

Unexpected products resulting from reactions of $\text{Cp}^* \text{Ir}(\eta^5\text{-2,5-Me}_2\text{T})^{2+}$ ($\text{Me}_2\text{T} = 2,5\text{-dimethylthiophene}$) with $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6^{2-}$ and $(\mu\text{-CO})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6^-$

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Abstract

The reactions of $\text{Cp}^* \text{Ir}(\eta^5\text{-2,5-Me}_2\text{T})^{2+}$ (**1**) with $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6^{2-}$ and $(\mu\text{-CO})(\mu\text{-}n\text{-BuS})\text{Fe}_2(\text{CO})_6^-$, which are expected to result in either reduction of **1** or nucleophilic attack on the $\eta^5\text{-2,5-dimethylthiophene}$ ring, yield products that contain the reduced $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T})$ (**2**) ligand. X-ray diffraction studies of the products $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T} \cdot \text{Fe}_2(\text{CO})_5(\mu\text{-S}_2))$ (**6**) and $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T} \cdot \text{Fe}_2(\text{CO})_5(\mu\text{-S}^n\text{Bu}_2))$ (**9**) show that the $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T})$ is coordinated through its sulfur atom to an Fe atom of the $\text{Fe}_2(\mu\text{-S})_2(\text{CO})_4$ dimer core. Reaction of **2** with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ (**4**) leads to a completely different product **7** in which the two bridging sulfur atoms of the $\text{Fe}_2(\mu\text{-S})_2(\text{CO})_4$ core are bonded at two carbons of a rearranged 2,5-Me₂T ligand. Characterization and mechanisms of formation of the new compounds are discussed.

Keywords: Iridium; Iron; Thiophene; Sulfur; Hydrodesulfurization; Pentamethylcyclopentadienyl

1. Introduction

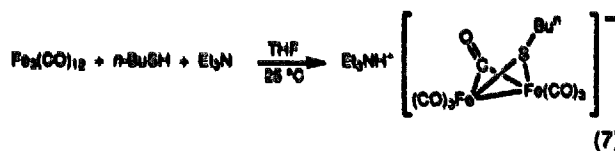
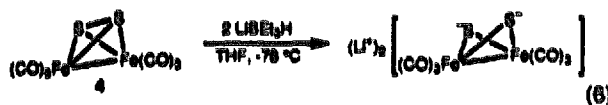
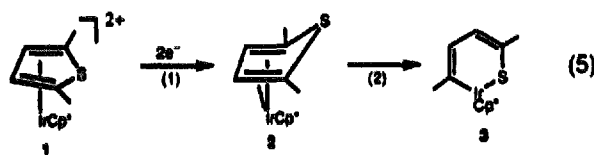
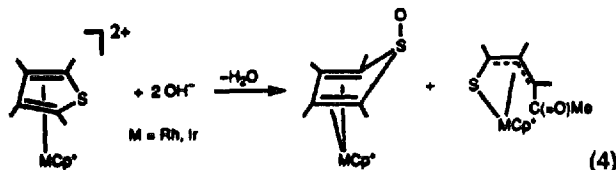
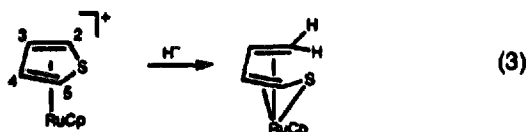
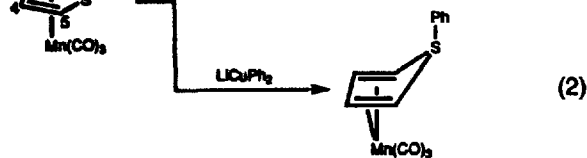
In connection with studies of the mechanism of thiophene hydrodesulfurization (HDS), we [1–4] and others [5–9] have explored reactions of thiophene coordinated in transition metal complexes. Among the many reported reactions are those that result from nucleophilic addition to $\eta^5\text{-thiophene}$ ligands. Examples include attack at C(2) [10,11] (Eq. (1)) or at sulfur [12] (Eq. (2)) in $(\eta^5\text{-T})\text{Mn}(\text{CO})_5^+$, at C(2) with C–S bond cleavage (Eq. (3)) [13,14] in $(\eta^5\text{-T})\text{RuCp}^+$, and at sulfur or C(2) (Eq. (4)) in $\text{Cp}^* \text{Rh}(\eta^5\text{-Me}_4\text{T})^{2+}$ (where Me₄T = tetramethylthiophene) [15,16]. Of special relevance to the present studies are reactions of $\text{Cp}^* \text{Ir}(\eta^5\text{-2,5-Me}_2\text{T})^{2+}$ (**1**), where 2,5-Me₂T is 2,5-dimethylthiophene. This dication reacts [17] with OH[−] to give products analogous to those obtained from $\text{Cp}^* \text{Rh}(\eta^5\text{-$

Me₄T)²⁺ (Eq. (4)). It reacts with two equivalents of LiR (R = Me, Ph) to give $\text{Cp}^* \text{Ir}(2,5\text{-Me}_2\text{T} \cdot 2\text{R})$ [17]. It undergoes a two-electron reduction (Eq. (5), step (1)) when treated with two equivalents of Cp₂Co or Na[H₂Al(OCH₂CH₂OMe)₂] [18,19]. Both isomers **2** and **3** are products of this reduction, but **3** is the more stable because **2** rearranges (Eq. (5), step (2)) to **3** in the presence of catalysts such as bases [19] or ultraviolet light [20].

In the present study, we explore reactions of the dication **1** with $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6^{2-}$ and $(\mu\text{-CO})(\mu\text{-}n\text{-BuS})\text{Fe}_2(\text{CO})_6^-$ in order to determine whether these iron-carbonyl-sulfide dimers react as nucleophiles or as reducing agents. The dianion $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6^{2-}$ is obtained from $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ (**4**) by reduction [21] with LiBEt₃H (Eq. (6)), while $(\mu\text{-CO})(\mu\text{-}n\text{-BuS})\text{Fe}_2(\text{CO})_6^-$ is generated [22] from $\text{Fe}_2(\text{CO})_{12}$ as shown in Eq. (7). In general [23], it is the bridging sulfides that are the nucleophilic centers in $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6^{2-}$. In contrast, in $(\mu\text{-CO})(\mu\text{-}n\text{-BuS})\text{Fe}_2(\text{CO})_6^-$ either the bridging carbonyl oxygen or the iron may be the nucleophilic

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center, depending on the other reactant [23,24]. In their reactions with $\text{Cp}^*\text{Ir}(\eta^5\text{-2,5-Me}_2\text{T})^{2+}$ (1), these nucleophiles do not give products resulting from simple nucleophilic attack or reduction; instead, quite unexpected tri-metal compounds are obtained.

2. Experimental section

2.1. General procedures

All reactions were performed under dry oxygen-free N_2 with use of standard Schlenk techniques. Solvents

employed were dried and distilled under N_2 ; tetrahydrofuran (THF) and diethyl ether (Et_2O) were dried over potassium or sodium benzophenone ketyl; hexanes and CH_2Cl_2 over CaH_2 . The neutral Al_2O_3 (Brockmann, Activity I) used for column chromatography was deoxygenated under high vacuum at room temperature for 16 h, deactivated with 5% (w/w) N_2 -saturated water, and stored under N_2 . Phenyl lithium (2.0 M solution in cyclohexane- Et_2O), lithium hydride, triethylborane (1.0 M solution in hexanes), 1-butanethiol ($n\text{-BuSH}$), Et_3N and $\text{Fe}_3(\text{CO})_{12}$ were purchased from Aldrich Chemical Co. $[\text{Cp}^*\text{Ir}(\eta^5\text{-2,5-Me}_2\text{T})](\text{BF}_4)_2$ (1), $\text{Cp}^*\text{Ir}(\eta^4\text{-2,5-Me}_2\text{T})$ (2), and $\text{Cp}^*\text{Ir}(\eta^4\text{-2,5-Me}_2\text{T})$ (3) were prepared as previously described [18,19]. $(\mu\text{-Dithio})\text{bis}(\text{tricarbonyliron})$, $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ (4), was prepared by the literature method [25]. All elemental analyses were performed by Galbraith Laboratory, Inc. The infrared spectra were recorded in the region $2200\text{--}1600\text{ cm}^{-1}$ on a Perkin-Elmer 681 spectrophotometer. All ^1H NMR spectra were recorded at ambient temperature on samples in CDCl_3 solution with CHCl_3 as an internal reference, using a Nicolet NT-300 spectrometer. Electron ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. The melting points were measured in sealed, nitrogen-filled capillaries and are uncorrected.

