Inorg. Chem. **1985**, *24*, 2209–2215

Contribution from the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Mono- and Dinuclear Thiocarbonyl Complexes of Iron, Including $[CpFe(CO)(CS)]_2$, $CpFe(CO)(CS)I$, and $CpFe(CS)_2I$

ROBERT J. ANGELICI* and JAN W. DUNKER[1]

Received July 24, 1984

The thiocarbonyl dimers, *cis*- and *trans*-$[CpFe(CO)(\mu\text{-}CS)]_2$, are prepared by reduction of $CpFe(CO)_2(CS)^+$ with NaH. The S atom of a bridging thiocarbonyl group can be alkylated with $MeOSO_2F$ or MeI to give $Cp_2Fe_2(CO)_2(CS)(CSMe)^+$. With $HgCl_2$ the $Cp_2Fe_2(CO)_2(CS)(CSHgCl_2)$ adduct is formed. The $[CpFe(CO)(CS)]_2$ dimer is cleaved by Br_2 to yield $CpFe(CO)(CS)Br$. Ultraviolet photolysis of $[CpFe(CO)_2(CS)]CF_3SO_3$ in CH_2Cl_2 yields an unstable but useful intermediate, $CpFe(CO)(CS)(CF_3SO_3)$, that reacts with KX (X = I, Br, Cl) to give $CpFe(CO)(CS)X$. With various neutral ligands L (PPh_3, pyridine, MeCN), $CpFe(CO)(CS)(CF_3SO_3)$ gives $[CpFe(CO)(CS)(L)]CF_3SO_3$. When photolyzed in the presence of MeCN or Me_2S, $[CpFe(CO)_2(CS)]PF_6$ is converted to $[CpFe(CS)(L)_2]PF_6$ (L = MeCN, Me_2S). The CO group in $CpFe(CO)(CS)I$ is substituted by L groups (PEt_3, PPh_3, $AsPh_3$, $SbPh_3$, $P(OMe)_3$, $P(OPh)_3$) to form the corresponding $CpFe(CS)(L)I$ products. One or two MeCN groups in $[CpFe(CS)(MeCN)_2]PF_6$ are substituted by neutral ligands L to give $[CpFe(CS)(L)(MeCN)]PF_6$ (L = $P(OMe)_3$, $P(OPh)_3$), $[CpFe(CS)(PPh_3)_2]PF_6$, $[CpFe(CS)(bpy)]PF_6$, and $[CpFe(CS)(phen)]PF_6$. The reaction of $[CpFe(CS)(MeCN)_2]PF_6$ with KI gives $CpFe(CS)_2I$, one of the few known dithiocarbonyl complexes. IR and ^1H and ^{13}C NMR spectra of the complexes are also reported.

Introduction

Although the first complex, $CpFe(CO)_2(CS)^+$, was reported in 1968,[2–4] still relatively few iron thiocarbonyl complexes are known today. Some substituted derivatives, $CpFe(CO)(L)(CS)^+$ and $CpFe(L)_2(CS)^+$,[5,6] have been described. The simple complex, $Fe(CO)_4(CS)$,[7] and the porphyrin complexes, Fe(porphyrin)(CS) and Fe(porphyrin)(CS)(L),[8–10] were reported in 1978. About the same time, the dinuclear $Cp_2Fe_2(CO)_2(CS)_2$[11] and $Cp_2Fe_2(CO)_3(CS)$[12,13] were described, and more recently, the clusters $Fe_4(CO)_{12}(CS)(S)$[14] and $Fe_5(CO)_{13}(CS)(S)_2$[15] were shown to have structures in which both the C and S atoms of the CS group are involved in bonding to the Fe atoms.

In the present paper, we describe details for the preparation of $Cp_2Fe_2(CO)_2(CS)_2$, some reactions of this dimer, and further studies of $CpFe(CO)_2(CS)^+$.

Experimental Section

General Methods. Unless stated otherwise, all reactions were performed under an atmosphere of prepurified nitrogen that was passed through Drierite prior to use. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ or $NaK_{2.8}$ (under nitrogen) prior to use. All solvents were reagent grade. Acetone and anhydrous Et_2O were used as received, while all other solvents were stored over 4A molecular sieves.

Infrared spectra were recorded on a Perkin-Elmer 337 or 237B grating spectrophotometer. Positions of the infrared absorption peaks were calibrated in the carbonyl region with CO gas and in the thiocarbonyl region with polystyrene. Peak positions are believed accurate to within 2 cm^{-1}. IR spectra of cationic complexes also showed absorptions due to the anions, either $CF_3SO_3^-$ (1269 vs, 1224 m, 1160 br m, and 1033 vs cm^{-1}) or PF_6^- (880 w and 845 vs cm^{-1}).

Proton NMR spectra were recorded with Varian A-60, Varian EM-360, or a Perkin-Elmer Hitachi R-20B instrument. ^{13}C NMR spectra were obtained on a Bruker HX-90 Fourier transform spectrometer. The shiftless, paramagnetic relaxation agent, $Cr(acac)_3$, was added to reduce data collection time. Deuteriochloroform (δ 77.09) or Me_4Si was used as the internal standard.

Photolysis reactions were conducted in a cylindrical 400-mL three-necked flask with two female 24/40 joints and a central 55/50 male joint which accepted a water-cooled quartz photolysis well in which a Hanovia photochemical immersion lamp (Ace Glass, Inc.) was placed. Small-scale (1 mmol) photolysis reactions were conducted in quartz Schlenk tubes, using a Bradford Scientific, Inc., photolysis reactor.

PPh_3, $AsPh_3$, and $SbPh_3$ were recrystallized from hexanes. $P(OMe)_3$ and PEt_3 were fractionally distilled. Triphenyl phosphite was recrystallized from the neat liquid. The cyclopentadienyliron dicarbonyl dimer, $[CpFe(CO)_2]_2$, was recrystallized from CH_2Cl_2/hexanes.

Preparation of Complexes. $[CpFe(CO)_2(CS)]CF_3SO_3$. Although the synthesis of $[CpFe(CO)_2(CS)]PF_6$ was described previously,[4] $[CpFe(CO)_2(CS)]CF_3SO_3$ was mentioned only briefly,[12] and its preparation is given in detail here. To an ether solution of $CpFe(CO)_2(CS_2Me)$[4] obtained from 10.0 g (28.3 mmol) of $Cp_2Fe_2(CO)_4$ according to ref 4 was added 5.6 mL (63 mmol) of CF_3SO_3H in 60 mL of Et_2O slowly and dropwise. After the mixture was stirred an additional 2 h, the precipitated $[CpFe(CO)_2(CS)]CF_3SO_3$ was filtered off and washed with Et_2O. The crude product was then dissolved in 150 mL of acetone, and 350 mL of hexane was added to reprecipitate the product. The yellow-brown powder was filtered and washed successively with Et_2O (50 mL), THF (30 mL), Et_2O (50 mL), THF (30 mL), and Et_2O (50 mL) to remove the brown impurity and yield the bright yellow powder $[CpFe(CO)_2(CS)]CF_3SO_3$ (79%) that was identified by its IR and NMR spectra (Table I).

***cis/trans*-$[CpFe(CO)(CS)]_2$.** A slurry of $[CpFe(CO)_2(CS)]CF_3SO_3$ (10.1 g, 27.3 mmol) and excess sodium hydride (1.43 g of a 57% mineral oil dispersion, 34.0 mmol) in 200 mL of THF was stirred at room temperature for 2 h. The mixture was then evaporated to dryness under reduced pressure, and the residue was extracted several times with hot benzene until the extracts no longer were green. The combined extracts were filtered through Celite, and the filtrate was chromatographed on a Florisil column (41 × 390 mm), eluting with benzene. A dark brown band with a blue leading edge developed and eventually colored the entire column. The eluent was collected, starting with the first colored material and continuing until all the dark green eluent had been collected. The solution was evaporated under reduced pressure to give a black solid containing a mixture of *cis*- and *trans*-$[CpFe(CO)(CS)]_2$, with small amounts of $[CpFe(CO)_2]_2$ and $Cp_2Fe_2(CO)_3(CS)$.

The black solid was dissolved in ~75 mL of $CHCl_3$, then 50 mL of 95% EtOH and 10 mL of concentrated aqueous HCl (120 mmol) were added, and O_2 gas was slowly bubbled through the solution for 1 h. (This oxidized the $[CpFe(CO)_2]_2$[16] and $Cp_2Fe_2(CO)_3(CS)$ to $CpFe(CO)_2Cl$

---

(1) Based on the Ph.D. dissertation submitted by J.W.D., Iowa State University, 1981.
(2) Busetto, L.; Angelici, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 3283.
(3) Busetto, L.; Belluco, U.; Angelici, R. J. *J. Organomet. Chem.* **1969**, *18*, 213.
(4) Dombek, B. D.; Angelici, R. J. *Inorg. Synth.* **1977**, *17*, 100.
(5) Busetto, L.; Palazzi, A. *Inorg. Chim. Acta* **1976**, *19*, 233.
(6) Ellermann, J.; Lietz, M. *J. Organomet. Chem.* **1981**, *213*, C4.
(7) Petz, W. *J. Organomet. Chem.* **1978**, *146*, C23.
(8) (a) Mansuy, D.; Battioni, J. P.; Chottard, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4311. (b) Battioni, J. P.; Chottard, J. C.; Mansuy, D. *Inorg. Chem.* **1982**, *21*, 2056.
(9) Buchler, J. W.; Kokisch, W.; Smith, P. D.; Tonn, B. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1371.
(10) Scheidt, W. R.; Geiger, D. K. *Inorg. Chem.* **1982**, *21*, 1208.
(11) Dunker, J. W.; Finer, J. S.; Clardy, J.; Angelici, R. J. *J. Organomet. Chem.* **1976**, *114*, C49.
(12) Quick, M. H.; Angelici, R. J. *J. Organomet. Chem.* **1978**, *160*, 231.
(13) Wagner, R. E.; Jacobson, R. A.; Angelici, R. J.; Quick, M. H. *J. Organomet. Chem.* **1978**, *148*, C35.
(14) Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 812.
(15) Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Am. Chem. Soc.* **1981**, *103*, 3198.
(16) Piper, T. S.; Cotton, F. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *1*, 165.

