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Hydride addition to and reduction of $Cp^*Ir(\eta^6\text{-BT})^{2+}$ and $Cp^*Ir(\eta^6\text{-DBT})^{2+}$, where BT = benzo[*b*]thiophene and DBT = dibenzothiophene *

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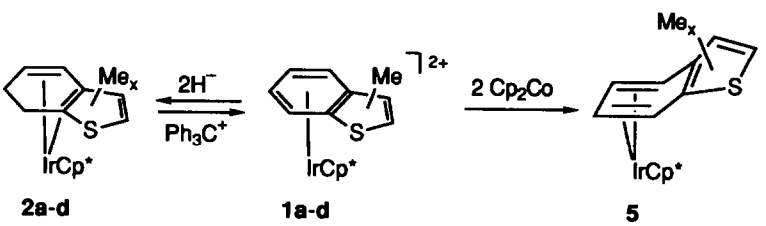
Abstract

The benzo[b]thiophene (BT) complexes $Cp^*Ir(\eta^6\text{-BTs})^{2+}$, where BTs is BT (**1a**), 2-MeBT (**1b**), 3-MeBT (**1c**) or 2,3-Me_2BT (**1d**), react with $H_2Al(OCH_2CH_2OMe)_2^-$ to add two H^- to the coordinated arene ring of the BTs to give the cyclohexadiene complexes $Cp^*Ir(\eta^4\text{-BTs}\cdot 2H)$, **2a–d**. The



dibenzothiophene complex $Cp^*Ir(\eta^6\text{-DBT})^{2+}$ (**3**) reacts similarly to give $Cp^*Ir(\eta^4\text{-DBT}\cdot 2H)$ (**4**). Both of these reactions can be reversed by adding Ph_3C^+. Two-electron reductions of **1c** and **3** give the η^4-arene complexes $Cp^*Ir(\eta^4\text{-3-MeBT})$ (**5**) and $Cp^*Ir(\eta^4\text{-DBT})$ (**6**). Compounds **2c** and **4** have been characterized by X-ray diffraction.

Introduction

Of the many areas of research pursued by Professor Beck, one that has been of special interest to our group is nucleophilic attack on coordinated ligands. A few of his recent papers described azide ion (N_3^-) attack on CO ligands [1], and metal carbonyl anion ($M(CO)_x^-$) attack on coordinated acetylenes [2] and on π-hydro-

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* Dedicated to Professor Wolfgang Beck on the occasion of his 60th birthday and in recognition of his many and diverse research contributions in organometallic chemistry.

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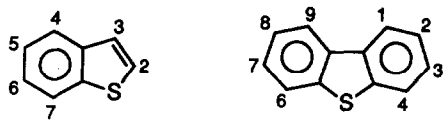

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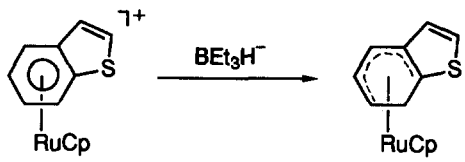

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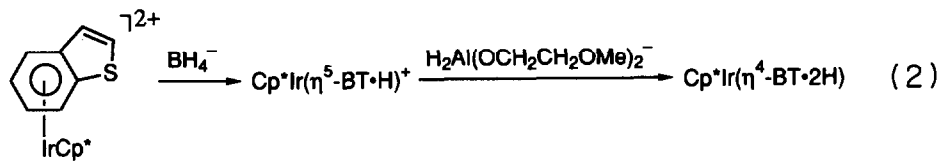
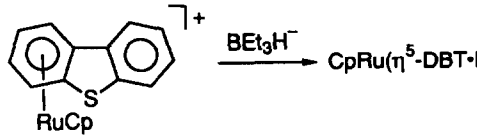


(2)

carbon ligands [3,4]. In the past few years, we have examined reactions of π-thiophenes with nucleophiles in connection with our investigations of the mechanism of the hydrodesulfurization (HDS) of thiophenes [5,6].

In this paper, we describe reactions of π-complexes of benzo[b]thiophene (BT) and dibenzothiophene (DBT). Previously, we reported [7] the reaction (eq. 1) of $CpRu(\eta^6\text{-BT})^+$ with the hydride source BEt_3H^- to give $CpRu(\eta^5\text{-BT} \cdot H)$ which is formed as a mixture of four isomeric cyclohexadienyl complexes; the major isomer (A in ref. 7) is shown in eq. 1. Similarly, $Cp^*Ir(\eta^6\text{-BT})^{2+}$ ($Cp^* = \eta^5\text{-}C_5Me_5$) reacts (eq. 2) with BH_4^- to give an inseparable mixture of four isomers of $Cp^*Ir(\eta^5\text{-BT} \cdot H)^+$ [7] This mixture reacts further with the more reactive hydride source $H_2Al(OCH_2CH_2OMe)_2^-$ to give an incompletely characterized mixture of isomers of the formula $Cp^*Ir(\eta^4\text{-BT} \cdot 2H)$ [7]. In the present paper, we describe the synthesis and establish the structure of one isomer of $Cp^*Ir(\eta^4\text{-BT} \cdot 2H)$, as well as the analogs containing the 2-, 3-, and 2,3-methyl-substituted benzo[b]thiophenes 2-MeBT, 3-MeBT, and 2,3-Me_2BT.

Previously, we had also examined [8] the reaction (eq. 3) of the dibenzothiophene complex $CpRu(\eta^6\text{-DBT})^+$ with BEt_3H^-; this gave a mixture of two cyclohexadienyl isomers of $CpRu(\eta^5\text{-DBT} \cdot H)$. Herein, we report the addition of two hydrides to $Cp^*Ir(\eta^6\text{-DBT})^{2+}$ and structurally characterize the one isolated isomer of $Cp^*Ir(\eta^4\text{-DBT} \cdot 2H)$.



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Finally, we describe the simple two-electron reductions of $Cp^*Ir(\eta^6\text{-3-MeBT})^{2+}$ and $Cp^*Ir(\eta^6\text{-DBT})^{2+}$ to give $Cp^*Ir(\eta^4\text{-3-MeBT})$ and $Cp^*Ir(\eta^4\text{-DBT})$, respectively.

Experimental section

General procedures. All manipulations were carried out under N_2 in reagent grade solvents by using standard Schlenk techniques. Solvents were distilled under N_2 from the following drying agents: tetrahydrofuran (THF) and diethyl ether from sodium/benzophenone, hexane and CH_2Cl_2 from CaH_2. The solvents were stored over 4-Å molecular sieves under N_2, except for acetone which was stored over $MgSO_4$ and purged with N_2 prior to use. The neutral alumina (Brockmann, Activity I) used for chromatography was deoxygenated at room temperature in high vacuum for 16 h, deactivated with 5% w/w N_2-saturated water, and stored under N_2. Benzo[*b*]thiophene (BT), dibenzothiophene (DBT), $Na[H_2Al(OCH_2CH_2OMe)_2]$ ("Red-Al", 3.4 *M* solution in toluene), cobaltocenium hexafluorophosphate $(Cp_2Co)PF_6$, $(Ph_3C)BF_4$, and $AgBF_4$ were purchased from Aldrich Chemical Co. $[Cp^*IrCl_2]_2$ [9], $[Cp^*Ir(BT)](BF_4)_2$ (**1a**) [10], $[Cp^*Ir(2\text{-MeBT})](BF_4)_2$ (**1b**) [7], $[Cp^*Ir(3\text{-MeBT})](BF_4)_2$ (**1c**) [10], $[Cp^*Ir(2,3\text{-Me}_2BT)](BF_4)_2$ (**1d**) [10], and the sodium potassium alloy $NaK_{2.8}$ [11] were prepared by literature methods.

