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# Nucleophilic addition to the $\eta^6$ -iridathiabenzene ligand in $[\eta^6$ -Cp\*Ir(C,S-2,5-Me\_2T)]FeCp<sup>+</sup>

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#### Abstract

The  $\eta^6$ -iridathiabenzene ring coordinated to CpFe<sup>+</sup> in  $[\eta^6$ -Cp\*Ir(C,S-2,5-Me<sub>2</sub>T)]FeCp<sup>+</sup> (**2**) undergoes attack by nucleophiles. Phosphorus-donors, C $\equiv$ N–Bu<sup>n</sup>, and CN<sup>-</sup> add to the Ir to give products with an  $\eta^5$ -coordinated iridathiabenzene ligand. Hydride (Et<sub>3</sub>BH<sup>-</sup>, HFe(CO)<sub>4</sub><sup>-</sup>) and Ph<sup>-</sup> nucleophiles attack at the sulfur to give products with Ir–SH and Ir–SPh groups and an iridacyclopentadiene unit. Other reactions of **2** are described together with structure determinations of key compounds. © 2005 Elsevier B.V. All rights reserved.

### 1. Introduction

Metallabenzenes are a relatively new class of compounds that incorporate a metal into the benzene ring as in A [1,2]. A less well-known family of related compounds is the metallathiabenzenes (**B**), which contain both a metal and a sulfur [1,3]. Previously, it was shown [4,5] that metallathiabenzenes are able to form  $\eta^6$ -complexes **C**, analogous to those of  $\eta^6$ -benzenes.



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Very limited studies show that such  $\eta^6$ -metallathiabenzene complexes undergo reactions with phosphines and CO that result in addition to either the metal in the  $L_xM$  unit (in structure C) or in the M'Y<sub>y</sub> unit. Examples of addition to the metal in the  $L_xM$  unit, Cp\*(C,S-2,5-Me<sub>2</sub>T) (1) in these cases, are given in Eqs. (1) and (2) [6,7].



Examples of addition to the  $M'Y_y$  unit are shown in Eqs. (3) and (4) [7,8].

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On the basis of these reactions, it appears that the most favorable sites of attack are either M or M' (structure C). On the other hand, if the M'Y<sub>y</sub> unit were cationic, one might consider the possibility that nucleophiles would add at a carbon of the  $\eta^6$ -metallathiabenzene ring as occurs in reactions of a variety of nucleophiles with cationic M( $\eta^6$ -arene)<sup>+n</sup> complexes [9,10].

In a previous communication [4], we briefly reported the synthesis and structural characterization of the cationic  $[\eta^6-Cp^*Ir(C,S-2,5-Me_2T)FeCp]^+$  (2) containing an  $\eta^6$  iridathiabenzene coordinated to CpFe<sup>+</sup>. In this paper, we present details of the synthesis of 2 as well as its reactions with a variety of nucleophiles/ligands that give products resulting from attack on the iridium or the sulfur.

#### 2. Experimental

#### 2.1. General procedures

All operations were performed under an N2 atmosphere following standard Schlenk techniques. All solvents employed were reagent grade and were dried by refluxing over appropriate drying agents; they were stored over 4-A molecular sieves under an N<sub>2</sub> atmosphere prior to use. Tetrahydrofuran (THF) and diethyl ether (Et<sub>2</sub>O) were distilled from sodium benzophenone ketyl, while hexanes and CH<sub>2</sub>Cl<sub>2</sub> were distilled from CaH<sub>2</sub>. Acetone was dried over 4-A molecular sieves and distilled under N2 atmosphere. The neutral Al2O3 (Brockman, Activity I, 80-100 mesh) used for chromatography was deoxygenated under vacuum at room temperature for 16 h, deactivated with 5% (w/w) N<sub>2</sub>saturated water, and stored under N<sub>2</sub>. Chromatography columns were  $1.5 \times (5-15)$  cm. The reagents PEt<sub>3</sub>, P(OEt)<sub>3</sub>, PPh<sub>2</sub>Me, HPPh<sub>2</sub>, LiBEt<sub>3</sub>H (1.0 M solution in THF), C<sub>6</sub>H<sub>5</sub>Li (1.8 M in cyclohexane–ether), n-butylisocyanide (n-C<sub>4</sub>H<sub>9</sub>NC), [Me<sub>3</sub>O]BF<sub>4</sub>, [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]I, [(n-

C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]CN, and HgCl<sub>2</sub> were purchased from Aldrich Chemical Co. The complex  $Cp*Ir(C,S-2,5-Me_2T)$  (1) was prepared as previously described [11]. The  $[(\eta^6 - \text{ClC}_6\text{H}_5)\text{FeCp}]^+\text{PF}_6^ [CpFe(\eta^5 - T)]^+$ [12],  $PF_6^{-}(T = thiophene)$  [13],  $[CpFe(\eta^5 - 2, 5 - Me_2T)]^+$  $PF_6^-$  (2,5-Me<sub>2</sub>T = 2,5-dimethylthiophene) [13], LiCo-(CO)<sub>4</sub> [14], (Me<sub>4</sub>N)HFe(CO)<sub>4</sub> [15], LiMn(CO)<sub>5</sub> [14],  $\{[(C_6H_5)_3P]_2N\}FeCo(CO)_8$  [16], and  $(\mu-S)_2Fe_2(CO)_6$ [17] were prepared by literature methods. All elemental analyses were performed by Galbraith Laboratory, Inc. or National Chemical Consulting, Inc. The IR spectra were measured on a Nicolet 710 FT-IR spectrophotometer using a solution cell with NaCl salt plates. All <sup>1</sup>H NMR spectra were recorded at ambient temperature in CDCl<sub>3</sub> solution with CHCl<sub>3</sub> as the internal reference or in acetone- $d_6$  solution with (CH<sub>3</sub>)<sub>2</sub>CO as the internal reference using a Nicolet NT-300 spectrometer. Electron ionization mass spectra (EIMS) and chemical ionization mass spectra (CIMS) were run on a Finnigan 4500 spectrometer at 70 eV, while fast atom bombardment (FAB) spectra were run on samples in a 3-nitrobenzyl alcohol/ CH<sub>3</sub>NO<sub>2</sub> matrix using a Kratos MS-50 mass spectrometer. Melting points were recorded in sealed nitrogenfilled capillaries and are uncorrected.

#### 2.2. Syntheses

2.2.1. Photolytic reaction of  $Cp^*Ir(C,S-2,5-Me_2T)$  (1) with  $[(\eta^6-C_6H_5Cl)FeCp](PF_6)$  to give  $\{[\eta^6-Cp^*Ir(C,S-2,5-Me_2T)]FeCp\}PF_6$  (2)

A solution of 1 (0.050 g, 0.114 mmol) and [( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>Cl)FeCp](PF<sub>6</sub>) (0.035 g, 0.092 mmol) in 25 mL of CH<sub>2</sub>Cl<sub>2</sub> in a quartz photolysis tube was photolyzed with a 450 W ultraviolet lamp for 4.5 h during which time the red solution gradually turned dark purple. The resulting solution was evaporated under vacuum to dryness, and the dark purple residue was redissolved in acetone and purified by passage through a short alumina (neutral, Activity I, 80-100 mesh) column. The acetone filtrate was reduced in vacuo to ca. 5 mL; 80 mL of Et<sub>2</sub>O was added to precipitate dark-purple 2, yield 0.052 g (80%, based on  $[(\eta^{6}-C_{6}H_{5}Cl)FeCp](PF_{6}));$  mp 199–200 °C (dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.81 (d, 1H), 5.99 (d, 1H), 4.46 (s, 5H), 3.15 (s, 3H), 2.96 (s, 3H), 2.14 (s, 15H). MS: m/e 561 (M<sup>+</sup>–PF<sub>6</sub>). Anal. Calc. for C<sub>21</sub>H<sub>28</sub>SPF<sub>6</sub>IrFe: C, 35.75; H, 4.00. Found: C, 36.35; H, 4.20.

