

## Cyclopentadienyl thiocarbonyl complexes of iron: $[\text{Cp}^*\text{Fe}(\text{CO})_2\text{CS}]^+$ , $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\text{CS})_2$ , $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$ , and $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})_2$

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### Abstract

Nucleophiles generally react with the new iron thiocarbonyl complex  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]^+$  ( $\text{Cp}^* = \eta\text{-C}_5\text{Me}_5$ ) by attacking at the carbon of the CS ligand. Thus,  $\text{SMe}^-$  gives the dithioester,  $\text{Cp}^*\text{Fe}(\text{CO})_2[(\text{C}=\text{S})\text{SMe}]$  and  $\text{N}_3^-$  gives N-bound thiocyanate,  $\text{Cp}^*\text{Fe}(\text{CO})_2(\text{NCS})$ . It is observed that  $\text{MeO}^-$  attacks initially at the carbon of the CO ligand but more slowly migrates to the carbon of the CS ligand giving  $\text{Cp}^*\text{Fe}(\text{CO})_2[\text{C}(\text{S})\text{OMe}]$ . The reaction of the thioesters with  $\text{MeOSO}_2\text{CF}_3$  yields the thiocarbene complexes,  $\{\text{Cp}^*(\text{CO})_2\text{Fe}[\text{C}(\text{SMe})\text{X}]\}^+$  ( $\text{X} = \text{OMe}, \text{SMe}$ ).

The thiocarbonyl dimer,  $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\text{CS})_2$ , is synthesized by reduction of  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]^+$  with NaH. Reactions of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$  and  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})_2$  with Raney Ni result in the conversion of the bridging CS ligands to  $\mu\text{-CH}_2$  groups in the complexes  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\mu\text{-CH}_2)$ ,  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\mu\text{-CH}_2)$  and  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CH}_2)_2$ . The thiocarbonyl dimers also react with  $\text{AgBF}_4$  to give  $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})_2]\text{Ag}^+\text{BF}_4^-$  and  $\{[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})]_3\text{Ag}\}\text{BF}_4$ ; the structure of the latter compound was determined by X-ray crystallography.

### Introduction

While metal carbonyl complexes were first discovered 100 years ago as celebrated in this issue, the first transition-metal thiocarbonyl complex was reported in 1966 [1]; since that time more than three hundred thiocarbonyl complexes have been described [2]. The first iron thiocarbonyl complex,  $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$ , was prepared in 1968 [3–5]. Bridging thiocarbonyl dinuclear iron complexes,  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})_2$  [6] and  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$  [7,8], were synthesized in the late 1970's. About the same time, other iron thiocarbonyl complexes,  $\text{Fe}(\text{CO})_4(\text{CS})$  [9],  $\text{Fe}(\text{porphyrin})(\text{CS})$  and

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Fe(porphyrin)(CS)(L) [10,11], were prepared. More recently,  $[\text{CpFe}(\text{CO})(\text{CS})(\text{L})]^+$  [12,13],  $[\text{CpFe}(\text{CS})(\text{L})_2]^+$  [13],  $\text{CpFe}(\text{CS})_2\text{I}$  [13],  $\text{Fe}(\text{CO})_3(\text{CS})(\text{L})$  [14],  $\text{Fe}(\text{CO})_2(\text{L})_2(\text{CS})$  [14,15], and the clusters  $\text{Fe}_4(\text{CO})_{12}(\text{CS})(\text{S})$  [16],  $\text{Fe}_5(\text{CO})_{13}(\text{CS})(\text{S})_2$  [17], and  $\text{Co}_3\text{FeCp}(\text{CO})_9(\text{CS})$  [18] were reported.

The chemistry of  $\text{Cp}^*$  ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) complexes [19–21] may be similar or dissimilar compared to the related Cp derivatives. In the present paper, we describe the preparations of the  $\text{Cp}^*$  thiocarbonyl complexes,  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]^+$  and  $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\text{CS})_2$ , and compare their reactions with those of the Cp analogs. Also, reactions of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$  and  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})_2$  with  $\text{Ag}^+$  and Raney Ni are reported.

## Experimental

*General procedures.* All reactions and distillations were carried out using Schlenk techniques under an atmosphere of prepurified nitrogen at room temperature unless otherwise noted. Methylene chloride and hexanes were dried over  $\text{CaH}_2$  and distilled. Tetrahydrofuran and  $\text{Et}_2\text{O}$  were distilled from Na-benzophenone prior to use. Prior to distillation,  $\text{CS}_2$  was dried with  $\text{P}_2\text{O}_5$  and MeOH was dried with Mg.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a Nicolet NT-300 spectrometer using deuterated solvents as internal locks. All  $^1\text{H}$  NMR chemical shifts were referenced to internal  $\text{Me}_4\text{Si}$ , and  $^{13}\text{C}$  NMR chemical shifts were referenced to  $\text{CDCl}_3$  ( $\delta$  77.0 ppm). Variable temperature  $^1\text{H}$  NMR spectra were recorded on a Bruker WM 300 MHz instrument. Infrared spectra were obtained using a Perkin–Elmer 281 or 681 spectrometer; the spectra were calibrated with the  $1944.0\text{ cm}^{-1}$  band of polystyrene. Electron-ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. Fast atom bombardment (FAB, 3-nitrobenzyl alcohol matrix) mass spectra were run on a Kratos MS-50 instrument. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

NaOMe was prepared from Na and dry MeOH under  $\text{N}_2$  and used in situ. NaSMe [22] and  $\text{NaK}_{2.8}$  alloy [23] were prepared by literature methods. The aluminum-nickel catalyst and  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  were purchased from Aldrich, and Raney-Ni [24] was made by a literature method.  $\text{Cp}^*_2\text{Fe}_2(\text{CO})_4$  [25],  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$  [7], and  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})_2$  [6,13] were prepared by published procedures.

*Preparation of  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})][\text{BF}_4]$ .* Crystals of  $\text{Cp}^*_2\text{Fe}_2(\text{CO})_4$  (1.00 g, 2.02 mmol) were dissolved in 40 ml of freshly distilled THF, and then 0.5 ml of  $\text{NaK}_{2.8}$  alloy was added by syringe. After the solution was stirred with a magnetic stirring bar for 2.5 h, the excess  $\text{NaK}_{2.8}$  alloy was filtered off using a coarse porosity frit filled with glass wool to yield a clear blood-red solution of  $\text{K}[\text{Cp}^*\text{Fe}(\text{CO})_2]$ . Carbon disulfide (0.30 ml, 5.00 mmol) was added rapidly to the solution, and the mixture was stirred for 10 s; MeI (0.35 ml, 5.62 mmol) was added immediately thereafter. The reaction mixture was stirred for 0.5 h and then filtered through a pad of Celite. The  $\text{Cp}^*\text{Fe}(\text{CO})_2[\text{C}(=\text{S})\text{SMe}]$  was isolated at this stage by evaporating off the solvent. The  $\text{Cp}^*\text{Fe}(\text{CO})_2[\text{C}(=\text{S})\text{SMe}]$  was dissolved in 20 ml of THF and a solution of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (85%, 1.00 ml, 4.83 mmol) in 20 ml of  $\text{Et}_2\text{O}$  was added slowly and dropwise. After the mixture was stirred an additional 3 h, the yellow precipitate  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]\text{BF}_4$  was filtered off and washed with  $\text{Et}_2\text{O}$  and THF to remove a brown impurity. The bright yellow powder (0.69–0.90 g, 45–59% yield,

based on  $\text{Cp}^*\text{Fe}_2(\text{CO})_4$ ) was collected. Analytically pure crystals were obtained by recrystallization from acetone/ether at  $-20^\circ\text{C}$ . FAB MS:  $M^+$ , 291 (100%);  $M^+ - \text{CO}$ , 263 (24%);  $M^+ - 2\text{CO}$ , 235 (26%). Anal. Found: C, 41.16; H, 4.11.  $\text{C}_{13}\text{H}_{15}\text{O}_2\text{SBF}_4$  calcd.: C, 41.31; H, 4.00%.

*Preparation of  $\text{Cp}^*\text{Fe}_2(\text{CO})_2(\text{CS})_2$ .* A slurry of  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]\text{BF}_4$  (2.10 g, 5.56 mmol) and excess sodium hydride (0.40 g of 50% mineral oil dispersion, 8.3 mmol) in 15 ml of THF was stirred for 2 h. The mixture was evaporated to dryness under reduced pressure. The brown-black residue was extracted with hot benzene. The extract was filtered through Celite, and the solution was chromatographed on a Florisil column (60–100 mesh,  $20 \times 400$  mm) eluting with benzene. The entire column was covered by a brown-green band. The eluent was collected until it was no longer green and was then evaporated under reduced pressure to give a black solid containing a mixture of *cis*- and *trans*- $\text{Cp}^*\text{Fe}_2(\text{CO})_2(\text{CS})_2$ , with small amounts of  $\text{Cp}^*\text{Fe}_2(\text{CO})_4$  and  $\text{Cp}^*\text{Fe}_2(\text{CO})_3(\text{CS})$ .