Elemental analyses were performed by Galbraith Laboratories, Inc. The ^1H NMR spectra were recorded on a Nicolet NT-300 spectrometer using deuterated solvents as internal locks. Electron ionization mass spectra (EI-MS) 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.

$Cp^*Ir(\eta^4\text{-BT}\cdot 2H)$ (2a). To a solution of 0.150 g (0.236 mmol) of **1a** dissolved in 30 mL of THF at room temperature was added 0.14 mL (0.476 mmol) of "Red-Al" with stirring. The solution turned from colorless to light yellow. After stirring for 16 h at room temperature, the solution was evaporated to dryness *in vacuo*. The orange-yellow residue was chromatographed on an alumina (neutral, 80–150 mesh) column (1.5 × 8 cm) at room temperature with hexanes/CH_2Cl_2 (10:1) as the eluant. After vacuum removal of the solvent from the yellow fraction, the crude product was recrystallized from hexanes/CH_2Cl_2 (15:1) at −80°C to give 0.039 g (36%, based on **1a**) of **2a** as light yellow crystals, m.p. 120–121°C (decomp.). EI-MS: *m/e* 464 (M^+). Anal. Found: C, 46.53; H, 5.05. $C_{18}H_{23}SIr$ calc.: C, 46.63; H, 5.00%.

$Cp^*Ir(\eta^4\text{-2-MeBT}\cdot 2H)$ (2b). To a stirred solution of **1b** (0.370 g, 0.570 mmol) in 40 mL of THF was added 0.34 mL (1.14 mmol) of "Red-Al" at room temperature. The solution immediately turned light yellow but was stirred at room temperature for 13 h. Subsequent treatment of the resulting mixture as described for **2a** gave 0.092 g (34%, based on **1b**) of light yellow crystals, **2b** (m.p. 58–59°C, decomp.). EI-MS: *m/e* 478 (M^+). Anal. Found: C, 48.11; H, 5.36. $C_{19}H_{25}SIr$ calc.: C, 47.78; H, 5.28%.

$Cp^*Ir(\eta^4\text{-3-MeBT}\cdot 2H)$ (2c). Similar to the preparation of **2a**, 0.320 g (0.493 mmol) of **1c** and 0.29 mL (0.984 mmol) of "Red-Al" were allowed to react with stirring at room temperature for 14 h. Further treatment of the resulting mixture as described for **2a** gave 0.070 g (30%, based on **1c**) of light yellow crystalline **2c** (m.p. 95–96°C, decomp.). EI-MS: *m/e* 478 (M^+). Anal. Found: C, 47.82; H, 5.25. $C_{19}H_{25}SIr$ calc.: C, 47.78; H, 5.28%.

$Cp^*Ir(\eta^4\text{-2,3-Me}_2BT\cdot 2H)$ (2d). This complex was prepared in a similar manner as that for **2a**. A solution of **1d** (0.352 g, 0.531 mmol) was reacted with

Table 1

^{1}H NMR data [a] for complexes **2–9** (δ, TMS as internal reference)

Complex	H1	H2	H3	H4	H5	H6	H7	H8	H9	BT–CH_3	$C_5(CH_3)_5$ or C_5H_5
$Cp^*Ir(BT\cdot 2H)$ (**2a**) [b]		6.62 (d)	6.39 (d)	4.87 (d)	2.76 (m)	1.49–1.40 (m, 2H)	1.38–1.30 (m, 2H)				1.77 (s)
[c]		6.72 (d)	6.41 (d)	4.91 (d)	2.79 (m)	1.48–1.44 (m, 2H)	1.37–1.33 (m, 2H)				1.77 (s)
$Cp^*Ir(2\text{-MeBT}\cdot 2H)$ (**2b**) [b]			6.09 (s)	4.78 (d)	2.67 (m)	1.75 (m, 2H)	1.52 (m, 2H)			2.30 (s)	1.82 (s)
$Cp^*Ir(3\text{-MeBT}\cdot 2H)$ (**2c**) [b]		6.19 (br)		4.77 (d)	2.76 (m)	1.74 (m, 2H)	1.56 (m 2H)			1.86 (br)	1.76 (s)
$Cp^*Ir(2,3\text{-Me}_2BT\cdot 2H)$ (**2d**) [b]				4.72 (d)	2.67 (m)	1.78 (m, 2H)	1.46 (m, 2H)			2.18 (s) 1.88 (s)	1.79 (s)
$[Cp^*Ir(DBT)](BF_4)_2$ (**3**) [c]	8.00 (d)	7.18 (t)	7.29 (t)	7.68 (d)		7.89 (d)	7.04 (m)	7.01 (m)	7.87 (d)		1.29 (s)
[f]	8.55 (d)	7.92 (t)	8.03 (t)	8.29 (d)		8.19 (d)	7.49 (m)	7.47 (m)	8.16 (d)		1.99 (s)
$Cp^*Ir(DBT\cdot 2H)$ (**4**) [c]	7.53 (m)	7.13–7.09 (m, 2H)		7.39 (m)		1.88 (m, 2H)	1.50 (m, 2H)	2.99 (m)	5.30 (d)		1.66 (s)
$Cp^*Ir(3\text{-MeBT})$ (**5**) [b]		6.37 (br)		3.34 (d)	5.81–5.78 (m, 2H)		3.40 (d)			2.13 (br)	1.96 (s)
$Cp^*Ir(DBT)$ (**6**) [b]	7.46 (d)	6.96 (t)	7.19 (t)	7.40 (d)		3.48 (d)	5.97–5.94 (m, 2H)		3.67 (d)		1.97 (s)
$CpCo(\eta^4\text{-}C_5H_5\cdot C_6H_5)$ (**7**) [b]	3.84 (t) [d], 5.26 (m, 2H) [d], 2.92 (m, 2H) [d], 7.13–7.00 (m, 3H) [e], 6.79–6.76 (m, 2H) [e]										4.79 (s)
$[Cp^*Ir(3\text{-MeBT}\cdot H)](BF_4)$ (**8**) [c]		7.30 (br)		7.14 (d)	5.60 (t)	4.07 (*t*)	5.00 (d, H_{exo}) 3.90 (m, H_{endo})			2.19 (br)	1.88 (s)
$[Cp^*Ir(DBT\cdot H)](BF_4)$ (**9**) [c]	8.21 (m)	7.95 (m)	7.70 (m)	7.58 (m)		5.10 (d, H_{exo}) 3.98 (m, H_{endo})	3.94 (m)	4.17 (t)	5.70 (d)		1.72 (s)
[f]	8.33 (m)	8.04 (m)	7.85 (m)	7.59 (m)		5.13 (d, H_{exo}) 3.89 (m, H_{endo})	3.80 (m)	4.08 (t)	5.52 (d)		1.69 (s)

[a] H atoms are labelled as shown in eqs. 4–9. [b] $CDCl_3$. [c] Acetone-d_6. [d] η^4-cyclopentadienyl proton. [e] phenyl proton. [f] CD_3NO_2.