0020-1669/85/1324-2209$01.50/0

Table I. Infrared and ^{1}H NMR Spectra of the Complexes

complex	ν(CS), cm^{-1}	ν(CO), cm^{-1}	δ(Cp)	other δ
$[CpFe(CO)_2(CO)]CF_3SO_3$	1353 (s)[a]	2105 (s), 2071 (s)[a]	6.05[b]	
cis-$[CpFe(CO)(CS)]_2$	1124 (s)[c]	2011 (vs), 1982 (m)[c]	4.78[c]	
trans-$[CpFe(CO)(CS)]_2$	1131 (s)[c]	1979 (s)[c]	4.68[c]	
$Cp_2Fe_2(CO)_2(CS)(CSHgCl_2)$	1177 (s, sh), 1168 (s)[d,e]	2028 (vs), 2019 (s, sh), 1995 (s)[d]	4.90 (11)[b,f] 5.13 (70)	
$[Cp_2Fe_2(CO)_2(CS)(CSMe)]PF_6$	1178 (s), 1070 (w)[g,h]	2043 (s), 2011 (m)[g]	5.73, 5.83[b]	3.80 (s, Me)
$CpFe(CO)(CS)I$	1306 (vs)[c]	2024 (s)[c]	5.07[c]	
$CpFe(CO)(CS)Br$	1309 (vs)[c]	2033 (s)[c]	5.00[c]	
$CpFe(CO)(CS)Cl$	1310 (vs)[c]	2036 (s)[c]		
$CpFe(CO)(CS)(CF_3SO_3)$	1318 (vs)[c] 1322 (vs)[g]	2054 (s)[c] 2051 (s)[g]	5.24[i]	
$[CpFe(CO)(CS)(PPh_3)]CF_3SO_3$	1323 (vs)[a]	2034 (s)[a]	5.55[b,j]	7.73–7.28 (m, Ph)[b]
$[CpFe(CO)(CS)(py)]CF_3SO_3$	1321 (vs)[a]	2045 (s)[a]	5.68[b]	8.93–7.57 (m, py)[b]
$[CpFe(CO)(CS)(MeCN)]CF_3SO_3$	1327 (vs)[a]	2056 (s)[a]	5.67[b]	2.51 (s, Me)[b]
$CpFe(CS)(PEt_3)I$	1272[c]		4.64[c,k]	2.32–1.73 (m, CH_2), 1.43–0.87 (m, CH_3)[c]
$CpFe(CS)(PPh_3)I$	1271[c]		4.42[c,l]	7.78–7.17 (m, Ph)[c]
$CpFe(CS)(AsPh_3)I$	1271[c]		4.50[c]	7.67–7.20 (m, Ph)[c]
$CpFe(CS)(SbPh_3)I$	1269[c]		4.61[c]	7.63–7.17 (m, Ph)[c]
$CpFe(CS)[P(OMe)_3]I$	1278[c]		4.69[c]	3.71 (d, J_{PH} = 11 Hz, Me)[c]
$CpFe(CS)[P(OPh)_3]I$	1289[c]		4.12[c]	7.45–7.08 (m, Ph)[c]
$[CpFe(CS)(MeCN)_2]PF_6$	1298[a]		5.16[b]	2.52 (Me)[b]
$CpFe(CS)(MeCN)(PEt_3)]PF_6$	1292[a]		5.16[b,j]	2.48 (MeCN),[j] 2.33–1.82 (m, CH_2), 1.52–0.93 (m, CH_3)[b]
$\{CpFe(CS)(MeCN)[P(OMe)_3]\}PF_6$	1304[a]		5.19[b,k]	2.45 (MeCN),[k] 3.85 (d, J_{PH} = 11.7 Hz, OMe)[b]
$\{CpFe(CS)(MeCN)[P(OPh)_3]\}PF_6$	1312[a]		4.72[b,k]	2.33 (d, J_{PH} = 1.1 Hz, MeCN), 7.60–7.08 (m, Ph)[b]
$[CpFe(CS)(PPh_3)_2]PF_6$	1285[a]		4.90[b,m]	7.62–7.07 (m, Ph)[b]
$[CpFe(CS)(Me_2S)_2]PF_6$	1287[a]		5.22[b]	2.40 (s, Me)[b]
$[CpMe(CS)(bpy)]PF_6$	1293[a]		5.35[b]	9.00–7.38 (m, bpy)[b]
$[CpFe(CS)(phen)]PF_6$	1290 (vs)[a]		5.42[b]	9.35–7.88 (m, phen)[b]
$CpFe(CS)_2I$	1337 (s), 1274 (vs)[c]		5.05[c]	
$CpFe(CS)_2Br$	1341 (s), 1276 (vs)[c]			

[a] CH_3N solvent. [b] $(CD_3)_2C{=}O$ solvent. [c] CS_2 solvent. [d] Nujol mull. [e] ν(C–$SHgCl_2$) at 1018 (s) cm^{-1}. [f] Relative intensities in parentheses. [g] CH_2Cl_2 solvent. [h] ν(C–SMe) at 1036 (m) cm^{-1}. [i] $CDCl_3$ solvent. [j] d, J_{PH} = 1.0 Hz. [k] d, J_{PH} = 0.8 Hz. [l] d, J_{PH} = 0.9 Hz. [m] t, J_{PH} = 1.3 Hz.

and $CpFe(CO)(CS)Cl$, while the $[CpFe(CO)(CS)]_2$ remained unreacted.) The solution volume was reduced to 50 mL under vacuum. Addition of ~200 mL of H_2O caused the $[CpFe(CO)(CS)]_2$ to precipitate. The resulting mixture was filtered and washed with H_2O to remove the water-soluble $CpFe(CO)_2Cl$ and $CpFe(CO)(CS)Cl$. The black residue was dissolved in ~50 mL of acetone and again precipitated by addition of ~200 mL of H_2O. The precipitate was again filtered and washed with H_2O. The residue was dissolved in CH_2Cl_2 and dried over anhydrous $MgSO_4$ overnight. After filtration through Celite, the green solution was reduced in volume to ~40 mL, and ~30 mL of heptanes was added. Crystallization at −20 °C yielded red to black crystals of $[CpFe(CO)(CS)]_2$ (thick crystals appeared black, while thin crystals appeared dark red). A second crop of crystals was obtained by concentrating and cooling the filtrate to give a total yield of 1.85 g (35%) of a mixture of *cis*- and *trans*-$[CpFe(CO)(CS)]_2$. Typical yields varied from 21% to 47%. IR spectra of the mixture in CS_2 solvent showed absorptions at 2011, 1978, and 1124 cm^{-1}, whose relative intensities depended on the cis/trans ratio in the product.

Separation of *cis*- and *trans*-$[CpFe(CO)(CS)]_2$. The *cis/trans*-$[CpFe(CO)(CS)]_2$ mixture was dissolved in benzene and chromatographed on a 41 × 400 mm Florisil/hexanes column eluting with 1:1 benzene/hexanes. Elution was fairly rapid, approximately 50 mL/min, as cis–trans isomerization occurred if the rate was too slow. The initial gray eluent was collected until the first appearance of a green color and then evaporated to dryness under reduced pressure. An infrared spectrum in CS_2 of this material indicated it was enriched in *trans*-$[CpFe(CO)(CS)]_2$. Crystallization from CS_2 at −20 °C three times gave black crystals of *trans*-$[CpFe(CO)(CS)]_2$ whose IR spectrum did not show the 2011-cm^{-1} absorption characteristic of *cis*-$[CpFe(CO)(CS)]_2$. The remaining material was eluted from the column and evaporated to dryness under reduced pressure. An infrared spectrum of this fraction in CS_2 indicated enrichment in *cis*-$[CpFe(CO)(CS)]_2$. Crystallization from CH_2Cl_2/hexanes at −20 °C was repeated until an infrared spectrum indicated that only the black crystals of *cis*-$[CpFe(CO)(CS)]_2$ were present. The mass spectrum of the product gave a parent ion at m/e 385.883. A detailed mass spectral study was reported previously.[17]

Anal. Calcd for $C_{14}H_{10}Fe_2O_2S_2$: C, 43.55; H, 2.61; S, 16.61. Found: C, 43.47; H, 2.69; S, 15.87.

$Cp_2Fe_2(CO)_2(CS)(CSHgCl_2)$. A solution of a *cis/trans*-$[CpFe(CO)(CS)]_2$ mixture (0.434 g, 1.12 mmol) and $HgCl_2$ (0.295 g, 1.09 mmol) in 40 mL of Et_2O was stirred for 9 h. Then, 80 mL of heptane was added, and the volume was reduced to ~25 mL on a rotary evaporator. The mixture was then filtered, and the precipitate was washed with pentane. Drying under high vacuum yielded 0.647 g (88%) of the black powder, $[Cp_2Fe_2(CO)_2(CS)(CSHgCl_2)]$. Anal. Calcd for $C_{14}H_{10}Cl_2Fe_2HgO_2S_2$: C, 25.57; H, 1.53. Found: C, 25.36; H, 1.74.

$[Cp_2Fe_2(CO)_2(CS)(CSMe)]PF_6$. From $MeSO_3F$. A solution of *cis*-$[CpFe(CO)(CS)]_2$ (0.205 g, 0.532 mmol) and CH_3SO_3F (2.0 mL, 25 mmol) in 100 mL of CH_2Cl_2 was stirred for 15 min. The solution was then taken to dryness on a rotary evaporator. The residue was dissolved in methanol, and the solution was passed through an anion-exchange column (Amberlite IRA-400) in the PF_6^- form. The green eluent was reduced in volume to ~25 mL, and Et_2O was added until a precipitate began to form. Crystallization at −20 °C gave black crystals of $[Cp_2Fe_2(CO)_2(CS)(CSMe)]PF_6$, 0.215 g (74%). Anal. Calcd for $C_{15}H_{13}F_6Fe_2O_2PS_2$: C, 33.00; H, 2.40. Found: C, 32.85; H, 2.43.

