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SYNTHESIS AND CLEAVAGE REACTIONS OF THIOCARBONYL-BRIDGED $Cp_2Fe_2(CO)_3CS$, AND PREPARATION OF THE CARBENE COMPLEXES $CpFe(CO)C(N_2C_2H_6)SnPh_3$ AND $[CpFe(CO)_2C(OMe)_2]PF_6$ *

MICHAEL H. QUICK and ROBERT J. ANGELICI *
Department of Chemistry, Iowa State University, Ames, Iowa 50011 (U.S.A.)

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Summary

The thiocarbonyl-bridged complex $Cp_2Fe_2(CO)_3CS$ is obtained by the reaction of $CpFe(CO)_2^-$ and $(PhO)_2CS$ in THF. Infrared and NMR spectra show that the compound exists in solution in interconverting *cis* and *trans* forms, but that the isomerization occurs more slowly than for the carbonyl analog $[CpFe(CO)_2]_2$. Most reagents which cleave $[CpFe(CO)_2]_2$, such as Br_2, $HgCl_2$, and O_2/HBF_4, do not give simple cleavage reactions with $Cp_2Fe_2(CO)_3CS$. Reductive cleavage of $Cp_2Fe_2(CO)_3CS$ with Na(Hg) gives the thiocarbonyl anion $CpFe(CO)(CS)^-$, which reacts with Ph_3SnCl to form $CpFe(CO)(CS)SnPh_3$. Methylamine reacts with $CpFe(CO)(CS)SnPh_3$ to give $CpFe(CO)(CN{-}Me)SnPh_3$, while ethylenediamine gives the carbene complex $CpFe(CO)C(N_2C_2H_6)SnPh_3$. The preparation of another new carbene complex, $[CpFe(CO)_2C(OMe)_2]PF_6$, is also described.

Introduction

Only a few metal thiocarbonyl complexes containing "thioketonic" bridging CS ligands are presently known [1—4]. Recently [4] we reported preliminary details of the preparation of one such compound, $Cp_2Fe_2(CO)_3CS$ ($Cp = \eta^5\text{-}C_5H_5$). In this paper we present a complete discussion of the synthesis and properties of the complex.

As part of our investigation of the reactivity of $Cp_2Fe_2(CO)_3CS$, it was of interest to determine if the thiocarbonyl-bridged complex would undergo the same cleavage reactions that are characteristic of its carbonyl analog, $[CpFe(CO)_2]_2$. This work also led to the isolation of two novel iron carbene complexes.

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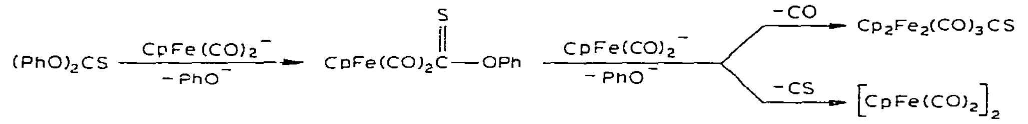
* Dedicated to Professor Ernst Otto Fischer on the occasion of his 60th birthday on November 10, 1978.

Results and discussion

Preparation and properties of $Cp_2Fe_2(CO)_3CS$

Reaction of $CpFe(CO)_2^-$ with $(PhO)_2CS$ (diphenyl thionocarbonate) in a 2/1 molar ratio in THF gives thiocarbonyl-bridged $Cp_2Fe_2(CO)_3CS$ in 40—45% yield. This reaction is the first example of the introduction of a CS ligand directly into a bridging position. An approximately equimolar amount of $[CpFe(CO)_2]_2$, which can be separated from the thiocarbonyl complex by column chromatography, is also formed. Other products observed are a small amount of $[CpFe(CO)_2]_2Hg$ [5] (produced during the generation of $CpFe(CO)_2^-$ from Na(Hg) and $[CpFe(CO)_2]_2$) and some brown, insoluble material.