An analogous photolytic (7 h) reaction of **1** (0.040 g, 0.091 mmol) and  $[CpFe(\eta^{5}-2,5-Me_{2}T)](PF_{6})$  (0.030 g, 0.079 mmol) in 25 mL of CH<sub>2</sub>Cl<sub>2</sub> gave 0.027 g (48%) of **2**, which was identified by its melting point and <sup>1</sup>H NMR spectrum.

An analogous photolytic (7 h) reaction of **1** (0.040 g, 0.091 mmol) and [CpFe( $\eta^5$ -T)]PF<sub>6</sub> (0.030 g, 0.086 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) yielded 0.019 g (32%) of **2**, which was identified by its melting point and <sup>1</sup>H NMR spectrum.

#### 2.2.2. Reaction of 2 with PEt<sub>3</sub> to give

$$\{ [Cp*Ir(C,S-2,5-Me_{2}T)(PEt_{3}) | FeCp \} PF_{6}(3) \}$$

To a solution of **2** (0.025 g, 0.035 mmol) in THF (20 mL) at -60 °C was added 0.024 g (0.030 mL, 0.203 mmol) of PEt<sub>3</sub>. The reaction solution was stirred for 8 h at -60 to -20 °C, during which time the dark-purple solution turned gradually dark red. After vacuum removal of the solvent, the residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O:hexanes (1:2:4) solution at -80 °C to give 0.021 g (72%, based on **2**) of dark-red crystals of **3** (m.p. 136–138 °C, dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.30 (d, 1H), 4.22 (d, 1H), 4.39 (s, 5H), 2.30 (s, 3H), 1.97 (s, 3H), 1.84 (s, 15H), 1.20 (m, 6H), 0.81 (m, 9H). MS: *mle* 737 (M<sup>+</sup>-3Et), 595 (M<sup>+</sup>-3Et-PF<sub>6</sub>). *Anal.* Calc. for C<sub>27</sub>H<sub>43</sub>SP<sub>2</sub>F<sub>6</sub>IrFeCH<sub>2</sub>Cl<sub>2</sub>: C, 37.01; H, 4.99. Found: C, 37.46; H, 5.03.

### 2.2.3. Reaction of 2 with $P(OEt)_3$ to give { $Cp*Ir(C,S-2,5-Me_2T)[P(OEt)_3]FeCp$ } $PF_6$ (4)

To a solution of **2** (0.030 g, 0.043 mmol) in THF (20 mL) was added P(OEt)<sub>3</sub> (0.028 g, 0.169 mmol) at -60 °C. The solution was stirred at -60 to -20 °C for 7 h during which time the dark-purple solution turned dark-red. Further treatment of the resulting mixture as described above for **3** gave 0.028 g (76%, based on **2**) of dark-red crystals of **4** (m.p. 178–180 °C, dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.18 (d, 1H), 4.39 (s, 5H), 3.76 (m, 6H), 3.46 (d, 1H), 2.31 (s, 3H), 2.22 (s, 3H), 1.83 (s, 15H), 1.32 (t, 9H). MS: *m/e* 626 (M<sup>+</sup>–PF<sub>6</sub>). *Anal.* Calc. for C<sub>27</sub>H<sub>43</sub>O<sub>3</sub>P<sub>2</sub>SF<sub>6</sub>IrFe: C, 37.21; H, 4.97. Found: C, 37.26; H, 5.01.

### 2.2.4. Reaction of 2 with $PPh_2Me$ to give { $[Cp*Ir(C,S-2,5-Me_2T)(PPh_2Me)]FeCp$ }PF<sub>6</sub> (5)

As in the reaction of **2** with PEt<sub>3</sub>, **2** (0.025 g, 0.035 mmol) was reacted with PPh<sub>2</sub>Me (0.035 g, 0.175 mmol) for 8 h at -60 to -20 °C. Subsequent workup of the reaction mixture as described for **3** gave dark-red crystals of **5** (m.p. 200–203 °C, dec); yield 0.021 g (66%, based on **2**). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.45–7.20 (m, 10H), 6.36 (d, 1H), 4.28 (s, 5H), 4.21 (d, 1H), 2.00 (s, 3H), 1.92 (s, 3H), 1.70 (d, 3H), 1.62 (s, 15H). MS: *m/e* 591 (M<sup>+</sup>–PF<sub>6</sub>-Ph<sub>2</sub>Me–H). *Anal.* Calc. for C<sub>34</sub>H<sub>41</sub>SP<sub>2</sub>F<sub>6</sub>IrFe: C, 45.09; H, 4.56. Found: C, 45.06; H, 4.88.

## 2.2.5. Reaction of 2 with PHPh<sub>2</sub> to give $\{[Cp*Ir(C,S-2,5-Me_2T)(PHPh_2)]FeCp\}PF_6$ (6)

The reaction of **2** (0.080 g, 0.113 mmol) for 10 h at -60 to -10 °C with PHPh<sub>2</sub> (0.042 g, 0.226 mmol) and Et<sub>3</sub>N (0.024 g, 0.237 mmol) was performed as described for the reaction of **2** with PEt<sub>3</sub>. Workup of the reaction mixture as described for **3** afforded 0.066 g (65%, based on **2**) of dark-red crystals of **6** (m.p. 202–204 °C, dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.42 (d, 1H), 7.41-7.28 (m, 10H), 4.85 (s, 1H), 4.36 (s, 5H), 4.26 (d, 1H), 2.01 (s, 3H), 1.74 (s, 3H), 1.61 (s, 15H). MS: *m/e* 747 (M<sup>+</sup>–PF<sub>6</sub>),

561 ( $M^+$ –PF<sub>6</sub>–HPPh<sub>2</sub>). *Anal.* Calc. for C<sub>33</sub>H<sub>39</sub>SP<sub>2</sub>-F<sub>6</sub>IrFe: C, 44.45; H, 4.41. Found: C, 44.40; H, 4.49. There was no evidence for a product in which the PHPh<sub>2</sub> ligand was deprotonated by the Et<sub>3</sub>N.

### 2.2.6. Reaction of **2** with $n-C_4H_9NC$ to give { $[Cp*Ir(C,S-2,5-Me_2T)(CN-Bu^n)]FeCp$ }PF<sub>6</sub>(7)

Compound 2 (0.030 g, 0.043 mmol) was dissolved in 20 mL of THF at -50 °C. To this solution was added *n*-C<sub>4</sub>H<sub>9</sub>NC (0.035 mL, 0.336 mmol). This solution was stirred at -50 to -40 °C for 3 h during which time the dark purple solution turned light purple red. After vacuum removal of the solvent, the residue was recrystallized from hexanes:CH<sub>2</sub>Cl<sub>2</sub> at -80°C to afford 0.029 g (85%, based on 2) of black crystals of 7 (m.p. 54–56 °C, dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 7.25 (d, 1H), 4.51 (d, 1H), 4.37 (s, 5H), 2.36 (s, 3H), 1.85 (s, 15H), 1.83 (s, 3H), 1.77–1.63 (m, 4H), 1.50-1.42 (m, 2H), 1.00 (t, 3H). MS: *m/e* 644 (M<sup>+</sup>–PF<sub>6</sub>), 561 (M<sup>+</sup>–PF<sub>6</sub>–CNC<sub>4</sub>H<sub>9</sub>). *Anal.* Calc. for C<sub>26</sub>H<sub>37</sub>-NSPF<sub>6</sub>IrFe: C, 39.60; H, 4.73; N, 1.78. Found: C, 39.45; H, 4.62; N, 1.49.