From MeI. The reaction of *cis*-$[CpFe(CO)(CS)]_2$ (0.0513 g, 0.133 mmol) and CH_3I (5 mL, 80 mmol) in 50 mL of CH_2Cl_2 was complete after ~10 h at 25 °C as determined by IR spectra. The solution was then reduced on a rotary evaporator to dryness. The product, $[Cp_2Fe_2(CO)_2(CS)(CSMe)]PF_6$ (0.0237 g, 33%), was isolated by anion exchange and crystallization in MeOH at −20 °C as described above.

$CpFe(CO)(CS)Br$. A solution of a *cis/trans*-$[CpFe(CO)(CS)]_2$ mixture (0.101 g, 0.261 mmol) and excess Br_2 (2.0 mL of a solution of 1.0 mL of Br_2 diluted to 100 mL with CCl_4, 0.390 mmol) in 50 mL of $CHCl_3$ was refluxed for 20 min. After cooling to room temperature, the solution was extracted with aqueous $Na_2S_2O_3$ (2 × 10 mL portions of 0.42 N $Na_2S_2O_3$) to destroy the excess Br_2. The organic layer was separated, dried overnight over anhydrous $MgSO_4$, filtered through Celite, and evaporated to dryness under reduced pressure. Crystallization from CS_2/hexane at −20 °C yielded tangerine crystals of $CpFe(CO)(CS)Br$, 0.0992 g (70%). Anal. Calcd for $C_7H_5BrFeOS$: C, 30.80; H, 1.85. Found: C, 30.89; H, 1.95.

$[CpFe(CS)(MeCN)_2]PF_6$. The photochemical flask charged with $[CpFe(CO)_2(CS)]PF_6$ (7.81 g, 21.3 mmol) was degassed by several cycles of alternate evacuation and filling with N_2 at atmospheric pressure.

---

[17] Efraty, A.; Liebman, D.; Huang, M. H. A.; Weston, C. A.; Angelici, R. J. *Inorg. Chem.* **1978**, *17*, 2831.

Table II. ^{13}C NMR Data[a] for the Complexes

	δ			
complex	CS	CO	Cp	other
cis-[CpFe(CO)(CS)]$_2$	374.5[b]	208.9	93.8	
trans-[CpFe(CO)-(CS)]$_2$	374.5	210.0	96.7	
CpFe(CO)(CS)I	322.5	212.5	87.6	
CpFe(CO)(CS)-(CF$_3$SO$_3$)	321.7	207.8	88.0	
CpFe(CS)(PPh$_3$)I	325.0[c]		87.1	134.9, 132.9[d] 129.5, 127.3[e] (Ph)
CpFe(CS)(PEt$_3$)I	324.4[f]		85.7	21.0[g] (CH$_2$) 8.4 (CH$_3$)
CpFe(CS)[P(OMe)$_3$]I	323.1[h]		86.5	54.0[i] (Me)
[CpFe(CS)(MeCN)$_2$]-PF$_6$[j]	329.4		87.4	222.6 (CN), 4.1 (Me)
CpFe(CS)$_2$I	323.4		90.6	

[a] Chemical shifts in ppm downfield from Me$_4$Si and coupling constants in Hz; complexes in CDCl$_3$ solvent. [b] The previously reported value (δ 287.6) was incorrect. [c] d, J_{PC} = 37.2. [d] d, J_{PC} = 7.4. [e] d, J_{PC} = 8.9. [f] d, J_{PC} = 37.8. [g] d,, J_{PC} = 28.1. [h] d, J_{PC} = 55.1. [i] d, J = 4.3. [j] (CD$_3$)$_2$C=O solvent.

Deoxygenated MeCN (350 mL) was added, and the solution was irradiated with 254-nm light for 8 h. After 2, 4, and 6 h, the probe was removed from the reaction vessel and cleaned of accumulated brown residue. After 8 h of irradiation, the amount of [CpFe(CS)(MeCN)$_2$]PF$_6$ in the air-stable, yellow-green solution was at a maximum as determined by the intensity of the 1298-cm^{-1} IR absorption. After the solution was evaporated to dryness under vacuum, the residue was dissolved in CH$_2$Cl$_2$, and the resulting solution was filtered through Celite, reduced in volume until precipitation began (~150 mL), and treated with 100 mL of CHCl$_3$. The volume was again reduced to the point of precipitation while heating in a water bath (~60 °C). Cooling to −20 °C gave shiny yellow-green crystals of [CpFe(CS)(MeCN)$_2$]PF$_6$. Repetition of this crystallization procedure gave a second batch of crystals for a total of 5.38 g (64% yield). Anal. Calcd for C$_{10}$H$_{11}$F$_6$FeN$_2$PS: C, 30.63; H, 2.83; S, 8.18. Found: C, 30.66; H, 2.94; S, 8.39.

[CpFe(CS)(Me$_2$S)$_2$]PF$_6$. Crystals of [CpFe(CO)$_2$(CS)]PF$_6$ (0.457 g, 1.25 mmol) were placed in a quartz Schlenk tube, and the apparatus was degassed by several cycles of alternate evacuation and filling with N$_2$. Then deoxygenated acetone (33 mL) and Me$_2$S (1.0 mL, 13.6 mmol) were added. The apparatus was fitted with a cooling probe and mineral oil bubbler and then irradiated for 5 h at 254 nm. The progress of the reaction was followed in the IR, and irradiation was continued until the intensity of the 1287-cm^{-1} band, due to [CpFe(CS)(Me$_2$S)$_2$]PF$_6$, was at a maximum. The dark green solution was then evaporated to dryness under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$ and filtered through Celite. Crystallization from CH$_2$Cl$_2$/CHCl$_3$ at −20 °C gave black crystals of [CpFe(CS)(Me$_2$S)$_2$]PF$_6$, 0.322 g (59% yield). Anal. Calcd for C$_{10}$H$_{17}$F$_6$FePS$_3$: C, 27.66; H, 3.95. Found: C, 28.34; H, 4.19.

CpFe(CO)(CS)(CF$_3$SO$_3$). Solid [CpFe(CO)$_2$(CS)]CF$_3$SO$_3$ (0.437 g, 1.18 mmol) was placed in a quartz Schlenk tube, and the apparatus was degassed by several cycles (4–5) of alternate evacuation and filling with N$_2$. Then, CH$_2$Cl$_2$ (35 mL) was added, the apparatus was fitted with a cooling probe and a mineral oil bubbler, and the solution was photolyzed with 254-nm radiation until the IR spectrum of the solution indicated that a maximum amount of CpFe(CO)(CS)(CF$_3$SO$_3$) was formed (~5 h). After irradiation, the red solution was transferred to a larger N$_2$-filled Schlenk tube (~150 mL). Ether (~95 mL) or hexane (~65 mL) was added to precipitate remaining starting material and any decomposition products. The solution was then filtered through Celite under N$_2$ to give a clear red solution of CpFe(CO)(CS)(CF$_3$SO$_3$).

Solutions of CpFe(CO)(CS)(CF$_3$SO$_3$) were used immediately after preparation for the synthesis of further products, as they decomposed rapidly in air and slowly under nitrogen. Attempts to isolate a crystalline product by evaporation of solutions of CpFe(CO)(CS)(CF$_3$SO$_3$) resulted in a red oil that slowly decomposed even at −20 °C under nitrogen. Because of its instability, it was characterized by its IR and ^{1}H and ^{13}C NMR spectra (Tables I and II).

CpFe(CO)(CS)I. An Et$_2$O solution of CpFe(CO)(CS)(CF$_3$SO$_3$) was produced by photolysis of [CpFe(CO)$_2$(CS)]CF$_3$SO$_3$ (0.402 g, 1.09 mmol) in 20 mL of CH$_2$Cl$_2$ as described above. To this solution were added KI (0.183 g, 1.10 mmol) and acetone (30 mL), and the mixture was stirred until all the KI had dissolved (typically overnight). The solution was evaporated to dryness, and the residue was extracted with CS$_2$ until all the green CpFe(CO)(CS)I had been extracted. This green solution was filtered, the volume was reduced to ~20 mL, and heptane was slowly added to the warmed solution until precipitation began. Cooling to −20 °C gave black crystals of CpFe(CO)(CS)I. Repetition of the crystallization step gave a second batch of crystals for a total of 0.223 g (64%). Anal. Calcd for C$_7$H$_5$FeIOS: C, 26.28; H, 1.58. Found: C, 25.91; H, 1.66.

The CpFe(CO)(CS)I produced by this synthesis typically contained ~3% CpFe(CO)$_2$I. For most purposes, this was sufficiently pure to use in subsequent studies. However, if a pure product was desired, as for elemental analyses, the CpFe(CO)(CS)I was separated from CpFe(CO)$_2$I by fractional crystallization using CS$_2$/hexanes. Pure CpFe(CO)(CS)I was also obtained by chromatography on Florisil eluting with CS$_2$.

CpFe(CO)(CS)Br. The same procedure and quantities as for the preparation of CpFe(CO)(CS)I were used, except KBr (0.17 g, 0.98 mmol) replaced KI. The isolated orange crystals of CpFe(CO)(CS)Br (0.154 g, 51%) commonly contained ~11% CpFe(CO)$_2$Br. As with CpFe(CO)(CS)I, pure CpFe(CO)(CS)Br could be obtained by fractional crystallization or chromatography. The compound was characterized by its IR and ^{1}H NMR spectra (Table I).

CpFe(CO)(CS)Cl. By the same procedure and with quantities as for CpFe(CO)(CS)I, except replacement of KI with KCl (0.0829 g, 1.11 mmol), CpFe(CO)(CS)Cl was isolated (0.0691 g, 31%) as a reddish powder that contained ~13% CpFe(CO)$_2$Cl. It was not purified further and was characterized by its IR spectrum (Table I).