2.2. Reaction of 1 with $(\mu\text{-LiS})_2\text{Fe}_2(\text{CO})_6$ to give $\text{Cp}^*\text{Ir}(\eta^4\text{-2,5-Me}_2\text{T})\text{Fe}_2(\text{CO})_4(\mu\text{-S}_2)$ (5) and $\text{Cp}^*\text{Ir}(\eta^4\text{-2,5-Me}_2\text{T})\text{Fe}_2(\text{CO})_5(\mu\text{-S}_2)$ (6)

To a suspension of LiH (0.042 g, 5.28 mmol) in THF (20 ml) was added 0.180 g (1.83 ml, 1.84 mmol) of BEt_3 (1.0 M solution in hexanes). The mixture was heated for 3–4 h at 65°C . The resulting solution was cooled to room temperature; then the excess of LiH was removed by filtration. The resulting solution of LiBEt_3H [26] was added dropwise with vigorous stirring to a solution of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ (0.260 g, 0.756 mmol) in THF (20 ml) cooled to -78°C over a period of 30 min. The dark-red solution quickly turned green. After 15 min stirring at -78°C , the resulting solution of $(\mu\text{-LiS})_2\text{Fe}_2(\text{CO})_6$ [21,25] was cooled to -100°C . To this solution was added 0.460 g (0.750 mmol) of 1 with vigorous stirring. The reaction solution was permitted to warm slowly to -78°C and was stirred at this temperature for 1 h and then warmed at -60 to -40°C for an additional 6 h during which time the green solution turned green-yellow gradually. After removal of the solvent under high vacuum at -20 to -10°C , the black residue was chromatographed on Al_2O_3 (neutral) with hexanes- CH_2Cl_2 (10:1) as the eluant. A purple-red band was eluted first; then a green band was eluted with hexanes- $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ (10:1:1). After vacuum re-

removal of the solvents from the above two eluates, the residues were recrystallized from hexanes-CH₂Cl₂ at -80°C. From the first fraction was obtained 0.251 g (44%, based on 1) of 6 as dark-red crystals (m.p. 237–240°C, decomp). IR(CH₂Cl₂)ν(CO): 2040 vs, 1978 vs, 1960 s, br, 1920 m cm⁻¹. ¹H NMR (CDCl₃): δ 4.48 (s, 2 H), 1.93 (s, 15 H), 1.25 (s, 6 H). MS: *m/e* 440 (M⁺ - (S₂)Fe₂(CO)₅), 316 ((S₂)Fe₂(CO)₅⁺). Anal. Found: C, 33.46; H, 3.23. C₂₁H₂₃Fe₂IrO₅S₃. Calc.: C, 33.39; H, 3.07%. From the second fraction, 0.084 g (15%, based on 1) of 5 were obtained (m.p. 218–220°C, decomp.). IR(CH₂Cl₂)ν(CO): 1970 s, br, 1935 vs, 1900 s, br cm⁻¹. ¹H NMR (CDCl₃): δ 4.66 (s, 2 H), 1.96 (s, 15 H), 1.34 (s, 6 H). MS: *m/e* 440 (M⁺ - (S₂)Fe₂(CO)₄). Anal. Found: C, 33.18; H, 3.29. C₂₀H₂₃Fe₂IrO₄S₃. Calc.: C, 32.99; H, 3.18%.

2.3. Reaction of Cp*Ir(η⁴-2,5-Me₂T) (2) with (μ-S₂)Fe₂(CO)₆ to give Cp*Ir(C(Me)=CHCH=C(Me))-(μ-S₂)Fe₂(CO)₅ (7)

To a solution of 2 (0.030 g, 0.068 mmol) dissolved in 30 ml of THF at -60°C was added 0.027 g (0.078 mmol) of (μ-S₂)Fe₂(CO)₆. The red solution immedi-

ately turned green. After the solution was stirred for 6 h at -60 to -50°C, the solvent was evaporated under vacuum and the residue was chromatographed on Al₂O₃ (neutral) with hexanes-CH₂Cl₂ (10:1) as the eluant. A green band was eluted and collected. After the solvent was removed in vacuo, the crude product was recrystallized from hexanes-CH₂Cl₂ at -80°C to give 0.024 g (48%, based on 2) of 7 as dark-green crystals (m.p. > 230°C, decomp.). IR(CH₂Cl₂)ν(CO): 2158 m, 2128 m, 2040 vs, 1928 vs, 1922 m cm⁻¹. ¹H NMR (CDCl₃): δ 3.66 (d, 1 H), 2.49 (d, 1 H), 1.86 (s, 15 H), 1.79 (s, 3 H), 1.58 (s, 3 H). MS: *m/e* 756 (M⁺), 728 (M⁺ - CO), 700 (M⁺ - 2CO), 672 (M⁺ - 3CO), 644 (M⁺ - 4CO), 616 (M⁺ - 5CO), 440 (M⁺ - Fe₂S₂(CO)₅). Anal. Found: C, 35.70; H, 3.80. C₂₁H₂₃Fe₂IrO₅S₃ · 0.5C₆H₁₄. Calc.: C, 36.10; H, 3.79%.

2.4. Reaction of Cp*Ir(C,S,-2,5-Me₂T) (3) with (μ-S₂)Fe₂(CO)₆ to give 7 and Cp*Ir(2,5-Me₂T)((μ-S₂)Fe₂(CO)₄) (8)

To a stirred solution of 3 (0.033 g, 0.075 mmol) in THF (30 ml) was added 0.030 g (0.087 mmol) of (μ-S₂)Fe₂(CO)₆ at -60°C. The red solution quickly

Table 1
Crystal and data collection parameters for 6, 7, and 9

	6	7	9
Empirical formula	IrFe ₂ S ₃ O ₅ C ₂₁ H ₂₃	IrFe ₂ S ₃ O ₅ C ₂₄ H ₃₀	IrFe ₂ S ₃ O ₅ C ₂₉ H ₄₁
Formula weight	755.50	798.59	869.70
Crystal color, habit	red, plate-like	black, chunk	red, irregular plate
Crystal system	triclinic	triclinic	triclinic
Crystal size (mm ³)	0.19 × 0.14 × 0.05	0.10 × 0.10 × 0.10	0.18 × 0.08 × 0.02
Lattice parameters			
<i>a</i> (Å)	10.013(2)	12.695(5)	9.679(4)
<i>b</i> (Å)	10.814(2)	13.419(6)	10.834(2)
<i>c</i> (Å)	13.136(2)	8.692(5)	16.712(3)
<i>α</i> (deg)	72.34(1)	97.92(5)	95.41(1)
<i>β</i> (deg)	67.13(2)	103.22(4)	102.10(3)
<i>γ</i> (deg)	84.64(1)	83.11(4)	94.59(3)
<i>V</i> (Å ³)	1248.3(4)	1422(1)	1696.9(8)
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>Z</i>	2	2	2
<i>d</i> (calc) (g cm ⁻³)	2.010	1.865	1.702
<i>μ</i> (cm ⁻¹)	67.16	59.03	162.02
Diffractionmeter	Enraf-Nonius CAD4	Rigaku AFC6R	Siemens P4RA
Radiation (monochromated)	Mo K α (λ = 0.71073 Å)	Mo K α (λ = 0.71069 Å)	Cu K α (λ = 1.5418 Å)
No. of reflections used for unit cell determination (2θ range)	25 (18.0–34.5°)	25 (20.2–24.4°)	25 (34.0–50.0°)
Temperature (°C)	-70(1)	23(1)	-60(1)
Scan method	θ-2θ	ω-2θ	ω-2θ
Data collection range, 2θ (deg)	4–50	3.0–50.1	5.4–113.9
No. unique data	4365 (3121, <i>I</i> > 3σ _{<i>I</i>})	5029 (1540, <i>I</i> > 3.0σ _{<i>I</i>})	4559 (3298, <i>I</i> > 3σ _{<i>I</i>})
No. parameters refined	289	187	401
Trans factors, max, min (ψ scans)	0.9996–0.6471	1.00–0.78	0.976–0.565
Extinction parameter	—	—	3.5 × 10 ⁻⁴
<i>R</i> , <i>R</i> _w ^a	0.032, 0.040	0.071, 0.079	0.064, 0.159
Goodness of fit ^b	1.00	1.80	1.17
Largest shift/esd, final cycle	< 0.01	0.79	0.018
Largest peak (e Å ⁻³)	1.5	1.8	1.8

^a *R* = Σ||*F*₀ - |*F*_c|| / Σ|*F*₀|; *R*_w = [Σw(|*F*₀ - |*F*_c||)² / Σw|*F*₀|]^{1/2}. ^b Goodness of fit = [w(|*F*₀ - |*F*_c||)² / (N_{obs} - N_{par})]^{1/2}.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for **6**