### 2.2.7. Reaction of **2** with $[(n-C_4H_9)_4N]CN$ to give $[Cp*Ir(C,S-2,5-Me_2T)(CN)]FeCp$ (**8**)

Following the procedure described for the reaction of **2** with  $[(n-C_4H_9)_4N]I$ , **2** (0.042 g, 0.060 mmol) was reacted with  $[(n-C_4H_9)_4N]CN$  (0.050 g, 0.186 mmol) at -60 to -40 °C for 3 h and worked up as described for **14** to give 0.026 g (74%, based on **2**) of black crystalline **8** (m.p. 64–66 °C, dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.24 (d, 1H), 4.35 (d, 1H), 4.19 (s, 5H), 2.32 (s, 3H), 1.82 (s, 15H), 1.80 (s, 3H). MS: *m/e* 587 (M<sup>+</sup>). *Anal.* Calc. for C<sub>22</sub>H<sub>28</sub>NSIrFe: C, 45.05; H, 4.81; N, 2.39. Found: C, 45.55; H, 5.10; N, 2.09.

### 2.2.8. Reaction of **2** with LiBEt<sub>3</sub>H to give $[C_{1} * F_{1} + C_{2} + M_{2}] = [C_{1} * F_{2} + C_{2} + M_{2}] = [C_{1} * F_{2} + C_{2} + M_{2}]$

### $[Cp*Ir(C_4Me_2H_2)(SH)]FeCp (9)$

To a solution of 2 (0.040 g, 0.057 mmol) in 25 mL of THF at -70 °C was added LiBEt<sub>3</sub>H (0.06 mL of 1.0 M solution, 0.057 mmol). The reaction solution turned immediately from dark-purple to dark red. After being stirred at -70 to 0 °C for 12 h, the solution was evaporated under vacuum to dryness, and the residue was chromatographed on  $Al_2O_3$  (neutral) with hexanes:  $CH_2Cl_2$  (15:1) as the eluant. After a small orange-yellow band, a dark band was eluted with hexanes:CH2Cl2:  $Et_2O$  (10:1:1). The dark red eluate was evaporated in vacuo and the red residue was recrystallized from hexanes:  $CH_2Cl_2$  at -80 °C to yield 0.020 g (63%, based on 2) of brick-red crystalline 9 (m.p. 110-112 °C, dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.31 (s, 2H), 3.98 (s, 5H), 2.90 (s, 6H), 1.81 (s, 15H), -3.30 (s, 1H). MS: m/e 562  $(M^+)$ , 561  $(M^+-H)$ . Anal. Calc. for  $C_{21}H_{29}SIrFe$ : C, 44.91; H, 5.21. Found: C, 45.35; H, 5.32.

2.2.9. Reaction of 2 with  $[Me_4N]HFe(CO)_4$  to give 9 and  $[Cp^*Ir(C_4Me_2H_2)(H)Fe(CO)_4]FeCp$  (11)

To compound 2 (0.040 g, 0.057 mmol) dissolved in 30 mL of THF at -60 °C was added 0.020 g (0.082 mmol) of  $[Me_4N]HFe(CO)_4$ . The mixture was stirred at -60 to 10 °C for 10 h during which time the dark solution turned gradually dark purple-red. After evaporation of the solvent under vacuum, the residue was chromatographed on  $Al_2O_3$  (neutral) with hexanes:  $CH_2Cl_2$ (15:1) as the eluant. A brick-red band was eluted first; then a dark-red band was eluted with hexanes:CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O (10:1:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from hexanes:CH<sub>2</sub>Cl<sub>2</sub> at -80 °C. From the first fraction, 0.017 g (41%, based on 2) of dark-red crystals of 11 were obtained (m.p. 137-139 °C, dec). IR (CH<sub>2</sub>Cl<sub>2</sub>) v(CO): 2051 (s), 2007 (vs.), 1979 (s), 1938 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.84 (s, 2H), 3.85 (s, 5H), 2.81 (s, 6H), 2.03 (s, 15H), -25.38 (s, 1H). MS: m/e 730 (M<sup>+</sup>). Anal. Calc. for C<sub>25</sub>H<sub>29</sub>O<sub>4</sub>SIrFe<sub>2</sub>: C, 41.16; H, 4.01. Found: C, 41.66; H, 3.95. From the second fraction, 0.012 g (38%, based on 2) of brick-red 9 were obtained; it was identified by its mp, <sup>1</sup>H NMR and MS spectra.

### 2.2.10. Reaction of **2** with $LiC_6H_5$ to give **1** and $[Cp*Ir(C_4Me_2H_2)(SC_6H_5)]FeCp$ (**10**)

A solution of 2 (0.020 g, 0.028 mmol) in THF (20 mL) was treated with LiC<sub>6</sub>H<sub>5</sub> (0.006 g, 0.032 mL of 1.8 M solution, 0.071 mmol) at -50 °C. The solution immediately turned from dark purple to dark red. After 8 h of stirring at -50 to -20 °C, the solvent was removed under vacuum. The residue was chromatographed on Al<sub>2</sub>O<sub>3</sub> (neutral) with hexanes:CH<sub>2</sub>Cl<sub>2</sub> (15:1) as the eluant. An orange-red band which eluted first was collected; then a dark-green band was eluted with hexanes:CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O (10:1:1). After vacuum removal of the solvent from the above two eluates, the residues were recrystallized from hexanes or hexanes:CH2Cl2 at -80 °C. From the first fraction, 0.003 g (25%, based on 2) of dark-red crystals of 1 were obtained and identified by the mp and <sup>1</sup>H NMR spectrum. From the second fraction, 0.010 g (50%, based on 2) of brick-red crystals of 10 were obtained (m.p. 93–95 °C, dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 6.93-6.76 (m, 5H), 5.32 (s, 2H), 3.98 (s, 5H), 2.93 (s, 6H), 1.87 (s, 15H). MS: m/e 638 (M<sup>+</sup>). Anal. Calc. for C<sub>27</sub>H<sub>33</sub>SIrFe: C, 50.86; H, 5.22. Found: C, 51.03; H, 5.07.

### 2.2.11. Reaction of **2** with $LiCo(CO)_4$ to give { $[\eta^6-Cp^*Ir(C,S-2,5-Me_2T)]FeCp$ }[ $Co(CO)_4$ ] (12)

To a solution of  $Co_2(CO)_8$  (0.012 g, 0.035 mmol) in 7 mL of THF at -20 °C was added 0.090 mL of 1.0 M Li-BEt<sub>3</sub>H solution (0.090 mmol). The mixture was stirred at -20 to 20 °C for 15 min. The resulting solution of Li-

 $Co(CO)_4$  was added to a solution of 2 (0.040 g, 0.057) mmol) in THF (30 mL) at -60 °C. This reaction solution was stirred at -60 to  $10 \,^{\circ}$ C for 10 h during which time the dark solution turned dark purple. After vacuum removal of the solvent, the residue was chromatographed on  $Al_2O_3$  (neutral) with hexanes:  $CH_2Cl_2$  (5:1) and then hexanes:CH2Cl2:Et2O (1:1:1) as the eluant. A dark purple band was eluted and collected. The solvent was removed in vacuo and the residue was recrystallized from hexanes:CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O (1:1:2) at -80 °C to yield 0.031 g (76%, based on 2) of dark-purple crystals of 12 (m.p. 132–134 °C, dec). IR (CH<sub>2</sub>Cl<sub>2</sub>): v(CO) 2026 (w), 1936 (m), 1889 (vs, br), 1712 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR  $(CDCl_3)$ :  $\delta$  6.74 (d, 1H), 5.96 (d, 1H), 4.43 (s, 5H), 3.17 (s, 3H), 2.95 (s, 3H), 2.15 (s, 15H). MS: m/e 648  $(M^+-3CO)$ , 561  $(M^+-Co(CO)_4)$ . Anal. Calc. for C<sub>25</sub>H<sub>28</sub>O<sub>4</sub>SIrFeCo: C, 41.05; H, 3.86. Found: C, 40.85; H, 3.92.