[CpFe(CO)(CS)(PPh$_3$)]CF$_3$SO$_3$. A solution of CpFe(CO)(CS)(CF$_3$SO$_3$) was prepared by photolysis of [CpFe(CO)$_2$(CS)]CF$_3$SO$_3$ (0.402 g, 1.09 mmol) in CH$_2$Cl$_2$ (20 mL). The volume of this solution was reduced to ~2 mL under an N$_2$ stream. Then, 25 mL of Et$_2$O was added, and the solution was filtered through Celite under N$_2$ to give a clear red solution of CpFe(CO)(CS)(CF$_3$SO$_3$). Upon addition of PPh$_3$ (0.288 g, 1.10 mmol), the color of the solution changed to yellow within 1 min and a precipitate formed. The solution was stirred for 5 min and then filtered. The precipitate was dissolved in acetone, the solution was filtered, and while warming, heptane was added to the point of precipitation. Cooling to −20 °C gave golden crystals of [CpFe(CO)(CS)(PPh$_3$)]CF$_3$SO$_3$, 0.399 g (61%). Anal. Calcd for C$_{26}$H$_{20}$F$_3$FePO$_4$S$_2$: C, 51.67; H, 3.34. Found: C, 51.61; H, 3.41.

[CpFe(CO)(CS)(L)]CF$_3$SO$_3$ (L = Pyridine, MeCN, P(OPh)$_3$, P(OMe)$_3$, (*n*-Bu)$_2$S). With similar procedures and quantities as for the preparation of [CpFe(CO)(CS)(PPh$_3$)]CF$_3$SO$_3$, IR evidence (Table I) for the generation of these complexes was obtained; however, in no case was it possible to isolate the products as solids. In some cases (L = P(OPh)$_3$, P(OMe)$_3$, (*n*-Bu)$_2$S), IR spectra of the product mixtures suggested that [CpFe(CS)(L)$_2$]CF$_3$SO$_3$ also formed, but they too could not be isolated from the oily mixtures.

CpFe(CS)(PEt$_3$)I. Triethylphosphine (150 μL, 1.02 mmol) was added to a solution of CpFe(CO)(CS)I (0.322 g, 1.02 mmol, containing traces of CpFe(CO)$_2$I) in benzene (50 mL), and the solution was refluxed for 1 h under N$_2$. The solution was cooled to room temperature and filtered to remove the yellow precipitate that had formed within the first 5 min of refluxing. The precipitate was washed with benzene and pentane to yield 0.083 g of what was probably [CpFe(CO)(CS)(PEt$_3$)]I (IR (MeCN): 2027 s, 1319 vs cm^{-1}) contaminated with [CpFe(CO)$_2$(PEt$_3$)]I (IR (MeCN): 2046, 2006 cm^{-1}). The green filtrate from above was evaporated to dryness, and the residue was dissolved in CS$_2$ (~15 mL). The solution was filtered, and hexane (~15 mL) was added. The solution was then slowly evaporated under a stream of N$_2$ until a precipitate began to form. Crystallization at −20 °C gave dark green crystals of CpFe(CS)(PEt$_3$)I, 0.134 g (33%). Anal. Calcd for C$_{12}$H$_{20}$FeIPS: C, 35.15; H, 4.92. Found: C, 35.30; H, 5.08.

CpFe(CS)(PPh$_3$)I. From CpFe(CO)(CS)I. A solution of CpFe(CO)(CS)I (1.51 g, 4.72 mmol, containing traces of CpFe(CO)$_2$I) and PPh$_3$ (1.24 g, 4.74 mmol) in benzene (80 mL) was refluxed for 3 h under N$_2$. The solution was cooled to room temperature and evaporated to dryness under reduced pressure. The residue was dissolved in CS$_2$ and chromatographed on a Florisil column (18 × 730 mm). Elution with CS$_2$ yielded an initial gray band identified as CpFe(CO)$_2$I impurity. Elution with 1% Et$_2$O (v/v) in CS$_2$ yielded a dark green band that was collected in fractions. Essentially all of the CpFe(CS)(PPh$_3$)I eluted before the CpFe(CO)(PPh$_3$)I; however, as both compounds are dark green, the composition of each fraction had to be monitored by infrared spectroscopy. The fractions containing only CpFe(CS)(PPh$_3$)I were combined and evaporated to dryness. The residue was dissolved in CH$_2$Cl$_2$ (~20 mL); the solution was filtered through Celite, and heptane (20 mL) was added. The solution was slowly evaporated under an N$_2$ stream until crystals began to form. Cooling at −20 °C gave green crystals of CpFe(CS)(PPh$_3$)I, 1.77 g (68%). Anal. Calcd for C$_{24}$H$_{20}$FeIPS; C, 52.01; H, 3.64. Found: C, 51.92; H, 3.68. The pure complex was also obtained by fractional crystallization from CS$_2$/heptane or CH$_2$Cl$_2$/heptane; however, yields were lower.

From $[CpFe(CS)(MeCN)_2]PF_6$. A solution of $[CpFe(CO)_2(CS)]PF_6$ (0.489 g, 1.33 mmol) in MeCN (35 mL) was irradiated in a quartz Schlenk tube for 7 h to produce $[CpFe(CS)(MeCN)_2]PF_6$ (vide ante). Potassium iodide (0.251 g, 1.51 mmol) was added, and the solution was stirred overnight to produce CpFe(CS)(MeCN)I. Then, PPh_3 (0.324 g, 1.43 mmol) was added, and the solution was stirred an additional 11 h. The green solution was evaporated to dryness, and the residue was dissolved in benzene. The resulting solution was filtered through Celite and placed on a Florisil chromatography column (16 × 290 mm). Elution, initially with benzene, then with $CHCl_3$, and finally with CH_2Cl_2, gave a dark green band that was collected and evaporated to dryness. An IR spectrum of the residue in CS_2 indicated that it was primarily $CpFe(CS)(PPh_3)I$ with traces of CpFe(CO)(CS)I and $CpFe(CO)_2I$. The residue was then dissolved in CH_2Cl_2 (~10 mL), the solution was filtered, and heptane (~10 mL) was added. The solution was placed under a slow stream of nitrogen until crystals began to form. Cooling to −20 °C gave crystals of pure $CpFe(CS)(PPh_3)I$, which were isolated by filtration and washed with pentane; 0.433 g (59%).

$CpFe(CS)(AsPh_3)I$. A solution of CpFe(CO)(CS)I (0.105 g, 0.329 mmol, containing traces of $CpFe(CO)_2I$) and $AsPh_3$ (0.155 g, 0.506 mmol) in benzene (25 mL) was refluxed under N_2 for 22 h. The solution was cooled to room temperature and placed on a Florisil column (12 × 340 mm). Elution with benzene first gave a brown band that was collected and evaporated to dryness. An IR spectrum showed this band to contain unreacted CpFe(CO)(CS)I and $CpFe(CO)_2I$. The second band was green and contained the product $CpFe(CS)(AsPh_3)I$ and some $CpFe(CO)(AsPh_3)I$; it was collected and evaporated to dryness under reduced pressure. The residue was dissolved in CS_2, the solution was filtered, and heptane (~10 mL) was added. The solution was evaporated under a slow nitrogen stream until crystals began to form and then cooled to −20 °C. This crystallization procedure was repeated again to yield green crystals of $CpFe(CS)(AsPh_3)I$ (0.099 g, 50%), which were characterized by its IR and ^1H NMR spectra (Table I).

$CpFe(CS)(SbPh_3)I$. The same procedures and quantities as used for the synthesis of $CpFe(CS)(AsPh_3)I$ were employed except for the following changes: (a) $SbPh_3$ (0.231 g, 0.653 mmol) replaced $AsPh_3$; (b) the reflux time was 37 h; (c) elution of the green product was accomplished by using benzene followed by CH_2Cl_2; (d) crystallization of the product was done using CH_2Cl_2 (~10 mL) to which heptane (~10 mL) was added. The yield of $CpFe(CS)(SbPh_3)I$ was 0.153 g (68%). Anal. Calcd for $C_{24}H_{20}FeISSb$: C, 44.69; H, 3.13. Found: C, 44.56; H, 3.02.

$CpFe(CS)[P(OMe)_3]I$. A solution of CpFe(CO)(CS)I (0.335 g, 1.05 mmol, containing traces of $CpFe(CO)_2I$) and $P(OMe)_3$ (1.0 mL, 8.48 mmol) in benzene (50 mL) was refluxed under N_2 for 11 h. The solution was reduced in volume in vacuo to ~2 mL and placed on a Florisil column (12 × 300 mm). Elution with benzene gave a single green band, which was collected and evaporated to dryness. An IR spectrum of the residue in CS_2 showed this to be a mixture of $CpFe(CS)[P(OMe)_3]I$, the major product, and $CpFe(CO)[P(OMe)_3]I$. Pure $CpFe(CS)[P(OMe)_3]I$ was then isolated by fractional crystallization. The residue was dissolved in a minimum of CH_2Cl_2 (~10 mL); the solution was filtered, and heptane (~15 mL) was added. The solution was placed under a slow nitrogen stream until crystals began to form and then cooled to −20 °C to complete the crystallization. The crystals were recovered by filtration and washed with pentane. After the crystallization was repeated three additional times, black crystals of pure $CpFe(CS)[P(OMe)_3]I$ (0.190 g, 44%) were obtained. Anal. Calcd for $C_9H_{14}FeIO_3PS$: C, 25.99; H, 3.39. Found: C, 26.20; H, 3.44.