Formation of the thiocarbonyl complex apparently occurs by stepwise replacement of phenoxide by the iron anion (eq. 1). Because the reaction is



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very fast, the proposed thioester intermediate $CpFe(CO)_2C(S)OPh$ cannot be detected in the reaction mixture. However, this compound can be obtained from NaOPh and $CpFe(CO)_2CS^+$ [6] in THF, and does react with $CpFe(CO)_2^-$ to give the same two products in yields comparable to those obtained with $(PhO)_2CS$. Evidently attack of the second iron anion can occur either at the thio ester carbon to give $Cp_2Fe_2(CO)_3CS$, phenoxide and CO, or at Fe to form $[CpFe(CO)_2]_2$, phenoxide and CS (the carbon monosulfide then decomposing to insoluble products [7,8]).

The thiocarbonyl complex can also be obtained from reactions of $CpFe(CO)_2^-$ with PhOC(S)Cl (5% yield), $(p\text{-}MeOC_6H_4O)_2CS$ (44%), $(p\text{-}ClC_6H_4O)_2CS$ (35%), and $CpFe(CO)_2CS_2Me$ [6] (25%). In contrast, other thiocarbonyl reagents, such as Cl_2CS, $(PhS)_2CS$, $(C_3H_3N_2)_2CS$ (thiocarbonyl diimidazole), $(p\text{-}NO_2C_6H_4O)_2CS$ and $CpFe(CO)_2CS^+$, give little or no $Cp_2Fe_2(CO)_3CS$ on reaction with the iron anion. Reduction of an equimolar mixture of $CpFe(CO)_3^+$ and $CpFe(CO)_2CS^+$ with NaH in THF also fails to produce usable amounts of $Cp_2Fe_2(CO)_3CS$. We have not detected thiocarbonyl complexes in reactions of other anions ($Re(CO)_5^-$, $W(CO)_5^{2-}$, $W_2(CO)_{10}^{2-}$, or $CpRu(CO)_2^-$) with $(PhO)_2CS$.

The monothiocarbonyl complex is an air-stable solid, and forms very dark red crystals that appear black to the unaided eye. The compound dissolves in all common organic solvents, its solubility being highest in CH_2Cl_2 and acetone, and lowest in aliphatic hydrocarbons. Solutions of $Cp_2Fe_2(CO)_3CS$ may be handled in air for brief periods, but prolonged exposure results in decomposition.

Spectra and structure of $Cp_2Fe_2(CO)_3CS$

Infrared spectra of $Cp_2Fe_2(CO)_3CS$ in the carbonyl region (Table 1) show two terminal $\nu(CO)$ bands and a single bridging carbonyl absorption. As can be seen from the data, the relative intensities of the terminal CO bands vary in a consistent manner with increasing solvent polarity. The $\nu(CS)$ absorption appears as a single, somewhat broad band at a position characteristic of "thioketonic" bridging CS ligands [1—3]; the absence of any bands in the 1400—1200 cm^{-1} region

TABLE 1

IR STRETCHING FREQUENCIES (cm^{-1}) FOR THE COMPLEXES

Compound	Solvent	$\nu(CO)^a$	$\nu(CS)^a$
$Cp_2Fe_2(CO)_3CS$	hexane	2012vs, 1972vs, 1813s	
	CS_2	2006vs, 1969s, 1809s	1130m
	CH_2Cl_2	2004vs, 1968m, 1805m	1124m
	CH_3CN	1999vs, 1962w, 1803m	1120m
CpFe(CO)(CS—Me)	CS_2	1960vs	
$CpFe(CO)(CS)SnPh_3$	CS_2	1978s	1289vs
$CpFe(CO)(CN—Me)SnPh_3$	hexane	2117m ^{b}, 1945s	
$CpFe(CO)C(N_2C_2H_6)SnPh_3$	CS_2	1893s	
$CpFe(CO)_2C(S)OPh$	hexane	2042s, 1996s	
$[CpFe(CO)_2C(OMe)_2]PF_6$	CH_2Cl_2	2068s, 2020s	