#### 2.2.12. Reaction of 2 with

 ${[(C_6H_5)_3P]_2N}$ [FeCo(CO)<sub>8</sub>] to give

 $\{[\eta^{6}-Cp^{*}Ir(C,S-2,5-Me_{2}T)FeCp]\}FeCo(CO)_{8}\}$  (13)

The reaction of 2 (0.050 g, 0.071 mmol) with  $\{[(C_6H_5)_3P]_2N\}FeCo(CO)_8$  (0.080 g, 0.091 mmol) was performed as described for the reaction of 2 with  $[Me_4N]HFe(CO)_4$  for 12 h at -50 to 10 °C. After removal of the solvent under vacuum, the residue was chromatographed on Al<sub>2</sub>O<sub>3</sub> (neutral) with hexanes:CH<sub>2</sub>Cl<sub>2</sub> (10:1) first and then CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O (5:1) as the eluant. A dark band was collected. The solvent was removed in vacuo, and the residue was recrystallized from hexanes:  $CH_2Cl_2$  at -80 °C to yield 0.040 g (62%, based on 2) of black crystals of 13 (m.p. 139-140 °C, dec). IR (CH<sub>2</sub>Cl<sub>2</sub>) v(CO): 2029 (w), 1892 (vs, br), 1886 (vs, br), 1864 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.83 (d, 1H), 6.01 (d, 1H), 4.46 (s, 5H), 3.16 (s, 3H), 2.97 (s, 3H), 2.15 (s, 15H). MS: m/e 561 (M<sup>+</sup>-FeCo(CO)<sub>8</sub>). Anal. Calc. for C<sub>29</sub>H<sub>28</sub>O<sub>8</sub>SIrFe<sub>2</sub>Co: C, 38.73; H, 3.14. Found: C, 38.67; H, 3.06.

### 2.2.13. Reaction of **2** with $[(n-C_4H_9)_4N]I$ to give $\{[\eta^6-Cp^*Ir(C,S-2,5-Me_2T)]FeCp\}I$ (14)

To a stirred, dark-purple solution of **2** (0.035 g, 0.050 mmol) in THF (20 mL) at -60 °C was added 0.030 g (0.081 mmol) of  $[(n - C_4H_9)_4N]I$ . The mixture was stirred at -60 to -20 °C for 7 h during which time the dark-purple solution turned dark red. After vacuum removal of the solvent, the residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>:THF:hexanes solution at -80 °C to give 0.027 g (79%, based on **2**) of black crystals of **14** (m.p. 128–130 °C, dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.04 (d, 1H), 6.09 (d, 1H), 4.54 (s, 5H), 3.17 (s, 3H), 3.01 (s, 3H), 2.15 (s, 15H). MS: *m/e* 688 (M<sup>+</sup>), 561 (M<sup>+</sup>–I). *Anal.* Calc. for C<sub>12</sub>H<sub>28</sub>ISIrFe: C, 36.69; H, 4.11. Found: C, 36.14; H, 3.82.

### 2.2.14. Reaction of **2** with $LiMn(CO)_5$ to give $\{[\eta^6-Cp^*Ir(C,S-2,5-Me_2T)]FeCp\}Mn(CO)_5$ (**15**)

To a solution of 2 (0.080 g, 0.113 mmol) in THF (30 mL) at  $-60 \,^{\circ}\text{C}$  was added fresh LiMn(CO)<sub>5</sub> prepared by the reaction of  $Mn_2(CO)_{10}$  (0.028 g, 0.072 mmol) with LiBEt<sub>3</sub>H (0.180 mL, 0.179 mmol) as described in the reaction of Co<sub>2</sub>(CO)<sub>8</sub> with LiBEt<sub>3</sub>H. The reaction solution was stirred for 8 h at -60 to 10 °C. During this time, the dark solution gradually turned dark red. After vacuum evaporation of the solvent, the residue was chromatographed on Al<sub>2</sub>O<sub>3</sub> (neutral) with hexanes:CH<sub>2</sub>Cl<sub>2</sub> (10:1) first and then hexanes:CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O (10:1:1) as the eluant. A dark band was collected. The solvent was removed in vacuo, and the residue was recrystallized from hexanes:CH2Cl2 at -80 °C to give 0.026 g (30%, based on 2) of black crystals of 15 (m.p. 131-133 °C, dec). IR (CH<sub>2</sub>Cl<sub>2</sub>) v(CO): 2035 (m), 2011 (s), 1927 (vs), 1834 (vs, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 6.57 (d, 1H), 5.84 (d, 1H), 3.96 (s, 5H), 2.82 (s, 3H), 2.44 (s, 3H), 2.14 (s, 15H). MS: 700 (M<sup>+</sup>-2CO), 561  $(M^+-Mn(CO)_5)$ . Anal. Calc. for  $C_{26}H_{28}O_5SIrFeMn$ : C, 41.33; H, 3.74. Found: C, 40.69; H, 3.26.

2.2.15. Reaction of **2** with  $(\mu - C_6H_5S)(\mu - LiS)Fe_2(CO)_6$ to give  $[Cp^*Ir(C,S-2,5-Me_2T)(\mu - C_6H_5S)(\mu - S)Fe_2-(CO)_6]FeCp$  (**16**)

To a solution of  $(\mu-S_2)Fe_2(CO)_6$  (0.030 g, 0.087 mmol) in THF (10 mL) at -78 °C was added 0.060 mL of 1.8 M LiC<sub>6</sub>H<sub>5</sub> solution (0.11 mmol) with vigorous stirring. The mixture was stirred at -78 °C for 0.5 h. The resulting emerald green solution of  $(\mu-C_6H_5S)(\mu$ LiS)Fe<sub>2</sub>(CO)<sub>6</sub> [18] was then added to a solution of 2(0.050 g, 0.071 mmol) dissolved in THF (20 mL) at -78 °C. The reaction solution was stirred at -78 to 0 °C for 20 h during which time the dark solution gradually turned dark-red. After vacuum removal of the solvent, the residue was chromatographed on Al<sub>2</sub>O<sub>3</sub> (neutral) with hexanes:  $CH_2Cl_2$  (10:1) as the eluant. The brick-red band was collected. The solvent was removed in vacuo, and the residue was recrystallized from hexanes:CH<sub>2</sub>Cl<sub>2</sub> at -80 °C to yield 0.048 g (69%, based on 2) of pink-red crystalline 16 (m.p. 70–72 °C, dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.37–7.17 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 6.67 (d, 1H), 5.78 (d, 1H), 5.44 (m, 2H, CH<sub>2</sub>Cl<sub>2</sub>), 4.97 (s, 5H), 2.68 (s, 3H), 2.29 (s, 3H), 1.88 (s, 15H). IR(hexane) v(CO): 2064 (s), 2024 (vs), 2011 (m), 1995 (s) cm<sup>-1</sup>. MS: *m/e* 561  $(M^{+}-(\mu-C_{6}H_{5}S)(\mu-S)(Fe_{2}(CO)_{6}))$ . Anal. Calc. for C<sub>33</sub>H<sub>33</sub>O<sub>6</sub>S<sub>3</sub>IrFe<sub>3</sub>CH<sub>2</sub>Cl<sub>2</sub>: C, 38.29; H, 3.31. Found: C, 37.62; H, 3.39.

### 2.2.16. Reaction of 2 with $HgCl_2$ to give $[Cp*Ir(C,S-2,5-Me_2T)FeCp(HgCl_2)]PF_6$ (17)

To a solution of **2** (0.020 g, 0.028 mmol) in THF (20 mL) at -30 °C was added 0.015 g (0.055 mmol) of HgCl<sub>2</sub>. The mixture was stirred at -30 to 20 °C for 48 h during which time the dark purple solution turned

gradually deep red. After vacuum removal of the solvent, the residue was recrystallized from THF:hexane at -80 °C to give 0.020 g (83%, based on **2**) of brick-red crystals of **17** (m.p. 172–174 °C, dec). <sup>1</sup>H NMR (acetone- $d_6$ ):  $\delta$  7.03 (d, 1H), 6.50 (d, 1H), 5.01 (s, 5H), 3.62 (m, 4H, THF), 3.32 (s, 3H), 3.06 (s, 3H), 2.53 (s, 15H), 1.79 (m, 4H, THF). MS: *m/e* 843 (M<sup>+</sup>–PF<sub>6</sub>), 561 (M<sup>+</sup>–PF<sub>6</sub>–HgCl<sub>2</sub>). *Anal.* Calc. for C<sub>21</sub>H<sub>28</sub>Cl<sub>2</sub>SPF<sub>6</sub>IrFeHg-C<sub>4</sub>H<sub>8</sub>O(THF): C, 28.62; H, 3.45. Found: C, 28.13; H, 3.55.

