The reaction of IX (0.030 g, 0.061 mmol) and $PhCH_2NH_2$ (14 μL, 0.13 mmol) afforded 0.015 g (56%) of VI[8] as yellow needles.

Reaction of IX with Piperidine. This reaction was carried out by using the method used to prepare IIb. From the reaction of IX (0.040 g, 0.082 mmol) and piperidine (16 μL, 0.16 mmol), 0.025 g (66%) of VII[8] was isolated as small yellow needles.

Reaction of $\{Cp(CO)_2Fe[C(SCH_3)SePh]\}PF_6$ (X) with Benzylamine. The method used to prepare IIb was also used in this reaction. Starting with X (0.024 g, 0.044 mmol) and $PhCH_2NH_2$ (10 μL, 0.092 mmol), 0.011 g (58%) of VI[8] was obtained as yellow needles.

Reaction of X with Piperidine. The reaction of X (0.028 g, 0.052 mmol) with piperidine (11 μL, 0.11 mmol), under the same conditions as used in the preparation of IIb, yielded 0.016 g (66%) of VII[8] as small yellow needles.

Reaction of $\{Cp(CO)_2Fe[\overline{CS(CH_2)_2S}]\}PF_6$ (XIa) with Benzylamine. This reaction was carried out by using the same procedure as used for IIb. The reaction of XIa (0.025 g, 0.059 mmol) with $PhCH_2NH_2$ (13 μL, 0.12 mmol) afforded 0.022 g (85%) of VI[8] as yellow needles.

Reaction of $\{Cp(CO)_2Fe[\overline{CS(CH_2)_3S}]\}PF_6$ (XIb) with Benzylamine. A solution of 15 mL of CH_2Cl_2 containing XIb (0.025 g, 0.057 mmol) and $PhCH_2NH_2$ (13 μL, 0.12 mmol) was stirred for 1 h. The resulting cloudy yellow solution was evaporated to dryness, and the residue was washed with Et_2O to remove an unidentified, neutral, yellow species. The remaining residue was then crystallized from CH_2Cl_2 with Et_2O at −20 °C to give 8.0 mg (32%) of VI[8] as yellow needles.

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Registry No. I, 76136-33-9; IIa, 76136-49-7; IIb, 76136-51-1; IIb (PF_6 salt), 76136-65-7; IIc, 76136-53-3; IId, 76136-55-5; IIe, 76136-57-7; IIf, 76136-59-9; IIIc, 76136-60-2; IV, 68868-37-1; V, 76136-30-6; VI, 69532-23-6; VII, 69532-34-9; VIII, 76136-62-4; IX, 76136-32-8; X, 76136-64-6; XIa, 76136-38-4; XIb, 76136-40-8.

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Substitution and S-Alkylation Reactions of Thiocarbonyl-Bridged $Cp_2Fe_2(CO)_3CS$

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In refluxing CH_3CN, $Cp_2Fe_2(CO)_3CS$ reacts with PEt_3, PMe_2Ph, $PMePh_2$, and $P(OMe)_3$ to give the monosubstituted derivatives $Cp_2Fe_2(CO)_2(PR_3)CS$, in which the CS group remains in the bridging position, as it does in all of the complexes described in this report. The reaction of MeNC with $Cp_2Fe_2(CO)_3CS$ in refluxing THF or cyclohexane gives $Cp_2Fe_2(CO)_2(MeNC)CS$ which exists predominantly as an isomer in which the MeNC is terminal. There is, however, spectroscopic evidence for a less abundant isomer in which the MeNC is bridging. The bissubstituted complex $Cp_2Fe_2(CO)(MeNC)_2CS$ may be obtained by refluxing $Cp_2Fe_2(CO)_3CS$ and MeNC in acetonitrile. This complex has been partially separated chromatographically into a major isomer, in which one MeNC is bridging and the other is terminal, and a minor bis-terminal MeNC isomer. The bridging thiocarbonyl sulfur atom of $CpFe_2(CO)_3CS$ may be alkylated at room temperature by reaction with alkyl iodides, benzyl bromide, allyl bromide, $MeOSO_2F$, and Et_3O^+ to give the $Cp_2Fe_2(CO)_3CSR^+$ complexes. The methyl derivative $Cp_2Fe_2(CO)_3CSMe^+$ reacts readily with ligands PEt_3, PMe_2Ph, $PMePh_2$, $P(OMe)_3$, and MeNC to give the CO-substituted products $Cp_2Fe_2(CO)_2(L)CSMe^+$. Both alkylation and substitution occur when $Cp_2Fe_2(CO)_3CS$ is refluxed in acetonitrile with MeI and NaI to give $Cp_2Fe_2(CO)_2(I)(CSMe)$. Only the CS-alkylated product $Cp_2Fe_2(CO)_2(MeNC)CSMe^+$ is obtained from the reaction of $Cp_2Fe_2(CO)_2(MeNC)CS$ with $MeOSO_2F$ or MeI. The bissubstituted complex $Cp_2Fe_2(CO)(MeNC)_2CS$ reacts with MeI to yield the CS-alkylated compound $Cp_2Fe_2(CO)(MeNC)_2CSMe^+$ in which both of the MeNC groups are terminal. With the stronger alkylating $MeOSO_2F$, this complex gives the dimethylated product $Cp_2Fe_2(CO)(MeNC)(Me_2NC)CSMe^{2+}$, in which both alkylated groups are bridging. All of the complexes are characterized by their IR and ^1H and ^{13}C NMR spectra, which give evidence of isomers in which the Cp rings are cis or trans to each other across the Fe–Fe bond. Mechanisms for the interconversion of several of the isomers are discussed.