The impurity complexes were removed by the following procedure. The black solid was dissolved in 10 ml of  $\text{CHCl}_3$ , then 5 ml of 90% EtOH and 1 ml of concentrated aqueous HCl were added. Air was slowly bubbled through the solution for 1 h. The air oxidized  $\text{Cp}^*\text{Fe}_2(\text{CO})_4$  and  $\text{Cp}^*\text{Fe}_2(\text{CO})_3(\text{CS})$  to  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{Cl}$  and  $\text{Cp}^*\text{Fe}(\text{CO})(\text{CS})\text{Cl}$ , while the  $\text{Cp}^*\text{Fe}_2(\text{CO})_2(\text{CS})_2$  did not react under these conditions. The solution was evaporated to reduce the volume to 5 ml. Addition of 20 ml of  $\text{H}_2\text{O}$  caused the  $\text{Cp}^*\text{Fe}_2(\text{CO})_2(\text{CS})_2$  to precipitate. The black powder was filtered off and washed with  $\text{H}_2\text{O}$  to remove the water soluble  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{Cl}$  and  $\text{Cp}^*\text{Fe}(\text{CO})(\text{CS})\text{Cl}$ . The black powder was dried under vacuum. Crystallization from  $\text{CH}_2\text{Cl}_2$ /hexanes at  $-20^\circ\text{C}$  yielded black crystals of  $\text{Cp}^*\text{Fe}_2(\text{CO})_2(\text{CS})_2$  (0.31 g, 21% yield). Typical yields varied from 15 to 25%. The IR spectrum of the *cis/trans* mixture in  $\text{CH}_2\text{Cl}_2$  solvent showed peaks at 1988 and  $1945\text{ cm}^{-1}$  whose relative intensities depended on the *cis/trans* ratio in the product. EIMS:  $M^+$ , 526 (3%);  $M^+ - 2\text{CO}$ , 470 (33%);  $\text{Cp}^* - \text{H}$ , 134 (79%);  $\text{Cp}^* - \text{Me}$ , 119 (100%). Anal. Found: C, 54.57; H, 6.03.  $\text{C}_{24}\text{H}_{30}\text{O}_2\text{S}_2\text{Fe}_2$  calcd.: C, 54.77; H, 5.75%.

*Reaction of  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]\text{BF}_4$  with NaOMe/MeOH.* A MeOH solution of NaOMe (1.00 ml, 0.26 mmol) prepared by adding 0.061 g (2.65 mmol) of Na in 10.0 ml of dry MeOH was added to  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]\text{BF}_4$  (0.10 g, 0.26 mmol) dissolved in 5 ml of  $\text{CH}_2\text{Cl}_2$ . The resulting mixture was stirred for a few seconds and then was evaporated immediately under vacuum to give a yellow precipitate which was extracted with  $\text{Et}_2\text{O}$ . The extract was filtered through Celite and evaporated under vacuum to yield a yellow powder (57 mg, 67%). IR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR (Table 1, 2, 3) showed only the  $\text{Cp}^*\text{Fe}(\text{CO})(\text{CS})[\text{C}(=\text{O})\text{OMe}]$  isomer. EIMS  $M^+$ , 322 (23%);  $M^+ - \text{CO}$ , 294 (100%);  $M^+ - 2\text{CO}$ , 266 (86%). When the same reaction mixture was stirred for 24 h at room temperature and worked up the same way, it yielded the  $\text{Cp}^*\text{Fe}(\text{CO})_2[\text{C}(=\text{S})\text{OMe}]$  isomer (50 mg, 59%) which was identified by its IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Table 1, 2, 3). The elemental analysis of the isomers was not obtained because they were air and thermally unstable.

*Reaction of  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]\text{BF}_4$  with  $\text{NaN}_3$ .* A solution of  $\text{NaN}_3$  (33 mg, 0.51 mmol) in 1 ml of  $\text{H}_2\text{O}$  was added to a solution of  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]\text{BF}_4$  (0.19 g, 0.50 mmol) in 15 ml of acetone. The solution turned from yellow to orange-red. After stirring for 20 min, evaporation of the solvent gave the product which was extracted with  $\text{CHCl}_3$ . The extract was filtered and concentrated. Addition of hexane and cooling to  $-20^\circ\text{C}$  gave orange-yellow crystals (0.11 g, 74%) of

Table 1  
Infrared spectra of the complexes

Complex	$\nu(\text{CO}), \text{cm}^{-1}$	$\nu(\text{CS}), \text{cm}^{-1}$	Complex	$\nu(\text{CO}), \text{cm}^{-1}$	$\nu(\text{CS}), \text{cm}^{-1}$	Ref
$[\text{Cp}^* \text{Fe}(\text{CO})_2(\text{CS})]\text{BF}_4^a$	2080(s), 2042(s)	1332(s)	$[\text{CpFe}(\text{CO})_2(\text{CS})\text{SO}_3\text{CF}_3]^g$	2105(s), 2071(s)	1353(s)	13
<i>cis</i> -, <i>trans</i> - $[\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\text{CS})_2]^a$	1988(m), 1945(s)	1108(m, br)	<i>cis</i> - $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})_2]^h$	2011(vs), 1982(m)	1124(s)	13
			<i>trans</i> - $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})_2]^h$	1979(s)	1131(s)	13
$\text{Cp}^* \text{Fe}(\text{CO})(\text{CS})[\text{C}(=\text{O})\text{OMe}]^{a,b}$	1992(s)	1292(s)	$\text{CpFe}(\text{CO})(\text{CS})[\text{C}(=\text{O})\text{OMe}]^{i,j}$	2020(s)	1316(s) <sup>h</sup>	30
$\text{Cp}^* \text{Fe}(\text{CO})_2[\text{C}(=\text{S})\text{OMe}]^{a,c}$	2012(s), 1958(s)		$\text{CpFe}(\text{CO})_2[\text{C}(=\text{S})\text{OMe}]^{i,k}$	2031(s), 1990(s)		30
$\text{Cp}^* \text{Fe}(\text{CO})_2[\text{C}(=\text{S})\text{SMe}]^a$	2008(s), 1955(s)		$\text{CpFe}(\text{CO})_2[\text{C}(=\text{S})\text{SMe}]^l$	2035(s), 1988(s)		5
$\text{Cp}^* \text{Fe}(\text{CO})_2(\text{NCS})^{a,d}$	2038(s), 1988(s)	820(m)	$\text{CpFe}(\text{CO})_2(\text{NCS})^m$	2072(s), 2031(s)	829(m) <sup>e</sup>	30
$[\text{Cp}^*(\text{CO})_2\text{Fe}[\text{C}(\text{SMe})_2]]\text{SO}_3\text{CF}_3^a$	2030(s), 1990(s)		$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SMe})_2]\}\text{SO}_3\text{CF}_3^a$	2055(s), 2014(s)		34
$[\text{Cp}^*(\text{CO})_2\text{Fe}[\text{C}(\text{SMe})(\text{OMe})]]\text{SO}_3\text{CF}_3^a$	2015(s), 1992(s)		$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SMe})(\text{OMe})]]\text{SO}_3\text{CF}_3^a$	2060(s), 2017(s)		34
$[\text{Cp}^*(\text{CO})_2\text{Fe}(\text{CNMe})]\text{SO}_3\text{CF}_3^{a,f}$	2055(s), 2018(s)		$[\text{Cp}(\text{CO})_2\text{Fe}(\text{CNMe})]\text{PF}_6^{a,n}$	2079(s), 2037(s)		o
$[\{\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})\}_3\text{Ag}]\text{BF}_4^a$	2020(s), 1990(sh), 1825(m)					
$\{[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})_2]\text{Ag}\}\text{BF}_4^e$	2040(vs), 2010(sh), 1030(m, br) 2000(s)					

<sup>a</sup>  $\text{CH}_2\text{Cl}_2$  solvent. <sup>b</sup>  $\nu(\text{C}=\text{O})\text{OMe}$  at 1634 (m)  $\text{cm}^{-1}$ . <sup>c</sup>  $\nu(\text{C}=\text{S})\text{OMe}$  at 1178 (m)  $\text{cm}^{-1}$ . <sup>d</sup>  $\nu(\text{CN})$  at 2110 (m)  $\text{cm}^{-1}$ . <sup>e</sup> Nujol mull. <sup>f</sup>  $\nu(\text{CN})$  at 2218 (m)  $\text{cm}^{-1}$ .  
<sup>g</sup> MeCN solvent. <sup>h</sup>  $\text{CS}_2$  solvent. <sup>i</sup> cyclohexane solvent. <sup>j</sup>  $\nu(\text{C}=\text{O})\text{OMe}$  at 1658 (m)  $\text{cm}^{-1}$ . <sup>k</sup>  $\nu(\text{C}=\text{S})\text{OMe}$  at 1196 (s)  $\text{cm}^{-1}$ . <sup>l</sup> Hexane solvent. <sup>m</sup>  $\nu(\text{CN})$  at 2133 (m)  $\text{cm}^{-1}$ . <sup>n</sup>  $\nu(\text{CN})$  at 2242 (m)  $\text{cm}^{-1}$ . <sup>o</sup> R.J. Angelici, P.A. Christian, B.D. Dombek and G.A. Pfeiffer, J. Organomet. Chem., 67 (1974) 287.

