$ and that at S is $117.2 (2)^\circ$; the interior angles at the four carbons range from $122.6 (5)$ to $130.2 (6)^\circ$. Bond distances in the six-membered ring suggest that the ring is best represented by a combination of the two following resonance forms.

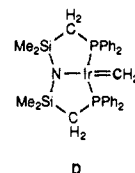


In A, the iridium is a 16-electron center, whereas in B it is 18-electron. Their contributions to the structure of **3d** are supported by the very similar C-C distances in the ring: C(2)-C(3), $1.375 (9)$; C(3)-C(4), $1.41 (1)$; C(4)-C(5), $1.394 (9) \text{ \AA}$. Also, the C(2)-S distance ($1.713 (6) \text{ \AA}$) is intermediate between a $\text{C}(\text{sp}^2)\text{-S}$ single bond distance (1.77 \AA)^{14,15} and a $\text{C}(\text{sp}^2)=\text{S}$ double bond

distance (1.61 \AA).¹⁶ The Ir-C(5) distance ($1.986 (6) \text{ \AA}$) is of special interest since it is a single bond in resonance form A but a double bond (carbene) in form B. The expected Ir-C(sp^2) single bond distance for A is found in

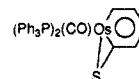


where this distance is $2.054 (4) \text{ \AA}$.¹⁷ The Ir-C(CF_3)=C(CF_3)H unit in $\text{Cp}^*\text{Ir}_2(\text{CO})_2[\text{C}_4(\text{CF}_3)_4][\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}]$ has an Ir-C(sp^2) length of $2.10 (2) \text{ \AA}$.¹⁸ The Ir-C(sp^2) distance to the ortho-metalated triphenylphosphine in $\text{Cp}^*\text{Ir}(\text{CH}_2\text{SiMe}_3)(\text{Ph}_2\text{PC}_6\text{H}_4)$ is $2.080 (5) \text{ \AA}$.¹⁹ The Ir-C(sp^2) bond length in the ortho-metalated benzoic acid complex $\text{Cp}^*\text{Ir}(\text{Me}_2\text{SO})(\text{C}_6\text{H}_4\text{CO}_2)$ is $2.08 (3) \text{ \AA}$.²⁰ All of these distances and their average (2.08 \AA) are longer than Ir-C(5) ($1.986 (6) \text{ \AA}$) in **3d**. Double bond Ir=C(sp^2) distances are found in



and $\text{IrCl}_3(\text{PPh}_3)_2=\text{CCl}_2$, where they are $1.868 (9)$ ²¹ and $1.872 (7) \text{ \AA}$,²² respectively. Thus, the Ir-C(5) bond distance ($1.986 (6) \text{ \AA}$) is intermediate between an Ir-C(sp^2) single bond (2.08 \AA) and an Ir=C(sp^2) double bond (1.87 \AA), consistent with the other evidence that supports the suggestion that the bonding in the six-membered ring can be represented by substantial contributions from both resonance forms A and B.

Features in the NMR spectra of **3d** also support a delocalized π -system in the six-membered ring. Thus, the position (180.99 ppm) of C(5) in the ^{13}C NMR spectrum (Table II) of **3d** is intermediate between those of Ir=CH₂ (200.1 ppm)²¹ in D and Ir-CH=CH₂ (129.2 ppm) in C. In the ^1H NMR spectrum of **3d**, H3 and H4 occur downfield (δ 7.34 and 7.47) in the region characteristic of delocalized or aromatic six-membered, benzene-type ring systems.²³ Considering the planar, delocalized bonding indicated by the X-ray results and the aromatic characteristics of the NMR spectrum, complex **3d** is reasonably described as a benzene derivative, perhaps best described as an "iridathiabenzene". To our knowledge, the only related type of ring is that²⁴ in the "osmabenzene",



which, however, also includes a sulfur group. Although a brief theoretical treatment of metallabenzene has been reported,²⁵ none

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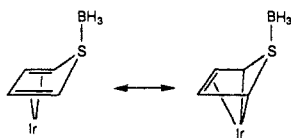
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is available for metallathiabenzenes.