Atom	x	y	z	$B(\text{\AA}^2)^a$
Ir	0.28555(3)	0.85222(3)	0.25616(3)	1.899(6)
Fe(1)	0.6135(1)	0.4812(1)	0.27427(9)	2.01(2)
Fe(2)	0.7920(1)	0.3681(1)	0.13314(9)	2.30(3)
S(1)	0.4542(2)	0.6321(2)	0.3226(2)	2.09(4)
S(2)	0.7407(2)	0.5794(2)	0.0875(2)	2.76(5)
S(3)	0.5813(2)	0.4524(2)	0.1225(2)	2.87(5)
O(31)	0.7948(6)	0.5264(6)	0.3888(5)	3.6(1)
O(32)	0.4456(8)	0.2694(7)	0.4674(6)	4.4(2)
O(33)	0.6934(8)	0.1123(7)	0.2961(6)	4.6(2)
O(34)	0.9566(7)	0.2977(7)	-0.0799(5)	4.3(2)
O(35)	1.0331(6)	0.3805(6)	0.2028(5)	3.5(2)
C(1)	0.6267(9)	0.8651(8)	0.2286(7)	3.1(2)
C(2)	0.5034(8)	0.7943(8)	0.2278(6)	2.2(2)
C(3)	0.4768(9)	0.8125(9)	0.1232(7)	2.8(2)
C(4)	0.3597(9)	0.7241(8)	0.1492(7)	2.7(2)
C(5)	0.3082(8)	0.6505(8)	0.2716(6)	2.4(2)
C(6)	0.1933(9)	0.5470(9)	0.3256(8)	3.5(2)
C(11)	0.0566(8)	0.9025(8)	0.3184(7)	2.7(2)
C(12)	0.110(1)	0.8850(9)	0.4077(7)	3.0(2)
C(13)	0.2216(8)	0.9817(8)	0.3674(6)	2.6(2)
C(14)	0.2357(8)	1.0583(8)	0.2550(7)	2.7(2)
C(15)	0.1328(9)	1.0111(8)	0.2249(7)	2.7(2)
C(21)	-0.068(1)	0.828(1)	0.3256(9)	5.0(3)
C(22)	0.056(1)	0.789(1)	0.5278(8)	5.2(3)
C(23)	0.308(1)	1.002(1)	0.4348(8)	5.4(2)
C(24)	0.336(1)	1.1798(9)	0.1842(9)	4.1(3)
C(25)	0.111(1)	1.068(1)	0.1136(7)	4.2(2)
C(31)	0.7220(9)	0.5090(8)	0.3455(6)	2.5(2)
C(32)	0.5101(9)	0.3536(8)	0.3916(7)	2.5(2)
C(33)	0.7316(9)	0.2125(9)	0.2302(7)	3.0(2)
C(34)	0.8883(9)	0.3288(9)	0.0004(7)	2.9(2)
C(35)	0.9387(9)	0.3744(8)	0.1754(7)	2.9(2)

^a In this and succeeding tables, anisotropically refined atoms are given in the form of the isotropic displacement parameter defined as: $B = 4/3(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ab\beta_{12}\cos\gamma + 2ac\beta_{13}\cos\beta + 2bc\beta_{23}\cos\alpha)$.

turned dark-green. After stirring for 6 h at -60 to -50°C , the solvent was removed under vacuum. The dark-green residue was chromatographed on Al_2O_3 (neutral) with hexanes- CH_2Cl_2 (10:1) as the eluant. The green band which eluted first was collected; then a purple-red band was eluted with hexanes- CH_2Cl_2 - Et_2O (10:1:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from hexanes- CH_2Cl_2 at -80°C . From the first fraction, 0.013 g (24%, based on **3**) of dark-green crystals of **7** were obtained (m.p. $> 230^\circ\text{C}$, decomp.); its IR and ^1H NMR spectra are the same as given above. From the second fraction was obtained 0.016 g (29%, based on **3**) of **8** as dark green crystals (m.p. 130 – 132°C , decomp.). IR(CH_2Cl_2) $\nu(\text{CO})$: 2159 m, 2127 m, 2053 s, 2000 vs cm^{-1} . ^1H NMR (CDCl_3): δ 7.69 (dd, 1 H), 7.52 (dd, 1 H), 2.29 (s, 3 H), 1.96 (s, 3

H), 1.88 (s, 15 H). MS: m/e 728 (M^+), 440 ($\text{M}^+ - \text{Fe}_2\text{S}_2(\text{CO})_4$). Anal. Found: C, 33.21; H, 3.07. $\text{C}_{20}\text{H}_{23}\text{Fe}_2\text{IrO}_4\text{S}_3$. Calc.: C, 32.90; H, 3.18%.

2.5. Reaction of **1 with $\text{Et}_3\text{NH}[(\mu\text{-CO})(\mu\text{-}n\text{-BuS})\text{Fe}_2(\text{CO})_6]$ to give $\text{Cp}^*\text{Ir}(\eta^5\text{-}2,5\text{-Me}_2\text{T} \cdot \text{Fe}_2(\text{CO})_5(\mu\text{-S}^n\text{Bu})_2)$ (**9**) and $\text{Cp}^*\text{Ir}(\text{C,S-}2,5\text{-Me}_2\text{T})(\text{CO})$ (**10**)**

To a solution of $\text{Fe}_3(\text{CO})_{12}$ (0.33 g, 0.66 mmol) in 25 ml of THF was added 0.060 g (0.67 mmol) of 1-butanethiol ($n\text{-BuSH}$) and 0.066 g (0.65 mmol) of Et_3N at room temperature. The mixture was stirred at room temperature for 30–40 min during which time the solution turned from green to orange-brown in color. The resulting brown-red solution of $\text{Et}_3\text{NH}[(\mu\text{-CO})(\mu\text{-}n\text{-BuS})\text{Fe}_2(\text{CO})_6]$ [**22**] was added to a suspension of **1**

Table 3
Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for **7**

Atom	x	y	z	B_{eq}^a
Ir	0.0638(2)	0.2263(2)	0.4017(2)	2.3(1)
Fe(1)	-0.2190(5)	0.2349(5)	0.0733(8)	3.3(4)
Fe(2)	-0.3774(5)	0.1886(6)	0.1684(8)	3.4(3)
S(1)	-0.249(1)	0.282(1)	0.317(1)	3.2(6)
S(2)	-0.230(1)	0.078(1)	0.136(1)	3.4(6)
S(3)	-0.035(1)	0.198(1)	0.135(1)	3.5(6)
O(1A)	-0.266(2)	0.164(2)	-0.265(4)	4.6(8)
O(1B)	-0.236(3)	0.441(4)	0.008(5)	9(1)
O(2A)	-0.524(3)	0.368(3)	0.109(5)	8(1)
O(2B)	-0.498(3)	0.081(3)	-0.122(4)	7(1)
O(2C)	-0.469(3)	0.114(3)	0.415(4)	6(1)
C(1A)	-0.250(3)	0.193(3)	-0.131(5)	3(1)
C(1B)	-0.229(5)	0.358(6)	0.038(7)	8(2)
C(2A)	-0.463(5)	0.299(5)	0.133(6)	6(1)
C(2B)	-0.456(5)	0.119(5)	-0.013(8)	8(2)
C(2C)	-0.432(4)	0.145(4)	0.327(6)	5(1)
C(3)	-0.011(4)	0.107(4)	0.288(5)	4(1)
C(3A)	0.042(4)	0.008(4)	0.233(5)	4(1)
C(4)	-0.124(3)	0.101(3)	0.323(4)	1.6(8)
C(5)	-0.151(3)	0.190(3)	0.436(5)	3(1)
C(6)	-0.046(4)	0.245(4)	0.500(6)	5(1)
C(6A)	-0.062(3)	0.307(3)	0.659(5)	3(1)
C(7)	0.225(3)	0.220(3)	0.340(4)	1.1(8)
C(7A)	0.252(4)	0.171(4)	0.191(6)	6(1)
C(8)	0.231(3)	0.179(4)	0.474(5)	3(1)
C(8A)	0.281(4)	0.077(4)	0.514(6)	5(1)
C(9)	0.207(3)	0.252(3)	0.589(5)	3(1)
C(9A)	0.212(5)	0.253(5)	0.765(8)	10(2)
C(10)	0.179(3)	0.346(4)	0.524(5)	3(1)
C(10A)	0.151(5)	0.451(5)	0.597(7)	8(2)
C(11)	0.189(3)	0.322(4)	0.375(5)	3(1)
C(11A)	0.169(5)	0.401(5)	0.247(7)	9(2)
C(12)	0.462(8)	0.456(6)	0.53(1)	14(7)
C(13)	0.535(7)	0.396(5)	0.635(9)	12(5)
C(14)	0.474(5)	0.331(5)	0.695(9)	9(4)

^a Only Ir, Fe, S, and C(12), C(13), C(14) atoms were refined anisotropically.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9**