"Red-Al" (0.31 mL, 1.06 mmol) at room temperature for 12 h to yield 0.102 g (39%, based on **1d**) of light yellow crystalline **2d** (m.p. 88–89°C decomp.). EI-MS: *m/e* 492 (M^+). Anal. Found: C, 48.71; K, 5.42. $C_{20}H_{27}SIr$ calc.: C, 48.85; H, 5.53%.

*[Cp*Ir(η^6-DBT)](BF$_4$)$_2$ (3).* This preparation was performed analogously to that for **1a–d** [7,10]. To a stirred solution of $[Cp^*IrCl_2]_2$ (0.500 g, 0.682 mmol) in 10 mL of acetone was added $AgBF_4$ (0.500 g, 2.57 mmol). The solution was stirred for 10 min at room temperature and filtered through Celite; the filter was rinsed with additional acetone (~ 5 mL). The volume of the filtrate was reduced to ~ 5 mL *in vacuo*, and then DBT (4.24 g, 23.0 mmol) was added. The reaction mixture was refluxed for 30 min and then cooled to room temperature. Approximately 50 mL of CH_2Cl_2 was added to precipitate the product. The solid was filtered from the solution and then dissolved in CH_3NO_2. The CH_3NO_2 solution was filtered to remove a black insoluble impurity. Addition of CH_2Cl_2 (~ 50 mL) to the filtrate gave the product **3** as a white solid that was separated by filtration and dried *in vacuo*; yield 0.640 g (74%). This complex is slightly sensitive to moisture and should be stored under N_2. FAB MS: *m/e* 512 (M^+). Anal. Found: C, 38.41; H, 3.45. $C_{22}H_{23}SB_2F_8Ir$ calc.: C, 38.56; H, 3.38%.

*Cp*Ir(η^4-DBT · 2H) (4).* To 0.300 g (0.437 mmol) of **3** dissolved in 30 mL of THF at room temperature was added 0.26 mL (0.876 mmol) of "Red-Al" with stirring. The solution immediately turned light yellow but was stirred at room temperature for 20 h. The solvent was removed *in vacuo*, and the residue was chromatographed on neutral Al_2O_3 with hexanes/CH_2Cl_2 (10:1) as the eluant. The yellow band was collected. After vacuum evaporation of the solvent, the crude product was recrystallized from hexanes/CH_2Cl_2 (20:1) at −80°C to give 0.079 g (35%, based on **3**) of **4** as yellow crystals (m.p. 93–94°C, decomp.). EI-MS: *m/e* 514 (M^+). Anal. Found: C, 51.51; H, 5.05. $C_{22}H_{25}SIr$ calc.: C, 51.44; H, 4.91%.

*Cp*Ir(η^4-3-MeBT) (5).* Compound **1c** (0.400 g, 0.616 mmol) was dissolved in 50 mL of THF at room temperature. To this solution was added Cp_2Co [7,12*] freshly prepared by reduction of $(Cp_2Co)PF_6$ (0.535 g, 1.60 mmol) in THF (20 mL) with $NaK_{2.8}$ (0.056 g, 1.60 mmol). The reaction solution was stirred for 12 h at room temperature. The solvent was evaporated *in vacuo*, and the black-purple residue was chromatographed on an Al_2O_3 (neutral) column with hexanes as the eluant. After removing the purple band (unreacted Cp_2Co) from the column, yellow and red bands were eluted separately with hexanes/CH_2Cl_2 (10:1) and collected. After removal of the solvents from the two eluates under vacuum, the residues were recrystallized from hexanes at −80°C. From the first yellow fraction precipitated 0.071 g (24%, based on **1c**) of **5** as yellow crystals (m.p. 130–132°C, decomp.). EI-MS: *m/e* 476 (M^+). Anal. Found: C, 47.77; H, 4.98. $C_{19}H_{23}SIr$ calc.: C, 47.98; H, 4.87%. From the second, red fraction, 0.028 g (21%, based on **1c**) of a red crystalline compound was obtained (m.p. 104–106°C, decomp.). EI-MS: *m/e* 218 (M^+). Anal. Found: C, 65.87; H, 6.63. $C_{12}H_{15}Co$ calc.: C, 66.06; H, 6.93%. ^1H NMR ($CDCl_3$): δ 3.45 (t, 1H), 5.29 (m, 2H), 3.38 (m, 2H), 2.67 (q, 2H), 1.24 (t, 3H), 4.70 (s, 5H). Although the elemental analysis of this red compound is the same as

* Reference number with asterisk indicates a note in the list of references.

that of $CpCo(\eta^4\text{-}C_5H_5 \cdot CH_2CH_3)$ [13], the ^1H NMR spectra of these compounds are clearly different. We were unable to obtain crystals of the red compound that were suitable for an X-ray diffraction study.

$Cp^*Ir(\eta^4\text{-}DBT)$ (6) and $CpCo(\eta^4\text{-}C_5H_5 \cdot C_6H_5)$ (7). To 0.350 g (0.511 mmol) of **3** dissolved in 50 mL of THF at room temperature was added fresh Cp_2Co prepared [12*] by reaction of $(Cp_2Co)PF_6$ (0.410 g, 1.23 mmol) with $NaK_{2.8}$ (0.043 g, 1.23 mmol) in THF solution. The solution was stirred for 12 h at room temperature. Further treatment of the resulting mixture as described above for **5** gave 0.052 g (20%, based on **3**) of yellow crystalline **6** and 0.025 g (18%, based on **3**) of **7** as red crystals. **6**: m.p. 98–100°C (decomp.). EI-MS: *m/e* 512 (M^+). Anal. Found: C, 51.65; H, 4.85. $C_{22}H_{23}SIr$ calc.: C, 51.64; H, 4.53%. **7**: m.p. 127–128.5°C (decomp.) (Lit. 128–129.5°C [14]). EI-MS: *m/e* 266 (M^+). Anal. Found: C, 72.02; H, 5.82. $C_{16}H_{15}Co$ calc.: C, 72.19; H, 5.68%.