Introduction

Recent research on metal thiocarbonyl complexes has led to the isolation of several compounds with bridging CS ligands.[1-5] One of these compounds is $Cp_2Fe_2(CO)_3CS$ (Cp = η^5-C_5H_5), which is a thiocarbonyl analogue of the well-known carbonyl complex $[CpFe(CO)_2]_2$. We have previously reported[5] the preparation of $Cp_2Fe_2(CO)_3CS$ and its reactions which result in cleavage of the Fe–Fe bond. In this paper, we discuss reactions leading to the alkylation of the bridging thiocarbonyl sulfur atom and reactions involving substitution of CO by other ligands.

Experimental Section

General Procedures. All reactions were conducted under prepurified N_2, with use of Schlenk ware (or similar apparatus) and standard inert-atmosphere techniques. Reactions were carried out at room temperature unless stated otherwise. Many compounds were conveniently isolated by a "slow evaporation" technique; in this method, the compound to be crystallized was dissolved in a suitable solvent, a higher boiling solvent in which the compound was less soluble was added, and the solution was evaporated to a small volume under reduced pressure (50–60 torr) at room temperature with a rotary evaporator. Exchange of PF_6^- for other anions was accomplished on a 10 × 25 cm column of Amberlite IRA-400 resin in acetone. Molar conductivities were determined in nitromethane solutions at 25 °C with use of an Industrial Instruments RC-16B2 conductivity bridge.

Infrared spectra were recorded on a Perkin-Elmer 337 or 237B instrument; NaCl cells with a 1-mm path length were used for most spectra. Band positions were determined with use of CO gas (CO region) and polystyrene (CS region) as references and are believed accurate to within 2 cm^{-1}. Proton NMR spectra were obtained with a Varian A-60 spectrometer; variable-temperature ^1H NMR spectra were run on a Varian HA-100 instrument. All ^{13}C NMR spectra were recorded on a Bruker HX-90 FT-NMR spectrometer; $Cr(acac)_3$ was added to the samples to reduce data collection time.[6] Tetramethylsilane was used as the internal reference for all NMR spectra.

Elemental analyses were performed by Galbraith Laboratories; analytical data are given below for representative compounds.

Solvents and Reagents. Tetrahydrofuran (THF) was distilled from $NaK_{2.8}$ under N_2 immediately before use. Nitromethane for conductivity measurements was dried over P_4O_{10}, fractionally distilled twice under N_2, and stored over type 4A molecular sieves under N_2.

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All other solvents were commercial reagent grade products and were stored over 4A sieves and purged with N_2 before use.

Commercially obtained phosphines and phosphites were fractionally distilled or, where appropriate, recrystallized. Methyl isocyanide (MeNC)[7] and phenyl isocyanide (PhNC)[8] were prepared by literature methods, as were the carbonyl complexes $Et_4N[M(CO)_5I]$ (M = Cr, W)[9] and $[CpFe(CO)_2(THF)]BF_4$.[10] The thiocarbonyl complex $Cp_2Fe_2(CO)_3CS$ was prepared as previously described.[5] All other reagents were commercial products of the highest purity available and were used as received.