$CpFe(CS)[P(OPh)_3]I$. A benzene (50 mL) solution of CpFe(CO)(CS)I (0.322 g, 1.01 mmol, containing traces of $CpFe(CO)_2I$) and $P(OPh)_3$ (1.0 mL, 3.8 mmol) was refluxed under N_2 for 12 h. The solution was evaporated to dryness under reduced pressure. The residue was dissolved in CS_2 and chromatographed on a Florisil column (12 × 350 mm), eluting with CS_2 until a single green band extended almost the entire length of the column. Elution was then continued with 10% $CHCl_3/CS_2$, and the green band was collected in fractions. Each fraction was analyzed by IR spectroscopy. Most of the band contained pure $CpFe(CS)[P(OPh)_3]I$; only the last few fractions were contaminated with $CpFe(CO)[P(OPh)_3]I$. The fractions containing only the thiocarbonyl complex were combined and evaporated to dryness under reduced pressure. The residue was dissolved in CH_2Cl_2 (~10 mL), and the solution was filtered and treated with heptane (~10 mL). The solution was then placed under a slow N_2 stream until crystals began to form. Cooling to −20 °C gave green crystals of $CpFe(CS)[P(OPh)_3]I$, 0.294 g (49%). Anal. Calcd for $C_{24}H_{20}FeIO_3PS$: C, 47.87; H, 3.35. Found: C, 47.63; H, 3.45.

$[CpFe(CS)(bpy)]PF_6$. A solution of 2,2′-bipyridine, bpy (0.171 g, 1.09 mmol), in CH_2Cl_2 (50 mL) was added dropwise very slowly (over ~30 min) to a solution of $[CpFe(CS)(MeCN)_2]PF_6$ (0.418 g, 1.07 mmol) in CH_2Cl_2 (40 mL). The solution was stirred an additional 30 min and then evaporated to dryness. The residue was extracted with CH_2Cl_2 until all the yellow-orange $[CpFe(CS)(bpy)]PF_6$ had been extracted, thereby effecting a partial separation from the less soluble, red $[Fe(bpy)_3](PF_6)_2$. After filtration, the solution was reduced in volume and chromatographed on alumina (12 × 300 mm column) with CH_2Cl_2. The initial orange-yellow band was collected and evaporated to dryness. Crystallization from $CH_2Cl_2/CHCl_3$ at −20 °C gave red crystals of $[CpFe(CS)(bpy)]PF_6$, 0.161 g (32%). Anal. Calcd for $C_{16}H_{13}F_6FeN_2PS$: C, 41.22; H, 2.81. Found: C, 41.16; H, 2.94.

$[CpFe(CS)(phen)]PF_6$. The procedures and quantities in this preparation were the same as in the synthesis of $[Cp(CS)(bpy)]PF_6$, except 1,10-phenanthroline, phen (0.208 g, 1.05 mmol), replaced bpy and the chromatography was carried out with mixtures of $CH_2Cl_2/MeCN$ (up to 50% MeCN). The brown crystalline product, $[CpFe(CS)(phen)]PF_6$, was obtained by recrystallization from CH_2Cl_2/hexanes at −20 °C; 0.093 g (18%). Anal. Calcd for $C_{18}H_{13}F_6FeN_2PS$: C, 44.11; H, 2.67. Found: C, 44.32; H, 2.60.

$[CpFe(CS)(PPh_3)_2]PF_6$. A solution of $[CpFe(CS)(MeCN)_2]PF_6$ (0.423 g, 1.08 mmol) and PPh_3 (0.566 g, 2.16 mmol) in CH_2Cl_2 (50 mL) was stirred for 6 h at room temperature. The initial yellow-green solution turned dark green in ~15 min and then red in ~1 h. Evaporation under reduced pressure gave a red tar, which was extracted with hot benzene, dissolving a red material and leaving behind orange crystals of $[CpFe(CS)(PPh_3)_2]PF_6 \cdot C_6H_6$, 0.330 g (34%). The analytical sample was crystallized from CH_2Cl_2/benzene at −20 °C. Anal. Calcd for $C_{48}H_{41}F_6FeP_3S$: C, 62.28; H, 4.53. Found: C, 62.17; H, 4.57.

$[CpFe(CS)[P(OMe)_3](MeCN)]PF_6$. Trimethyl phosphite (2.0 mL, 17 mmol) was added to a solution of $[CpFe(CS)(MeCN)_2]PF_6$ (0.461 g, 1.17 mmol) in CH_2Cl_2 (50 mL). After stirring for 9 h, the orange solution was evaporated to dryness under reduced pressure. The residue was dissolved in CH_2Cl_2; the solution was filtered, and hexanes were added to the point of precipitation. Crystallization at −20 °C gave orange crystals of $[CpFe(CS)[P(OMe)_3](MeCN)]PF_6$, 0.233 g (42%). The analytical sample was recrystallized from acetone/hexane. Anal. Calcd for $C_{11}H_{17}F_6FeNO_3P_2S$: C, 27.81; H, 3.61. Found: C, 27.83; H, 3.70.

$[CpFe(CS)[P(OPh)_3](MeCN)]PF_6$. Triphenyl phosphite (1.0 mL, 3.8 mmol) was added to a solution of $[CpFe(CS)(MeCN)_2]PF_6$ (0.466 g, 1.19 mmol) in CH_2Cl_2 (50 mL). The initial yellow-green solution turned orange in approximately 2 h but was stirred overnight. The solution was then evaporated to dryness under reduced pressure. The residue was dissolved in a minimum of CH_2Cl_2 (~15 mL), the solution was filtered, and then hexanes (~100 mL) were added to precipitate the product. The orange product was recrystallized from CH_2Cl_2/benzene at −20 °C as the monobenzene solvate, $[CpFe(CS)[P(OPh_3)_3](MeCN)]PF_6 \cdot C_6H_6$, 0.634 g (72%). Anal. Calcd for $C_{32}H_{29}F_6FeNO_3P_2S$: C, 51.98; H, 3.95. Found: C, 51.62; H, 3.91.

$CpFe(CS)_2I$. Methanol (25 mL) was added to a nitrogen-filled Schlenk tube containing $[CpFe(CS)(MeCN)_2]PF_6$ (0.434 g, 1.11 mmol) and KI (0.186 g, 1.12 mmol). The mixture was stirred for 6 h (if the reaction was conducted in CH_3CN, the progress of the reaction could be followed in the IR and indicated that the reaction is complete in ~90 min), to produce an air-stable solution of what appears to be CpFe(CS)(MeCN)I, on the basis of its spectra (IR (MeCN): 1277 cm^{-1}. ^1H NMR (MeCN): δ 4.88 (Cp)). After CH_2Cl_2 (50 mL) was added, the solution was extracted with aqueous $Na_2S_2O_3$ (0.42 M, in two 10-mL portions) to destroy the byproduct, I_2. The organic phase was collected, dried overnight over anhydrous $MgSO_4$, and then filtered through Celite to produce a green solution of $CpFe(CS)_2I$. The volume of the solution was reduced in vacuo to ~10 mL, heptane was added to the point of precipitation, and the product was crystallized at −20 °C to yield black crystals of $CpFe(CS)_2I$, 0.105 g (57%). The analytical sample was recrystallized from CS_2/hexanes. The mass spectrum of the complex showed a molecular ion at m/e 335.5. Anal. Calcd for $C_7H_5FeIS_2$: C, 25.02; H, 1.50. Found: C, 25.28; H, 1.58.

Attempts to isolate the intermediate, CpFe(CS)(MeCN)I, were unsuccessful. Extraction of a CH_3CN solution of CpFe(CS)(MeCN)I with CS_2 initially showed the presence of CpFe(CS)(MeCN)I (by IR); however, this rapidly converted to $CpFe(CS)_2I$.

Results and Discussion

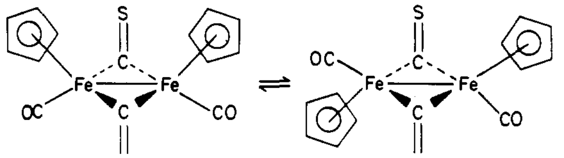
Synthesis and Characterization of *cis*- and *trans*-$[CpFe(CO)(CS)]_2$. The reduction (eq 1) of $[CpFe(CO)_2(CS)]CF_3SO_3$

$$2CpFe(CO)_2(CS)^+ + 2NaH \rightarrow [CpFe(CO)(CS)]_2 + 2Na^+ + \{H_2\} + 2\{CO\} \quad (1)$$

with NaH in THF solvent yields air-stable *cis-trans*-$[CpFe(CO)(CS)]_2$ (35%) with much smaller amounts of $[CpFe(CO)_2]_2$ and $Cp_2Fe_2(CO)_3(CS)$. The separation of these very similar dimers is achieved best by oxidizing the mixture with O_2 in

$HCl/EtOH/CHCl_3$. This treatment cleaves the Fe–Fe bond in the latter dimers[16] to give $CpFe(CO)_2Cl$ and CpFe(CO)(CS)Cl, which are easily separated from *cis/trans*-$[CpFe(CO)(CS)]_2$, which is stable to these oxidizing conditions. Separation of the cis and trans isomers of $[CpFe(CO)(CS)]_2$ is accomplished by careful chromatography and recrystallization. The structure of the cis isomer, as established by an X-ray diffraction study, was reported earlier[11] and shows both CS groups in bridging positions. IR spectra (Table I) of the isomers show ν(C=S) absorptions at 1124 and 1131 cm^{-1} for the bridging CS groups, and the ^{13}C NMR resonance (Table II) of the bridging CS groups lies far downfield at 374.5 ppm, as was observed for $Cp_2Fe_2(CO)_3(CS)$ at 378.1 ppm.[12] The preference of the CS groups for bridging positions was discussed previously[18] in terms of the weak C–S π bonds, which favor the bridging position where there are more metal–CS bonds and less C–S π bonding.

The fact that the isomers can be separated chromatographically indicates that cis–trans interconversion is a relatively slow process (eq 2). A qualitative measure of this rate was obtained by noting the time (~28 min) required for the 2011-cm^{-1} absorption of the cis isomer to reach half its maximum intensity when a xylene solution of *trans*-$[CpFe(CO)(CS)]_2$ was heated at 50 °C. At this point, both the cis and trans isomers were present and at equilibrium. During the isomerization, there was no IR evidence for other CO- or CS-containing intermediates.