Reaction of 2c with $(Ph_3C)BF_4$ to give $[Cp^*Ir(\eta^5\text{-}3\text{-}MeBT \cdot H)]BF_4$ (8). To a solution of **2c** (0.020 g, 0.042 mmol) in 5 mL of CH_2Cl_2 was added $(Ph_3C)BF_4$ (0.014 g, 0.042 mmol). After being stirred for 15 min at room temperature, the pale yellow product **8** was precipitated from the resulting solution by addition of Et_2O (~ 6 mL). Yield 0.020 g (83%, based on **2c**). The ^1H NMR and FAB MS spectra of **8** are essentially identical with those previously reported [7] for isomer **A**.

Reaction of 2c with 2 equiv. of $(Ph_3C)BF_4$ to give 1c. To a solution of **2c** (0.020 g, 0.042 mmol) in 5 mL of CH_2Cl_2 was added $(Ph_3C)BF_4$ (0.028 g, 0.084 mmol). The reaction solution was stirred for 15 min at room temperature. The pale yellow product that precipitated from the solution was filtered and dried *in vacuo* to give 0.023 g (85%, based on **2c**) of **1c** as a pale yellow solid. ^1H NMR (CD_3NO_2): δ 8.42 (q, 1H), 8.16 (m, 1H), 7.94 (m, 1H), 7.38 (m, 2H), 2.13 (s, 15H), 2.58 (d, 3H).

Reaction of 4 with $(Ph_3C)BF_4$ to give 3 and $[Cp^*Ir(DBT \cdot H)]BF_4$ (9). 0.025 g (0.049 mmol) of **4** was dissolved in 5 mL of CH_2Cl_2 at room temperature. To this solution was added 0.016 g (0.049 mmol) of $(Ph_3C)BF_4$. The solution was stirred for 15 min at room temperature. The resulting white precipitate was separated by filtration, washed with CH_2Cl_2 (~ 0.5 mL), and dried *in vacuo* to give white, solid **3**; yield 0.010 g (30%, based on **4**). ^1H NMR (CD_3NO_2): δ 8.55 (d, 1H), 8.29 (d, 1H), 8.19 (d, 1H), 8.16 (d, 1H), 8.04 (t, 1H), 7.92 (t, 1H), 7.49 (m, 1H), 7.47 (m, 1H), 1.99 (s, 15H). The filtrates were combined and reduced to ~ 4 mL *in vacuo*. To this filtrate was added 5 mL of Et_2O to precipitate the product which was filtered and dried *in vacuo* to give 0.016 g (55%, based on **4**) of **9** as a white solid. FAB MS: *m/e* 513 (M^+). Anal. Found: C, 44.31; H, 4.17. $C_{22}H_{24}SBF_4Ir$ calc.: C, 44.08; H, 4.04%.

Reaction of 4 with 2 equiv. of $(Ph_3C)BF_4$ to give 3. To a solution of **4** (0.022 g, 0.043 mmol) in 5 mL of CH_2Cl_2 was added $(Ph_3C)BF_4$ (0.028 g, 0.086 mmol) at room temperature. The reaction solution was stirred for 15 min at this temperature. Further treatment of the resulting mixture as described in the reaction of **2c** with 2 equiv. of $(Ph_3C)BF_4$ gave 0.027 g (90%, based on **4**) of white solid, **3**, which was identified by its ^1H NMR spectrum.

X-ray structure determinations of 2c and 4. Light yellow crystals of **2c** and **4** suitable for X-ray diffraction study were obtained by recrystallization from hexanes/CH_2Cl_2 solution at −80°C. For each compound, a single crystal of approximate dimensions 0.3 × 0.4 × 0.5 mm was mounted on the end of a glass fiber and coated with a thin layer of epoxy cement. All measurements were made at −80°C

Table 2

Crystallographic data for **2c** and **4**

	2c	**4**
Empirical formula	$C_{19}H_{25}SIr$	$C_{22}H_{25}SIr$
Formula weight	477.67	513.70
Crystal system	Monoclinic	Monoclinic
Lattice parameters	$a = 10.786(4)$ Å	$a = 8.62(7)$ Å
	$b = 10.039(10)$ Å	$b = 10.37(2)$ Å
	$c = 15.214(4)$ Å	$c = 20.954(8)$ Å
	$\beta = 100.26(2)°$	$\beta = 92.6(1)°$
	$V = 1782(2)$ Å^3	$V = 1872(13)$ Å^3
Space group	$P2_1/a$ (#14)	$P2_1/n$ (#14)
Z value	4	4
D_{calc}	1.77 g/cm^3	1.82 g/cm^3
$F(000)$	920	992
μ(Mo-K_α)	80.49 cm^{-1} (correction applied)	76.73 cm^{-1} (correction applied)
Diffractometer	Rigaku AFC6	Rigaku AFC6
Radiation	Mo-K_α ($\lambda = 0.71069$) Graphite-monochromated	Mo-K_α ($\lambda = 0.71069$) Graphite-monochromated
Temperature	−80°C	−80°C
$2\theta_{max}$	60.0°	60.0°
No. observations ($I > 3.00\sigma(I)$)	2585	3632
No. variables	190	217
Residuals: R^a; $R_w{}^b$	0.051; 0.068	0.053; 0.071
Goodness of Fit Indicator [c]	1.57	2.05
Maximum shift in final cycle	0.02	0.01

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

on a Rigaku AFC6 diffractometer with graphite-monochromated Mo-K_α radiation and a 12 kW rotating anode generator. Using a search procedure, 25 reflections were selected within the range of $14° < 2\theta < 50°$ and centered carefully. Indices for these reflections were obtained from an automatic indexing program INDEX and cell parameters were determined using 13 high angle ($25° < 2\theta < 35°$) reflections and their Friedel counterparts. 5715 reflections were measured for **2c** and 6223 for **4** using the ω–2θ scan technique. 2740 out of the measured 5715 reflections for **2c** and 4000 out of 6223 for **4** were considered to be "observed" reflections with $I \geq 3\sigma(I)$. After averaging, 2585 and 3632 reflections remained and were used for subsequent structure determinations for **2c** and **4**, respectively. The space groups were uniquely determined to be $P2_1/a$ for **2c** and $P2_1/n$ for **4** from the conditions limiting possible reflections: **2c**: $h01$, $h = 2n$; $0k0$, $k = 2n$ and **4**: $h01$, $h + 1 = 2n$; $0k0$, $k = 2n$. Further experimental details are given in Table 2.

The structures were solved by direct methods and refined by full-matrix least-squares refinement to conventional residual indices of 5.53% for **2c** and 5.56% for **4** [15a]. The final positional and equivalent isotropic thermal parameters, bond distances and angles for **2c** and **4** are given in Tables 3–5; ORTEP drawings [15b] of **2c** and **4** are shown in Figs. 1 and 2, respectively.