Atom	x	y	z	U_{eq}^a
Ir	998(1)	1953(1)	4014(1)	44(1)
S(1)	2012(4)	364(3)	2799(2)	41(1)
C(1)	4191(18)	1119(14)	4224(9)	67(5)
C(2)	2638(15)	817(12)	3883(8)	41(3)
C(3)	1683(20)	233(13)	4292(9)	57(5)
C(4)	282(23)	9(13)	3812(10)	66(5)
C(5)	337(14)	516(13)	3048(8)	38(3)
C(6)	-949(18)	467(15)	2335(11)	72(5)
Fe(1)	2394(2)	-1538(2)	2295(1)	41(1)
C(101)	709(20)	-2350(14)	2219(8)	55(4)
O(101)	-406(14)	-2873(11)	2191(8)	83(4)
C(102)	3125(17)	-1959(12)	3277(9)	44(4)
O(102)	3588(13)	-2242(9)	3910(6)	62(3)
Fe(2)	4520(3)	-854(2)	1734(2)	55(1)
C(201)	4833(19)	808(17)	1970(13)	72(5)
O(201)	5060(16)	1840(12)	2094(10)	100(5)
C(202)	5515(23)	-1028(20)	947(13)	89(7)
O(202)	6159(19)	-1139(17)	442(10)	128(6)
C(203)	5730(20)	-1044(16)	2630(11)	68(5)
O(203)	6523(14)	-1107(12)	3254(8)	84(4)
S(2)	3533(5)	-2861(3)	1614(2)	53(1)
C(21)	4613(24)	-3837(16)	2287(10)	84(6)
C(22)	5883(28)	-4300(24)	1933(15)	121(9)
C(23)	5655(34)	-4937(30)	1175(14)	157(13)
C(24)	6819(32)	-5579(32)	939(16)	178(16)
S(3)	2244(5)	-618(4)	1117(2)	57(1)
C(31)	1566(25)	-1676(17)	185(9)	84(6)
C(32)	-73(23)	-1997(17)	72(10)	84(6)
C(33)	-714(40)	-2787(22)	-718(14)	137(12)
C(34)	-2146(50)	-3125(62)	-821(25)	79(23)
C(33')	-714(40)	-2787(22)	-718(14)	137(12)
C(34')	-1019(102)	-4613(47)	-582(35)	256(66)
C(11)	1637(20)	360(23)	4991(10)	44(7)
C(12)	74(20)	3317(23)	4810(11)	42(7)
C(13)	-490(18)	3470(22)	3935(13)	49(8)
C(14)	732(18)	3841(21)	3565(11)	48(8)
C(15)	2058(17)	3918(20)	4213(12)	52(8)
C(16)	2614(32)	3759(37)	5815(14)	77(8)
C(17)	-795(37)	3064(40)	5435(20)	107(12)
C(18)	-2013(23)	3282(39)	3497(21)	94(10)
C(19)	614(41)	4162(33)	2707(13)	98(12)
C(20)	3525(10)	4348(8)	4154(5)	83(9)
C(11')	1968(10)	3767(10)	4767(5)	49(8)
C(12')	715(10)	3308(10)	5065(5)	48(8)
C(13')	-578(10)	3245(8)	4364(7)	52(8)
C(14')	-145(10)	3600(11)	3609(6)	44(7)
C(15')	1432(10)	3967(11)	3877(6)	42(7)
C(16')	3419(10)	3899(10)	5324(5)	94(10)
C(17')	619(31)	3084(25)	5906(11)	98(12)
C(18')	-2076(18)	2921(27)	4420(17)	83(9)
C(19')	-984(25)	3672(27)	2776(11)	77(8)
C(20')	2359(28)	4467(27)	3357(15)	107(12)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(0.20 g, 0.33 mmol) in 30 ml of THF at -70°C with vigorous stirring. The reaction solution turned red immediately. After the mixture was stirred at -70 to 10°C

for 8 h, the solvent was removed in vacuo, and the dark-red residue was chromatographed on Al_2O_3 (neutral) with hexanes- CH_2Cl_2 (10:1) as the eluant. A deep-red band eluted first; then an orange band was eluted with hexanes- CH_2Cl_2 - Et_2O (10:1:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from hexanes- CH_2Cl_2 at -80°C . From the first fraction, 0.185 g (65%, based on **1**) of **9** as deep-red crystals were obtained (m.p. 132 – 134°C , decomp.). IR(hexanes) $\nu(\text{CO})$: 2031 vs, 1980 vs, 1965 s, 1952 s, 1918 m cm^{-1} . $^1\text{H NMR}$ (CDCl_3): δ 4.64 (d, 1 H), 4.59 (d, 1 H), 1.34 (s, 6 H), 1.92 (s, 15 H), 1.56 (m, 4 H), 1.34 (m, 8 H), 0.87 (t, 6 H). MS: m/e 813 ($\text{M}^+ - \text{C}_4\text{H}_9$), 758 ($\text{M}^+ - \text{C}_4\text{H}_9 - 2\text{CO}$). Anal. Found: C, 40.69; H, 4.95. $\text{C}_{29}\text{H}_{41}\text{Fe}_2\text{IrO}_5\text{S}_3$. Calc.: C, 40.05; H, 4.75%. From the second fraction, 0.031 g (20%, based on **1**) of **10** [27] as orange crystals were obtained (m.p. 121 – 122°C , decomp.). IR(hexane) $\nu(\text{CO})$: 2020 s cm^{-1} . $^1\text{H NMR}$ (CDCl_3): δ 5.79 (d, 1 H), 5.45 (d, 1 H), 2.29 (s, 3 H), 1.97 (s, 3 H), 1.88 (s, 15 H). MS: m/e 468 (M^+).

2.6. Photolytic reaction of **9** to give **10**

A solution of **9** (0.025 g, 0.029 mmol) in 20 ml of THF in a quartz photolysis tube was photolyzed with a 450 W, 254-nm lamp for 20 h during which time the deep-red solution gradually turned orange-red. The solvent was removed in vacuo, and the residue was chromatographed on Al_2O_3 (neutral) with hexanes- CH_2Cl_2 (10:1) as the eluant. The orange band was eluted and collected. After removal of the solvent, the residue was recrystallized from hexanes- CH_2Cl_2 at -80°C to give 0.010 g (80%, based on **9**) of orange crystals of **10** which was identified by its melting point, and IR and $^1\text{H NMR}$ spectra [27].

2.7. X-ray crystal structure determinations of **6**, **7**, and **9**

Crystals of complexes **6**, **7** and **9** suitable for X-ray diffraction studies were obtained by recrystallization

Table 5
Selected bond lengths (\AA) for $\text{Cp}^* \text{Ir}(\eta^1\text{-}2,5\text{-Me}_2\text{T})\text{Fe}_2(\text{CO})_4(\mu\text{-S}_2)$ (**6**) with e.s.d.s

Fe(1)–Fe(2)	2.553(2)	Ir–C(2)	2.132(8)
Fe(1)–S(1)	2.228(2)	Ir–C(3)	2.146(9)
Fe(1)–S(2)	2.239(3)	Ir–C(4)	2.150(8)
Fe(1)–S(3)	2.252(3)	Ir–C(5)	2.128(9)
Fe(1)–C(31)	1.780(9)	C(1)–C(2)	1.52(1)
Fe(1)–C(32)	1.76(1)	C(2)–C(3)	1.45(1)
Fe(2)–S(2)	2.243(3)	C(3)–C(4)	1.45(1)
Fe(2)–S(3)	2.257(3)	C(4)–C(5)	1.46(1)
Fe(2)–C(33)	1.76(1)	C(5)–C(6)	1.48(1)
Fe(2)–C(34)	1.79(1)	S(1)–C(2)	1.797(9)
Fe(2)–C(35)	1.77(1)	S(1)–C(5)	1.804(8)

Table 6
Selected bond angles (deg) for $\text{Cp}^* \text{Ir}(\eta^4\text{-}2,5\text{-Me}_2\text{T})\text{-Fe}_2(\text{CO})_5 (\mu\text{-S}_2)$ (6) with e.s.d.s

C(31)–Fe(1)–C(32)	94.5(4)	Fe(2)–Fe(1)–S(1)	154.42(8)
Fe(1)–Fe(2)–S(2)	55.19(7)	Fe(2)–Fe(1)–S(2)	55.36(7)
Fe(1)–Fe(2)–S(3)	55.41(7)	Fe(2)–Fe(1)–S(3)	55.60(7)
Fe(1)–Fe(2)–C(33)	92.5(3)	Fe(2)–Fe(1)–C(31)	101.2(3)
Fe(1)–Fe(2)–C(34)	159.0(3)	Fe(2)–Fe(1)–C(32)	104.3(3)
Fe(1)–Fe(2)–C(35)	95.6(3)	S(1)–Fe(1)–S(2)	101.51(9)
S(2)–Fe(2)–S(3)	53.5(1)	S(1)–Fe(1)–S(3)	103.29(9)
S(2)–Fe(2)–C(33)	145.7(3)	S(1)–Fe(1)–C(31)	94.6(3)
S(2)–Fe(2)–C(34)	107.4(3)	S(1)–Fe(1)–C(32)	94.2(3)
S(2)–Fe(2)–C(35)	100.2(3)	S(2)–Fe(1)–S(3)	53.6(1)
S(3)–Fe(2)–C(33)	100.8(3)	S(2)–Fe(1)–C(31)	103.7(3)
S(3)–Fe(2)–C(34)	105.8(3)	S(2)–Fe(1)–C(32)	154.7(3)
S(3)–Fe(2)–C(35)	147.8(3)	S(3)–Fe(1)–C(31)	153.3(3)
C(33)–Fe(2)–C(34)	101.0(5)	S(3)–Fe(1)–C(32)	103.7(3)
C(33)–Fe(2)–C(35)	93.5(4)	S(1)–C(5)–C(4)	110.0(7)
C(34)–Fe(2)–C(35)	99.5(4)	S(1)–C(5)–C(6)	118.6(7)
Fe(1)–S(1)–C(2)	115.4(3)	C(4)–C(5)–C(6)	123.1(9)
Fe(1)–S(1)–C(5)	115.7(3)	S(1)–C(2)–C(1)	118.4(6)
C(2)–S(1)–C(5)	83.3(4)	S(1)–C(2)–C(3)	111.4(7)
Fe(1)–S(2)–Fe(2)	69.45(8)	C(1)–C(2)–C(3)	122.0(8)
Fe(1)–S(3)–Fe(2)	68.99(8)	C(2)–C(3)–C(4)	108.4(8)
		C(3)–C(4)–C(5)	109.2(7)

from hexanes- CH_2Cl_2 solution at -80°C . In each case, a crystal of the compound whose structure was to be determined was mounted on the end of a glass fiber in a random orientation. The crystal was then placed on a four-circle diffractometer and cell constants and crystal system determined by an automated search routine. Each of the molecules was found to crystallize in the triclinic crystal system.

Data were collected within a 2θ sphere of 50° for 6 and 7 using Mo $\text{K}\alpha$ radiation and within a 2θ sphere of 114° for 9 using Cu $\text{K}\alpha$ radiation (Table 1). In order to try to partially compensate for small crystal size and weak diffracting power, rotating anode sources were used for 7 and 9. In all cases intensity data were

corrected for absorption using empirical ψ scans and also corrected for Lorentz-polarization effects. Compound 9 was also corrected for extinction. Equivalent data were merged.