^{a} Abbreviations: s = strong, m = medium, w = weak, v = very. ^{b} $\nu(CN)$ absorption.

shows that there is no significant amount of any species with a terminal CS group. These data indicate that $Cp_2Fe_2(CO)_3CS$ is isostructural with its close analogs $[CpM(CO)_2]_2$ (M = Fe, Ru) [9,10], $[CpM(CO)(CS)]_2$ (M = Fe, Ru) [1,3] and $Cp_2Ru_2(CO)_3CS$ [3], and that the compound exists in solution as a mixture of *cis* and *trans* isomers, the *cis* form being favored in polar media. Interconversion of the isomers can occur by the same mechanism proposed by Adams and Cotton [11] for the isomerization of $[CpFe(CO)_2]_2$, as shown in eq. 2. However, this process is much slower for $Cp_2Fe_2(CO)_3CS$ than for its carbonyl analog [12,13], since ^1H NMR spectra of the thiocarbonyl complex in most solvents show two Cp resonances at ambient temperatures (Table 2). The lower-field peak becomes

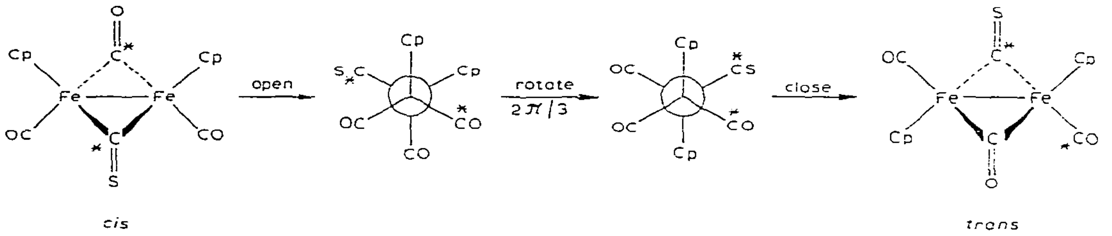

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TABLE 2

^1H NMR CHEMICAL SHIFTS (δ, ppm) FOR THE COMPLEXES

Compound	Solvent	δ(Cp)	$\delta(R)^a$
$Cp_2Fe_2(CO)_3CS$	C_6D_6	4.26, 4.33(2 : 1) ^{b}	
	CS_2	4.65, 4.73(4 : 7) ^{b}	
	$CDCl_3$	4.79, 4.85(2 : 5) ^{b}	
	acetone-d_6	5.01	
CpFe(CO)(CS—Me)	CS_2	4.57	2.53(Me)
$CpFe(CO)(CS)SnPh_3$	CS_2	4.78	7.20—7.70(m, Ph)
$CpFe(CO)(CN—Me)SnPh_3$	CS_2	4.48	2.70(Me), 7.10—7.60(m, Ph)
$CpFe(CO)C(N_2C_2H_6)SnPh_3$	CS_2	4.38	3.05(br, CH_2), 5.45 (br, NH), 7.10—7.60 (m, Ph)
$[CpFe(CO)_2C(OMe)_2]PF_6$	acetone-d_6	5.65	4.42(Me)

^{a} Abbreviations: m = multiplet, br = broad. ^{b} Relative peak areas in parentheses.

more intense as the solvent polarity increases, and thus may be assigned to the *cis* isomer. In the very polar solvent acetone, the spectrum consists of a single peak, indicating that only the *cis* form is present. The two Cp resonances observed for $Cp_2Fe_2(CO)_3CS$ in C_6D_6 solution coalesce at +53°C, which is about 100°C higher than the coalescence temperature found for $[CpFe(CO)_2]_2$ [12]. This retarding effect of the bridging CS ligand on the rate of *cis*—*trans* isomerization was also observed for $[CpM(CO)(CS)]_2$ (M = Fe, Ru) [1,3] and $Cp_2Ru_2(CO)_3CS$ [3].