Table 2

<sup>1</sup>H NMR data (δ) for the complexes in CDCl<sub>3</sub>

Complex	C <sub>3</sub> Me <sub>3</sub> or C <sub>5</sub> H <sub>5</sub>	other
[Cp*Fe(CO) <sub>2</sub> (CS)]BF <sub>4</sub>	2.03	
<i>cis, trans</i> -[Cp* <sub>2</sub> Fe <sub>2</sub> (CO) <sub>2</sub> (CS) <sub>2</sub> ]	1.58, 1.64	
Cp*Fe(CO)(CS)[C(=O)OMe]	1.77	3.60 (OMe)
Cp*Fe(CO) <sub>2</sub> [C(=S)OMe]	1.75	4.14 (SMe)
Cp*Fe(CO) <sub>2</sub> [C(=S)SMe]	1.76	2.62 (SMe)
Cp*Fe(CO) <sub>2</sub> (NCS)	1.80	
{Cp*(CO) <sub>2</sub> Fe[=C(SMe) <sub>2</sub> ]}SO <sub>3</sub> CF <sub>3</sub>	1.88	3.18 (SMe)
{Cp*(CO) <sub>2</sub> Fe[=C(SMe)(OMe)]}SO <sub>3</sub> CF <sub>3</sub>	1.93	4.80 (OMe), 2.67 (SMe)
[Cp*(CO) <sub>2</sub> Fe(CNMe)]SO <sub>3</sub> CF <sub>3</sub>	1.97	3.66 (CNMe)
{[Cp <sub>2</sub> Fe <sub>2</sub> (CO) <sub>3</sub> (CS)] <sub>3</sub> Ag}BF <sub>4</sub> <sup>a</sup>	5.20	

<sup>a</sup> Acetone-*d*<sub>6</sub>.

Cp\*Fe(CO)<sub>2</sub>(NCS). EIMS: *M*<sup>+</sup>, 305 (16%); *M*<sup>+</sup> – CO, 277 (14%); *M*<sup>+</sup> – 2CO, 249 (23%); Cp\*, 135 (100%). Anal. Found: C, 51.01; H, 5.04; N, 4.30. C<sub>13</sub>H<sub>15</sub>O<sub>2</sub>NSFe calcd.: C, 51.17; H, 4.95; N, 4.59%.

*Reaction of [Cp\*Fe(CO)<sub>2</sub>(CS)]BF<sub>4</sub> with NaSMe.* A solution of [Cp\*Fe(CO)<sub>2</sub>(CS)]BF<sub>4</sub> (50 mg, 0.13 mmol) and NaSMe (10 mg, 0.14 mmol) in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> was stirred for 15 min. After evaporating the solvent under vacuum, the residue was extracted with Et<sub>2</sub>O. The extract was filtered through Celite; evaporation of the solvent yielded a brown powder (30 mg, 67%) of Cp\*Fe(CO)<sub>2</sub>[C(=S)SMe]. The <sup>1</sup>H NMR and IR spectra agreed with those reported [26] for this compound which was prepared by a different method.

*Preparation of {Cp\*(CO)<sub>2</sub>Fe[=C(SMe)<sub>2</sub>]}PF<sub>6</sub>.* The methyl thioester, Cp\*Fe(CO)<sub>2</sub>[C(=S)SMe] (0.35 g, 1.0 mmol), dissolved in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> was stirred with MeOSO<sub>2</sub>CF<sub>3</sub> (0.13 ml, 1.1 mmol) for 1 h. The resulting solution was evaporated to give an oily solid which was washed with Et<sub>2</sub>O. The resulting yellow powder was

Table 3

<sup>13</sup>C NMR data (δ) for the complexes in CDCl<sub>3</sub>

Complex	Me(Cp*)	C <sub>5</sub> (Cp*)	CS	CO	Other
[Cp*Fe(CO) <sub>2</sub> (CS)]BF <sub>4</sub> <sup>a</sup>	9.9	106.6	317.2	206.6	
<i>cis</i> -[Cp* <sub>2</sub> Fe <sub>2</sub> (CO) <sub>2</sub> (CS) <sub>2</sub> ]	8.3	100.0	388.0	211.5	
<i>trans</i> -[Cp* <sub>2</sub> Fe <sub>2</sub> (CO) <sub>2</sub> (CS) <sub>2</sub> ]	9.0	101.3	390.3	213.3	
Cp*Fe(CO)(CS)[C(=O)OMe]	9.3	99.1	329.4	214.7	52.4 (C(=O)OMe) 204.6 (C(=O)OMe)
Cp*Fe(CO) <sub>2</sub> [C(=S)OMe]	9.3	97.0		214.7	61.2 (C(=S)OMe) 291.0 (C(=S)OMe)
Cp*Fe(CO) <sub>2</sub> [C(=S)SMe]	9.0	97.2		214.4	25.1 (C(=S)SMe) 305.1 (C(=S)SMe)
{Cp*(CO) <sub>2</sub> Fe[=C(SMe) <sub>2</sub> ]}SO <sub>3</sub> CF <sub>3</sub>	9.5	100.1		211.1	29.4 (SMe) 310.5 (Fe=C)
{Cp*(CO) <sub>2</sub> Fe[=C(SMe)(OMe)]}SO <sub>3</sub> CF <sub>3</sub>	9.6	100.2		210.7	21.4 (SMe) 70.4 (OMe) 302.7 (Fe=C)

<sup>a</sup> In CD<sub>3</sub>NO<sub>2</sub>.

dissolved in a minimum amount of acetone; adding Et<sub>2</sub>O and cooling to -20 °C yielded yellow crystals. The crystals were washed with Et<sub>2</sub>O and dried under vacuum to give {Cp<sup>+</sup>(CO)<sub>2</sub>Fe[=C(SMe)<sub>2</sub>]}SO<sub>3</sub>CF<sub>3</sub> (0.33 g, 63%). Anion exchange was performed as follows to give the more stable PF<sub>6</sub><sup>-</sup> salt. The compound was dissolved in a minimum amount of acetone, placed on an anion-exchange column (Amberlite IRA-400, 25 × 1 cm) in the PF<sub>6</sub><sup>-</sup> form, and eluted slowly with acetone. The yellow fraction was collected and concentrated. Adding Et<sub>2</sub>O and cooling to -20 °C gave yellow crystals. FAB MS: M<sup>+</sup>, 353 (100%); M<sup>+</sup> - CO, 325 (33%); M<sup>+</sup> - 2CO, 297 (11%); M<sup>+</sup> - (2CO + Me), 282 (25%). Anal. Found: C, 36.27; H, 3.96. C<sub>15</sub>H<sub>21</sub>O<sub>2</sub>PF<sub>6</sub>Fe calcd.: C, 36.16; H, 4.25%.

*Preparation of {Cp<sup>+</sup>(CO)<sub>2</sub>Fe(=C(SMe)(OMe))}PF<sub>6</sub>.* This complex was prepared by the same method as described above. Starting with Cp<sup>+</sup>Fe(CO)<sub>2</sub>[C(=S)OMe] (80 mg, 0.25 mmol) and MeOSO<sub>2</sub>CF<sub>3</sub> (0.029 ml, 0.26 mmol), the product (78 mg, 65%) was obtained as yellow crystals. Anion exchange and crystallization were performed as described above. FAB MS: M<sup>+</sup>, 337 (100%); M<sup>+</sup> - CO, 309 (6%); M<sup>+</sup> - (2CO + Me), 266 (33%). Anal. Found: C, 37.39; H, 4.11. C<sub>15</sub>H<sub>21</sub>O<sub>3</sub>SFePF<sub>6</sub> calcd.: C, 37.36; H, 4.39%.

*Preparation of [Cp<sup>+</sup>(CO)<sub>2</sub>Fe(CNMe)]SO<sub>3</sub>CF<sub>3</sub>.* Methylamine was slowly bubbled through 40 ml of CH<sub>2</sub>Cl<sub>2</sub> containing {Cp<sup>+</sup>(CO)<sub>2</sub>Fe[=X(SMe)<sub>2</sub>]}SO<sub>3</sub>CF<sub>3</sub> (0.20 g, 0.44 mmol) for 10 min. After an additional 30 min of stirring, the bright yellow solution was concentrated, and yellow crystals (0.12 g, 70%) were obtained by adding Et<sub>2</sub>O and cooling to -20 °C. FAB MS: M<sup>+</sup>, 288 (100%); M<sup>+</sup> - CO, 260 (17%); M<sup>+</sup> - 2CO, 232 (41%). Anal. Found: C, 40.86; H, 4.35; N, 3.06. C<sub>15</sub>H<sub>18</sub>O<sub>6</sub>NSF<sub>3</sub>Fe calcd.: C, 41.21; H, 4.15; N, 3.20%.

*Reaction of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS) with AgBF<sub>4</sub>.* The bridged thiocarbonyl compound (0.20 g, 0.54 mmol) was dissolved in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> and AgBF<sub>4</sub> (0.10 g, 0.54 mmol) was added to the stirred solution. The dark green color changed to red within a few minutes. The resulting mixture was stirred for 30 min and then filtered. The filtrate was evaporated under vacuum to give a red solid product. Crystallization in either CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O or MeCN/Et<sub>2</sub>O yielded dark red crystals (0.14 g, 47%). Anal. Found **1**: C, 35.90; H, 2.36. Found **2**: C, 37.60; H, 2.64. Found **3**: C, 36.97; H, 2.68; Ag, 7.36. C<sub>42</sub>H<sub>30</sub>Fe<sub>6</sub>O<sub>9</sub>S<sub>3</sub>AgBF<sub>4</sub> calcd.: C, 38.67; H, 2.64; Ag, 8.27%. The nature of this compound is discussed in the Results and discussion section.