### 2.2.17. Reaction of **2** with NalHg and then $[Me_3O]BF_4$ to give $[Cp*Ir(C,S-2,5-Me_2T)]FeCp(CH_3)$ (18)

Compound 2 (0.050 g, 0.071 mmol) was reacted with 0.006 g (0.261 mmol) of Na in Na/Hg (1%), prepared by the reaction of Na (0.006 g, 0.261 mmol) with Hg (0.394 mmol)g), at -40 to -30 °C for 3 h during which time the dark solution turned deep brown. After separation from Na/ Hg, the solution was treated with 0.015 g (0.101 mmol) of  $[Me_3O]BF_4$ . The mixture was stirred at -30 to -20 °C for 3 h. After evaporation of the solvent under vacuum to dryness, the residue was chromatographed on Al<sub>2</sub>O<sub>3</sub> (neutral) with hexanes:CH<sub>2</sub>Cl<sub>2</sub> (10:1) as the eluant. After the purple-red band was eluted and collected, the solvent was removed in vacuo, and the pinkred residue was recrystallized from hexanes:CH<sub>2</sub>Cl<sub>2</sub> at -80 °C to give 0.013 g (41%, based on 2) of pink-red crystals of **18** (m.p. 118–120 °C, dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.84 (d, 1H), 4.01 (d, 1H), 3.86 (s, 3H), 3.07 (s, 3H), 2.81 (s, 5H), 2.04 (s, 15H), 1.79 (s, 3H). MS: m/e 576 (M<sup>+</sup>), 561 (M<sup>+</sup>–CH<sub>3</sub>). Anal. Calc. for C<sub>22</sub>H<sub>31</sub>SIrFe: C, 45.91; H, 5.43. Found: C, 46.22; H, 5.32.

### 2.3. X-ray crystal structure determinations of complexes 3, 9, and 12

The single crystals of complexes **3**, **9**, and **12** suitable for X-ray diffraction study were obtained by recrystallization from hexanes:  $CH_2Cl_2$  solution at -80 °C. The single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data for **3**, **9**, and **12** were collected with Enraf-Nonius CAD4, Siemens P4RA, and Rigaku AFC7R diffractometers, respectively.

The structures of complexes 3, 9, and 12 were solved by direct methods and expanded using Fourier techniques. For 3, many non-hydrogen atoms were placed directly from the E-map. The remaining atoms were located in several difference-Fourier maps. One molecule of  $CH_2Cl_2$  was located in addition to the subject of study. For 9 and 12, all non-hydrogen atoms were placed directly from the E-map. For the four complexes, all non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms for complexes 3 and 12 were treated as riding-atoms with individual isotopic displacement parameters. For complex 9, the hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-PLUS programs or the TEXSAN crystallographic software package of the Molecular Structure Corporation.

Crystallographic data and procedures for data collection and reduction for complexes 3, 9, and 12 are given in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3. Molecular structures of 2, 3, 9, and 12 are given in Figs. 1-4, respectively. Structure solution details were previously reported for 2 [4].

### 3. Results and discussion

### 3.1. Synthesis and characterization of $\{ [\eta^6 - Cp^* Ir(C, S-2, 5-Me_2T)] FeCp \} PF_6(2)$

Complex 2 was prepared by UV-photolytic substitution of the  $\eta^6$ -C<sub>6</sub>H<sub>5</sub>Cl,  $\eta^5$ -thiophene (T) or  $\eta^5$ -2,5-dimethylthiophene (2,5-Me<sub>2</sub>T) ligand in CpFe(arene)<sup>+</sup> by  $Cp*Ir(C,S-2,5-Me_2T)$  (1) according to Eq. (5). Yields

Table 1 Crystal data and experimental details for complexes 3, 9 and 12

of 2 ranged from 32% to 80% depending on the starting complex.

$$[CpFe(arene)]PF_{6} + Cp^{*-Ir} \\ 1$$

$$\xrightarrow{hv (UV)}_{- \text{ arene}} Cp^{*-Ir} \\ S \\ \downarrow \\ Fe \\ 2$$

$$(5)$$

arene =  $\eta^{6}$ -C<sub>6</sub>H<sub>5</sub>Cl,  $\eta^{5}$ -T, or  $\eta^{5}$ -2,5-Me<sub>2</sub>T

The highest yield is achieved with the  $\eta^6$ -C<sub>6</sub>H<sub>5</sub>Cl complex which suggests that  $Cp*Ir(C,S-2,5-Me_2T)$  (1) is more strongly coordinating than C<sub>6</sub>H<sub>5</sub>Cl. The molecular structure of 2 determined by X-ray diffraction studies [4], shows (Fig. 1) that the six-membered iridathiabenzene ring is planar ( $\pm 0.07$  Å) as it is in 1, and the bond distances within this ring are the same, within experimental error, as those in uncoordinated 1.

	3	9	12
Formula	C <sub>28</sub> H <sub>45</sub> Cl <sub>2</sub> F <sub>6</sub> P <sub>2</sub> SirFe	C <sub>21</sub> H <sub>29</sub> SIrFe	C <sub>25</sub> H <sub>28</sub> O <sub>4</sub> SCoIrFe
Formula weight	908.59	561.59	731.5
Space group	$P_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
Unit cell dimensions			
a (Å)	11.059(2)	8.308(4)	9.555(2)
b (Å)	14.539(2)	15.698(7)	21.989(6)
c (Å)	20.875(4)	15.934(5)	12.787(2)
β(°)	90.79(1)	101.31(3)	104.07(2)
$V(Å^3)$	3356.1(10)	2037(1)	2606.0(9)
Ζ	4	4	4
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	1.798	1.830	1.865
Crystal size (mm)	$0.55 \times 0.50 \times 0.45$	$0.20 \times 0.20 \times 0.30$	$0.36 \times 0.20 \times 0.08$
Absorption coefficient $(mm^{-1})$	14.439		6.383
$F(0 \ 0 \ 0)$	1800	1096	1424
Radiation (monochromated in incident beam)	Cu K $\alpha$ ( $\lambda$ = 1.54178 Å)	Mo K $\alpha$ ( $\lambda$ = 0.71069 Å)	Mo K $\alpha$ ( $\lambda = 0.71073$ Å)
Diffractometer	Siemens P4RA	Rigaku AFC7R	Enraf-Nonius CAD4
Temperature (°C)	-60(1)	20.0	-60(1)
Scan method	20-0	ω–2θ	2θ–ω
Data collected range, $2\theta(^{\circ})$	3.70-56.96	5-50.0	4.0-50.0
No. of unique data, total	4506	3296	4594
With $I > 3.00\sigma(I)$	3741 $(I \ge 2\sigma(I))$	2501	2997 ( $F \ge 4.0\sigma(F)$ )
No. of parameters refined	391	217	309
Correction factors, maximum minimum	0.435-1.000	0.9050-1.2140	0.5474-0.6542
R <sup>a</sup>	0.0414	0.025	0.0595
$R_{ m w}$	0.1055 <sup>b</sup>	0.032 <sup>c</sup>	0.0653 <sup>a</sup>
Quality-of-fit indicator <sup>d</sup>	1.08	1.27	1.61
Largest shift/esd. final cycle	0.001	0.00	0.005
Largest peak (e <sup>-</sup> /Å <sup>3</sup> )	1.321	1.11	2.90
Minimum peak (e <sup>-</sup> /Å <sup>3</sup> )	-2.198	-0.47	-3.65

 $\begin{array}{l} ^{a} & R = \Sigma \|F_{o}| - |F_{c}||/\Sigma |F_{o}|. \\ ^{b} & wR_{2} = [\Sigma [w(|F_{o}^{2}| - F_{c}^{2})^{2}]/\Sigma [w(F_{o}^{2})^{2}]]^{0.5}. \\ ^{c} & R_{w} = [\Sigma w(|F_{o}| - |F_{c}|)^{2}/\Sigma W |F_{o}|^{2}]^{1/2}; \ w = 1/\sigma^{2}(|F_{o}|). \end{array}$ 

<sup>d</sup> Quality-of-fit =  $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$ .