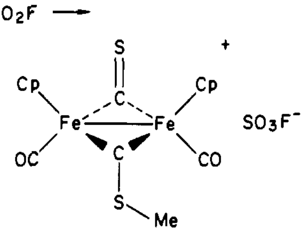
(2)

This rate of isomerization is much slower than that of $Cp_2Fe_2(CO)_3(CS)$, whose cis and trans isomers interconvert too rapidly to separate but do show a coalescence temperature of 53 °C in ^1H NMR studies.[12] This coalescence temperature is about 100 °C higher than that of $[CpFe(CO)_2]_2$.[19] Thus, the rate of cis $\rightleftharpoons$ trans isomerization decreases in the order $[CpFe(CO)_2]_2$ > $Cp_2Fe_2(CO)_3(CS)$ > $[CpFe(CO)(CS)]_2$. This is the same order found in the analogous Ru series.[18]

The $[CpFe(CO)_2]_2$ and $Cp_2Fe_2(CO)_3(CS)$ isomerizations[12] presumably occur by the Adams–Cotton mechanism[20] in which the bridging ligands move to terminal positions, which allows rotation around the Fe–Fe bond to the other isomer followed by closure of the bridging ligands. Such a mechanism for $[CpFe(CO)(CS)]_2$ leads to the formation of dimers with terminal CS ligands, which are not observed. Therefore, some other mechanism is required. Two possible mechanisms[18] were previously proposed for $[CpRu(CO)(CS)]_2$, and these are likely mechanisms for $[CpFe(CO)(CS)]_2$. One involves direct exchange of a bridging CS and a terminal CO followed by an Adams–Cotton rotation. The other involves cleavage of an Fe–CS and the Fe–Fe bond, which allows rotation and isomerization. Both of these mechanisms account for the CS groups remaining in the bridging position in both the cis and trans isomers; however, there is no definitive experimental evidence to support either. Whatever the mechanism, the isomerization occurs much slower for $[CpFe(CO)(CS)]_2$ than for $[CpRu(CO)(CS)]_2$, which isomerizes within seconds at room temperature.[18]

Reactions of $[CpFe(CO)(CS)]_2$. The S atom of the terminal CS ligand in electron-rich complexes such as $CpW(CO)_2(CS)^-$,[21,22] $[HB(pz)_3]W(CO)_2(CS)^-$,[21,22] $W(diphos)_2(CO)(CS)$,[23] and $CpCo(PPh_3)(CS)$[24] is known to add electrophiles such as carbonium ions and, in some cases, metal salts such as $HgCl_2$ and Ag^+. The S atom of the bridging thiocarbonyl ligand in the following complexes also forms adducts with electrophiles: $[CpFe(CO)(CS)]_2$,[11] $Cp_2Fe_2(CO)_3(CS)$,[12,13,25,26] $Cp_3Co_3(\mu_3\text{-}S)(\mu_3\text{-}CS)$,[24,27] $CpMPt(\mu\text{-}CS)(CO)_2(PR_3)_2$ (M = Mn, Re),[28] and $Cp_2CoMn(CO)(\mu\text{-}CO)(\mu\text{-}CS)(PMe_3)$.[29] As communicated earlier,[11] *cis*-$[CpFe(CO)(CS)]_2$ reacts in 15 min with $MeOSO_3F$ to give the black, air-stable *S*-methyl bridging carbyne complex, $[Cp_2Fe_2(CO)_2(CS)(CSMe)]^+$ (eq 3). Methylation of the second CS group does not occur even when stirring the dimer in excess, neat $MeOSO_2F$.

cis-$[CpFe(CO)(CS)]_2$ + $MeOSO_2F$ $\longrightarrow$



(3)

The cis structure of the product shown in eq 3 is supported by the familiar strong, medium pattern[18] of the terminal ν(CO) absorptions (Table I) and an X-ray structural study of $Cp_2Fe_2(CO)_3(CSEt)^+$.[13] The ν(CO) values (Table I) of the carbyne complex increase ~30 cm^{-1} from those of the starting dimer, while the unalkylated bridging CS frequency increases by ~50 cm^{-1}. These increases are expected for the addition of an electron-withdrawing CH_3^+ group on a bridging CS. The ν(CS) frequency of the alkylated CS group decreases by ~90 cm^{-1}, which is similar to the decrease reported for the methylation of $Cp_2Fe_2(CO)_3(CS)$.[25] Separate ^1H resonances for the two Cp rings in the NMR spectrum of the carbyne complex are consistent with a bent C–S–Me group and a slow rate of inversion or rotation at the S atom, as noted previously for the related $Cp_2Fe_2(CO)_3(CSR)^+$ complexes.[25]

The reaction of *cis*-$[CpFe(CO)(CS)]_2$ with MeI also gives $Cp_2Fe_2(CO)_3(CSMe)^+$, although a longer reaction time is required. It was observed that the rate of reaction with MeI is different for the cis and trans isomers, as determined by noting the decrease in the ν(CO) absorptions of the dimers in neat MeI at room temperature. Under these conditions, 8 min was required for one-fourth of the *cis*-$[CpFe(CO)(CS)]_2$ to react, while ~60 min was necessary for the trans isomer. In both reactions, the same cis product (eq 3) was observed. During the reaction of the trans isomer, there was extensive decomposition, and a band at 2004 cm^{-1} characteristic of *cis*-$[CpFe(CO)(CS)]_2$ was observed, which suggests that the trans isomer is converting to the cis which is actually reacting with the MeI. These results indicate that the cis isomer is more reactive toward MeI than the trans, a conclusion that was tentatively proposed for the cis and trans isomers of $Cp_2Fe_2(CO)_3(CS)$.[30] It is not obvious why the cis isomer reacts with MeI substantially faster than does the trans form.

With the Lewis acid $HgCl_2$, a *cis/trans*-$[CpFe(CO)(CS)]_2$ mixture reacts to form the black, air-stable adduct (eq 4). Excess

$$[CpFe(CO)(CS)]_2 + HgCl_2 \rightarrow Cp_2Fe_2(CO)_2(CS)(CSHgCl_2) \qquad (4)$$

$HgCl_2$ also gives only the 1:1 adduct. The number and intensities of the ν(CO) absorptions (Table I) suggest that $HgCl_2$ adducts

---

(18) Wnuk, T. A.; Angelici, R. J. *Inorg. Chem.* **1977**, *16*, 1173.

(19) Bullitt, J. G.; Cotton, F. A.; Marks, T. J. *Inorg. Chem.* **1972**, *11*, 671.

(20) Adams, R. D.; Cotton, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6589.

(21) Greaves, W. W.; Angelici, R. J.; Helland, B. J.; Klima, R.; Jacobson, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7618.

(22) Greaves, W. W.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 2983.

(23) Dombek, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 1261. Dombek, B. D.; Angelici, R. J. *Inorg. Chem.* **1976**, *15*, 2397.

(24) Fortune, J.; Manning, A. R. *Organometallics* **1983**, *2*, 1719.

(25) (a) Quick, M. H.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 1123. (b) Howell, J. A. S.; Mathur, P.; Kumar, R.; Manning, A. R.; Stephens, F. S. *J. Organomet. Chem.* **1984**, *262*, 227.

(26) Quick, M. H.; Angelici, R. J. *Inorg. Chem.* **1982**, *21*, 1674.

(27) Werner, H.; Leonhard, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 627. Werner, H.; Leonard, K.; Kolb, O.; Rottinger, E.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 1654.

(28) Jeffrey, J. C.; Razay, H.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1733.

(29) Kolb, O.; Werner, H. *Angew. Chem.* **1982**, *94*, 207.

(30) Quick, M. H. Ph.D. Dissertation, Iowa State University, Ames, IA, 1978.

of both the cis and trans isomers form. The ν(CO) frequencies are ~17 cm^{-1} higher in the adduct than the starting dimers, while the ν(CS) of the unreacted bridging CS ligand increases ~50 cm^{-1}. The ν(CS) absorbance of the $CSHgCl_2$ group is ~110 cm^{-1} lower than in the dimers. Very similar IR changes were observed in the formation of the $Cp_2Fe_2(CO)_3(CSHgCl_2)$ adduct.[25] When NH_3 is bubbled through a solution of the adduct, the $HgCl_2$ is removed by complexation and $[CpFe(CO)(CS)]_2$ is liberated.

Terminal CS ligands in electron-poor complexes react with primary amines (RNH_2) to give the corresponding isocyanide (CNR) complexes and H_2S.[5,12,22,31-33] We attempted the reaction of $[CpFe(CO)(CS)]_2$ with methyl- and cyclohexylamine at room temperature to form the known $Cp_2Fe_2(CO)_2(CS)(CNMe)$[25] or $Cp_2Fe_2(CO)_2(CNMe)_2$.[34] Unfortunately, there was no reaction; nor was there a reaction with water to give $Cp_2Fe_2(CO)_3(CS)$ or $[CpFe(CO)_2]_2$.

Bromine reacts with $[CpFe(CO)(CS)]_2$ in refluxing $CHCl_3$ to give orange, air-stable CpFe(CO)(CS)Br in 70% yield (eq 5). The

$$[CpFe(CO)(CS)]_2 + Br_2 \rightarrow 2CpFe(CO)(CS)Br \quad (5)$$

IR spectrum of the product shows one ν(CO) (2033 cm^{-1}) and one ν(CS) absorption (1309 cm^{-1}), as expected. When reaction 5 was conducted at 0 °C in CS_2, a black precipitate (IR (MeCN): 2104 (w, sh), 2084 (s), 2039 (m), 1325 (s) cm^{-1}) formed. Upon standing in MeCN, this precipitate slowly converted to CpFe(CO)(CS)Br. The IR spectrum and the conversion to CpFe(CO)(CS)Br suggest that the black precipitate contains $\{[CpFe(CO)(CS)]_2Br\}^+$, a complex in which Br^- bridges two $CpFe(CO)(CS)^+$ units. Although we were unable to fully characterize this material, it is known[35] that reactions of $[CpFe(CO)_2]_2$ with halogens to form $CpFe(CO)_2X$ proceed via an isolable $\{CpFe(CO)_2]_2X\}X$ intermediate.