*Reaction of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(CS)<sub>2</sub> with AgBF<sub>4</sub>.* Crystals of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(CS)<sub>2</sub> (50 mg, 0.13 mmol) were dissolved in 10 ml of benzene, and AgBF<sub>4</sub> (25 mg, 0.13 mmol) was added to the solution with stirring. After the reaction mixture was stirred for 15 min, the dark green solution turned colorless and a dark red precipitate formed at the bottom of the flask. The product was filtered and then washed with Et<sub>2</sub>O to give a dark red powder of {[Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(CS)<sub>2</sub>]Ag}BF<sub>4</sub> (0.55 g, 73%). Anal. Found: C, 28.61; H, 2.01. C<sub>14</sub>H<sub>10</sub>O<sub>2</sub>S<sub>2</sub>BF<sub>4</sub>Fe<sub>2</sub>Ag calcd.: C, 28.96; H, 1.74%.

*Reaction of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS) with Raney Ni.* A Raney Ni slurry (1.5 ml) was added to a solution of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS) (0.10 g, 0.27 mmol) in 5 ml of xylenes, and the resulting mixture was stirred for 10 min. The dark green color changed to red. Filtration of the solution and evaporation yielded a red powder (10 mg, 11%). The product showed the same IR, <sup>1</sup>H NMR and mass spectra as reported for Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(μ-CO)(μ-CH<sub>2</sub>) [27].

*Reaction of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(CS)<sub>2</sub> with Raney Ni.* The same procedure as above was used for the reaction of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(CS)<sub>2</sub> (50 mg, 0.13 mmol) with Raney Ni

slurry (1.0 ml). Only trace amounts of a mixture of  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CS})(\mu\text{-CH}_2)$  and  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CH}_2)_2$  were obtained. These products were identified by  $^1\text{H}$  NMR, mass, and IR spectrometry. Spectral data for the mixture follow.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  10.52, 9.91, 9.89, 9.62, 8.68, 7.97 ( $\mu\text{-CH}_2$ ); 4.90, 4.80, 4.70, 4.66 (Cp). MS:  $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CH}_2)(\mu\text{-CS})]$ ,  $M_1^+$ , 356 (2%);  $[M_1^+ - \text{CO}]$ , 328 (6%);  $[M_1^+ - 2\text{CO}]$ , 300 (14%);  $[M_1^+ - (2\text{CO} + \text{CH}_2)]$ , 286 (2%);  $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CH}_2)_2]$ ,  $M_{11}^+$ , 326 (1%);  $[M_{11}^+ - \text{CO}]$ , 298 (6%);  $[M_{11}^+ - 2\text{CO}]$ , 270 (6%);  $[M_{11}^+ - (2\text{CO} + \text{CH}_2)]$ , 256 (1%);  $[M_{11}^+ - (2\text{CO} + 2\text{CH}_2)]$ , 242 (5%). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  1985(s), 1965(s), 1925(w);  $\nu(\text{CS})$  1155 (w), 1135 (w)  $\text{cm}^{-1}$ .

*Crystal structure determination of  $\{[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})]_3\text{Ag}\}\text{BF}_4$*

*Data collection and reduction.* A dark red crystal of  $\{[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})]_3\text{Ag}\}\text{BF}_4$ , formed by diffusion of  $\text{Et}_2\text{O}$  into a MeCN solution at  $-20^\circ\text{C}$ , was mounted on a glass fiber in a random orientation. The cell constants were determined from a list

Table 4

Crystal and data collection parameters for  $\{[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})]_3\text{Ag}\}\text{BF}_4$

Formula	$\text{C}_{42}\text{H}_{30}\text{O}_9\text{AgBF}_4\text{Fe}_6\text{S}_3$
Formula weight	1304.65
Space group	$P\bar{1}$
$a$ , Å	13.771(4)
$b$ , Å	15.047(7)
$c$ , Å	12.544(4)
$\alpha$ , deg	109.55(3)
$\beta$	93.77(3)
$\gamma$	90.76(3)
$V$ , Å <sup>3</sup>	2442(3)
$Z$	2
$d_{\text{calc}}$ , g/cm <sup>3</sup>	1.774
Crystal size, mm	0.15 × 0.20 × 0.20
$\mu(\text{Mo-K}\alpha)$ , cm <sup>-1</sup>	23.1
Data collection instrument	Enraf-Nonius CAD4
Radiation (monochromated in incident beam)	Mo-K $\alpha$ ( $\lambda_a$ 0.71073 Å)
Orientation reflections, number, range ( $2\theta$ )	25, $20 < 2\theta < 34$
Temperature, °C	$22 \pm 1$
Scan method	$\theta - 2\theta$
Data col. range, $2\theta$ , deg	4–50
No. unique data, total:	7949
with $F_o^2 > 2.5 \sigma(F_o^2)$ :	3980
Number of parameters refined	542 (no more than 320 in any given cycle)
Trans. factors, max., min. ( $\psi$ -scans)	0.997, 0.726
$R^a$	0.0758
$R_w^b$	0.0978
Quality-of-fit indicator <sup>c</sup>	2.12
Largest shift/esd, final cycle	0.02
Largest peak, e/Å <sup>3</sup>	1.65

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

Table 5

Selected bond distances (Å) for  $[\{Cp_2Fe_2(CO)_3(CS)\}_3Ag]^+$ 

Fe(1)–Fe(2)	2.505(3) <sup>a</sup>	Fe(6)–C(3S)	1.85(2)
Fe(1)–C(1S)	1.90(1)	Fe(6)–C(6)	1.75(2)
Fe(1)–C(1)	1.77(2)	Fe(6)–C(9)	1.92(2)
Fe(1)–C(7)	1.90(2)	Ag–S(1)	2.517(5)
Fe(2)–C(1S)	1.86(1)	Ag–S(2)	2.482(6)
Fe(2)–C(2)	1.77(2)	Ag–S(3)	2.496(7)
Fe(2)–C(7)	1.92(2)	S(1)–C(1S)	1.61(2)
Fe(3)–Fe(4)	2.501(3)	S(2)–C(2S)	1.61(2)
Fe(3)–C(2S)	1.87(1)	S(3)–C(3S)	1.64(2)
Fe(3)–C(3)	1.72(2)	O(1)–C(1)	1.15(2)
Fe(3)–C(8)	1.93(2)	O(2)–C(2)	1.14(3)
Fe(4)–C(2S)	1.90(2)	O(3)–C(3)	1.12(2)
Fe(4)–C(4)	1.78(2)	O(4)–C(4)	1.14(2)
Fe(4)–C(8)	1.93(2)	O(5)–C(5)	1.17(2)
Fe(5)–Fe(6)	2.502(4)	O(6)–C(6)	1.16(2)
Fe(5)–C(3S)	1.85(2)	O(7)–C(7)	1.17(2)
Fe(5)–C(5)	1.75(2)	O(8)–C(8)	1.18(2)
Fe(5)–C(9)	1.90(2)	O(9)–C(9)	1.17(2)

<sup>a</sup> The numbers in parentheses are estimated standard deviations.

of reflections found by an automated search routine. Pertinent data collection and reduction information is given in Table 4.

*Structure solution and refinement.* The positions of the Ag and Fe atoms were given by a Patterson interpretation routine [28]. The remainder of the structure was

Table 6

Selected bond angles (deg) for  $[\{Cp_2Fe_2(CO)_3(CS)\}_3Ag]^+$ 

Fe(2)–Fe(1)–C(1S)	47.7(4) <sup>a</sup>	Fe(2)–C(1S)–S(1)	142.8(8)
Fe(2)–Fe(1)–C(1)	99.9(5)	Fe(3)–C(2S)–Fe(4)	83.2(7)
Fe(2)–Fe(1)–C(7)	49.3(5)	Fe(3)–C(2S)–S(2)	143(1)
C(1S)–Fe(1)–C(1)	89.0(7)	Fe(4)–C(2S)–S(2)	133.5(8)
C(1S)–Fe(1)–C(7)	95.5(7)	Fe(5)–C(3S)–Fe(6)	85.3(7)
C(1)–Fe(1)–C(7)	91.7(8)	Fe(5)–C(3S)–S(3)	140(1)
Fe(1)–Fe(2)–C(1S)	48.8(4)	Fe(6)–C(3S)–S(3)	135(1)
Fe(1)–Fe(2)–C(2)	99.0(6)	Fe(1)–C(7)–Fe(2)	81.9(8)
Fe(1)–Fe(2)–C(7)	48.8(5)	Fe(1)–C(7)–O(7)	139(1)
C(1S)–Fe(2)–C(2)	89.5(8)	Fe(2)–C(7)–O(7)	139(1)
C(1S)–Fe(2)–C(7)	96.2(6)	Fe(3)–C(8)–Fe(4)	80.9(7)
C(2)–Fe(2)–C(7)	89.7(8)	Fe(3)–C(8)–O(8)	138(1)
C(2S)–Fe(3)–C(8)	96.5(6)	Fe(4)–C(8)–O(8)	141(1)
C(2S)–Fe(4)–C(8)	95.7(7)	Fe(5)–C(9)–Fe(6)	81.9(7)
C(3S)–Fe(6)–C(9)	95.0(8)	Fe(5)–C(9)–O(9)	140(2)
S(1)–Ag–S(2)	126.6(2)	Fe(6)–C(9)–O(9)	138(2)
S(1)–Ag–S(3)	109.9(2)	Fe(1)–Fe(2)–Cp <sup>b</sup>	136.2(1)
S(2)–Ag–S(3)	118.2(2)	Fe(2)–Fe(1)–Cp <sup>b</sup>	134.3(1)
Ag–S(1)–C(1S)	116.6(5)	Fe(3)–Fe(4)–Cp <sup>b</sup>	136.1(1)
Ag–S(2)–C(2S)	113.4(6)	Fe(4)–Fe(3)–Cp <sup>b</sup>	136.8(1)
Ag–S(3)–C(3S)	114.4(7)	Fe(5)–Fe(6)–Cp <sup>b</sup>	137.4(1)
Fe(1)–C(1S)–Fe(2)	83.5(6)	Fe(6)–Fe(5)–Cp <sup>b</sup>	137.1(1)
Fe(1)–C(1S)–S(1)	133.7(8)		