Table 8
Selected bond angles (deg) for $\text{Cp}^* \text{Ir}(\text{C}(\text{Me})=\text{CHCH}=\text{C}(\text{Me}))\mu\text{-SX}(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_5$ (7) with e.s.d.s

Ir–C(6)–C(6A)	132(3)	C(2C)–Fe(2)–S(1)	100(2)
Ir–C(6)–C(5)	123(3)	C(2C)–Fe(2)–S(2)	106(2)
C(6A)–C(6)–C(5)	105(4)	S(1)–Fe(2)–S(2)	82.3(5)
C(6)–Ir–C(3)	83(2)	S(1)–Fe(2)–Fe(1)	55.7(4)
C(6)–Ir–S(3)	99(2)	S(2)–Fe(2)–Fe(1)	56.4(4)
C(3)–Ir–S(3)	50(1)	Fe(1)–S(1)–Fe(2)	68.5(4)
C(1B)–Fe(1)–C(1A)	92(3)	C(4)–S(2)–Fe(1)	91(1)
C(1B)–Fe(1)–S(1)	91(2)	C(4)–S(2)–Fe(2)	106(1)
C(1B)–Fe(1)–S(2)	171(2)	Fe(1)–S(2)–Fe(2)	66.8(4)
C(1B)–Fe(1)–S(3)	101(2)	C(3)–S(3)–Fe(1)	105(2)
C(1B)–Fe(1)–Fe(2)	114(2)	C(3)–S(3)–Ir	54(1)
C(1A)–Fe(1)–S(1)	157(1)	Fe(1)–S(3)–Ir	120.5(6)
C(1A)–Fe(1)–S(2)	92(2)	C(3A)–C(3)–C(4)	114(4)
C(1A)–Fe(1)–S(3)	102(1)	C(3A)–C(3)–S(3)	111(3)
C(1A)–Fe(1)–Fe(2)	103(1)	C(3A)–C(3)–Ir	126(3)
S(1)–Fe(1)–S(2)	82.6(5)	C(4)–C(3)–S(3)	105(3)
S(1)–Fe(1)–S(3)	99.6(5)	C(4)–C(3)–Ir	115(3)
S(1)–Fe(1)–Fe(2)	55.8(4)	S(3)–C(3)–Ir	76(2)
S(2)–Fe(1)–S(3)	86.4(5)	C(5)–C(4)–C(3)	110(3)
S(2)–Fe(1)–Fe(2)	56.8(4)	C(5)–C(4)–S(2)	115(3)
S(3)–Fe(1)–Fe(2)	135.7(4)	C(3)–C(4)–S(2)	112(3)
C(2A)–Fe(2)–C(2B)	91(3)	C(4)–C(5)–C(6)	107(4)
C(2A)–Fe(2)–C(2C)	101(2)	C(4)–C(5)–S(1)	108(3)
C(2A)–Fe(2)–S(1)	90(2)	C(6)–C(5)–S(1)	104(3)
C(2A)–Fe(2)–S(2)	153(2)	C(6A)–C(6)–C(5)	105(4)
C(2A)–Fe(2)–C(2C)	101(2)	C(6A)–C(6)–Ir	132(3)
C(2B)–Fe(2)–S(1)	158(2)	C(5)–C(6)–Ir	123(3)
C(2B)–Fe(2)–S(2)	88(2)	C(12)–C(13)–C(14)	109(9)

Table 7
Selected bond lengths (Å) for $\text{Cp}^* \text{Ir}(\text{C}(\text{Me})=\text{CHCH}=\text{C}(\text{Me}))\mu\text{-SX}(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_5$ (7) with e.s.d.s

Ir–S(3)	2.38(1)	Fe(2)–C(2C)	1.87(5)
Ir–C(3)	1.98(5)	S(1)–C(5)	1.88(4)
Ir–C(6)	1.77(5)	S(2)–C(4)	1.87(4)
Fe(1)–Fe(2)	2.514(9)	S(3)–C(3)	1.88(5)
Fe(1)–S(1)	2.23(1)	C(3)–C(3A)	1.49(6)
Fe(1)–S(2)	2.28(1)	C(3)–C(4)	1.55(5)
Fe(1)–S(3)	2.28(1)	C(4)–C(5)	1.50(5)
Fe(1)–C(1A)	1.76(4)	C(5)–C(6)	1.56(6)
Fe(1)–C(1B)	1.70(7)	C(6)–C(6A)	1.55(5)
Fe(2)–S(1)	2.23(1)	C(12)–C(12)*	1.6(2) ^a
Fe(2)–S(2)	2.29(1)	C(12)–C(13)	1.4(1) ^a
Fe(2)–C(2A)	1.75(6)	C(13)–C(14)	1.4(1) ^a
Fe(2)–C(2B)	1.86(7)		

^a C(12), C(13), and C(14) are carbons in the lattice *n*-hexane molecules. C(12)* is the symmetry generated partner of C12.

Table 9
Selected bond lengths (Å) for $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T})\cdot\text{Fe}_2(\text{CO})_5(\mu\text{-S}^n\text{Bu})_2$ (9) with e.s.d.s

Ir–C(3)	2.09(2)	S(3)–C(31)	1.81(2)
Ir–C(5)	2.09(1)	S(2)–C(21)	1.84(2)
Ir–C(2)	2.12(1)	Fe(1)–C(102)	1.76(2)
Ir–C(4)	2.14(2)	Fe(1)–C(101)	1.76(2)
S(1)–C(5)	1.77(1)	Fe(2)–C(203)	1.74(2)
S(1)–C(2)	1.79(1)	Fe(2)–C(202)	1.79(2)
S(1)–Fe(1)	2.240(4)	Fe(2)–C(201)	1.79(2)
C(1)–C(2)	1.49(2)	Fe(2)–S(3)	2.274(5)
C(2)–C(3)	1.40(2)	Fe(2)–S(2)	2.276(5)
C(3)–C(4)	1.41(2)	Fe(1)–S(2)	2.244(4)
C(4)–C(5)	1.45(2)	Fe(1)–S(3)	2.271(4)
C(5)–C(6)	1.53(2)	Fe(1)–Fe(2)	2.521(3)

In each case intensity statistics indicated $P\bar{1}$ as the most probable space group and this was later confirmed by successful refinement. The positions of the heavier atoms were found either by direct methods or by a combination of Patterson and direct methods. Remaining non-hydrogen atoms were found by difference electron density calculations; the largest residual peak was adjacent to the iridium atom. The structures were refined using full matrix least squares techniques [28] minimizing the function $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma_F^2$. All non-hydrogen atoms were refined anisotropically for 6 and 9. Owing to the poor scattering power of 7 and the lower number of observations, primarily the heavier atoms were refined anisotropically for 7.

Atomic coordinates and equivalent isotropic displacement parameters for 6, 7, and 9 are given in Tables 2, 3, and 4 respectively. Selected bond lengths and bond

angles for 6 are given in Tables 5 and 6 respectively, for 7 in Tables 7 and 8 respectively, and for 9 in Tables 9 and 10 respectively.

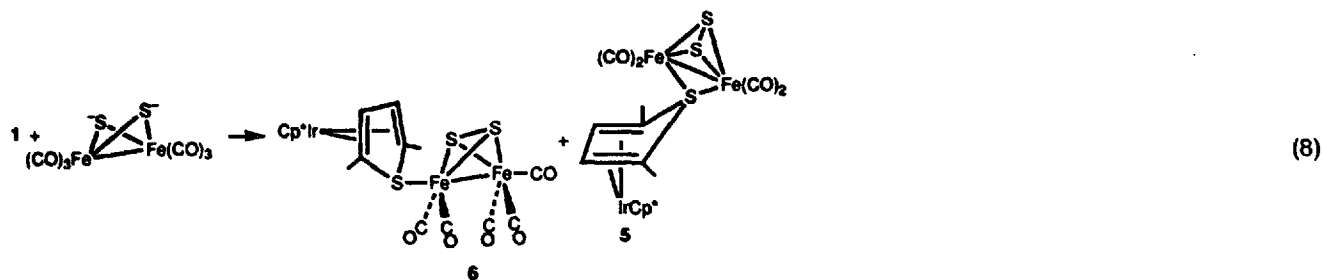
3. Results and discussion

3.1. Reaction of $\text{Cp}^* \text{Ir}(\eta^5\text{-2,5-Me}_2\text{T})^{2+}$ (1) with $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6^{2-}$

At -60° to -40°C in THF solvent, 1 reacts with $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6^{2-}$ over a 6 h period to give two products 5 and 6, which were isolated in 15% and 44% yield respectively (Eq. (8)). The molecular structure (Fig. 1) of the higher yield product 6 was established by X-ray diffraction studies, which show that it is a derivative of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ (4) in which one of the CO ligands is substituted by the S-donor $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T})$ (2). This sulfur lies approximately along the Fe(1)–Fe(2) axis with an Fe(2)–Fe(1)–S(1) angle of $154.42(8)^\circ$. Except for this $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T})$ substitution, the structures of 4 [29] and the $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_5$ portion of 6 are nearly the same as illustrated by the following parameters (the value for 6 is followed by the same parameter for 4): Fe(1)–Fe(2) (2.553(2), 2.552(2) Å), S(1)–S(2) (2.025(5), 2.007(5)), average Fe–S (2.242, 2.228), average Fe–S–Fe (69.23 , 69.88°). The Fe(1)–S(1) distance (2.228(2) Å) to the sulfur of the $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T})$ ligand is slightly shorter than the distances (2.239(3), 2.252(3) Å) between Fe(1) and the bridging sulfur atoms, S(2) and S(3). The structural