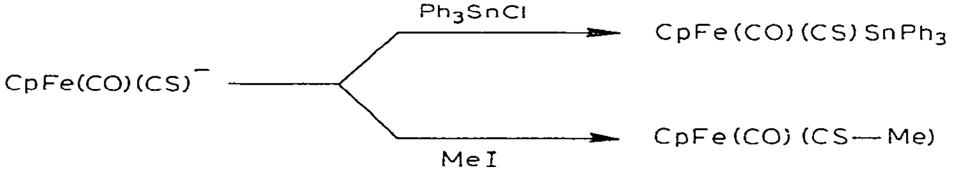
The ^{13}C NMR spectrum of $Cp_2Fe_2(CO)_3CS$ in $CDCl_3$ solution shows two Cp resonances (90.0 and 92.1 ppm downfield from TMS, ~5/2 ratio) and two terminal CO resonances (208.5 and 209.3 ppm, ~5/2 ratio), again indicating two isomers; the bridging CO and CS resonances appear as single peaks (267.7 and 378.1 ppm, respectively). In the more polar solvent acetone-d_6, all of the ligands give single resonances (92.1, 211.4, 268.1 and 380.8 ppm), as expected, since only the *cis* isomer is present. The thiocarbonyl carbon in $Cp_2Fe_2(CO)_3CS$ absorbs at much lower field than the bridging CS groups in $[CpFe(CO)(CS)]_2$ (287.6 ppm) [1], and in fact has the largest ^{13}C chemical shift yet observed for a CS ligand [14].

The preference of the CS ligand for a bridging position in $Cp_2Fe_2(CO)_3CS$ and similar thiocarbonyl complexes is understandable in view of the relative bond strengths in CO and CS. Formation of "ketonic" and "thioketonic" bridges requires some sacrifice of π-bonding in the terminal C≡X groups, as shown by the lower $\nu(CX)$ frequencies observed for bridging CX ligands. However, the C—X π-bonding is much weaker in CS [15], and the stabilization gained by formation of a second M—CS bond evidently more than compensates for any loss in C—S π-bonding. This may also account for the slower isomerization of $Cp_2Fe_2(CO)_3CS$, since the more stable CS-bridged structure would be expected to dissociate less readily to the non-bridged form required by this process.

Cleavage reactions of $Cp_2Fe_2(CO)_3CS$

The thiocarbonyl complex differs markedly from its carbonyl analog in its behavior toward oxidative cleavage. For example, $Cp_2Fe_2(CO)_3CS$ does not react with Me_2S_2 in refluxing benzene, while under the same conditions $[CpFe(CO)_2]_2$ gives the thiomethoxide-bridged compound $[CpFe(CO)(SMe)]_2$ [16]. The thiocarbonyl complex reacts rapidly with X_2 (X = Br, I) in CS_2, but, unlike $[CpFe(CO)_2]_2$ [17], gives only small amounts of the expected cleavage products, $CpFe(CO)_2X$ and $CpFe(CO)(CS)X$ [19]. The major product of these reactions is an insoluble black tar, which was not characterized but seems likely to consist in part of CS polymer [7,8]. Reaction of $Cp_2Fe_2(CO)_3CS$ with $HgCl_2$ in Et_2O or CH_2Cl_2 gives the S-adduct complex $Cp_2Fe_2(CO)_3CS \cdot HgCl_2$, rather than cleavage products as with $[CpFe(CO)_2]_2$ [18]. Reaction with O_2 and aqueous HBF_4 in acetone, which with $[CpFe(CO)_2]_2$ gives $CpFe(CO)_2(H_2O)^+$ [20], results in only partial cleavage of $Cp_2Fe_2(CO)_3CS$, the ultimate products being H_2S and another S-adduct complex, $[Cp_2Fe_2(CO)_3CS \cdot CpFe(CO)_2]BF_4$. The last two reactions illustrate the tendency of the bridging thiocarbonyl group in $Cp_2Fe_2(CO)_3CS$ to undergo electrophilic addition at the sulfur atom; a complete discussion of the S-adducts and the related S-alkyl derivatives [4] of $Cp_2Fe_2(CO)_3CS$ will be given in a separate paper [21].