$Cp_2Fe_2(CO)_2(L)CS$ (L = PEt_3, PMe_2Ph, $PMePh_2$, $P(OMe)_3$). A solution of $Cp_2Fe_2(CO)_3CS$ (0.20 g, 0.54 mmol) and PEt_3 (0.12 mL, 0.10 g, 0.82 mmol) in 30 mL of acetonitrile was refluxed for 30 min. The solvent was evaporated under reduced pressure, the residue was extracted with 40 mL of CS_2, and the solution was chromatographed on a 10 × 120 mm Florisil column; the product was eluted as a green band with 10:1 CS_2/Et_2O. The solution was evaporated under reduced pressure, the residue was dissolved in 20 mL of CH_2Cl_2, and the solution was filtered. Addition of 50 mL of hexane followed by slow evaporation gave black crystals of $Cp_2Fe_2(CO)_2(PEt_3)CS$ (0.22 g, 87%). An analytical sample was recrystallized from hexane at −20 °C. Anal. Calcd for $C_{19}H_{25}Fe_2O_2PS$: C, 38.74; H, 4.55; S, 5.17. Found: C, 38.80; H, 4.55; S, 5.03.

Reaction of $Cp_2Fe_2(CO)_3CS$ (0.20 g, 0.54 mmol) with PMe_2Ph (0.13 mL, 0.13 g, 0.91 mmol) in acetonitrile as above, followed by the same isolation procedure, gave black crystals of $Cp_2Fe_2(CO)_2(PMe_2Ph)CS$ (0.22 g, 83%). The sample for analysis was recrystallized from 1:1 hexane/Et_2O at −78 °C. Anal. Calcd for $C_{21}H_{21}Fe_2O_2PS$: C, 52.53; H, 4.41. Found: C, 52.49; H, 4.48.

The similar reaction of the thiocarbonyl complex with $PMePh_2$ (0.20 mL, 0.20 g, 1.0 mmol) required 8 h and gave dark green $Cp_2Fe_2(CO)_2(PMePh_2)CS$ (60% yield). Reaction of $P(OMe)_3$ (0.11 mL, 0.11 g, 0.93 mmol) with $Cp_2Fe_2(CO)_3CS$ under the same conditions for 1.5 h afforded brown $Cp_2Fe_2(CO)_2[P(OMe)_3]CS$ (56%). These latter two complexes were identified by their IR and NMR spectra (see below).

$Cp_2Fe_2(CO)_2(MeNC)CS$ and $Cp_2Fe_2(CO)(MeNC)_2CS$. A solution of $Cp_2Fe_2(CO)_3CS$ (0.20 g, 0.54 mmol) and MeNC (0.10 mL, 0.071 g, 1.7 mmol) in 30 mL of THF was refluxed for 1 h. The mixture was evaporated under reduced pressure, the residue was extracted with 30 mL of CS_2, and the solution was filtered. Addition of 60 mL of hexane followed by slow evaporation gave the red-brown monosubstituted complex $Cp_2Fe_2(CO)_2(MeNC)CS$ (0.17 g, 83%). The sample for analysis was recrystallized from 5:1 hexane/Et_2O at −78 °C. Anal. Calcd for $C_{15}H_{13}Fe_2NO_2S$: C, 47.04; H, 3.42; N, 3.66. Found: C, 46.95; H, 3.53; N, 3.66.

To obtain the disubstituted compound, a mixture of $Cp_2Fe_2(CO)_3CS$ (0.37 g, 1.0 mmol) and MeNC (0.20 mL, 0.14 g, 3.4 mmol) in 30 mL of acetonitrile was refluxed for 20 min. The solvent was removed under reduced pressure, the residue was extracted with 40 mL of CS_2, and the mixture was filtered; the solution was then stirred for 24 h at room temperature. After filtration, 80 mL of hexane was added, and slow evaporation gave purple crystals of the bridge-terminal isomer (see Results and Discussion) of $Cp_2Fe_2(CO)(MeNC)_2CS$ (0.31 g, 78%). An analytical sample was recrystallized from 4:1 hexane/Et_2O at −78 °C. Anal. Calcd for $C_{16}H_{16}Fe_2N_2OS$: C, 48.52; H, 4.07; N, 7.07. Found: C, 48.59; H, 3.95; N, 6.95.