Table 3

Table 2 Selected bond lengths  $(\mathring{A})^a$  and angles  $(\circ)^a$  for **2**, **3**, and **12** 

	2	3	12
Fe–S	2.332(2)	2.269(2)	2.348(5)
Fe–C(2)	2.091(9)	2.043(8)	2.09(2)
Fe-C(3)	2.073(8)	2.011(8)	2.06(2)
Fe-C(4)	2.097(8)	2.041(7)	2.07(2)
Fe-C(5)	2.207(9)	2.283(7)	2.20(2)
Ir–Fe	2.758(1)		2.744(2)
Ir–S	2.212(2)	2.310(2)	2.211(5)
Ir-C(5)	2.004(8)	2.085(7)	1.98(2)
Ir-P(31)		2.292(2)	
S-C(2)	1.742(9)	1.735(8)	1.67(2)
C(2)–C(3)	1.37(1)	1.39(1)	1.39(3)
C(3)–C(4)	1.41(1)	1.42(1)	1.43(3)
C(4)–C(5)	1.39(1)	1.42(1)	1.46(2)
C(1)–C(2)	1.51(2)	1.51(1)	1.52(3)
C(5)-C(6)	1.51(1)	1.50(1)	1.45(3)
Ir–C(Cp*) (avg.)	2.204	2.275	2.213
Fe-C(Cp) (avg.)	2.047	2.031	2.038
Co-C(CO) (avg.)			1.731
Fe–Ir–S	54.6(1)		55.3(1)
Fe-Ir-C(5)	52.4(3)		52.6(5)
S-Ir-C(5)	92.7(2)	79.8(2)	93.7(6)
S-C(2)-C(1)	114.6(7)	117.5(6)	116(2)
S-C(2)-C(3)	122.9(7)	120.2(6)	125(2)
C(2)–C(3)–C(4)	127.8(8)	124.3(7)	126 (2)
C(3)–C(4)–C(5)	129.0(7)	127.4(7)	129(2)
Ir-C(5)-C(4)	129.5(6)	128.3(5)	128(2)
Ir-C(5)-Fe	81.7(3)	102.7(3)	81.8(6)
Ir-C(5)-C(6)	118.4(6)	117.5(5)	123(1)
Ir–S-Fe	74.7(1)	96.36(8)	73.9(2)
Ir-S-C(2)	116.9(3)	117.3(3)	59.9(7)
S-Ir-P(31)		99.09(7)	
C(5)–Ir–P(31)		93.8(2)	

<sup>a</sup> Estimated standard deviations in the least significant figure are given in parentheses.

### 3.2. Addition of nucleophiles to iridium in $\{[\eta^6-Cp^*Ir(C,S-2,5-Me_2T)]FeCp\}PF_6(2)$

A series of phosphorus-donor and carbon-donor ligands react (Eq. (6)) with 2 below room temperature to give adducts in which the ligand is bonded to the iridium.



The products **3–8** were isolated in 66–85% yields and characterized by their elemental analyses, <sup>1</sup>H NMR and mass spectra. The structure of **3**, determined by X-ray diffraction, shows (Fig. 2) that the PEt<sub>3</sub> ligand

Ir(1)-Fe(1)	2.623(1)
Ir(1)-S(1)	2.374(2)
Ir(1)–C(20)	2.025(7)
Ir(1)–C(21)	2.035(7)
Fe(1)-C(17)	2.000(8)
Fe(1)–C(18)	2.020(8)
Fe(1)–C(20)	2.004(7)
Fe(1)–C(21)	2.006(7)
C(17)–C(18)	1.41(1)
C(18)–C(21)	1.40(1)
C(17)–C(20)	1.38(1)
C(16)–C(20)	1.52(1)
C(19)–C(21)	1.52(1)
Ir(1)–C(Cp*) (avg.)	2.262
Fe(1)–C(Cp) (avg.)	2.063
Fe(1)–Ir(1)–S(1)	115.62(6)
S(1)–Ir(1)–C(20)	84.6(2)
S(1)–Ir(1)–C(21)	85.3(2)
Fe(1)-Ir(1)-C(20)	49.1(2)
Fe(1)-Ir(1)-C(21)	49.1(2)
C(20)-Ir(1)-C(21)	78.6(3)
Ir(1)-C(20)-C(16)	122.3(5)
Ir(1)–C(21)–C(19)	123.4(5)
Fe(1)-C(20)-C(16)	128.1(6)
Fe(1)-C(21)-C(19)	129.1(6)
Ir(1)–C(20)–C(17)	114.0(6)
Ir(1)–C(21)–C(18)	113.6(5)
C(18)-C(17)-C(20)	115.1(6)
C(17)–C(18)–C(21)	114.0(7)
C(16)-C(20)-C(17)	122.4(6)
C(18)-C(21)-C(19)	121.2(7)

Selected bond lengths  $(\text{\AA})^a$  and angles  $(^{\circ})^a$  for **9** 

<sup>a</sup> Estimated standard deviations in the least significant figure are given in parentheses.

C(11)

C(18)

C(20)

C(16)

C(13) C(17) C(12 C(19) Ir C(6) C(23 C(24) C(5) C(4) C(25) C(2) C(22)C(3) C(21) C(1)

Fig. 1. Molecular structure of 2, showing the atom-numbering scheme.



Fig. 2. Molecular structure of 3, showing the atom-numbering scheme.

adds to the iridium on the opposite side of the six-membered ring from the CpFe<sup>+</sup> unit. This same *exo* addition occurred in the reaction of  $[\eta^6$ -Cp\*Ir(C,S-2,5-Me<sub>2</sub>T)]Cr(CO)<sub>3</sub> with PEt<sub>3</sub> (Eq. (2)). The long Ir–Fe distance (3.413 Å) in **3** is non-bonding as compared with a bonding Ir–Fe distance (2.758(1) Å) in **2**.

The C–C bond distances (Table 2) in the iridathiabenzene ring are the same, within experimental error, in both 2 and 3. These C–C distances are all similar indi-



Fig. 3. Molecular structure of 9, showing the atom-numbering scheme.

cating that there is considerable delocalization in this portion of the ring of both 2 and 3. The Ir–C(5) and Ir–S bond distances are significantly longer in 3 than in 2, suggesting that the addition of the PEt<sub>3</sub> to Ir weakens the bonding between Ir and the C(5) and S atoms. The addition of PEt<sub>3</sub> shortens the Fe bonds to S, C(2),



Fig. 4. Molecular structure of 12, showing the atom-numbering scheme.

C(3), and C(4), which suggests that these atoms in the  $\eta^5$ -iridathiabenzene in **3** are stronger donors toward CpFe<sup>+</sup> than in **2**. In contrast to these shorter bond distances to Fe, the Fe–C(5) distance is longer in **3** (2.283(7) Å) than in **2** (2.207(9) Å). It is not clear why this distance is longer, but the Cr–C(5) distance in  $[\eta^5-Cp^*Ir(C,S-2,5-Me_2T)(PEt_3)]Cr(CO)_3$  (the product in Eq. (2)) is also longer than this same distance in  $[\eta^6-Cp^*Ir(C,S-2,5-Me_2T)]Cr(CO)_3$ .