Table 3

Positional parameters and equivalent isotropic thermal parameters for **2c** and **4**

Atom	**2c**				**4**			
	x	*y*	*z*	B_{eq} [a]	*x*	*y*	*z*	B_{eq} [a]
Ir	0.72290(4)	0.01301(3)	0.71494(3)	2.04(1)	0.92877(5)	0.31468(4)	0.65025(2)	1.82(2)
S	0.5510(3)	0.0187(3)	0.8888(2)	3.5(1)	0.8969(5)	−0.0122(3)	0.6317(2)	3.3(1)
C1	0.561(1)	−0.027(1)	0.7787(8)	2.5(4)	0.943(1)	0.118(1)	0.6858(5)	2.3(5)
C2	0.642(1)	-0.134(1)	0.7828(7)	2.4(4)	0.793(1)	0.182(1)	0.6996(5)	2.3(4)
C3	0.669(1)	−0.175(1)	0.695(1)	3.4(5),	0.815(1)	0.296(1)	0.7386(5)	2.5(5)
C4	0.604(1)	−0.111(1)	0.625(1)	4.3(7)	0.974(1)	0.324(1)	0.7504(5)	2.7(5)
C5	0.466(1)	−0.078(2)	0.619(1)	4.8(7)	1.090(2)	0.221(1)	0.7746(7)	3.4(6)
C6	0.443(1)	−0.016(1)	0.706(1)	4.2(6)	1.059(1)	0.094(1)	0.7390(7)	3.3(6)
C7	0.654(1)	−0.094(1)	0.934(1)	3.8(6)	0.696(2)	0.020(1)	0.6275(6)	3.2(6)
C8	0.696(1)	−0.170(1)	0.8744(9)	3.2(5)	0.657(2)	0.123(1)	0.6675(6)	3.0(6)
C9	0.788(1)	−0.270(1)	0.895(1)	4.7(7)	0.503(2)	0.161(1)	0.6699(6)	3.1(6)
C10					0.389(2)	0.097(2)	0.6326(8)	4.6(8)
C11					0.428(2)	−0.005(2)	0.5947(7)	4.3(7)
C12					0.585(2)	−0.045(1)	0.5901(7)	4.1(7)
C13	0.796(1)	0.194(1)	0.7646(7)	2.2(4)	0.995(2)	0.323(1)	0.5500(5)	2.6(5)
C14	0.736(1)	0.280(1)	0.822(1)	3.7(6)	1.064(2)	0.215(1)	0.5136(6)	4.2(7)
C15	0.772(1)	0.1939(9)	0.6672(7)	1.9(4)	1.087(1)	0.413(1)	0.5884(5)	2.1(4)
C16	0.688(1)	0.277(1)	0.6074(9)	3.1(5)	1.261(1)	0.425(1)	0.5948(7)	3.8(6)
C17	0.854(1)	0.100(1)	0.6391(7)	2.1(4)	0.980(2)	0.508(1)	0.6110(6)	2.7(5)
C18	0.863(1)	0.073(1)	0.5420(8)	3.3(5)	1.021(2)	0.622(1)	0.6550(6)	3.2(6)
C19	0.928(1)	0.047(1)	0.7200(8)	2.5(4)	0.827(1)	0.473(1)	0.5875(6)	2.5(5)
C20	1.024(1)	−0.051(1)	0.717(1)	4.5(6)	0.680(1)	0.547(2)	0.5995(7)	3.8(7)
C21	0.893(1)	0.106(1)	0.7945(8)	2.7(4)	0.836(1)	0.360(1)	0.5520(6)	2.8(5)
C22	0.944(1)	0.082(1)	0.890(1)	4.3(6)	0.709(2)	0.287(1)	0.5162(7)	4.1(7)

[a] $B_{eq} = 4/3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}2ab \cos\gamma + \beta_{13}2ac \cos\beta + \beta_{23}2bc \cos\alpha]$ while the anisotropic temperature factor is defined as: $\exp[-\Sigma(\beta_{ij}h_ih_j)]$, and $i, j = 1$–3.

Table 4

Bond distances (Å) [a] for **2c** and **4**

	2c	**4**		**2c**	**4**
Ir–C2	2.16(1)	2.11(1)	C5–C6	1.53(2)	1.53(2)
Ir–C4	2.17(1)	2.12(1)	C7–C12		1.39(2)
Ir–C3	2.13(1)	2.14(1)	C7–C8	1.35(2)	1.41(2)
Ir–C1	2.17(1)	2.18(1)	C8–C9	1.47(2)	1.38(2)
Ir–C15	2.19(1)	2.18(1)	C9–C10		1.40(2)
Ir–C13	2.20(1)	2.20(1)	C10–C11		1.37(2)
Ir–C17	2.18(1)	2.22(1)	C11–C12		1.42(3)
Ir–C21	2.26(1)	2.22(1)	C13–C21	1.44(1)	1.43(2)
Ir–C19	2.23(1)	2.26(1)	C13–C15	1.45(1)	1.45(2)
S–C7	1.72(1)	1.76(2)	C13–C14	1.50(2)	1.50(2)
S–C1	1.75(1)	1.79(1)	C15–C17	1.46(1)	1.45(2)
C1–C6	1.55(2)	1.48(2)	C15–C16	1.48(1)	1.50(2)
C1–C2	1.45(1)	1.49(2)	C17–C19	1.46(1)	1.43(2)
C2–C3	1.47(2)	1.44(2)	C17–C18	1.51(1)	1.53(2)
C2–C8	1.46(2)	1.46(2)	C19–C21	1.39(2)	1.39(2)
C3–C4	1.36(2)	1.42(2)	C19–C20	1.50(2)	1.51(2)
C4–C5	1.52(2)	1.54(2)	C21–C22	1.47(2)	1.51(2)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

Table 5

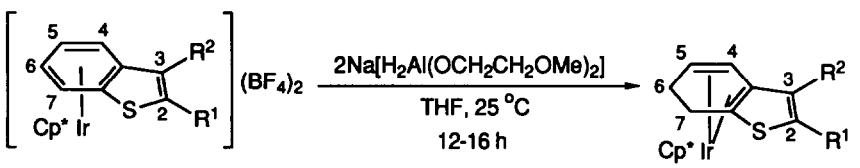
Selected bond angles [a] for 2c and 4

	2c	4
C(7)–S–C(1)	92. (6)	94.5(6)
C(2)–C(1)–C(6)	121. (1)	119. (1)
C(2)–C(1)–S	108.6(8)	107. (1)
C(6)–C(1)–S	118.7(9)	118. (1)
C(1)–C(2)–C(8)	113. (1)	114. (1)
C(1)–C(2)–C(3)	114. (1)	113. (1)
C(8)–C(2)–C(3)	132. (1)	133. (1)
C(4)–C(3)–C(2)	113. (1)	112. (1)
C(3)–C(4)–C(5)	122. (1)	122. (1)
C(4)–C(5)–C(6)	110. (1)	110. (1)
C(5)–C(6)–C(1)	110. (1)	109. (1)
C(8)–C(7)–S	116. (1)	112. (1)
C(7)–C(8)–C(2)	110. (1)	112. (1)
C(7)–C(8)–C(9)	127. (1)	120. (1)
C(2)–C(8)–C(9)	123. (1)	128. (1)
C(8)–C(9)–C(10)		120. (1)
C(11)–C(10)–C(9)		120. (2)
C(10)–C(11)–C(12)		122. (1)
C(7)–C(12)–C(11)		117. (1)
C(12)–C(7)–C(8)		122. (1)
C(12)–C(7)–S		126. (1)
C(13)–C(15)–C(17)	106.2(9)	106. (1)
C(19)–C(17)–C(15)	107.7(9)	108. (1)
C(19)–C(21)–C(13)	109. (1)	109. (1)
C(21)–C(13)–C(15)	109. (1)	108. (1)
C(21)–C(19)–C(17)	108. (1)	109. (1)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Results and discussion