Table 10
Selected bond angles (deg) for $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T})\cdot\text{Fe}_2(\text{CO})_5(\mu\text{-S}^n\text{Bu})_2$ (9)

C(5)–S(1)–Fe(1)	116.7(5)	S(2)–Fe(1)–Fe(2)	56.7(1)
C(2)–S(1)–Fe(1)	117.8(5)	S(3)–Fe(1)–Fe(2)	56.4(1)
C(3)–C(2)–C(1)	125(1)	C(203)–Fe(2)–C(202)	104(1)
C(3)–C(2)–S(1)	108(1)	C(203)–Fe(2)–C(201)	90.5(9)
C(1)–C(2)–S(1)	119(1)	C(202)–Fe(2)–C(201)	98.4(9)
C(2)–C(3)–C(4)	113(1)	C(203)–Fe(2)–S(3)	147.9(7)
C(4)–C(5)–C(6)	124(1)	C(202)–Fe(2)–S(3)	107.9(7)
C(4)–C(5)–S(1)	111(1)	C(201)–Fe(2)–S(3)	88.4(6)
C(6)–C(5)–S(1)	117(1)	S(3)–Fe(2)–S(2)	80.2(2)
C(102)–Fe(1)–C(101)	94.8(7)	C(203)–Fe(2)–Fe(1)	93.7(6)
C(102)–Fe(1)–S(1)	93.3(4)	C(202)–Fe(2)–Fe(1)	149.3(8)
C(102)–Fe(1)–S(2)	95.0(4)	C(201)–Fe(2)–Fe(1)	106.6(6)
C(101)–Fe(1)–S(2)	104.3(5)	S(3)–Fe(2)–Fe(1)	56.3(1)
S(1)–Fe(1)–S(2)	153.3(2)	S(2)–Fe(2)–Fe(1)	55.5(1)
C(102)–Fe(1)–S(3)	159.3(5)	C(21)–S(2)–Fe(1)	113.3(6)
C(101)–Fe(1)–S(3)	105.9(5)	C(21)–S(2)–Fe(2)	113.3(7)
S(1)–Fe(1)–S(3)	82.3(2)	Fe(1)–S(2)–Fe(2)	67.8(1)
S(2)–Fe(1)–S(3)	80.9(2)	C(31)–S(3)–Fe(1)	114.0(6)
C(102)–Fe(1)–Fe(2)	104.5(5)	C(31)–S(3)–Fe(2)	113.3(7)
C(101)–Fe(1)–Fe(2)	153.6(5)	Fe(1)–S(3)–Fe(2)	67.4(1)
S(1)–Fe(1)–Fe(2)	96.7(1)		



features of the $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T})$ unit in **6** are very similar to those of this same unit when coordinated through sulfur to $\text{Fe}(\text{CO})_4$ [30]; η^4 -thiophene ligands in $\text{Cp}^* \text{Rh}(\eta^4\text{-Me}_4\text{T})$ [31], $(\eta^5\text{-Me}_4\text{T})\text{Ru}(\eta^4\text{-Me}_4\text{T})$ [32], and $(\text{CO})_3\text{Fe}(\eta^4\text{-T})$ [33] also form sulfur-coordinated complexes and their structures are very similar to that of $\eta^4\text{-2,5-Me}_2\text{T}$ in **6**. The strong donor ability of the sulfur in these η^4 -thiophene ligands has been explained in terms of an antibonding interaction between the metal and the sulfur [34]. In **6**, the fold angle of the thiophene ring, defined as the dihedral angle between the $\text{C}(2)\text{-C}(3)\text{-C}(4)\text{-C}(5)$ and $\text{C}(2)\text{-S}(1)\text{-C}(5)$ planes, is 36.6° ; $\text{S}(1)$ is 0.803 \AA above the four-carbon plane. The $\text{C}(2)\text{-through-C}(5)$ and $\text{C}(11)\text{-through-C}(15)$ planes are nearly co-planar, as indicated by the 10.2° dihedral angle between them. The $\text{C}(2)\text{-S}$ and $\text{C}(5)\text{-S}$ distances ($1.797(9)$, $1.804(8) \text{ \AA}$) are the same, within experimental error, as those in the $\text{Fe}(\text{CO})_4$ [30] complex but longer than the C-S bonds ($1.714(1) \text{ \AA}$) in thiophene itself [4].

In the ^1H NMR spectrum of **6**, the $\text{H}(3)$ and $\text{H}(4)$ protons are observed at δ 4.48, while the CH_3 protons are at δ 1.25. These chemical shifts are very similar to

those in $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T} \cdot \text{Fe}(\text{CO})_4)$ whose corresponding chemical shifts are δ 4.54 and 1.35 [30]. The infrared spectrum of **6** in the $\nu(\text{CO})$ region (2040 vs. 1978 vs. 1960 s.br, 1920 m cm^{-1} in CH_2Cl_2) is very similar to that of the mono-phosphine-substituted derivative of **4**, $(\text{Ph}_3\text{P})\text{Fe}_2(\text{CO})_5(\mu\text{-S}_2)$ (2055 s, 1996 s, 1986 s, 1975 w.sh, 1942 w in CCl_4) [35]. However, the generally lower $\nu(\text{CO})$ values in **6** indicate that the sulfur of $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T})$ is a better electron-donor than PPh_3 .

Crystals of **5**, the other product of reaction (8), were not suitable for X-ray studies. However, its ^1H NMR spectrum shows a singlet for $\text{H}(3)$ and $\text{H}(4)$ at δ 4.66 and another singlet (δ 1.34) for the CH_3 groups at carbons 2 and 3. The lack of splitting and the positions (δ) of these signals are characteristic of a $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T})$ ligand that is coordinated through the sulfur to one metal or possibly bridging two metals as in $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T} \cdot \text{Fe}_2(\text{CO})_7)$ [30] or $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T} \cdot \text{Mo}_2(\text{CO})_4\text{Cp}_2)$ [20,36]. The chemical shifts of $\text{H}(3,4)$ and the CH_3 groups in $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T} \cdot \text{Fe}_2(\text{CO})_7)$ occur at very similar values (δ 4.80 and 1.24). The elemental analysis (C and H) of **5** is similar

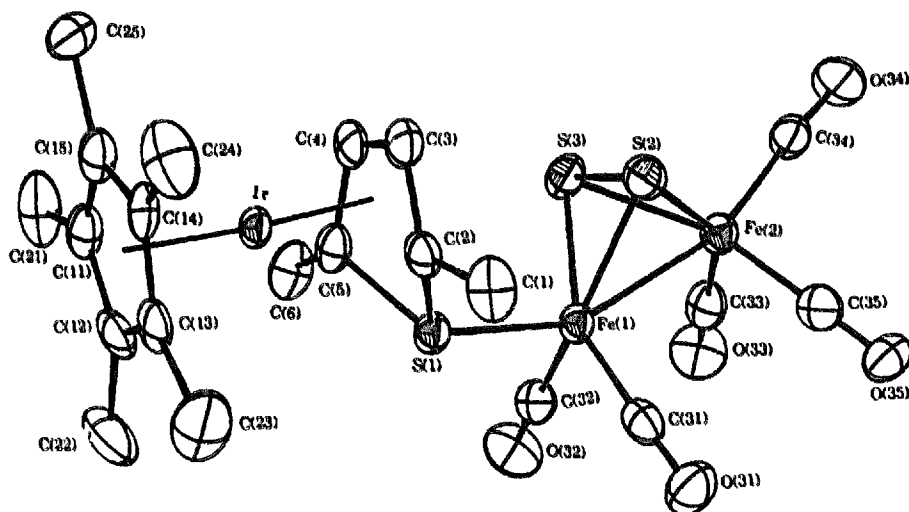
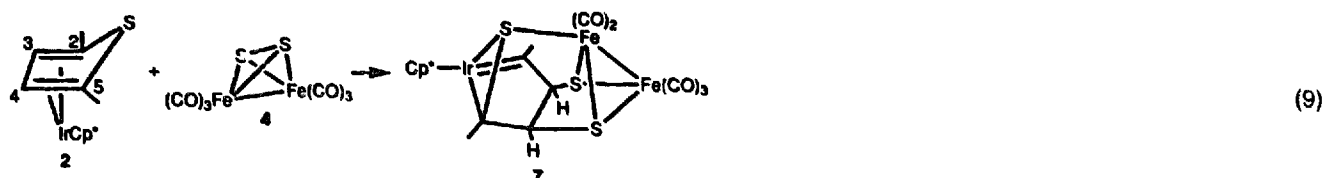


Fig. 1. Molecular structure of $\text{Cp}^* \text{Ir}(\eta^4\text{-2,5-Me}_2\text{T} \cdot \text{Fe}_2(\text{CO})_5(\mu\text{-S}_2))$ (**6**).



to that of **6** but $\nu(\text{CO})$ bands in the infrared spectrum (1970 s,br, 1935 vs. 1900 s,br cm^{-1} in CH_2Cl_2) of **5** are at lower wavenumbers than those in **6**, which is consistent with the replacement of a CO group in **6** by a sulfur donor ligand. The infrared spectrum of **5** is similar to the bis-phosphine-substituted **4**, $(\text{Ph}_3\text{P})_2\text{Fe}_2(\text{CO})_4(\mu\text{-S}_2)$, which has $\nu(\text{CO})$ bands at 2006 s, 1958 m, and 1943 s cm^{-1} in CCl_4 [35]. Taken altogether, the spectroscopic data are consistent with the sulfur-bridging structure for **5** shown in Eq. (8), but this assignment must be regarded as tentative.