Like its carbonyl analog [22], $Cp_2Fe_2(CO)_3CS$ is readily cleaved by Na(Hg) in THF, apparently giving a mixture of $CpFe(CO)_2^-$ and $CpFe(CO)(CS)^-$. Of the few metal thiocarbonyl anions known [23,24], $CpFe(CO)(CS)^-$ is the first to be produced by reduction of a thiocarbonyl complex. The anion reacts rapidly with Ph_3SnCl to form the metal—metal bonded derivative $CpFe(CO)(CS)SnPh_3$, (see below) and in this respect is similar to $CpFe(CO)_2^-$ [25]. However, reaction with MeI gives a low yield of an orange compound which appears to be the S-methyl thiocarbonyl complex CpFe(CO)(CS—Me) rather than the anticipated metal-alkylated product [22].



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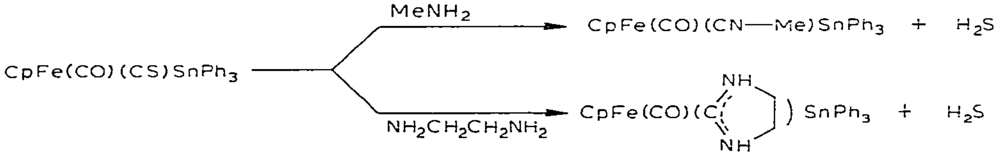
The compound is rather unstable, and as yet has not been obtained in sufficient quantity for crystallization and analysis. The proposed structure is based on the absence of a terminal ν(CS) band in the IR spectrum (Table 1) and the similarity of the Me chemical shift (Table 2) to that observed for $IW(CO)_4$-(CS—Me) [26]. Additionally, our current investigation of the thiocarbonyl anion $CpW(CO)_2CS^-$ [27] indicates that this species also undergoes alkylation at the thiocarbonyl sulfur rather than the metal. The reaction of $CpFe(CO)(CS)^-$ with MeI also gives a small amount of a second compound which has not yet been characterized. Further work on the alkylation reactions of $CpFe(CO)(CS)^-$ will be necessary to determine unequivocally the identitites of these products.

Reactions of $CpFe(CO)(CS)SnPh_3$ and $CpFe(CO)_2C(S)OPh$

Like the terminal thiocarbonyl groups of certain other thiocarbonyl complexes [28,29], the CS ligand in $CpFe(CO)(CS)SnPh_3$ reacts with primary aliphatic amines (eq. 4). Methylamine converts the CS group to a methyl isocyanide ligand, whereas ethylenediamine gives a cyclic diaminocarbene complex; spectroscopic data for these derivatives are given in Tables 1 and 2. These reactions are catalyzed to some extent by pyridine, as was observed for $W(CO)_5CS$ [29], but are still quite slow with amines other than $MeNH_2$. The compound is unreactive toward secondary amines. Presumably these results are attributable to steric hindrance by the rather bulky $SnPh_3$ group.



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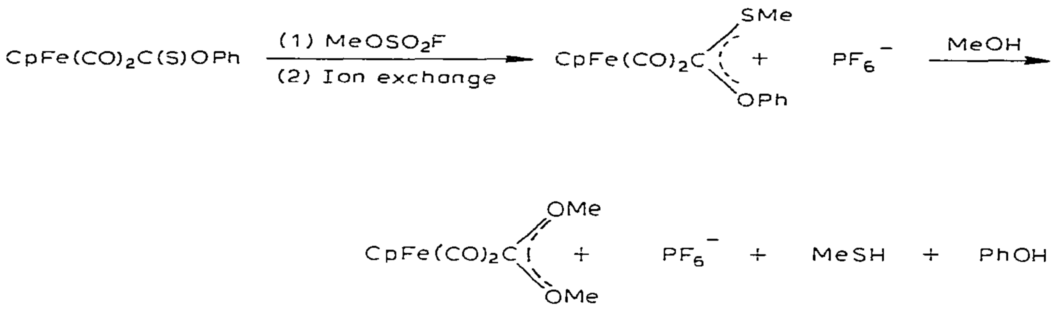
The thio ester complex $CpFe(CO)_2C(S)OPh$, mentioned above, is a somewhat unstable brown oil that could not be obtained in pure form. This compound was characterized indirectly by conversion to a cationic carbene complex, as shown in (eq. 5). Although the dimethoxycarbene product gave a somewhat high carbon analysis, even after several recrystallizations, the IR and ^1H NMR data (Tables 1