*Preparation of complexes Cp*Ir(η^4-BTs · 2H) (2a–d) and Cp*Ir(η^4-DBT · 2H) (4).* The η^6 benzo[b]thiophene and methyl-substituted benzo[*b*]thiophene complexes of iridium, $[Cp^*Ir(\eta^6\text{-BTs})](BF_4)_2$ ($Cp^* = C_5Me_5$, BTs = BT (**1a**), 2-MeBT (**1b**), 3-MeBT (**1c**), 2,3-Me_2BT (**1d**), react with two moles of $Na[H_2Al(OCH_2CH_2OMe)_2]$ ("Red-Al", 3.4 *M* solution in toluene) at room temperature for 12 to 16 h according to eq. 4 to give complexes **2a–d** in 30–39% yields.



1a-d **2a-d** (4)

a: $R^1 = R^2 = H$
b: $R^1 = CH_3$, $R^2 = H$
c: $R^1 = H$, $R^2 = CH_3$
d: $R^1 = R^2 = CH_3$

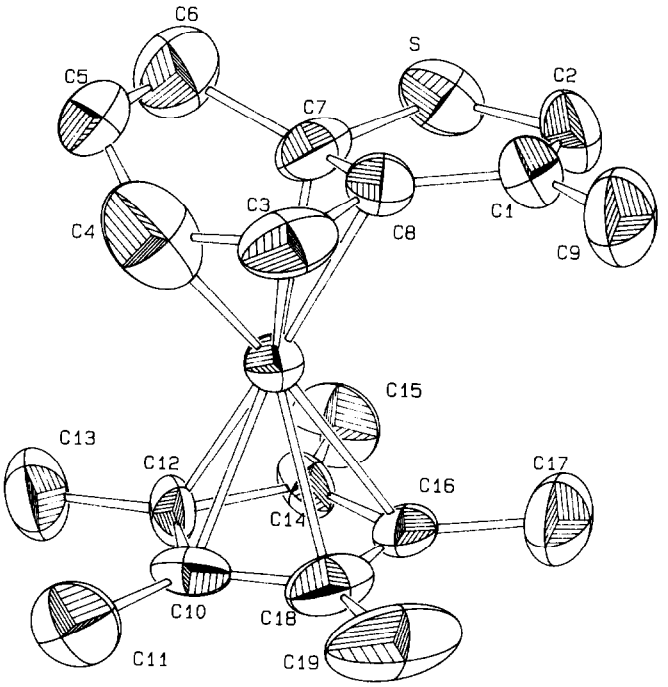
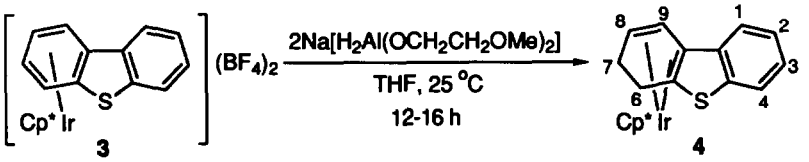


Fig. 1. ORTEP drawing of $Cp^*Ir(\eta^4\text{-}3\text{-}MeBT\cdot 2H)$ (**2c**).

Product **2c** was established by an X-ray crystallographic study (see below) to have a structure in which the two added hydrides (H^-) are at the 6 and 7 positions (eq. 4) and the Ir is coordinated to the diene portion of the resulting cyclohexadiene ring. The solution ^1H NMR spectrum (Table 1) is consistent with this structure; it shows high-field multiplets (δ 1.74, 1.56 ppm) for the protons on the saturated carbons at positions 6 and 7, a low-field quartet (δ 6.19 ppm) for the uncoordinated thiophene H2 proton, and intermediate signals (δ 2.76 and 4.77 ppm) for H4 and H5 of the coordinated diene system. Comparable ^1H NMR signals for complexes **2a**, **2b** and **2d** have been assigned (Table 1); these assignments are also consistent with upfield shifts observed [7] when one hydride (H^-) is added to **1a–d** [7,10] to give the mono-hydride derivatives $Cp^*Ir(\eta^5\text{-}BTs\cdot H)^+$ (eq. 2).

A reaction analogous to that (eq. 4) of $Cp^*Ir(\eta^6\text{-}BTs)^{2+}$ also occurs with the dibenzothiophene complex $Cp^*Ir(\eta^6\text{-}DBT)^{2+}$ (eq. 5). Thus, two equivalents of $Na[H_2Al(OCH_2CH_2OMe)_2]$ react at room temperature during 20 h to afford complex **4** in 35% yield. The structure of **4** as determined by X-ray crystallography (see below) shows that the two added hydrides are at the 6 and 7 positions. Thus, like **2a–d**, **4** is a cyclohexadiene complex. The ^1H NMR spectrum of **4** shows the expected high-field multiplets for H6 and H7, down-field signals for the uncoordinated aromatic ring protons (H1–H4), and intermediate field signals for H8 and H9 of the coordinated diene. These proton assignments are consistent with those of $Cp^*Ir(\eta^6\text{-}DBT)^{2+}$ (**3**), $CpRu(\eta^6\text{-}DBT)^+$ [8] and $CpRu(\eta^5\text{-}DBT\cdot H)$ [8].



(5)

Complexes **2a–d** and **4** are soluble in both polar and non-polar organic solvents and are air-stable for short periods in the solid state. In the ^1H NMR spectra of **2a–d**, there is evidence for only one isomer even though the addition of one H^- to compounds **1a–d** gives four isomers. One would expect the addition of a second H^- to give at least two isomers of $Cp^*Ir(\eta^4\text{-BTs} \cdot 2H)$. It seems likely that more than one isomer is actually formed, as suggested by our earlier studies (eq. 2) [7], but the chromatographic purification procedure leads to the isolation of only one isomer. The formation of **4** (eq. 5) presumably proceeds via the mono-hydride $Cp^*Ir(\eta^5\text{-DBT} \cdot H)^+$. This compound has not been prepared previously; however, the analogous $CpRu(\eta^5\text{-DBT} \cdot H)$ has been prepared [8] and exists in two isomeric forms. Thus, reaction 5 may occur via more than one isomer of $Cp^*Ir(\eta^5\text{-DBT} \cdot H)^+$; however, only one isomer of **4** is isolated.