In several cases the CS_2 extract of the above reaction mixture was immediately chromatographed on a 10 × 120 mm column of Grade III Woelm alumina. Carbon disulfide usually eluted a green band, which proved to be a small amount of the monosubstituted complex $Cp_2Fe_2(CO)_2(MeNC)CS$. Elution with 20:1 CS_2/Et_2O gave a second green band containing the major product, the bridge-terminal isomer of $Cp_2Fe_2(CO)(MeNC)_2CS$. Continued elution brought down a third green band, which yielded a small amount (~10% yield) of a brown-purple product consisting mainly of the bis-terminal isomer of $Cp_2Fe_2(CO)(MeNC)_2CS$ (see Results and Discussion). When this product was stirred in CS_2 at room temperature, it was converted almost entirely into the bridge-terminal isomer within 24 h. This isomerization prevented isolation of the bis-terminal isomer in pure form.

$[Cp_2Fe_2(CO)_3CS\text{-}Me]FSO_3$. Methyl fluorosulfonate (0.20 mL, 0.36 g, 2.5 mmol) was added to a solution of $Cp_2Fe_2(CO)_3CS$ (0.40 g, 1.1 mmol) in 20 mL of CH_2Cl_2, and the mixture was stirred for 1 h; the majority of the product precipitated during this period. Addition of 30 mL of Et_2O followed by filtration gave dark red microcrystals of $[Cp_2Fe_2(CO)_3CSMe]FSO_3$ (0.51 g, 96%). The analytical sample was recrystallized from 1:1 acetone/hexane at −20 °C. Molar conductivity in nitromethane Λ = 82.1 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{15}H_{13}FFe_2O_6S_2$: C, 37.22; H, 2.71; S, 13.25. Found: C, 37.10; H, 2.73; S, 13.42.

$[Cp_2Fe_2(CO)_3CSEt]BF_4$. A solution of the thiocarbonyl complex (0.20 g, 0.54 mmol) and $[Et_3O]BF_4$ (0.10 g, 0.53 mmol) in 15 mL of CH_2Cl_2 was stirred for 30 min. The product was precipitated by addition of 40 mL of Et_2O; recrystallization from 1:1 CH_2Cl_2/hexane at −20 °C gave red-brown crystals of the *S*-ethyl thiocarbonyl compound (0.21 g, 81%). Molar conductivity in nitromethane Λ = 89.4 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{16}H_{15}BF_4Fe_2O_3S$: C, 39.55; H, 3.11. Found: C, 39.30; H, 3.05.

$[Cp_2Fe_2(CO)_3CSR]PF_6$ (R = Me, Et, Pr, Bu, All, Bz). A mixture of $Cp_2Fe_2(CO)_3CS$ (0.20 g, 0.54 mmol) and MeI (3 mL) was stirred for 12 h. Addition of 40 mL of Et_2O and filtration gave $[Cp_2Fe_2(CO)_3CSMe]I$ as a red powder. The product was dissolved in 150 mL of acetone, and the solution was passed slowly through a PF_6^- ion-exchange column. The eluate was evaporated to about 50–60 mL under reduced pressure, 30 mL of heptane was added, and the solution was evaporated slowly to give small dark red crystals of $[Cp_2Fe_2(CO)_3CSMe]PF_6$ (0.27 g, 94%).

Other *S*-alkyl complexes were obtained in the same fashion by stirring $Cp_2Fe_2(CO)_3CS$ for 24 h with EtI (90% yield), *n*-PrI (90%), and *n*-BuI (85%). The greater solubility of the Pr and Bu derivatives permitted use of only 30–40 mL of acetone in the ion-exchange step.

For the *S*-benzyl derivative to be obtained, the thiocarbonyl complex (0.37 g, 1.0 mmol) was stirred with BzBr (3 mL) for 8 h. Addition of 40 mL of Et_2O and filtration gave the Br^- salt, which was washed 10 times with 20 mL of Et_2O to remove excess BzBr. The product was dissolved in 30 mL of acetone; anion exchange and crystallization by slow evaporation as above gave dark red $[Cp_2Fe_2(CO)_3CSBz]PF_6$ (0.54 g, 89%). An analytical sample was obtained from 3:1 Et_2O/acetone at −20 °C. Molar conductivity in nitromethane Λ = 82.4 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{21}H_{17}F_6Fe_2PO_3S$: C, 41.62; H, 2.83; S, 5.29. Found: C, 41.83; H, 2.80; S, 5.01.