The mechanism of reaction (8) might be considered to involve an initial 2-electron transfer from $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6^{2-}$ to $\text{Cp}^*\text{Ir}(\eta^5\text{-2,5-Me}_2\text{T})^{2+}$ to give $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_5$ (**4**) and $\text{Cp}^*\text{Ir}(\eta^5\text{-2,5-Me}_2\text{T})$ as either isomer **2** or **3**. Then, **4** could react with **2** or **3** to give the products **5** and **6**. However, this cannot be the mechanism since **4** reacts with **2** or **3** to give products other than **5** and **6**, as discussed in the next section. At this point, any proposed mechanism for reaction (8) would be highly speculative.

3.2. Reactions of 2 and 3 with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ (4**)**

In order to explore the possibility that reaction (8) proceeds via $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ (**4**) and $\text{Cp}^*\text{Ir}(\eta^5\text{-2,5-Me}_2\text{T})$ (**2** or **3**) as intermediates, **4** was allowed to react separately with **2** and **3**. The reaction (Eq. (9)) with **2** run at -60°C in THF solvent gave a new compound **7** in 48% isolated yield. While **7** has the same chemical composition as **6**, their structures are completely different. In **7** (Fig. 2), the Ir is part of a five-membered ring including C(3), C(4), C(5) and C(6). All of the carbons in this ring are saturated except C(6), which is planar as indicated by the sum (360°) of the three angles around it. The short Ir=C(6) bond distance (1.77(5) Å) suggests that C(6) is a carbene carbon; this distance is even shorter than the Ir=C double bonds (1.868(9) and 1.872(7) Å) in $\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{Ir}=\text{CH}_2$ [37] and $(\text{Ph}_3\text{P})_2\text{Cl}_3\text{Ir}=\text{CCl}_2$ [38], although the errors in **7** are relatively large. The S(3) atom, which was presumably part of the 2,5-Me₂T ligand in reactant **2**, bridges the Ir–C(3) bond like an episulfide but also coordinates to Fe(1). The S(1) and S(2) atoms, assumed to be part of **4** originally, are attached at C(4) and C(5). A similar attachment of the two sulfur atoms was reported [39] for complex **A** which forms in the reaction of **4** with cyclohexene. In fact, the structures of **A** and the $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_5$ portion of **7** are very similar, except that one of the two end CO groups in **A** is replaced by the

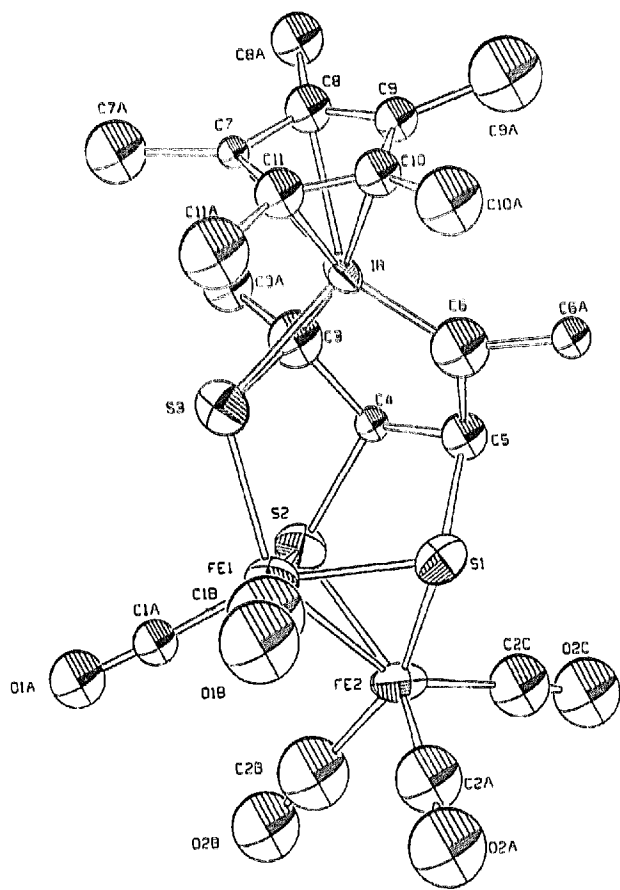
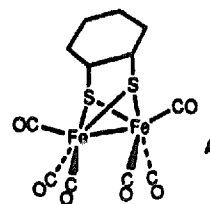
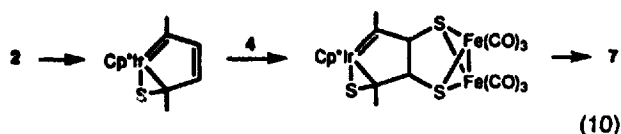


Fig. 2. Molecular structure of $\text{Cp}^*\text{Ir}(\eta^5\text{-CH}(\text{Me})=\text{CHCH}=\text{C}(\text{Me}))(\mu\text{-S})_2\text{Fe}_2(\text{CO})_5$ (**7**).





(10)

episulfide in **7**. A comparison of structural parameters follows (values for **7** are given first, then for **A**): Fe(1)–Fe(2) (2.514(9), 2.496(2) Å), average Fe(1)–S–Fe(2) (67.6, 67.6°), and average S(1)–Fe–S(2) (82.4, 80.2°). The structure of the thiophene ring in **7**, with the sulfur atom bent out of the thiophene plane, is similar to that [**40**] of the tetramethylthiophene ring in $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{CpRu}(\text{SC}_4\text{Me}_4))]^+$; it was suggested [**40**] that the bent sulfur form may illustrate an intermediate in the process of the HDS of thiophenes.

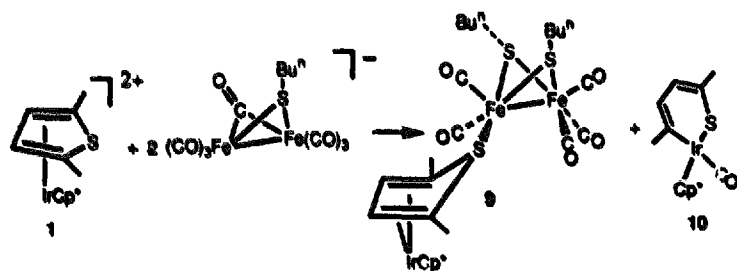
The very mild conditions (-60°C) of reaction (9) and reasonable yield (48%) of **7** suggest that there is a facile pathway for this reaction. Complex **4** is known to undergo oxidative reactions [23,39] at the S–S or Fe–Fe bonds with electron-rich metal complexes; however, they seem not to be involved in reaction (9) since they do not lead to the observed product **7**. In fact, there is no simple route involving preceded reactions of **2** and **4** that lead to **7**. Eq. (10) gives an outline of a pathway that may serve as a framework for an initial understanding of reaction (9).

The ring-opened isomer **3** reacts with **4** under the same conditions (-60 to -50°C in THF for 6 h) as reaction (9) to give **7** and a new complex **8** in 24% and 29% isolated yields respectively. The formation of **7** is not surprising since **2** and **3** often react to give the same products [20,30]. The structure of **8** is not known since we were unable to obtain X-ray quality crystals. The parent ion (M^+) in its mass spectrum and C,H elemental analyses indicate a composition $\text{Cp}^*\text{Ir}(\eta^5\text{-2,5-Me}_2\text{T})(\text{S}_2)\text{Fe}_2(\text{CO})_4$. The far downfield signals (δ 7.69, 7.52) in the ^1H NMR spectrum of **8** are similar to those for H(3) and H(4) in **3** (δ 7.47, 7.37). The $\nu(\text{CO})$ absorptions (2159 m, 2127 m, 2053 s, 2000 vs cm^{-1}) of **8** are at higher values than those of **4** [41] or its mono- or bis-phosphine-substituted derivatives [35], which suggests that the Fe atoms in **8** have been oxidized. At

this point, there is not sufficient evidence to assign the structure of **8**.