(5)

and 2), and the ^{13}C NMR spectrum in acetone-d_6, which shows a typical carbene resonance [30] at −248.6 ppm, establish it as $[CpFe(CO)_2C(OMe)_2]PF_6$. Carbene complexes of this type are presently under investigation in our research group, and will be discussed in a forthcoming publication [31].

Experimental

All reactions were carried out under prepurified nitrogen using standard inert atmosphere techniques. Tetrahydrofuran (THF) was distilled from $NaK_{2.8}$ [25] under N_2 immediately before use; other commercial reagent-grade solvents were stored over type 4A molecular sieves and purged with N_2. Ethylenediamine was fractionally distilled from KOH under N_2. Cyclopentadienyliron dicarbonyl dimer ($[CpFe(CO)_2]_2$) was recrystallized from 2/1 hexane/CH_2Cl_2 at −20°C. The thiocarbonyl cation $CpFe(CO)_2CS^+$ was conveniently obtained as the $CF_3SO_3^-$ salt by the reaction of $CpFe(CO)_2CS_2Me$ [6] with CF_3SO_3H in Et_2O; $[CpFe(CO)_3]CF_3SO_3$ was prepared similarly from $CpFe(CO)_2CO_2Me$ [32]. The thiocarbonyl reagents PhO—C(S)—Cl [33] and $(PhS)_2CS$ [34] were obtained by literature methods; aryl thionocarbonates were prepared as described below for $(PhO)_2CS$. Other reagents were commercial products of the highest purity available and were used as received.

Infrared spectra were recorded on a Perkin—Elmer 237B or 337 instrument, and were referenced on an expanded scale with CO (carbonyl region) or polystyrene (thiocarbonyl region). Proton NMR spectra were recorded on a Varian A-60 spectrometer, except for the variable-temperature spectrum of $Cp_2Fe_2(CO)_3CS$ which was obtained with a Varian HA-100. Carbon-13 spectra were run on a Bruker HX-90 FTNMR spectrometer; $Cr(acac)_3$ (~0.1 *M*) was added to the solutions to reduce data collection time [35]. Tetramethylsilane (TMS) was employed as the internal reference for all NMR spectra; chemical shifts are given in δ ppm downfield from TMS.

$(PhO)_2CS$. A solution of NaOPh was prepared by addition of NaH (3.84 g, 160 mmol, or 6.75 g of 57% NaH oil dispersion) in small portions to a solution of phenol (15.0 g, 160 mmol) in 175 ml of THF. Thiophosgene (5.75 ml, 8.65 g, 75.2 mmol) in 25 ml of THF was then added dropwise over a period of 1 h to the vigorously stirred (paddle-type stirrer) solution at room temperature. The mixture was then refluxed for an additional 1 h, and the solvent was removed under reduced pressure. The product was extracted from the residue with 300 ml of Et_2O and recrystallized from boiling hexane. A typical yield was 14.0 g

(60.9 mmol, 81%). This procedure was found to be much more satisfactory than the previously published method [36] for the preparation of $(PhO)_2CS$ and also $(p\text{-}XC_6H_4O)_2CS$ (X = Cl, MeO, NO_2).