The reaction of $[CpFe(CO)(CS)]_2$ with Cl_2 in CCl_4 at 0 °C gave an unstable emerald green precipitate, perhaps $\{[CpFe(CO)(CS)]_2Cl\}^+$, which decomposed in MeCN solution; however, no CpFe(CO)(CS)Cl was formed. Iodine reacts with $[CpFe(CO)(CS)]_2$ in refluxing MeCN for 1 h to give a poor yield (19%) of CpFe(CO)(CS)I contaminated with ~10% $CpFe(CO)_2I$. The product, which was not purified, can be made by a more efficient method (vide infra).

Although $[CpFe(CO)_2]_2$ can be cleaved by reducing agents such as Na/Hg to give $CpFe(CO)_2^-$ and $Cp_2Fe_2(CO)_3(CS)$ can be reduced to $CpFe(CO)(CS)^-$ and $CpFe(CO)_2^-$,[12] the reduction of $[CpFe(CO)(CS)]_2$ is much more complicated. When a THF solution of $[CpFe(CO)(CS)]_2$ reacts with excess (>2 equiv) Na/Hg, C_8K,[36] or $NaK_{2.8}$, a gray to brown precipitate, which is insoluble in common solvents, forms. It shows no apparent reaction with MeI or Ph_3SnCl even in hexamethylphosphoramide solvent, in which it gives a dark red air-sensitive solution. Excess sodium naphthalide[37] reacts with $[CpFe(CO)(CS)]_2$ to give an olive green solution, which when reacted with Ph_3SnCl did not yield a product. Sodium hydride does not react with the dimers during a 2-day period at 25 °C.

Reactions of $[CpFe(CO)_2(CS)]^+$. Complexes containing both CO and CS groups generally react with other ligands to substitute a CO rather than a CS.[38-40] This behavior has been rationalized in terms of a stronger metal–CS bond as compared with the metal–CO bond. Specific CO substitution is not observed for $CpFe(CO)_2(CS)^+$. Busetto and Palazzi[5] found that $CpFe(CO)_2(CS)^+$ reacts with phosphines and related ligands to give both the CO-substituted, $CpFe(CO)(L)(CS)^+$, and the CS-substituted products, $CpFe(CO)_2(L)^+$. Likewise, we observe that $CpFe(CO)_2(CS)^+$ reacts with halide salts at room temperature in THF to give both CpFe(CO)(CS)X and $CpFe(CO)_2X$. The $CpFe(CO)(CS)X/CpFe(CO)_2X$ ratio, as estimated by their ν(CO) intensities, varied depending upon the halide salt as follows: KI (2.9), LiI (3.3), Et_4NI (0.55), LiCl (4.4), LiBr (0.19). There seems to be no logical explanation for the ratio changes, but since CpFe(CO)(CS)X and $CpFe(CO)_2X$ are difficult to separate, these reactions are not as desirable a route to the thiocarbonyl derivatives as other methods (vide infra).

The CO may be substituted specifically by irradiating with UV light a CH_2Cl_2 solution of $[CpFe(CO)_2(CS)]CF_3SO_3$ (eq 6). The

$$[CpFe(CO)_2(CS)]CF_3SO_3 \xrightarrow{h\nu} CpFe(CO)(CS)(CF_3SO_3) + CO \quad (6)$$

product, like $(Me_5C_5)Fe(CO)_2(CF_3SO_3)$,[41] probably contains an O-coordinated $CF_3SO_3^-$ ligand. It is soluble in CS_2, in which its IR spectrum shows one ν(CO) (2054 (s) cm^{-1}) and one ν(CS) (1318 (vs) cm^{-1}) absorption. Although the compound was not sufficiently stable to be isolated pure, its solutions are very useful for the preparation of other thiocarbonyl complexes, as described in the next section. When THF or acetone is used in reaction 6, yields of the product are much lower.

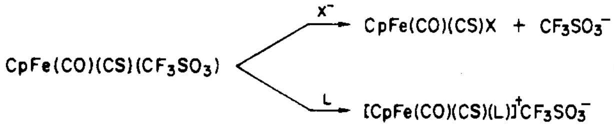
While the irradiation of $[CpFe(CO)_2(CS)]PF_6$ in acetone, THF, or CH_2Cl_2 solvents gives only very unstable materials, the reaction in MeCN gives $[CpFe(CS)(MeCN)_2]PF_6$ as yellow-green crystals in 64% yield (eq 7). This compound is useful for the synthesis

$$[CpFe(CO)_2(CS)]PF_6 + 2L \xrightarrow{h\nu} [CpFe(CS)(L)_2]PF_6 + 2CO \quad (7)$$

$$L = MeCN,\ Me_2S$$

of other substituted products (vide infra). A similar reaction of Me_2S in acetone gives black crystals (59%) of $[CpFe(CS)(Me_2S)_2]PF_6$. Photolysis of $[CpFe(CO)_2(CS)]PF_6$ in acetone with PPh_3 gives a mixture of $[CpFe(CO)(CS)(PPh_3)]PF_6$[5] and $[CpFe(CS)(PPh_3)_2]PF_6$, which were not purified. Both of these complexes can be prepared more specifically by methods described below.

Reactions of $CpFe(CO)(CS)(CF_3SO_3)$. When $CpFe(CO)(CS)(CF_3SO_3)$ is stirred in CH_2Cl_2 with the halide salts, KX, the air-stable CpFe(CO)(CS)X complexes are obtained (eq 8) in



(8)

yields that decrease with X in the order I (64%) > Br (51%) > Cl (31%). Since the approximate amount of $CpFe(CO)_2X$ impurity increases with X, I (3%) < Br (11%) < Cl (13%), CpFe(CO)(CS)I is the easiest complex to isolate in highest yield and highest purity. For this reason, it was used in the studies described in the next section. The $CpFe(CO_2)X$ impurity may be removed with considerable loss in yield by fractional crystallization or chromatography.

The monosubstituted cationic complexes $[CpFe(CO)(CS)(L)]CF_3SO_3$ are produced in reactions of neutral ligands, L, with $CpFe(CO)(CS)(CF_3SO_3)$ (eq 8). For L = PPh_3, the product was isolated (61%) as an air-stable solid and was fully characterized including elemental analyses. This complex was reported previously,[5] but the present method gives a higher yield without the $CpFe(CO)_2(PPh_3)^+$ contaminant. For L = pyridine and MeCN, the products could only be obtained as brownish oils, which were characterized only by their IR and ^1H NMR spectra (Table I). IR spectra of mixtures resulting from reactions where L = P-

---

(31) Dombek, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 7516.
(32) Dombek, B. D.; Angelici, R. J. *Inorg. Chem.* **1976**, *15*, 2403.
(33) Faraone, F.; Piraino, P.; Marsala, V.; Sergi, S. *J. Chem. Soc., Dalton Trans.* **1977**, 859.
(34) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209.
(35) Haines, R. J.; du Preez, A. L. *J. Chem. Soc. A* **1970**, 2341. Haines, R. J.; du Preez, A. L. *J. Chem. Soc., Dalton Trans.* **1972**, 944.
(36) Ottmers, D. M.; Rase, H. F. *Carbon* **1966**, *4*, 125.
(37) Classon, W. D.; Wriede, P.; Bank, S. *J. Am. Chem. Soc.* **1966**, *88*, 1581.
(38) Butler, I. S.; Fenster, A. E. *J. Organomet. Chem.* **1974**, *66*, 161.
(39) Butler, I. S. *Acc. Chem. Res.* **1977**, *10*, 359.
(40) Yaneff, P. V. *Coord. Chem. Rev.* **1977**, *23*, 183.
(41) Humphrey, M. B.; Lamanna, W. M.; Brookhart, M.; Husk, G. R. *Inorg. Chem.* **1983**, *22*, 3355.

$(OPh)_3$, $P(OMe)_3$, and $(n\text{-}Bu)_2S$ indicated that both $[CpFe(CO)(CS)(L)]CF_3SO_3$ and $[CpFe(CS)(L)_2]CF_3SO_3$ formed; pure products were not isolated from these mixtures. No reaction occurred between $CpFe(CO)(CS)(CF_3SO_3)$ and the olefins cyclopentene or norbornadiene at room temperature.

Reactions of CpFe(CO)(CS)I. The carbonyl complexes, $CpFe(CO)_2X$ (X = Cl, Br, I), react thermally with phosphines and phosphites to form CpFe(CO)(L)X and $[CpFe(CO)_2(L)]X$.[42-44] The analogous reactions of CpFe(CO)(CS)I with ligands L in refluxing benzene give the CO-substituted products CpFe(CS)(L)I in 33–68% yield (eq 9). Only for the reaction of L = PEt$_3$ is there any evidence for the I$^-$-substituted product $[CpFe(CO)(CS)(PEt_3)]I$. All of the CpFe(CS)(L)I products contained trace amounts of the analogous CpFe(CO)(L)I complex, presumably from the reaction of the small amount of $CpFe(CO)_2I$ present in the CpFe(CO)(CS)I starting material.

$$\mathrm{CpFe(CO)(CS)I + L \rightarrow CpFe(CS)(L)I + CO} \qquad (9)$$

$$\mathrm{L = PEt_3,\ PPh_3,\ AsPh_3,\ SbPh_3,\ P(OMe)_3,\ P(OPh)_3}$$

Attempts to reduce CpFe(CO)(CS)I with Zn/Hg and MeLi gave predominantly $[CpFe(CO)(CS)]_2$. There was no reaction with Mg or Mg/Hg. An attempt to prepare $Cp(CO)(CS)FeCo(CO)_4$ by reaction of CpFe(CO)(CS)I with $Na[Co(CO)_4]$ gave no identifiable CS-containing products.