A precedent for addition of two hydrides to $Cp^*Ir(arene)^{2+}$ complexes is the reaction of $Cp^*Ir(\eta^6\text{-}C_6H_6)^{2+}$ with $Na[H_2Al(OCH_2CH_2OMe)_2]$ to give the cyclohexadiene complex $Cp^*Ir(\eta^4\text{-}C_6H_8)$ [16]. Arenes in $Cp^*Ir(\eta^6\text{-arene})^{2+}$ complexes are unusually susceptible [16] to nucleophilic attack [17] as compared with arenes in other η^6-arene complexes. The free 6,7-dihydrobenzo[*b*]thiophenes generated as ligands in **2** have been prepared previously [18] by lengthy procedures. The 6,7-dihydrodibenzothiophene produced as a ligand in **4** was previously unknown, based on a literature search.

Structure of $Cp^*Ir(\eta^4\text{-3-MeBT} \cdot 2H)$ (2c). The structure (Fig. 1) of **2c** is generally similar to that of other cyclohexadiene complexes [19]. The saturated carbons C(5) and C(6) lie 0.97 and 0.85 Å, respectively, out of the plane defined by C(1), C(2), C(3) and C(4). The dihedral angle between this plane and the C(1), C(4), C(5), C(6) plane is 38.7°. Except for C(5) and C(6), the 3-MeBT · 2H ligand is essentially planar as indicated by the small 4.5° angle between the C(1), C(2), C(3), C(4) plane and that defined by C(1), C(2), C(7), C(8) and S. The sulfur and four carbon atoms of the thiophene lie in a plane (±0.02 Å), while the methyl carbon C(9) is 0.074 Å out of this plane away from the Ir.

Structure of $Cp^*Ir(\eta^4\text{-DBT} \cdot 2H)$ (4). Like **2c**, **4** is a cyclohexadiene complex (Fig. 2) in which the saturated carbons C(5) and C(6) lie above (0.92 and 1.02 Å, respectively) the plane of the coordinated carbon atoms C(1), C(2), C(3), and C(4). The dihedral angle between this plane and that defined by C(1), C(4), C(5), and C(6) is 43.4°. The atoms S, C(1), C(2), C(7)–C(12) lie (±0.02 Å) in a plane that forms a dihedral angle of 8.43° with the C(1), C(2), C(3), C(4) plane. The Cp^* ring carbon plane is essentially parallel (5.3° dihedral angle) to that of C(1), C(2), C(3), C(4).

Reduction of $Cp^*Ir(\eta^6\text{-3-MeBT})^{2+}$ (1c) and $Cp^*Ir(\eta^6\text{-DBT})^{2+}$ (3) with Cp_2Co. Complex **1c** reacts (eq. 6) with 2 equivalents of Cp_2Co at room temperature during a 12 h period to give in 24% yield $Cp^*Ir(\eta^4\text{-3-MeBT})$ (**5**), which is air-sensitive and also not very stable thermally as the solid or in solution. Compound **5** is assigned the η^4-arene structure based primarily on the upfield doublets for H4 and H7 at 3.34 and 3.40 ppm and the somewhat less upfield multiplets assigned to H5 and

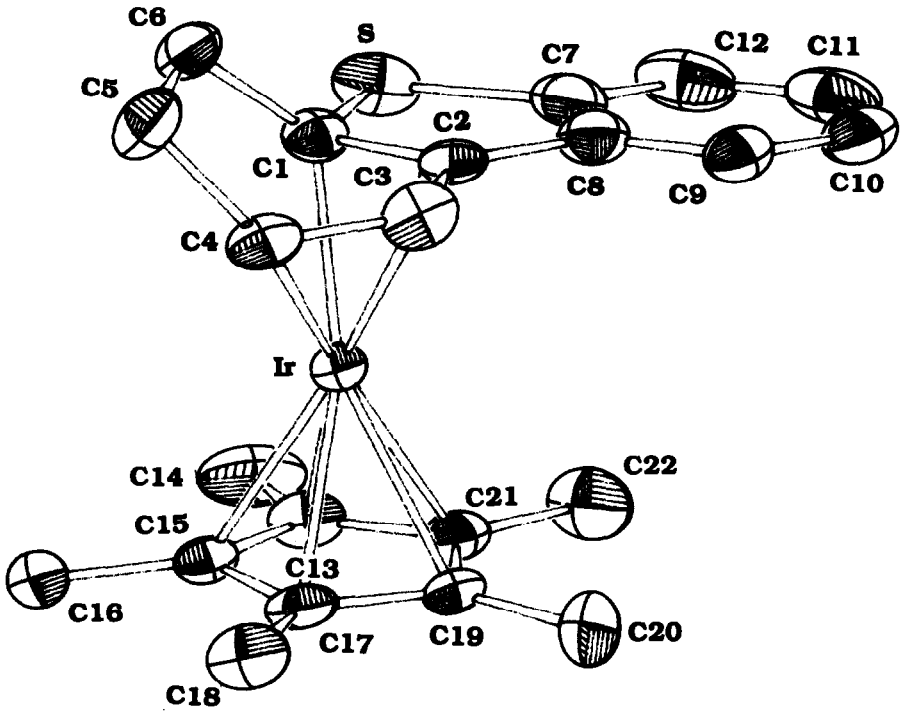
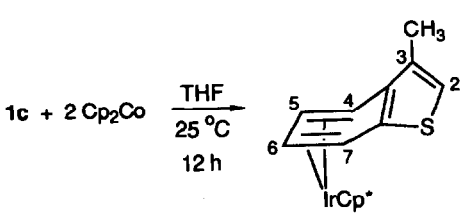


Fig. 2. ORTEP drawing of Cp*Ir(η^4-DBT·2H) (4).

H6. The quartet at 6.37 assigned to H2 is the furthest downfield as expected for the uncomplexed thiophene part of the ligand. All of the protons in the η^4-3-MeBT ligand in **5** are upfield of those (δ 7.3–8.4 ppm) in Cp*Ir(η^6-3-MeBT)$^{2+}$ [10]. The benzo[*b*]thiophene ring is probably bent at C4 and C7, so that the thiophene ring does not lie in the plane defined by C4–C7. Such a bending is observed in the η^4-naphthalene complex (5–8-η^4-1,4-dimethylnaphthalene)Fe[P(OMe)$_3$]$_3$ [20]. The upfield shift of the protons on the coordinated carbons in **5** is characteristic of other η^4-arene complexes such as the ironnaphthalene complex above [20], Cr(η^4-naphthalene)(CO)$_3^{2-}$ [21] and (arene)Ru(η^4-naphthalene) [22,23].



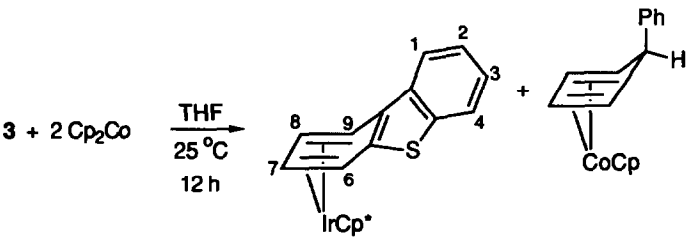
(6)

5

In related systems, Cp*Ir(η^6-C$_6$Me$_6$)$^{2+}$ has been reduced electrochemically and chemically [24,25] to Cp*Ir(η^4-C$_6$Me$_6$). The electrochemical reduction of Cp*Ir(η^6-BT)$^{2+}$ was previously reported [7] to be quasi-reversible.