$Cp_2Fe_2(CO)_3CS$. In a typical preparation, a solution of $Na[CpFe(CO)_2]$ was prepared by stirring $[CpFe(CO)_2]_2$ (11.5 g, 31.5 mmol) in 150 ml of THF in an amalgam reduction flask [22] of 250 ml capacity with 1% Na(Hg) (14 ml, ~80 mmol Na) for 45 min. (Longer stirring resulted in appreciable contamination by $[CpFe(CO)_2]_2Hg$ and a significantly lower yield.) After the excess amalgam was drained off, a solution of $(PhO)_2CS$ (6.90 g, 30.0 mmol) in 30 ml of THF was added to the stirred reaction mixture from an pressure-equalised dropping funnel over a period of 5—10 min. A mildly exothermic reaction with vigorous CO evolution occurred, giving a dark brown solution. After another 10 min, the solvent was evaporated under reduced pressure, and the residue was dried in vacuo for 15—20 min. The residue was stirred with 250 ml of CS_2 for 30 min, and the mixture was filtered through Celite; the gummy residue was washed with another 50 ml of CS_2. The volume of the CS_2 filtrate was reduced to about 120 ml, using a rotary evaporator and a room temperature water bath. (Any solid that precipitated at this point consisted almost entirely of $[CpFe(CO)_2]_2$ and was filtered off.) The solution was then chromatographed on a 25 mm × 1 m Florisil column by eluting first with 100 ml of CS_2, and thereafter with 5/1 CS_2/CH_2Cl_2. A broad black $Cp_2Fe_2(CO)_3CS$ band developed, preceded by much smaller bands of $[CpFe(CO)_2]_2Hg$ (light orange) and $(PhO)_2CS$ (pale yellow), and followed very closely by a broad, dark red $[CpFe(CO)_2]_2$ band. For reactions on this scale, resolution of the thiocarbonyl and dimer bands was usually incomplete, but only a small amount of $Cp_2Fe_2(CO)_3CS$ remained on the column when $[CpFe(CO)_2]_2$ began to elute, and product loss was minimal. The thiocarbonyl solution was filtered and then evaporated slowly under reduced pressure (rotary evaporator) to give shiny black crystals of $Cp_2Fe_2(CO)_3CS$. The product was transferred to a frit, washed three times with ice-cold hexane and dried in vacuo. Yield was 4.77 g (12.9 mmol, 43%). The analytical sample was recrystallized from hexane at —20°C. (Found: C, 45.32; H, 2.70, S, 9.19. $C_{14}H_{10}Fe_2O_3S$ calcd.: C, 45.45; H, 2.72; S, 8.66%.) Mass spectrum: *m/e* 370 (M^+), 342, 314, 286, 186 (Cp_2Fe^+). M.p. 159—161°C with some dec.

$CpFe(CO)(CS)SnPh_3$. A solution of $Cp_2Fe_2(CO)_3CS$ (1.11 g, 3.00 mmol) in 40 ml of THF was stirred vigorously with 1% Na(Hg) (2.0 ml, ~11 mmol Na) in a 100 ml amalgam reduction flask for 7—8 min to give a red-brown solution of $Na[CpFe(CO)_2]$ and $Na[CpFe(CO)(CS)]$. (Prolonged stirring resulted in the gradual destruction of the thiocarbonyl anion.) The excess amalgam, which had become a sand, was drained off, and Ph_3SnCl (2.31 g, 6.00 mmol) was added, causing an immediate color change to yellow-brown. After 10 min the solvent was removed under reduced pressure, and the residue was extracted with 30 ml of CS_2. Chromatography on a Florisil column (18 × 700 mm) with CS_2 gave a bright yellow band ($CpFe(CO)(CS)SnPh_3$) followed closely by a pale yellow band ($CpFe(CO)_2SnPh_3$ plus some unreacted Ph_3SnCl). Evaporation of the thiocarbonyl solution gave a sticky yellow-brown residue, which was crystallized from hexane at —20°C to give golden yellow needles of $CpFe(CO)(CS)SnPh_3$ (0.94 g, 1.74 mmol, 58%). (Found: C, 55.61; H, 3.85; S, 6.19. $C_{25}H_{20}FeOSSn$ calcd.: C, 55.29; H, 3.71; S, 5.90%.) M.p. 124—126°C.