<sup>a</sup> See Table 5 for footnote. <sup>b</sup> Calculated centers of the Cp ligands.



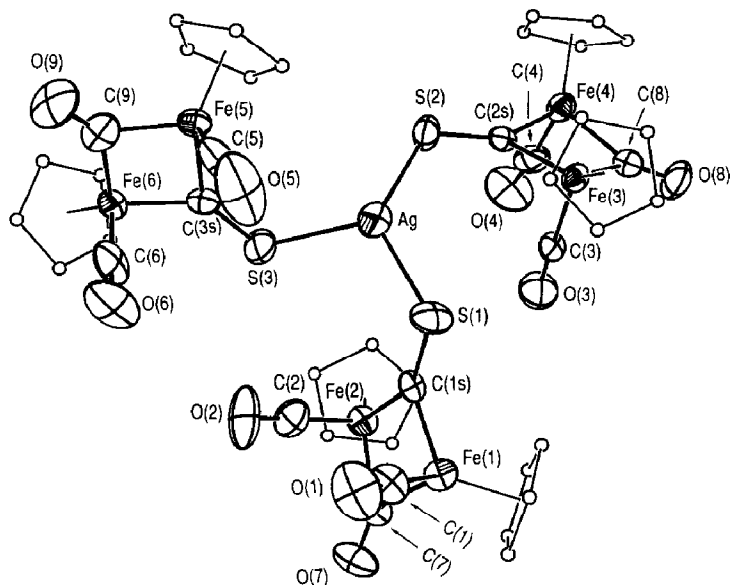


Fig. 1. ORTEP drawing of  $[\{Cp_2Fe_2(CO)_3(CS)\}_3Ag]^+$  with ellipsoids drawn at the 50% probability level. Ring carbon atoms have been drawn as arbitrary small spheres for clarity.

located by subsequent least-squares refinement and difference Fourier techniques. Because of the low data/parameter ratio, the cyclopentadienyl rings were refined as rigid groups, although it was possible to refine the ring atoms with anisotropic thermal parameters. Inclusion of hydrogen atoms in calculated positions for structure factor calculations did not improve the residuals, so the hydrogen atoms were not used. Although a total of 512 parameters were included in the least-squares refinement, no more than 320 were refined in any given cycle.

Refinement of the structure was carried out using the SHELX76 package [29]. Selected bond lengths and angles are presented in Tables 5 and 6 and an ORTEP drawing of the compound is given in Fig. 1. In Table 7 are given the dihedral angles and in Table 8 atomic coordinates and averaged temperature factors.

## Results and discussion

*Preparation of  $[Cp^*Fe(CO)_2(CS)]^+$ .* The complex,  $[Cp^*Fe(CO)_2(CS)]^+$ , is prepared following a procedure similar to that used to prepare  $[CpFe(CO)_2(CS)]^+$

Table 7

Dihedral angles (deg) for  $[\{Cp_2Fe_2(CO)_3(CS)\}_3Ag]^+$

Planes defined by atoms	Dihedral angles
$[Fe(1), Fe(2), (C1S)], [Fe(1), Fe(2), (C7)]$	17(2) <sup>a</sup>
$[Fe(3), Fe(4), (C2S)], [Fe(3), Fe(4), (C8)]$	19(2)
$[Fe(5), Fe(6), (C3S)], [Fe(5), Fe(6), (C9)]$	14(2)
$[S(1), Ag, S(3)], [Ag, S(1), C(1S)]$	38(1)
$[S(1), Ag, S(2)], [Ag, S(2), C(2S)]$	3(7)
$[S(2), Ag, S(3)], [Ag, S(3), C(3S)]$	82(1)

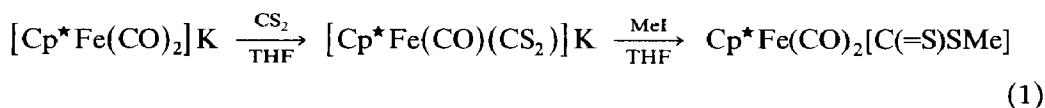
<sup>a</sup> See Table 5 for footnote.

Table 8. Atom coordinates and average temperature factor for  $[(Cp_2Fe_2(CO)_3(CS))_3Ag]BF_4$ 

Atom <sup>a</sup>	x	y	z	B(A <sup>2</sup> ) <sup>b</sup>	Atom <sup>a</sup>	x	y	z	B(A <sup>2</sup> ) <sup>b</sup>
Fe(1)	0.1267(2)	0.1745(2)	0.1015(2)	2.79(6)	O(7)	0.2657(9)	0.3164(9)	0.091(1)	5.3(4)
Fe(2)	0.1002(2)	0.3393(2)	0.2283(2)	2.72(6)	O(8)	-0.0787(9)	0.0340(8)	0.653(1)	5.1(4)
Fe(3)	-0.1733(2)	0.0953(1)	0.4757(2)	2.64(6)	O(9)	-0.508(1)	0.584(1)	0.109(1)	6.6(5)
Fe(4)	-0.2090(2)	0.1907(2)	0.6736(2)	3.09(7)	C(1S)	0.019(1)	0.2313(9)	0.181(1)	2.4(4)
Fe(5)	-0.4096(2)	0.4801(2)	0.2381(2)	2.95(6)	C(2S)	-0.221(1)	0.2165(9)	0.535(1)	2.5(4)
Fe(6)	-0.3063(2)	0.6013(2)	0.1973(2)	2.91(6)	C(3S)	-0.277(1)	0.505(1)	0.252(1)	3.0(4)
Ag	-0.1954(1)	0.3092(1)	0.3213(2)	5.71(6)	C(1)	0.064(1)	0.176(1)	0.176(1)	4.0(5)
S(1)	-0.0869(3)	0.1919(3)	0.1962(4)	4.4(1)	C(2)	0.035(1)	0.381(1)	0.129(2)	4.8(6)
S(2)	-0.2546(4)	0.3066(3)	0.5029(4)	3.9(1)	C(3)	-0.061(1)	0.144(1)	0.471(1)	2.8(5)
S(3)	-0.1756(4)	0.4650(4)	0.2936(6)	6.3(2)	C(4)	-0.105(1)	0.269(1)	0.718(1)	4.2(5)
O(1)	0.024(1)	0.173(1)	-0.111(1)	6.8(5)	C(5)	-0.398(2)	0.383(1)	0.116(2)	5.1(6)
O(2)	-0.004(1)	0.407(1)	0.064(1)	9.0(7)	C(6)	-0.272(2)	0.536(1)	0.063(2)	4.9(6)
O(3)	0.013(1)	0.1753(9)	0.470(1)	5.3(4)	C(7)	0.196(1)	0.290(1)	0.121(1)	3.5(5)
O(4)	-0.043(1)	0.324(1)	0.743(1)	7.3(5)	C(8)	-0.128(1)	0.084(1)	0.619(1)	3.3(5)
O(5)	-0.385(2)	0.317(1)	0.037(1)	10.4(7)	C(9)	-0.441(1)	0.561(1)	0.154(1)	4.0(5)
O(6)	-0.247(1)	0.4918(9)	-0.026(1)	7.4(5)	C(11)	0.133(1)	0.0288(9)	0.041(2)	6.5(8)
C(12)	0.114(1)	0.0576(9)	0.158(2)	6.1(8)	C(44)	-0.270(2)	0.127(1)	0.781(2)	17(2)
C(13)	0.194(1)	0.1157(9)	0.222(2)	5.5(7)	C(45)	-0.244(2)	0.223(1)	0.841(2)	9(1)
C(14)	0.263(1)	0.1227(9)	0.145(2)	7.5(9)	C(51)	-0.532(1)	0.415(2)	0.278(1)	6.3(8)
C(15)	0.225(1)	0.0690(9)	0.033(2)	6.5(8)	C(52)	-0.447(1)	0.399(2)	0.339(1)	5.3(7)
C(21)	0.2171(8)	0.379(1)	0.359(1)	5.2(6)	C(53)	-0.407(1)	0.488(2)	0.410(1)	8.1(9)
C(22)	0.1370(8)	0.338(1)	0.395(1)	4.6(6)	C(54)	-0.467(1)	0.559(2)	0.392(1)	9(1)
C(23)	0.0557(8)	0.395(1)	0.395(1)	5.2(6)	C(55)	-0.544(1)	0.514(2)	0.311(1)	8(1)
C(24)	0.0855(8)	0.471(1)	0.359(1)	5.1(6)	C(61)	-0.196(1)	0.694(1)	0.309(1)	5.8(7)
C(25)	0.1852(8)	0.461(1)	0.337(1)	5.2(6)	C(62)	-0.288(1)	0.713(1)	0.355(1)	5.3(6)
C(31)	-0.305(1)	0.034(1)	0.394(2)	7.5(8)	C(63)	-0.351(1)	0.740(1)	0.278(1)	5.4(6)
C(32)	-0.246(1)	0.054(1)	0.315(2)	7.8(9)	C(64)	-0.298(1)	0.738(1)	0.184(1)	5.7(7)
C(33)	-0.161(1)	0.000(1)	0.308(2)	7.3(8)	C(65)	-0.202(1)	0.709(1)	0.203(1)	7.6(9)
C(34)	-0.168(1)	-0.053(1)	0.382(2)	6.6(8)	B	0.442(1)	0.1713(9)	0.392(1)	7(1)
C(35)	-0.256(1)	-0.032(1)	0.436(2)	8.1(9)	F(1)	0.379(1)	0.241(2)	0.393(1)	13.3(7)
C(41)	-0.298(2)	0.280(1)	0.789(2)	7.3(9)	F(2)	0.504(1)	0.201(1)	0.487(1)	15.4(8)
C(42)	-0.357(2)	0.218(1)	0.696(2)	6.8(9)	F(3)	0.391(1)	0.092(1)	0.386(2)	19(1)
C(43)	-0.340(2)	0.124(1)	0.691(2)	10(1)	F(4)	0.495(1)	0.153(1)	0.298(1)	17(1)