Structure of Cp*Ir(η^4 -2,5-Me₂T·BH₃) (4d). Previously⁵ we reported the structure of **2d**, which is very similar to that (Figure 2) of **4d**, except for the BH₃ group on the sulfur. In fact, the following features of **4d** are essentially the same as those in **2d**: (1) The two ligand planes C(2) through C(5) and C(11) through C(15) are nearly parallel with a $7.5 \pm 2.2^\circ$ angle between them. (2) The four Ir–C distances to the 2,5-Me₂T ligand average 2.13 ± 0.02 Å. (3) The methyl groups (C(1) and C(6)) lie slightly (0.047 Å average) below the C(2)–C(3)–C(4)–C(5) plane toward Ir, while the S lies 0.867 Å out of this plane away from Ir with an Ir–S distance of 2.937 (3) Å. (4) The dihedral angle between the C(2)–C(3)–C(4)–C(5) and C(2)–S–C(5) planes is $39.8 \pm 0.6^\circ$. (5) The interior ring angles at carbon atom (C(2) through C(5)) are essentially all the same (108–111°), while the interior angle at S is much more acute (82.6 (5)°) than it is in free thiophene (91°)²⁶ and in (Ph₃P)₂Rh(η^5 -thiophene)⁺ (90°).²⁷ (6) The three C–C distances (1.47 (2), 1.42 (1), and 1.43 (10)) are the same within experimental error, which suggests that the bonding of the ligand can be represented by the two resonance forms put forward for other diene complexes.²⁸



An apparent difference in the structures of **2d** and **4d** is the longer C–S bonds in **4d** (1.81 (1) and 1.80 (1) Å) as compared to **2d** (1.76 (2) and 1.79 (2) Å). Thus, the BH₃ lengthens the C–S bonds even further from the C–S distance (1.72 Å)²⁶ in free thiophene; these distances in **4d** are essentially the same as a normal C(sp³)–S single bond length (1.81 Å).²⁹ The S–BH₃ distance (1.97 (1) Å) in **4d** is comparable to that (1.941 (5) Å) in Fe[η^3 -HC(SMe)SBH₃](CO)(PMe₃)₂.³⁰

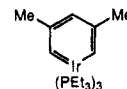
Relevance to Thiophene HDS. The η^4 -coordination mode of the thiophene in complexes **2** is imposed by the electronic saturation (18 electrons) of the Ir. It is possible that such a coordination mode could be forced on thiophene when it adsorbs to an HDS catalyst. If so, a low oxidation state of the metal as in

complexes **2** could favor ring-opening of the thiophene, especially when catalyzed by basic sites on the catalyst, to give the six-membered metallathiabenzene as in eq 3, which would be a first step in the cleavage of carbon–sulfur bonds in thiophene to eventually lead to its complete desulfurization. A ring-opening reaction somewhat related to that in eq 3 may also be involved as a step in the reaction of Fe₃(CO)₁₂ with thiophenes and benzothiophene to give the ring-opened thiophenes in dinuclear thiaferroles, e.g., Fe₂(2,5-Me₂C₄H₂S)(CO)₆.³¹

It is especially interesting that in the reduced state, the Cp*Ir(thiophene) is thermodynamically more stable in the ring-opened form **3**; this ring-opening process occurs readily and essentially quantitatively when catalyzed by basic Al₂O₃. On the other hand, the oxidation of the ring-opened complex (**3d**) immediately and essentially quantitatively gives the η^5 -thiophene complex (**1d**). The ease with which the open ring in **3d** reforms the C–S bond to produce the η^5 -thiophene complex (**1d**) is remarkable. Clearly in the oxidized state the complex is most stable with thiophene ring closed; this may be due in part or perhaps entirely to the η^5 -thiophene's ability to donate six electrons which would bring the electron count on Ir to 18 electrons. However, it may be that other electronic factors, including the oxidation state and electron richness of the Ir, favor the closed-ring form over an open-ring isomer. Regardless of the fundamental reasons, it is clear that C–S bond cleavage and reformation is a facile process which depends on the oxidation state of the complex. While we have demonstrated this type of reactivity only in this iridium–thiophene system, these results suggest that similar reactions may also occur at metal centers during the HDS of thiophene.

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Note Added in Proof. An interesting iridabenzene complex



which has several structural and NMR similarities to Cp*Ir(η^2 -2,5-Me₂T), **3d**, was recently reported. Bleeke, J. R.; Xie, Y.-F.; Peng, W.-J.; Chiang, M. *J. Am. Chem. Soc.* **1989**, *111*, 4118.

Supplementary Material Available: Tables of bond angles, displacement parameters, and least-squares planes (13 pages); tables of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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