Because the structure of uncoordinated Cp\*Ir(C,S-2,5-Me<sub>2</sub>T)(PEt<sub>3</sub>) is not known, we compare the structure of Cp\*Ir(C,S-2,5-Me<sub>2</sub>T)(PMe<sub>2</sub>Ph) [19] with that of **3**. In the PMe<sub>2</sub>Ph complex, the C(2)–C(3)–C(4) bond distances in the 6-membered ring have a short (1.347(8) Å)–long (1.458(8) Å)–short (1.330(6) Å) pattern which indicates that the  $\pi$ -bonds are localized, as described earlier [3,19]. On the other hand, these C–C distances in **3** are nearly all the same (1.37–1.41 Å) indicating that the ring is more delocalized when it is  $\eta^5$ -coordinated to CpFe<sup>+</sup>. This  $\eta^5$ -coordination changes the Ir–S (2.310(2) Å) and Ir–C(5) bonds (2.085(7) Å) in **3** very little as compared with those (2.348(1) and 2.074(5) Å) in Cp\*Ir(C,S-2,5-Me<sub>2</sub>T)(PMe<sub>2</sub>Ph).

A comparison of the <sup>1</sup>H NMR spectra of **2** and **3** shows that the difference between chemical shifts for H(3) and H(4) is relatively small (~0.8 ppm) in **2**. On the other hand, this difference is substantially larger (~3 ppm) in **3**. In fact, this difference is also large (2–3.6 ppm) in the other phosphorus ligand adducts **4–6**, where the ligand is P(OEt)<sub>3</sub>, PPh<sub>2</sub>Me, or PHPh<sub>2</sub>. It is this relatively large difference in the H(3)–H(4) chemical shifts that leads to the conclusion that the C $\equiv$ N–Bu<sup>n</sup> (~2.7 ppm) and CN<sup>-</sup> (~2.9 ppm) adducts, **7** and **8**, also have the same structure (Eq. (6)).

The difference between the H(3) and H(4) chemical shifts in Cp\*Ir(C,S-2,5-Me<sub>2</sub>T)(PMe<sub>2</sub>Ph) is also small (~0.5 ppm), which is characteristic of the other Cp\*Ir(C,S-2,5-Me<sub>2</sub>T)(PR<sub>3</sub>) adducts, where PR<sub>3</sub> = PMe<sub>3</sub> PMePh<sub>2</sub>, PPh<sub>3</sub>, or P(OPh)<sub>3</sub> [19]; in this series of complexes, the difference between the H(3) and H(4) chemical shifts is only 0.2–0.5 ppm. However, when Cp\*Ir(C,S-2,5-Me<sub>2</sub>T)(PEt<sub>3</sub>) is  $\eta^5$ -coordinated to CpFe<sup>+</sup> in **3**, H(3) and H(4) are separated by ~3 ppm. Although the origin of this large separation upon coordination to CpFe<sup>+</sup> is not obvious, it is helpful for the assignment of structures to adducts with this <sup>1</sup>H NMR signature.

## 3.3. Addition of nucleophiles to sulfur in $\{[\eta^6-Cp^*Ir(C,S-2,5-Me_2T)]FeCp\}PF_6(2)$

Unlike the nucleophiles described in the previous section,  $Et_3BH^-$  reacts below room temperature with **2** to give a product **9** (63% yield) in which H<sup>-</sup> has added to the S of the coordinated iridathiabenzene ring, and the sulfur is cleaved from the ring to give a terminal SH<sup>-</sup> ligand (Eq (7)). The structure of **9**, established by X-ray diffraction studies (Fig. 3), shows an  $\eta^5$ iridacyclopentadiene group coordinated to the Fe and an SH ligand bound to the Ir; each metal center has an 18-electron count.



The Ir–Fe bond (2.623(1) Å) is relatively short as compared with that in 2 (2.758(1) Å). The Ir-SH distance (2.374(2) A) is the same as those (2.370(2) and 2.380(2))Å) in the previously reported  $Cp*Ir(PMe_3)(SH)_2$  [20]. The Ir-SH distance is also similar to those in other less-closely-related complexes containing Ir-SH groups [21]. The Ir–C bonds to C(20) (2.025(7) Å) and C(21)(2.035(7) Å) in the iridacyclopentaliene ring are distinctly shorter than those (2.080(5), 2.081(5) Å) in **D** [22]. While the C-C distances in the iridacyclopentadiene ring in D have alternating short-long-short distances (1.326(8), 1.445(9), 1.345(9) Å), these distances (1.38(1), 1.41(1), 1.40(1) Å) in 9 are very similar. This difference in C-C bond distance patterns was also observed (see Section 3.2) in the comparison of C-C distances in the iridathiabenzene ring of Cp\*Ir(C,S-2,5-Me<sub>2</sub>T)(PMe<sub>2</sub>Ph) and 3, where the  $\eta^5$ -C,S-2,5-Me<sub>2</sub>T ring in 3 has nearly equal C–C distances. Thus,  $\eta^5$  complex formation of both the iridathiabenzene and iridacyclopentadiene rings causes delocalization of the bonding in the C-C-C-C portion of the ring.



The <sup>1</sup>H NMR spectrum of **9** shows equivalent methyl groups (2.90 ppm) and C–H hydrogens (5.31 ppm) in the iridacyclopentadiene ring, which is consistent with the solid state structure. The Ir–SH signal occurs upfield at -3.30 ppm, which is similar to that (-1.93 ppm) for Cp\*Ir(PMe<sub>3</sub>)(SH)<sub>2</sub> [20] and is in the range typical of M–SH groups [21].

Complex 9 is also formed (38% yield) in the reaction of  $HFe(CO)_4^-$  with 2 below room temperature. Another

product **11** whose composition corresponds to  $[Cp*Ir(C_4Me_2H_2)(H)Fe(CO)_4]FeCp$  on the basis of its elemental analysis and parent ion in the mass spectrum, is also formed. Like **9**, its <sup>1</sup>H NMR spectrum shows equivalent methyl (2.81 ppm) and C–H (4.84 ppm) protons, which suggests the presence of an iridacyclopentadiene unit. The fact that it is formed along with **9** and has the composition of a 1:1 adduct of **9** and Fe(CO)<sub>4</sub> suggests that its structure, may be related to that of **9**. The presence of a <sup>1</sup>H NMR peak at –25.38 ppm corresponding to one proton suggests that there is a metal–metal bridging hydride ligand. Unfortunately, we were unable to obtain X-ray quality crystals for a definitive structure determination.

In a reaction analogous to that of  $Et_3BH^-$  and  $HFe(CO)_4^-$  (Eq. (7)), LiPh reacts with **2** below room temperature to give red crystals of **10** in 50% yield. Although its structure was not determined by X-ray studies, its elemental analyses and mass spectrum (which shows M<sup>+</sup>) are consistent with the proposed composition. Especially important for the structural assignment are the equivalent methyl and C–H groups of the iridacyclopentadiene ring in the <sup>1</sup>H NMR spectrum. Moreover, the chemical shifts of the methyl and C–H groups in **9** and **10** are nearly identical (2.90, 5.31 ppm in **9** vs. 2.93, 5.32 ppm in **10**).

Although the mechanism for the reactions in Eq. (7) is not obvious, one possible pathway is direct attack of  $H^-$  or  $Ph^-$  on the sulfur in the iridathiabenzene which is activated to such an attack by the cationic CpFe<sup>+</sup> unit. Subsequent cleavage of the C–S bond and formation of the Ir–C bond gives the product 9 or 10.