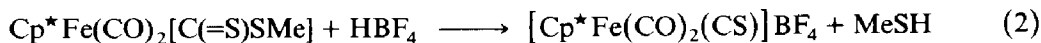
<sup>a</sup> Atom labels as shown in Fig. 1. <sup>b</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$ .

[5,13]. When a THF solution of  $\text{K}[\text{Cp}^*\text{Fe}(\text{CO})_2]$  is treated successively with  $\text{CS}_2$  and  $\text{MeI}$ , the dithioester,  $\text{Cp}^*\text{Fe}(\text{CO})_2[\text{C}(=\text{S})\text{SMe}]$  is produced (eq. 1).



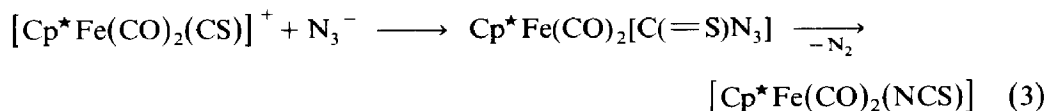
The dithioester is isolated by evaporating the solvent and extracting the residue with hexanes. Evaporation of the filtered solution yields the brown dithioester complex which is air stable. The infrared spectrum in  $\text{CH}_2\text{Cl}_2$  shows two strong  $\nu(\text{CO})$  bands at 2008 and 1955  $\text{cm}^{-1}$  (Table 1) which identify it as this previously reported [26] complex. Its  $^1\text{H}$  NMR spectrum shows a single methyl resonance for the  $\text{Cp}^*$  ring at 1.76 ppm and a resonance at 2.62 ppm assigned to the  $\text{SMe}$  (Table 2).

Several routes for preparing  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]^+$  from  $\text{Cp}^*\text{Fe}(\text{CO})_2[\text{C}(=\text{S})\text{SMe}]$  were tried. Reaction of the dithioester with  $\text{AgBF}_4$  or  $(\text{Ph}_3\text{C})\text{BF}_4$  leads to solid  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]\text{BF}_4$ . Triflic acid yields a brown oily product  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]\text{SO}_3\text{CF}_3$  identified by its IR spectrum. Addition of a  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  solution to a THF solution of  $\text{Cp}^*\text{Fe}(\text{CO})_2[\text{C}(=\text{S})\text{SMe}]$  gives the best results (eq. 2). The characterization of  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]\text{BF}_4$  was based on analytical (experimental section) and



spectroscopic results. The infrared spectrum exhibits two  $\nu(\text{CO})$  bands at 2080 and 2042  $\text{cm}^{-1}$  and a  $\nu(\text{CS})$  band at 1332  $\text{cm}^{-1}$  (Table 1). In comparison with the  $\text{Cp}$  analog (Table 1), these carbonyl and thiocarbonyl bands are shifted about 15–30  $\text{cm}^{-1}$  to lower wave numbers. The methyl groups of the  $\text{Cp}^*$  ligand provide more electron density to the metal, increasing  $\pi$  back bonding from the metal to the CO and CS, thus accounting for the lower  $\nu(\text{CO})$  and  $\nu(\text{CS})$  bands in the  $\text{Cp}^*$  complex. The  $^1\text{H}$  NMR spectrum shows a single methyl resonance for the  $\text{Cp}^*$  ring at 2.03 ppm (Table 2). The  $^{13}\text{C}$  NMR resonance (Table 3) of the terminal CS group at  $\delta$  317.2 ppm, is similar to that of the CS in the  $\text{Cp}$  analog ( $\delta$  307.9 ppm) [12].

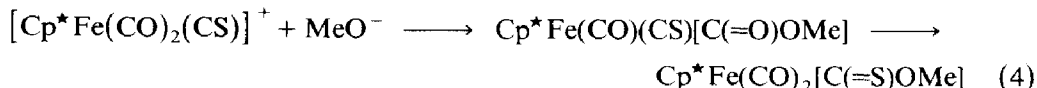
*Reactions of  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]^+$  with nucleophiles.* Nucleophiles react with  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]^+$  by attacking the carbon atom of the CS rather than that of the CO [30]. This is also generally the case for  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]^+$ . Thus,  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]^+$  reacts immediately with  $\text{NaSMe}$  in  $\text{CH}_2\text{Cl}_2$  to yield the known [26] dithioester complex,  $\text{Cp}^*\text{Fe}(\text{CO})_2[\text{C}(=\text{S})\text{SMe}]$ , which was identified by its IR and NMR spectra. The reaction appears to be quantitative as determined by IR spectroscopy but is isolated in 67% yield. The reaction of  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]^+$  with  $\text{NaN}_3$  in acetone produces the orange N-bound  $\text{Cp}^*\text{Fe}(\text{CO})_2(\text{NCS})$ , presumably via  $\text{N}_3^-$  attack on the CS carbon to form the reactive thioacyl azide intermediate which rearranges giving off  $\text{N}_2$  to form the stable  $\text{Cp}^*\text{Fe}(\text{CO})_2(\text{NCS})$  (eq. 3).



Assignment of N-bound coordination to the NCS ligand is based on the IR band in a Nujol mull at 820  $\text{cm}^{-1}$  which is characteristic of N-bound thiocyanate complexes [31].

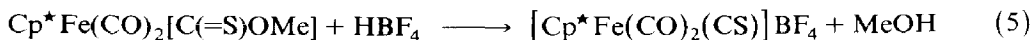
In contrast to its reactions with  $\text{MeS}^-$  and  $\text{N}_3^-$ ,  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]^+$  undergoes attack by  $\text{MeO}^-$  at the CO rather than the CS carbon. With time the  $\text{MeO}^-$

migrates to the CS ligand (eq. 4).



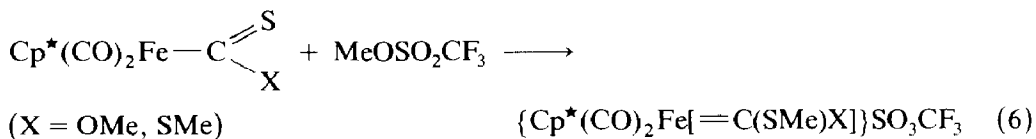
Immediately upon addition of  $\text{MeO}^-$ , the two  $\nu(\text{CO})$  bands at 2080 and 2042  $\text{cm}^{-1}$  of  $[\text{Cp}^*\text{Fe}(\text{CO})_2\text{CS}]^+$  disappear and new absorptions ( $\nu(\text{CO})$  1992  $\text{cm}^{-1}$ ,  $\nu[\text{C}(=\text{O})\text{OMe}]$  1634  $\text{cm}^{-1}$ ) for  $\text{Cp}^*\text{Fe}(\text{CO})(\text{CS})[\text{C}(=\text{O})\text{OMe}]$  appear. The terminal  $\nu(\text{CS})$  band also shifts from 1332 to 1292  $\text{cm}^{-1}$ . As the reaction mixture is stirred, two new  $\nu(\text{CO})$  bands at 2012 and 1958  $\text{cm}^{-1}$  for  $\text{Cp}^*\text{Fe}(\text{CO})_2[\text{C}(=\text{S})\text{OMe}]$  increase with time (10 to 24 h at room temperature) and the bands for  $\text{Cp}^*\text{Fe}(\text{CO})(\text{CS})[\text{C}(=\text{O})\text{OMe}]$  disappear. The  $\nu(\text{CS})$  band at 1292  $\text{cm}^{-1}$  shifts to 1178  $\text{cm}^{-1}$  and is assigned to  $\nu[\text{C}(=\text{S})\text{OMe}]$ .