$CpFe(CO)(CN{-}Me)SnPh_3$ and $CpFe(CO)C(N_2C_2H_6)SnPh_3$. A slow stream of $MeNH_2$ was bubbled through a solution of $CpFe(CO)(CS)SnPh_3$ (0.27 g, 0.50 mmol) in 50 ml of Et_2O for 5 min; a green color developed immediately. On stirring the mixture for 3 h, a yellow solution and a small amount of greenish precipitate were obtained. The mixture was evaporated in vacuo, the residue was extracted with 30 ml of 1/1 hexane/CS_2, and the solution was filtered and evaporated. Slow crystallization (2—3 weeks) of the product from hexane at —20°C gave golden needles of the methyl isocyanide complex, $CpFe(CO)(CN{-}Me)SnPh_3$ (0.20 g, 0.37 mmol, 74%). (Found: C, 57.98; H, 4.20. $C_{26}H_{23}FeNOSn$ calcd.: C, 57.83; H, 4.29%.) M.p. 90—91°C.

To obtain the cyclic diaminocarbene complex, a mixture of $CpFe(CO)(CS)SnPh_3$ (0.27 g, 0.50 mmol), ethylenediamine (0.20 ml, 0.18 g, 3.0 mmol) and pyridine (0.10 ml) in 40 ml of Et_2O was stirred for 12 h. Evaporation under reduced pressure, extraction with 30 ml of CS_2, and filtration gave a yellow solution of $CpFe(CO)C(N_2C_2H_6)SnPh_3$. The product was obtained as yellow-brown crystals from 9/1 hexane/Et_2O at —20°C (0.13 g, 0.23 mmol, 46%). (Found: C, 56.86; H, 4.62; N, 4.95. $C_{27}H_{26}FeN_2OSn$ calcd.: C, 56.99; H, 4.61; N, 4.92%.) M.p. 125—130°C (dec.).

$CpFe(CO)_2C(S)OPh$ and $[CpFe(CO)_2C(OMe)_2]PF_6$. To a solution of NaOPh, prepared from phenol (2.35 g, 25.0 mmol) and NaH (0.60 g, 25.0 mmol) in 75 ml of THF, $[CpFe(CO)_2CS]CF_3SO_3$ (9.25 g, 25.0 mmol) was added, and the mixture was stirred for 1 h. The dark brown solution was evaporated under reduced pressure, and the residue was extracted with 100 ml of CS_2. After filtration, the solvent was removed in vacuo to give the thio ester complex $CpFe(CO)_2C(S)OPh$ as a dark yellow-brown oil which could not be made to crystallize. Attempted purification by chromatography on Florisil led to decomposition; the compound also decomposed upon storage in air for 4—5 days.

The product from another such reaction (5.0 mmol) was dissolved in 30 ml of CH_2Cl_2. Methyl fluorosulfonate (0.50 ml, 0.70 g, 6.2 mmol) was added, and the mixture was stirred for 30 minutes. An IR spectrum at this point showed bands at 2059vs and 2019s, presumably from the cationic carbene $[CpFe(CO)_2C(SMe)(OPh)]FSO_3$. The solvent was removed in vacuo, leaving a yellow-brown oil that would not crystallize. Ion exchange in acetone (Amberlite IRA-400, column, PF_6^- form) gave the PF_6^- salt, which also was an oil. Addition of MeOH caused an immediate reaction, giving the solid dimethoxycarbene complex and MeSH. The product was recrystallized three times from MeOH at —20°C to give pale yellow crystals of $[CpFe(CO)_2C(OMe)_2]PF_6$ (0.87 g, 2.2 mmol, 44%). (Found: C, 31.78; H, 2.98. $C_{10}H_{11}F_6FeO_4P$ calcd.: C, 30.33; H, 2.80%.) M.p. 200—205°C (dec.).

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