### 3.4. Exchange of the $PF_6^-$ anion in { $[\eta^6-Cp^*Ir(C,S-2,5-Me_2T)]FeCp$ } $PF_6(2)$

Considering the reactivities of **2** toward phosphorus, carbon and hydride nucleophiles shown in Eqs. (6) and (7), we explored reactions of **2** with the metal carbonyl anions  $Co(CO)_4^-$  and  $FeCo(CO)_8^-$  [Eq. (8)]. The reactions were performed under conditions (below room temperature) very similar to those used in Eqs. (6) and (7).

Rather than obtaining products resulting from nucleophilic addition to the  $\eta^6$ -iridathiabenzene ligand, only exchange of the PF<sub>6</sub><sup>-</sup> anion for the metal carbonyl anion occurred in yields ranging from 30% to 76%. The Co(CO)<sub>4</sub><sup>-</sup> salt **12** was obtained as crystals that were suitable for X-ray diffraction studies (Fig. 4). The structural parameters (bond distances and angles) for the {[ $\eta^6$ -Cp\*Ir(C,S-2,5-Me\_2T)]FeCp}<sup>+</sup> cation in **12** are nearly identical (Table 2) to those of the same cation in **2**. The Co(CO)<sub>4</sub><sup>-</sup> anion in **12** has a tetrahedral structure with average C–Co–C angles of 109.4° (average deviation = 1.1°). The Co–CO bond distances average 1.73 Å. All of these structural parameters are very similar to those reported for Co(CO)<sub>4</sub><sup>-</sup> in other compounds [23].

The <sup>1</sup>H NMR spectrum of **12** in CDCl<sub>3</sub> shows signals for the inequivalent methyl groups at 3.17 and 2.95 ppm and the C–H groups at 6.74 d and 5.96 d ppm, which are very similar to those of **2** in CDCl<sub>3</sub> at 3.15, 2.96, 6.81 d, 5.99 d ppm. It is the similarity of the chemical shifts and splittings of these peaks that allows us to assign the same structure to the cation in **13**, which must therefore contain the FeCo(CO)<sub>4</sub><sup>-</sup> anion. The <sup>1</sup>H NMR spectrum of **14** is also essentially the same as those of **2**, **12**, and **13**, which means that the I<sup>-</sup> in **14** is simply the anion in the compound.

It is surprising that  $Co(CO)_4^-$ ,  $FeCo(CO)_8^-$ , and I<sup>-</sup> do not attack the cation in **2**, while the other nucleophiles (Eqs. (6) and (7)) do. On the other hand,  $Mn(CO)_5^-$  does react with **2** to give a product **15** whose analysis indicates that it has the composition {[n<sup>6</sup>-Cp\*Ir(C,S-2,5-Me<sub>2</sub>T)]FeCp}Mn(CO)<sub>5</sub>. However, the positions of the methyl groups at 2.82 and 2.44 ppm and C–H groups at 6.57 d and 5.84 d are distinctly different from those of the cation in **2**, **12**, **13**, and **14**; they are also different than those of **8** in which the CN<sup>-</sup> has added to the Ir. Therefore,  $Mn(CO)_5^-$  does react with the cation in **2**, but the structure of the product **15** is unknown because suitable crystals for X-ray diffraction could not be obtained.

Another metal carbonyl anion ( $\mu$ -PhS)( $\mu$ -S)Fe<sub>2</sub>(Co)<sub>6</sub>, that is known [17,24] to act as a nucleophile, also reacts with **2**. The product **16** has the composition [Cp\*Ir(C,S-2,5-Me<sub>2</sub>T)( $\mu$ -PhS)( $\mu$ -S)Fe<sub>2</sub>(CO)<sub>6</sub>]FeCp as established by elemental analyses. Its <sup>1</sup>H NMR spectrum shows peaks at 2.68 and 2.29 ppm for the inequivalent methyl groups and at 6.67 d and 5.78 d ppm for the inequivalent C–H protons. However, we were unable to obtain X-ray quality crystals for **16** that would allow its structure to be established.

3.5. Other Reactions of  $\{[\eta^6-Cp^*Ir(C,S-2,5-Me_2T)]FeCp\}PF_6(2)$ 

From the reaction of 2 with  $HgCl_2$  in THF was isolated a compound 17 whose composition [Cp\*Ir(C,S- 2,5-Me<sub>2</sub>T)FeCp(HgCl<sub>2</sub>)]PF<sub>6</sub>THF includes one molecule of THF, which was identified in the <sup>1</sup>H NMR spectrum of 17. This spectrum also shows inequivalent methyl groups (3.32, 3.06 ppm) and C-H groups (7.03 d, 6.50 d) with chemical shifts that are downfield of the analogous signals (3.15, 2.96, 6.81 d, 5.99 d ppm) in 2. In addition, the Cp\* methyl groups (2.53 ppm) and Cp protons (5.01 ppm) are downfield of the corresponding peaks (2.14, 4.46 pm) in 2. These significant downfield shifts of both the Cp\* and Cp ligands suggest that both the Ir and Fe metals are oxidized upon reaction with  $HgCl_2$ . Therefore, a possible structure for 17 is one resulting from oxidative-addition of HgCl<sub>2</sub> across the Ir-Fe bond to give a product with one of the -HgCl and -Cl ligands bound to each of the metal atoms. Lack of good crystals prevented its structure from being established definitively.

With the goal of cleaving the Ir–Fe bond in 2 by reduction with Na/Hg and then methylating the resulting anion, the sequence of reactions in Eq. (9) was performed. The final product 18 was isolated in 41% yield and has a composition that corresponds to  $[Cp*Ir(C,S-2,5-Me_2T)]FeCp(Me)$  on the basis of its elemental analyses and parent ion in the mass spectrum.

$$2 \xrightarrow{2 \text{ Na/Hg}}_{\text{THF}} Cp^* \text{Ir} \xrightarrow{\text{S}}_{\text{FeCp}} \xrightarrow{\text{Me}_3 O^+} 18$$
(9)

The <sup>1</sup>H NMR spectrum displays three methyl singlet signals (3.86, 3.07, 1.79 ppm) that may be assigned to the two methyl groups in the Ir(C,S-2,5-Me<sub>2</sub>T) unit and the Me group added by Me<sub>3</sub>O<sup>+</sup>. The site of the added Me<sup>+</sup> group could be the Ir, Fe, or S of the putative anionic intermediate in Eq. (9). Since the <sup>1</sup>H NMR signal of the methyl group in CpFe(CO)<sub>2</sub>CH<sub>3</sub> occurs at  $\delta$  0.17 ppm and at -0.17 in CpFe(CO)(PPh<sub>3</sub>)CH<sub>3</sub> [25] and none of the methyl signals in **18** are at such high field, it seems unlikely that the Me<sup>+</sup> adds at Fe. On the other hand, the methyl signal for CpFe(CO)<sub>2</sub>(SMe) occurs at 1.58 ppm [26], which is similar to 1.79 ppm in **18**. Thus, **18** probably contains a methylated sulfur but its exact structure is unknown because suitable crystals could not be obtained.

#### 3.6. Conclusions

One of the two most definitive and interesting conclusions of the studies reported in this paper is that phosphorus-donor ligands,  $C \equiv N-Bu^n$ , and  $CN^-$  react with the  $\eta^6$ -Cp\*Ir(C,S-2,5-Me\_2T) ligand in [ $\eta^6$ -Cp\*Ir(C,S-2,5-Me\_2T)]FeCp<sup>+</sup> (2) by adding to the Ir atom (Eq. (6)). The other interesting result is that hydride (from Et<sub>3</sub>BH<sup>-</sup> and HFe(CO)<sub>4</sub><sup>-</sup>) and Ph<sup>-</sup> add to the sulfur of the six-membered ring to give a product that contains a –SH or –SPh ligand and an iridacyclopentadiene unit (Eq. (7)). This latter reaction represents a very different type of reactivity for the  $\eta^6$ -Cp\*Ir(C,S-2,5-Me<sub>2</sub>T) ligand than has been previously reported.

### 4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 254454 (3), 254455 (9), 254456 (12). Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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