3.3. Reaction of $\text{Cp}^*\text{Ir}(\eta^5\text{-2,5-Me}_2\text{T})^{2+}$ (**1**) with $(\mu\text{-CO})(\mu\text{-}n\text{-BuS})\text{Fe}_2(\text{CO})_6^-$

Since the bridging carbonyl oxygen and Fe atoms in the $(\mu\text{-CO})(\mu\text{-}n\text{-RS})\text{Fe}_2(\text{CO})_6^-$ anions are known to be the nucleophilic centers toward a variety of electrophilic substrates [22–24,42,43], we expected the anion, where $\text{R} = n\text{-Bu}$, to react with **1** by nucleophilic attack on the $\eta^5\text{-2,5-Me}_2\text{T}$ ring. However, a totally different reaction (Eq. (11)) occurs at -70° to 10°C ; it gives **9** as the major product (65% yield) which is accompanied by a small amount (20%) of by-product **10**. The formation of **9** and **10** clearly indicate that **1** is reduced to **2** and **3**, which are incorporated into products **9** and **10** respectively. Since CO must also be liberated from $(\mu\text{-CO})(\mu\text{-}n\text{-BuS})\text{Fe}_2(\text{CO})_6^-$ in order to form **9**, product **10** probably forms by reaction of **3** with this CO; **3** is known [27,30] to react with CO at -30°C to form **10**. The formation of **9** requires the transfer of an $n\text{-BuS}^-$ group from one anion dimer to another to give the $(\mu\text{-}n\text{-BuS})_2\text{Fe}_2$ core. It has been previously reported [22a,42,43] that reactions of the $(\mu\text{-CO})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6^-$ anions with organomercury compounds, HgR_2 and $\text{Hg}(\text{R})(\text{X})$, often give $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_6$ by-products; yields of these by-products range from 9 to 82%, usually exceeding 40%. Thus, there is an oxidative pathway that converts $(\mu\text{-CO})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6^-$ to $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_6$. Details of the transfer of an RS^- group from one anion to another under these oxidative conditions are not known, but they appear to be occurring in both reaction (11) and the reactions with organomercury compounds. It is unlikely that $(\mu\text{-}n\text{-BuS})_2\text{Fe}_2(\text{CO})_6$ is actually formed in reaction (11) as an intermediate which subsequently undergoes CO substitution by **2** to give **9** since substitution of CO in $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_6$ by phosphines requires [44] more vigorous conditions (refluxing benzene or toluene); however, substitution reactions of $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_6$ by sulfur donor ligands (SR_2) have not been tried. Thus, the formation of **9** in reaction (11) probably results from initial electron-transfer to **1** giving **2** and **3**, as well as some oxidized form of $(\mu\text{-CO})(\mu\text{-}n\text{-BuS})\text{Fe}_2(\text{CO})_6^-$



(11)

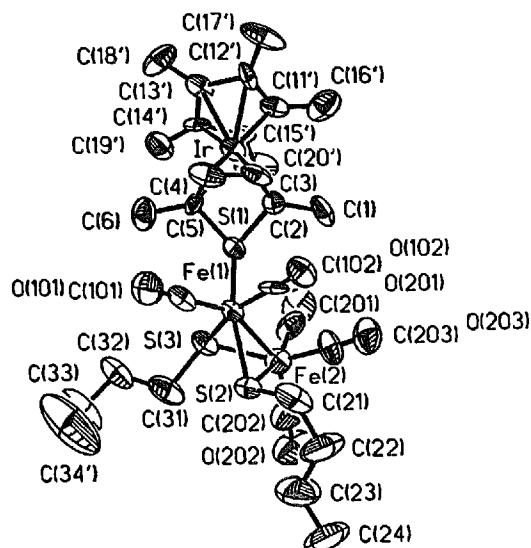
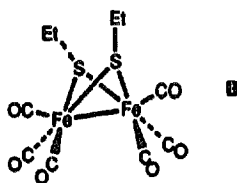


Fig. 3. Molecular structure of $\text{Cp}^* \text{Ir}(\eta^4\text{-}2,5\text{-Me}_2\text{T})\text{-Fe}_2(\text{CO})_5(\mu\text{-S}^n\text{Bu})_2$ (**9**).

which allows $n\text{-BuS}^-$ transfer and substitution of a CO group by **2**.

The molecular structure (Fig. 3) established by X-ray diffraction studies shows that **9** is a derivative of $(\mu\text{-}n\text{-BuS})_2\text{Fe}_2(\text{CO})_6$ in which one of the four equivalent CO groups approximately trans to the bridging sulfur atoms is substituted by a sulfur-bound $\text{Cp}^* \text{Ir}(\eta^4\text{-}2,5\text{-Me}_2\text{T})$ (**2**) ligand. The structure of the $(\mu\text{-}n\text{-BuS})_2\text{Fe}_2(\text{CO})_5$ part of **9** is very similar to that of $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ (**B**) [45]. In both **B** and **9**, the alkyl groups (Et or $n\text{-Bu}$) are anti with respect to each other. In **9**, the $n\text{-Bu}$ group on the same side of the molecule as the $\text{Cp}^* \text{Ir}(\eta^4\text{-}2,5\text{-Me}_2\text{T})$ (**2**) ligand points away from this bulky ligand. The $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_5$ portions of the molecules have basically the same geometries as indicated by the following parameters (the values for **9** are given first, then those for **B**): Fe–Fe (2.521(3); 2.54(1) Å), Fe–S–Fe (67.8, 67.4; 67.8, 68.9°), S–Fe–S (80.9, 80.2; 81.6, 80.3°), C(102)–Fe(1)–S(3) (159.3; 160.0°).

The structure of the $\text{Cp}^* \text{Ir}(\eta^4\text{-}2,5\text{-Me}_2\text{T})$ (**2**) portion of **9** is very similar to that in **6** and the related molecules discussed with **6** above. The dihedral angle (39.9°) between the C(2)–C(3)–C(4)–C(5) and C(2)–S(1)–C(5) planes in **9** is similar to that (36.6°) in **6**. The S(1) atom in **9** is 0.862 Å out of the C(2)–C(3)–C(4)–C(5) plane, which compares with 0.803 Å in **6**. Thus, the overall structures of **9** (Fig. 3) and **6** (Fig. 1) are similar except



for the different sulfur bridging ligands, $(\mu\text{-S}_2)$ in **6** and $(\mu\text{-}n\text{-BuS})_2$ in **9**. Also, the sulfur donor atom of the $\text{Cp}^* \text{Ir}(\eta^4\text{-}2,5\text{-Me}_2\text{T})$ ligand is coordinated at an end position (nearly on the Fe–Fe axis) in **6** but in one of the four positions trans to the bridging sulfur atoms in **9**.

The ^1H NMR spectrum of **9** contains doublets at δ 4.64 and 4.59 for H(3, 4) in the 2,5-Me₂T ligand; the inequivalence of H(3) and H(4) presumably results from their diastereotopic character in this asymmetric structure. The methyl groups at C(2) and C(5) occur as a singlet at δ 1.34. These chemical shifts for H(3, 4) and the methyl groups are very similar to those (δ 4.48 and 1.25) of **6** and related $\eta^4, \eta^1(\text{S})\text{-}2,5\text{-Me}_2\text{T}$ complexes.

The infrared spectrum of **9** exhibits $\nu(\text{CO})$ bands at 2031 vs., 1980 vs., 1965 s, 1952 s, 1918 m cm^{-1} ; these compare with absorptions (2045 s, 1985 s, 1978 sh, 1969 m, 1935 w, 1929 sh) for the mono-phosphine analog $(\mu\text{-MeS})_2\text{Fe}_2(\text{CO})_5(\text{PPh}_3)$ [44].

Although the structure of $(\mu\text{-MeS})\text{Fe}_2(\text{CO})_5(\text{PPh}_3)$ has not been established, the similarity of its infrared spectrum to that of **9** suggests that it has the same structure. The positions of the $\nu(\text{CO})$ bands in **9** are 5–15 cm^{-1} lower than those in $(\mu\text{-MeS})_2\text{Fe}_2(\text{CO})_5(\text{PPh}_3)$, which suggests that $\text{Cp}^* \text{Ir}(\eta^4\text{-}2,5\text{-Me}_2\text{T})$ is a better electron-donor ligand than PPh_3 , a conclusion that was reached in the discussion of **6** in Section 3.1.

4. Conclusions

Reactions of the cation $\text{Cp}^* \text{Ir}(\eta^4\text{-}2,5\text{-Me}_2\text{T})^{2+}$ (**1**) with $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6^{2-}$ (Eq. (8)) and with $(\mu\text{-CO})(\mu\text{-}n\text{-BuS})\text{Fe}_2(\text{CO})_6^-$ (Eq. (11)) lead to products which contain either the $\text{Cp}^* \text{Ir}(\eta^4\text{-}2,5\text{-Me}_2\text{T})$ (**2**) or $\text{Cp}^* \text{Ir}(\text{C},\text{S-}2,5\text{-Me}_2\text{T})$ (**3**) units. Thus, both reactions result in the reduction of **1** to **2** or **3**, a process that occurs more directly with reducing agents such as Cp_2Co or $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})_2]$ (Eq. (5)). However, in products of reactions (8) and (11), the reduced $\text{Cp}^* \text{Ir}(\eta^4\text{-}2,5\text{-Me}_2\text{T})$ (**2**) is coordinated through its sulfur to the $\text{Fe}_2(\mu\text{-S})_2(\text{CO})_4$ dimer core in complexes **5**, **6** and **9**. In neither reaction (8) nor (11) is there evidence for nucleophilic attack of the $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6^{2-}$ or $(\mu\text{-CO})(\mu\text{-}n\text{-BuS})\text{Fe}_2(\text{CO})_6^-$ anion on the $\eta^5\text{-}2,5\text{-Me}_2\text{T}$ ligand of **1**. The reaction (Eq. (9)) of **2** with the neutral $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ (**4**) gives a totally different product (**7**) than that obtained from the corresponding cation and anion (Eq. (8)), which demonstrates that reaction (8) does not proceed via **2** and **4** as intermediates.

5. Supplementary material

Tables of anisotropic displacement parameters for **6**, **7**, and **9** (5 pages) are available.

Acknowledgments

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