The initial complex  $\text{Cp}^*\text{Fe}(\text{CO})(\text{CS})[\text{C}(=\text{O})\text{OMe}]$  is isolated by immediate solvent evaporation. The  $^1\text{H}$  NMR spectrum of  $\text{Cp}^*\text{Fe}(\text{CO})(\text{CS})[\text{C}(=\text{O})\text{OMe}]$  exhibits an OMe resonance at 3.60 ppm, whereas the OMe resonance of  $\text{Cp}^*\text{Fe}(\text{CO})(\text{CS})[\text{C}(=\text{S})\text{OMe}]$  occurs at 4.14 ppm (Table 2). In the  $^{13}\text{C}$  spectrum of  $\text{Cp}^*\text{Fe}(\text{CO})(\text{CS})[\text{C}(=\text{O})\text{OMe}]$ , the OMe resonance lies at 52.4 ppm, and the C=O carbon resonance is at 204.6 ppm. The terminal CO and CS resonances occur at 214.7 and 329.4 ppm, respectively (Table 3). In the  $^{13}\text{C}$  spectrum of  $\text{Cp}^*\text{Fe}(\text{CO})_2[\text{C}(=\text{S})\text{OMe}]$ , the OMe resonance appears at 61.2 ppm and the terminal CO resonance at 214.7 ppm. The resonance at 291.0 ppm is assigned to the thioester carbon. Treatment of the thioester  $\text{Cp}^*\text{Fe}(\text{CO})_2[\text{C}(=\text{S})\text{OMe}]$  in  $\text{CH}_2\text{Cl}_2$  with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  reforms  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]^+$  (eq. 5) quantitatively as established by an IR spectrum of the reaction mixture.



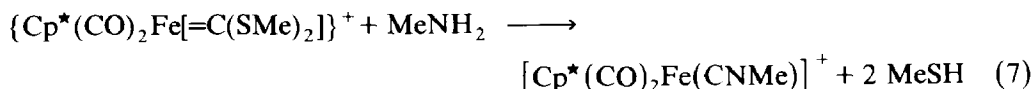
It has been reported [30] that the Cp analog,  $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$ , reacts with  $\text{MeO}^-$  in anhydrous methanol to give exclusively the thioester  $\text{CpFe}(\text{CO})_2[\text{C}(=\text{S})\text{OMe}]$ , while in nondried methanol it gives a mixture of the  $[\text{C}(=\text{S})\text{OMe}]$  and  $[\text{C}(=\text{O})\text{OMe}]$  isomers. In contrast,  $[\text{Ir}(\text{CO})_2(\text{CS})(\text{PPh}_3)]^+$  undergoes nucleophilic addition by  $\text{MeO}^-$  only at a CO ligand, giving  $\text{Ir}(\text{CO})(\text{CS})(\text{PPh}_3)_2[\text{C}(=\text{O})\text{OMe}]$  [32]. Lichtenberger and Fenske [33], on the basis of MO calculations, concluded that nucleophilic attack at the carbon of CS or CO is frontier orbital rather than charged controlled. Perhaps subtle differences in the frontier orbitals of the nucleophiles and the thiocarbonyl complexes cause the different behaviors in the reactions of the complexes above.

*Preparations and reactions of carbene complexes.* Just as  $\text{CpFe}(\text{CO})_2[\text{C}(=\text{S})\text{SMe}]$  can be methylated to give the carbene complex  $\{\text{CpFe}(\text{CO})_2[=\text{C}(\text{SMe})_2]\}^+$  [34], so are  $\text{Cp}^*\text{Fe}(\text{CO})_2[\text{C}(=\text{S})\text{SMe}]$  and  $\text{Cp}^*\text{Fe}(\text{CO})_2[\text{C}(=\text{S})\text{OMe}]$  methylated to give the corresponding cationic carbene products (eq. 6). Anionic exchange is performed on the carbene salts to give the more stable  $\text{PF}_6^-$  complexes.



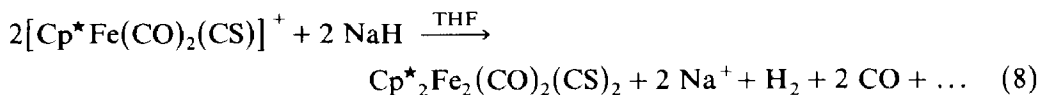
The IR spectra of  $\{\text{Cp}^*(\text{CO})_2\text{Fe}[\text{C}(\text{SMe})_2]\}^+$  and  $\{\text{Cp}^*(\text{CO})_2\text{Fe}[\text{C}(\text{SMe})(\text{OMe})]\}^+$  show two  $\nu(\text{CO})$  bands at 2030, 1990 and 2015, 1992  $\text{cm}^{-1}$ , respectively (Table 1). Comparison of these values with the  $\nu(\text{CO})$  bands observed for  $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SMe})_2]\}^+$  (2055, 2014  $\text{cm}^{-1}$ ) [34] and  $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SMe})(\text{OMe})]\}^+$  (2060, 2017  $\text{cm}^{-1}$ ) (Table 1) [34], show that the more strongly electron-donating  $\text{Cp}^*$  [35] causes a shift of about 25–45  $\text{cm}^{-1}$  toward lower wavenumber.

As for the reaction of  $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SMe})_2]\}^+$  with amines [36], the product resulting from the reaction of  $\{\text{Cp}^*(\text{CO})_2\text{Fe}[\text{C}(\text{SMe})_2]\}^+$  with methylamine is the cationic isocyanide complex (eq. 7).



The IR spectrum of  $[\text{Cp}^*(\text{CO})_2\text{Fe}(\text{CNMe})]^+$  shows a characteristic  $\nu(\text{CN})$  band at 2218  $\text{cm}^{-1}$  and two  $\nu(\text{CO})$  bands at 2055, 2018  $\text{cm}^{-1}$  (Table 1).

*Preparation of  $\text{Cp}_2^*\text{Fe}_2(\text{CO})_2(\text{CS})_2$ .* The reaction of  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CS})]^+$  with NaH in THF yields a mixture of *cis*- and *trans*- $\text{Cp}_2^*\text{Fe}_2(\text{CO})_2(\text{CS})_2$  (eq. 8)

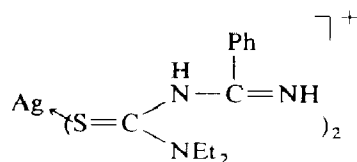


with small amounts of  $\text{Cp}_2^*\text{Fe}_2(\text{CO})_4$  and  $\text{Cp}_2^*\text{Fe}_2(\text{CO})_3(\text{CS})$ . These minor products can be oxidized with air in a HCl/EtOH/ $\text{CHCl}_3$  mixture to give water-soluble  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{Cl}$  and  $\text{Cp}^*\text{Fe}(\text{CO})(\text{CS})\text{Cl}$ , while the major product,  $\text{Cp}_2^*\text{Fe}_2(\text{CO})_2(\text{CS})_2$ , does not react under these conditions (details in experimental section). The separation of these compounds is achieved by washing with  $\text{H}_2\text{O}$ . The IR spectrum of *cis/trans*- $\text{Cp}_2^*\text{Fe}_2(\text{CO})_2(\text{CS})_2$  (Table 1) shows a broad, medium-intensity  $\nu(\text{C}=\text{S})$  absorption at 1108  $\text{cm}^{-1}$  for the bridging CS groups. The  $^{13}\text{C}$  NMR resonances of the bridging CS groups lie far downfield at 388.0 ppm (*cis*) and 390.3 ppm (*trans*) which is about 15 ppm further downfield than that for the Cp analog, *cis*- and *trans*- $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})_2$ , at 374.5 ppm [13].

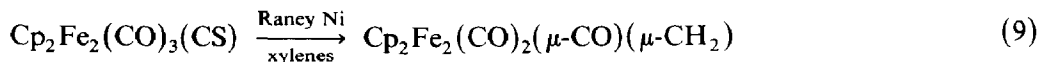
In dinuclear carbonyl thiocarbonyl complexes, the CS group always prefers a bridging position [37–39]. A possible reason for this preference is the weak 2*p*–3*p*  $\pi$ -bond between the C and S. Because of this weak bonding, the migration of CS from a terminal ( $\text{C}\equiv\text{S}$ ) to a bridging ( $\text{C}=\text{S}$ ) position results in the loss of relatively little C–S  $\pi$ -bond stabilization. The stabilization gained by forming a bond to another metal apparently more than compensates for the loss in  $\text{C}\equiv\text{S}$   $\pi$ -bonding. The  $^1\text{H}$  NMR spectrum of  $\text{Cp}_2^*\text{Fe}_2(\text{CO})_2(\text{CS})_2$  in  $\text{CDCl}_3$  shows two singlets at 1.64 and 1.58 ppm. The higher field peak can be assigned to the *cis* isomer, since its relative intensity decreases with decreasing solvent polarity (from  $\text{CDCl}_3$  to benzene- $d_6$ ). The relative intensities of the 1.64 ppm: 1.58 ppm signals is approximately 1/1.3 in  $\text{CDCl}_3$ . Temperature dependent  $^1\text{H}$  NMR studies show a coalescence of these resonances at 90 °C in benzene- $d_6$  in a sealed NMR tube. The  $^{13}\text{C}$  NMR spectrum of  $\text{Cp}_2^*\text{Fe}_2(\text{CO})_2(\text{CS})_2$  in  $\text{CDCl}_3$  shows two singlets at 100.0 and 101.3 ppm for the ring carbons of the  $\text{Cp}^*$  ligands, two terminal CO resonances at 211.5 and 213.3 ppm, and two bridging CS resonances at 388.0 and 390.3 ppm (Table 3), again indicating two isomers.