Reactions of [CpFe(CS)(MeCN)$_2$]PF$_6$. As is commonly observed in other nitrile complexes,[45] the MeCN ligands in $[CpFe(CS)(MeCN)_2]^+$ are replaced by several ligands L (eq 10).

$$\mathrm{CpFe(CS)(MeCN)_2^+ + 2L \rightarrow [CpFe(CS)(L)_2]^+ + 2MeCN} \qquad (10)$$

$$\mathrm{2\ L = bpy,\ phen,\ 2\ PPh_3}$$

Yields of the 2,2′-bipyridine (32%) and *o*-phenanthroline (18%) complexes are low primarily because of the formation of $Fe(bpy)_3^{2+}$ and $Fe(phen)_3^{2+}$ as byproducts, even when stoichiometric amounts of the bidentate ligands are used. In MeCN solvent, the IR spectrum of $[CpFe(CS)(phen)]PF_6$ shows a shoulder at 1299 cm^{-1} that is apparently due to the replacement of phen by 2 MeCN to give some $CpFe(CS)(MeCN)_2^+$. Reaction 10 with PPh_3 gives a 34% yield of the orange, air-stable $[CpFe(CS)(PPh_3)_2]PF_6$, which crystallizes as the C_6H_6 solvate. When benzene is not present, only an oil is obtained. When reacted with the less basic $P(OMe)_3$ and $P(OPh)_3$ ligands, only one MeCN ligand is substituted to give the orange, air-stable $[CpFe(CS)(L)(MeCN)]PF_6$ products in modest yields, 42% and 72%, respectively.

When $[CpFe(CS)(MeCN)_2]PF_6$ is reacted with KI in MeCN at room temperature, an air-stable solution of what appears to be CpFe(CS)(MeCN)I (IR (MeCN): 1277 cm^{-1}. ^1H NMR (CH_3CN): δ 4.88 (Cp)) is produced. When PPh_3 is added to this solution, $CpFe(CS)(PPh_3)I$ is isolated in 59% yield, which is the best method for preparing this complex. Attempts to isolate the CpFe(CS)(MeCN)I intermediate were unsuccessful; evaporation of the MeCN solvent gives the new and unexpected product $CpFe(CS)_2I$. This product is also formed when CH_2Cl_2 or CS_2 is added to the MeCN solution of CpFe(CS)(MeCN)I. It seems that a decrease in the MeCN concentration causes $CpFe(CS)_2I$ to form. On a preparative scale, $CpFe(CS)_2I$ is generated in 57% yield (eq 11) by reacting $CpFe(CS)(MeCN)_2^+$ with KI in MeOH

$$\mathrm{2CpFe(CS)(MeCN)_2^+ + I^- \rightarrow CpFe(CS)_2I + ?} \qquad (11)$$

and adding CH_2Cl_2 to this solution. This is a complicated reaction, and the other products have not been identified, but it is clear that a CS group has been transferred from one Fe to another, such transfers being rare[46] for the CS group. The analogous reaction of $[CpFe(CS)(MeCN)_2]PF_6$ with KBr gives a poor yield (~4%) of $CpFe(CS)_2Br$, which is contaminated with CpFe(CO)(CS)Br and $CpFe(CO)_2Br$. This complex, $CpFe(CS)_2Br$, was not purified but only characterized by its IR spectrum.

Only a few other mononuclear, dithiocarbonyl complexes, $CpMn(CO)(CS)_2$,[39,40,47] $CpRe(CO)(CS)_2$, $OsX_2(CS)_2(PPh_3)_2$ [X = Cl, Br],[40] and $Os(S_2CNEt_2)(CS)_2(PPh_3)_2^+$,[48] are known, and their syntheses are generally more difficult and proceed in lower yields than for $CpFe(CS)_2I$. The molecular structure of $CpFe(CS)_2I$ is presumably very similar to that established for $(MeC_5H_4)Mn(CS)(NO)I$.[49] The mass spectrum of $CpFe(CS)_2I$ shows a molecular ion, and its IR spectrum shows the expected two ν(CS) bands at 1341 (s) and 1276 (vs) cm^{-1} (Table I); the average (1308 cm^{-1}) of these values is very close to the ν(CS) frequency (1306 cm^{-1}) for CpFe(CO)(CS)I, indicating that CO and CS have essentially the same effect on ν(CS). The ^{13}C NMR spectrum of $CpFe(CS)_2I$ shows the CS resonance at 323.4 ppm, which is in the range (321.7–329.4 ppm) observed for the other terminal CS-containing complexes (Table I) reported in this paper. These values are considerably upfield from the bridging CS resonance (374.5 ppm) in $[CpFe(CO)(CS)]_2$.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. $[CpFe(CO)_2(CS)]CF_3SO_3$, 60817-01-8; *cis*-$[CpFe(CO)(CS)]_2$, 60764-49-0; *trans*-$[CpF(CO)(CS)]_2$, 60802-41-7; *cis*-$[Cp_2Fe_2(CO)_2(CS)(CSHgCl_2)]$, 96307-23-2; *trans*-$[Cp_2Fe_2(CO)_2(CS)(CSHgCl_2)]$, 96391-82-1; *cis*-$[Cp_2Fe_2(CO)_2(CS)(CSMe)]PF_6$, 96307-25-4; CpFe(CO)(CS)I, 96307-26-5; CpFe(CO)(CS)Br, 96307-27-6; CpFe(CO)(CS)Cl, 96307-28-7; $CpFe(CO)(CS)(CF_3SO_3)$, 96307-29-8; $[CpFe(CO)(CS)(PPh_3)]CF_3SO_3$, 96307-30-1; $[CpFe(CO)(CS)(py)]CF_3SO_3$, 96307-32-3; $[CpFe(CO)(CS)(MeCN)]CF_3SO_3$, 96307-34-5; $CpFe(CS)(PEt_3)I$, 96307-35-6; $CpFe(CS)(PPh_3)I$, 96307-36-7; $CpFe(CS)(AsPh_3)I$, 96307-37-8; $CpFe(CS)(SbPh_3)I$, 96307-38-9; $CpFe(CS)[P(OMe)_3]I$, 96307-39-0; $CpFe(CS)[P(OPh)_3]I$, 96307-40-3; $[CpFe(CS)(MeCN)_2]PF_6$, 96307-42-5; $[CpFe(CS)(MeCN)(PEt_3)]PF_6$, 96326-06-6; $\{CpFe(CS)(MeCN)[P(OMe)_3]\}PF_6$, 96307-44-7; $\{CpFe(CS)(MeCN)[P(OPh)_3]\}PF_6$, 96307-46-9; $[CpFe(CS)(PPh_3)_2]PF_6$, 96307-48-1; $[CpFe(CS)(Me_2S)_2]PF_6$, 96307-50-5; $[CpFe(CS)(bpy)]PF_6$, 96307-52-7; $[CpFe(CS)(phen)]PF_6$, 96307-54-9; $CpFe(CS)_2I$, 96307-55-0; $CpFe(CS)_2Br$, 96307-56-1; $[CpFe(CO)_2]_2$, 12154-95-9; $Cp_2Fe_2(CO)_3(CS)$, 67113-80-8; $CpFe(CO)_2Cl$, 12107-04-9; $[Cp_2Fe_2(CO)_2(CS)(CSMe)]FSO_3$, 96391-83-2; $[Cp_2Fe_2(CO)_2(CS)(CSMe)]I$, 96391-84-3; $CpFe(CO)_2I$, 12078-28-3; $CpFe(CO)_2Br$, 12078-20-5; $[CpFe(CO)(CS)(P(OPh)_3)]CF_3SO_3$, 96307-58-3; $[CpFe(CO)(CS)(P(OMe)_3)]CF_3SO_3$, 96307-60-7; $[CpFe(CO)(CS)(PPh_3)]CF_3SO_3$, 96307-62-9; $[CpFe(CS)(P(OPh)_3)_2]CF_3SO_3$, 96307-64-1; $[CpFe(CS)(P(OMe)_3)_2]CF_3SO_3$, 96307-66-3; $[CpFe(CS)((n\text{-}Bu)_2S)_2]CF_3SO_3$, 96307-68-5; $[CpFe(CO)(CS)(PEt_3)]I$, 96307-69-6; $[CpFe(CO)_2(PEt_3)]I$, 41611-01-2; $CpFe(CO)(PPh_3)I$, 12099-18-2; CpFe(CS)(MeCN)I, 96307-70-9; $CpFe(CO)(AsPh_3)I$, 31781-34-7; $CpFe(CO)[P(OMe)_3]I$, 31781-71-2; $CpFe(CO)[P(OPh)_3]I$, 31988-05-3; $[Fe(bpy)_3](PF_6)_2$, 70811-29-9; $\{[CpFe(CO)(CS)]_2Br\}Br$, 96307-71-0; $\{[CpFe(CO)(CS)]_2Cl\}Cl$, 96307-72-1; $[CpFe(CO)_2(CS)]^+$, 32626-61-2; $[CpFe(CO)(CS)(PPh_3)]PF_6$, 61113-61-9; $[Fe(phen)_3](PF_6)_2$, 17112-07-1; $CpFe(CO)(PEt_3)I$, 33154-70-0; $CpFe(CO)(SbPh_3)I$, 31975-95-8; $CpFe(CO)_2(CS_2Me)$, 59654-63-6; $SbPh_3$, 603-36-1; CS_2, 75-15-0.

---

(42) Treichel, P. M.; Shubkin, R. L.; Barnett, K. W.; Reichard, D. *Inorg. Chem.* **1966**, *5*, 1177.
(43) Haines, R. J.; du Preez, A. L.; Marais, I. L. *J. Organomet. Chem.* **1971**, *28*, 405.
(44) Brown, D. A.; Lyons, H. J.; Manning, A. R.; Rowley, J. M. *Inorg. Chim. Acta* **1969**, *3*, 346.
(45) Storhoff, B. N.; Lewis, C. H., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1.
(46) Kuhlmann, E. J.; Alexander, J. J. *Inorg. Chim. Acta* **1979**, *34*, 197.
(47) Fenster, A. E.; Butler, I. S. *Inorg. Chem.* **1974**, *13*, 915.
(48) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1977**, *139*, C9.
(49) Potenza, J. A.; Johnson, R.; Rudich, S.; Efraty, A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 1933.