The two-electron reduction of Cp*Ir(η^6-DBT)$^{2+}$ (**3**) gives (eq. 7) in 20% yield Cp*Ir(η^4-DBT) (**6**), an analog of **5**. The observation in the ^{1}H NMR spectrum

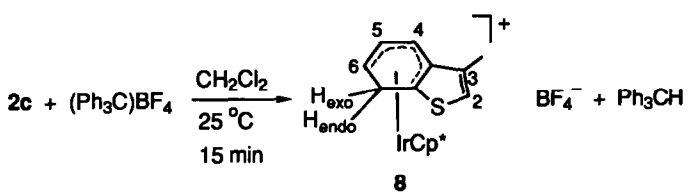
(Table 1) of **6** that four of the proton signals are substantially upfield of the other four indicates that the Ir coordinates through four carbons of one arene ring (eq. 7). As for **5**, the outermost protons H6 and H9 are further upfield than H7 and H8. The ^{1}H NMR assignments in Table 1 were made by comparison with those in $Cp^*Ir(\eta^6\text{-DBT})^{2+}$ (**3**) [8] and free DBT [27*]. In (η^4-anthracene)$Co(PMe_3)_2(SnPh_3)$ [26] as well as in the η^4-naphthalene complexes cited above, the arene ring is not planar. Thus, the DBT ring in **6** is likely to be bent at C6 and C9, as shown in eq. 7.



6 **7** (7)

The other product $CpCo(\eta^4\text{-}C_5H_5 \cdot C_6H_5)$ (**7**) was characterized by a comparison of its ^{1}H NMR spectrum with that [13] of the compound prepared by the reaction of $Cp_2Co^+X^-$ with PhLi according to a literature procedure [14]; also the melting point of **7** is the same as that previously reported [14] for this compound. The route to the formation of **7** in reaction 7 is not known; however, it presumably involves transfer of a phenyl group from DBT.

Reaction of $Cp^*Ir(\eta^4\text{-}3\text{-}MeBT \cdot 2H)$ (2c) with $(Ph_3C)BF_4$. One hydride (H^-) is abstracted from **2c** when it reacts with equimolar Ph_3C^+ in CH_2Cl_2. Within 15 min, $Cp^*Ir(\eta^5\text{-}3\text{-}MeBT \cdot H)^+$ (**8**) is produced in 83% isolated yield (eq. 8) as the only 3-MeBT-containing product. Complex **8** was previously prepared [7] as one in a mixture of four isomers resulting from hydride addition to the C4, C5, C6, or C7 atoms of the coordinated arene ring of $Cp^*Ir(\eta^6\text{-}3\text{-}MeBT)^{2+}$ (**1c**) (see eq. 2). In reaction 8, only the **A** isomer (labelled **8** here) is formed; its identity was established by comparison of its ^{1}H NMR spectrum with that of **A** [7]. Thus, the H^- abstracted from **2c** in eq. 8 is H6 and not H7. It is interesting that selective H^- abstraction from $Cp^*Ir(\eta^5\text{-}BT \cdot H)^+$ by $HBF_4 \cdot Et_2O$ removes H4, H5, and H6 in preference to H7. Thus, the same selectivity is observed in reaction 8.

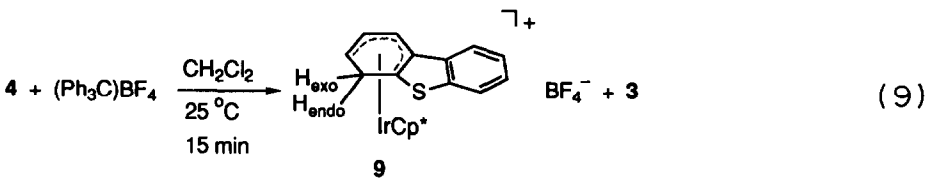


8 (8)

When **2c** reacts with 2 equivalents of $(Ph_3C)BF_4$ under the same conditions, two hydrides are removed from the cyclohexadiene portion of the η^4-3-MeBT · 2H ligand to give $Cp^*Ir(\eta^6\text{-}3\text{-}MeBT)^{2+}$ (**1c**). Thus, the hydride addition reaction (eq. 4) is reversed by Ph_3C^+.

Reaction of $Cp^*Ir(\eta^4\text{-}DBT \cdot 2H)$ (4) with $(Ph_3C)BF_4$. As for the reactions of **2c** with $(Ph_3C)BF_4$, **4** reacts (eq. 9) with one equivalent of $(Ph_3C)BF_4$ to give

predominantly the monohydride abstraction product **9** (55% yield) but also some $Cp^*Ir(\eta^6\text{-DBT})^{2+}$ (**3**) (30% yield). The structure of **9** is assigned based on the similarity of the ^1H NMR spectrum to that of isomer **A** of $CpRu(\eta^5\text{-DBT}\cdot H)$ [8] (eq. 3). As in reaction 8, only one isomer of $Cp^*Ir(\eta^5\text{-DBT}\cdot H)^+$ (**10**) is produced, whereas two isomers of $CpRu(\eta^5\text{-DBT}\cdot H)$ were formed in the reaction of $CpRu(\eta^6\text{-DBT})^+$ with BEt_3H^- (eq. 3). The reaction of **4** with two equivalents of $(Ph_3C)BF_4$ removes both hydrides to give $Cp^*Ir(\eta^6\text{-DBT})^{2+}$ (**3**) in 90% yield.



(9)

Conclusion

The additions (eqs. 4 and 5) of two hydrides to the arene rings of $Cp^*Ir(\eta^6\text{-BTs})^{2+}$, **1a–d**, and $Cp^*Ir(\eta^6\text{-DBT})^{2+}$ (**3**) demonstrate that the Cp^*Ir^{2+} group strongly activates [17] the arene to nucleophilic attack. The products **2a–d** and **4** are cyclohexadiene complexes in which the double bonds are conjugated. There is no evidence for migration of the Cp^*Ir group to the thiophene part of the ligand. The two-electron reductions (eqs. 6 and 7) of **1c** and **3** give air-sensitive η^4-arene complexes, which are also thermally rather unstable. In these reductions, there is also no migration of the Cp^*Ir unit to the thiophene moiety. Thus, in these studies, in contrast to those [28] involving reduction of $Cp^*Ir(\eta^5\text{-thiophene})^{2+}$, there is no evidence for C–S cleavage of the thiophene ring. The reactivity of the ligand is typical of that in other $Cp^*Ir(\eta^6\text{-arene})^{2+}$ complexes.

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Supplementary material available. Tables of additional angles, thermal parameters, least-squares planes, and molecular mechanics calculations for **2c** and **4** (16 pages), as well as structure factors (43 pages) for **2c** and **4**, are available from R.J. Angelici.

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