*Reactions of  $Cp_2Fe_2(CO)_3(CS)$  and  $Cp_2Fe_2(CO)_2(CS)_2$  with  $AgBF_4$ .* It is known that electrophilic attack occurs at the S atom of the terminal CS ligand in electron-rich complexes such as  $\{[HB(Me_2pz)_3]Mo(CO)_2(CS)\}^-$  [40],  $[CpCo(PPh_3)_3(CS)]$  [41],  $\{[HB(pz)_3]W(CO)_2(CS)\}^-$  [42],  $[CpIr(PPh_3)_3(CS)]$  [43]. The S atom of the bridging thiocarbonyl ligands ( $\mu_2$ -CS,  $\mu_3$ -CS) in the following complexes also form adducts with electrophiles:  $Cp_2Fe_2(CO)_2(CS)_2$  [6],  $Cp_2Fe_2(CO)_3(CS)$  [8,38],  $Cp_3Co_3(\mu_3-S)(\mu_3-CS)$  [41,44],  $CpMPt(\mu-CS)(CO)_2(PR_3)_2$  (M = Mn, Re) [45] and  $Cp_2CoMn(CO)(\mu-CO)(\mu-CS)(PMe_3)$  [46]. Both thiocarbonyl-bridged dimers,  $Cp_2Fe_2(CO)_3(CS)$  and  $Cp_2Fe_2(CO)_2(CS)_2$ , react with  $Ag^+$  to form adducts. In the  $Cp_2Fe_2(CO)_2(CS)_2$  case, elemental analysis suggests formation of a 1/1 adduct  $[Cp_2Fe_2(CO)_2(CS)_2]Ag^+ BF_4^-$ . The Nujol mull spectrum shows a  $\nu(C=S)$  band for  $Ag^+$  coordinated bridging CS groups at  $1030\text{ cm}^{-1}$  but none in the region for uncoordinated bridging CS groups. Thus, the structure of this insoluble adduct is presumably a polymer with  $Ag^+$  bridging two  $Cp_2Fe_2(CO)_2(CS)_2$  units by coordinating to the sulfur atoms of the bridging thiocarbonyl ligands. When this adduct dissolves in polar solvents ( $CH_2Cl_2$ , acetone), it dissociates rapidly to  $Cp_2Fe_2(CO)_2(CS)_2$  and  $AgBF_4$ .

When  $Cp_2Fe_2(CO)_3(CS)$  reacts with  $AgBF_4$ , it forms adducts  $\{[Cp_2Fe_2(CO)_3(CS)]_nAg\}BF_4$  with elemental analyses which indicate a variable composition ranging from  $n = 1.87$  to 2.38. This compound is stable in air in the solid state, but it decomposes in solution at room temperature.  $^1H$  NMR studies of the adducts in acetone- $d_6$  show a single Cp signal at 5.20 ppm. If more  $Cp_2Fe_2(CO)_3(CS)$  is added to the solution, the Cp resonance moves to 5.06 ppm, which is nearer the resonance (5.03 ppm) of pure  $Cp_2Fe_2(CO)_3(CS)$  in acetone- $d_6$ ; also there is still only one Cp signal in the spectrum. These results suggest that  $Ag^+$  and  $Cp_2Fe_2(CO)_3(CS)$  form a rapidly equilibrating mixture of  $\{[Cp_2Fe_2(CO)_3(CS)]_nAg\}BF_4$  adducts in solution. The variable elemental analyses of the adducts precipitated from solutions reflect the mixtures of complexes present in solution. In order to establish the nature of these adducts, a single crystal was isolated, and its structure was determined by X-ray diffraction methods. The structure of the cation in  $\{[Cp_2Fe_2(CO)_3(CS)]_3Ag\}BF_4$  (Fig. 1) clearly shows that three  $Cp_2Fe_2(CO)_3(CS)$  molecules coordinate to a  $Ag^+$  through the S atom of the bridging thiocarbonyl ligand. Within each  $Cp_2Fe_2(CO)_3(CS)$  ligand the Cp rings are cis to each other. Tables 5 and 6 list selected interatomic distances and angles. The silver atom lies slightly above (0.33 Å) the plane defined by S(1), S(2), and S(3). The structure of the  $Cp_2Fe_2(CO)_3(CS)$  ligands is essentially the same as the free *cis*- $Cp_2Fe_2(CO)_3(CS)$  [47]. In the ethylated  $[Cp_2Fe_2(CO)_3(\mu-C-S-Et)]^+$ , the C-S bond is lengthened 0.06 Å [8] from that in the original dimer. This presumably results from reduced C-S  $\pi$ -bonding upon alkylation. Coordination of  $Ag^+$  to the bridging CS group, also appears to cause some C-S bond lengthening, but the effect is spread over three ligand molecules, and the bond lengthening is so small (0.02 Å) as to be insignificant. The Ag-S bond distances (avg. 2.498(6) Å) are somewhat longer than those (avg. 2.403(4) Å) [48] in

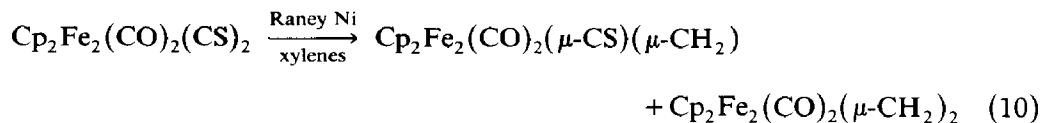


*Reactions of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS) and Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(CS)<sub>2</sub> with Raney Ni.* Raney Ni is one of the most commonly used reagents for desulfurization and hydrogenation in organosulfur chemistry [49,50]. The reaction (eq. 9) of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS)



with Raney Ni in xylenes solution results in the desulfurization and hydrogenation of the bridging CS group to produce the known [27]  $\mu\text{-CH}_2$  complex in low yield (11%).

The same reaction (eq. 10) of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(CS)<sub>2</sub> causes desulfurization and hydrogenation of either one or both CS groups to yield the  $\mu\text{-CH}_2$  complexes but in only trace amounts.



The <sup>1</sup>H NMR spectrum of this mixture in CDCl<sub>3</sub> shows six far downfield singlets at 10.52, 9.91, 9.89, 9.62, 8.68, 7.97 ppm characteristic [27,51] of bridging methylene protons. Both compounds exist as *cis*- and *trans*-isomers. In the *cis*-isomers, the  $\mu\text{-CH}_2$  protons are inequivalent and give two signals while the  $\mu\text{-CH}_2$  protons in the *trans*-isomers are equivalent and give only one signal. There are four singlet Cp resonances at 4.90, 4.80, 4.70, 4.66 ppm corresponding to the four compounds. The mass spectrum of the mixture shows a parent ion peak for each of the compounds, [Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>( $\mu\text{-CS}$ )( $\mu\text{-CH}_2$ )] and [Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>( $\mu\text{-CH}_2$ )<sub>2</sub>], and typical fragmentation patterns involving loss of CO and CH<sub>2</sub> groups.

Other reactions of the iron thiocarbonyl dimers were also examined. Like the protonation of the Fe-Fe bond in Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> [52], Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS) reacts with HBF<sub>4</sub> · Et<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub> causing a ~ 50 cm<sup>-1</sup> shift (toward higher wave number) in the  $\nu(\text{CO})$  bands and a color change from dark green to red; however, the product was not sufficiently stable to be isolated and fully characterized. In an attempt to form the sulfoxide (C=S=O) of the bridging thiocarbonyl, Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS) was reacted with 3-chloroperoxybenzoic acid in Et<sub>2</sub>O at 0 °C. Although a red-brown precipitate with  $\nu(\text{CO})$  bands approximately 20–40 cm<sup>-1</sup> higher than in the starting dimer formed, the <sup>1</sup>H NMR spectrum showed no proton signals. Since Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> and Cp<sup>\*</sup><sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> form tripoly-carbonyl-bridging species, Cp<sub>2</sub>Fe<sub>2</sub>( $\mu\text{-CO}$ )<sub>3</sub> [53] and Cp<sup>\*</sup><sub>2</sub>Fe<sub>2</sub>( $\mu\text{-CO}$ )<sub>3</sub> [54], under UV photolysis, Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS) and Cp<sup>\*</sup><sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(CS)<sub>2</sub> were photolyzed in cyclohexane at room temperature; however, no new  $\nu(\text{CO})$  bands were observed; only decomposition occurred.

#### Supplementary material available

Tables containing additional bond distances, bond angles, least-squares planes and structure factors (39 pages) are available from R.J. Angelici.

#### Acknowledgments

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