Reaction of $Cp_2Fe_2(CO)_3CS$ (0.20 g, 0.54 mmol) with allyl bromide, AllBr (3 mL), in the above manner, followed by ion-exchange and crystallization from CH_2Cl_2/hexane by slow evaporation, gave red-gold $[Cp_2Fe_2(CO)_3CSAll]PF_6$ (0.26 g, 86%), which was characterized by its IR and NMR spectra.

$[Cp_2Fe_2(CO)_2(L)CSMe]PF_6$ (L = PEt_3, PMe_2Ph, $PMePh_2$, $P(OMe)_3$, MeNC). Triethyl phosphine (0.11 mL, 0.88 g, 0.75 mmol) was added to a stirred solution of $[Cp_2Fe_2(CO)_3CSMe]FSO_3$ (0.24 g, 0.50 mmol) in 15 mL of acetonitrile. Evolution of CO commenced immediately, and the solution became yellow-green within a few minutes. After 30 min the solvent was removed under reduced pressure at 50 °C; the residue was then dried in vacuo at this temperature for 1 h. The residue was extracted with 20 mL of acetone, and, after filtration, the solution was eluted through a PF_6^- ion-exchange column. The eluate was evaporated under reduced pressure, the residue was dissolved in 30 mL of CH_2Cl_2, and 20 mL of hexane was added. Slow evaporation gave brown crystals of $[Cp_2Fe_2(CO)_2(PEt_3)CSMe]PF_6$ (0.29 g, 95%). A sample for analysis was recrystallized from 1:1 acetone/Et_2O at −20 °C. Molar conductivity in nitromethane Λ = 84.6 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{20}H_{28}F_6Fe_2O_2P_2S$: C, 38.74; H, 4.55; S, 5.17. Found: C, 38.80; H, 4.55; S, 5.03.

Reaction of $[Cp_2Fe_2(CO)_3CSMe]FSO_3$ (0.24 g, 0.50 mmol) with PMe_2Ph (0.10 mL, 0.097 g, 0.70 mmol) in the above manner gave $[Cp_2Fe_2(CO)_2(PMe_2Ph)CSMe]PF_6$ as brown needles (0.30 g, 95%). Anal. Calcd for $C_{22}H_{24}F_6Fe_2O_2P_2S$: C, 41.28; H, 3.78. Found: C, 41.59; H, 3.94.

The analogous MeNC complex was prepared by refluxing a solution of the *S*-methyl thiocarbonyl compound (0.24 g, 0.50 mmol) in 15 mL of acetonitrile with MeNC (0.10 mL, 0.071 g, 1.8 mmol) for 35 min. Workup as for the PEt_3 derivative gave red crystals of $[Cp_2Fe_2(CO)_2(MeNC)CSMe]PF_6$ (0.25 g, 93%). Anal. Calcd for $C_{16}H_{16}F_6Fe_2NO_2PS$: C, 35.39; H, 2.97; N, 2.58. Found: C, 35.59; H, 3.06; N, 2.63. Heating was also required to obtain substitution

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products with $PMePh_2$ (4-h reflux, 63% yield) and $P(OMe)_3$ (1.5 h, 56%).

All of the preceding derivatives also could be prepared by reaction of the $Cp_2Fe_2(CO)_2(L)CS$ complexes with $MeOSO_2F$ or MeI in CH_2Cl_2, followed by ion exchange and crystallization as above.

$[Cp_2Fe_2(CO)_2(PEt_3)CSBz]PF_6$. A mixture of $Cp_2Fe_2(CO)_2(PEt_3)CS$ (0.20 g, 0.43 mmol) and BzBr (3 mL) was stirred for 3 h. The product was precipitated with 40 mL of Et_2O, filtered off, and washed repeatedly with Et_2O. Anion exchange in acetone and slow evaporation of a CH_2Cl_2/hexane solution gave black crystals of the complex (0.26 g, 87%).

S-Benzyl derivatives of the $Cp_2Fe_2(CO)_2(L)CS$ compounds were necessarily prepared by the above method, owing to the lability of the Bz group (see Results and Discussion).

$Cp_2Fe_2(CO)_2(I)(CS\text{-}R)$ (R = Me, Et). A mixture of $Cp_2Fe_2(CO)_3CS$ (0.40 g, 1.1 mmol), MeI (0.12 mL, 0.28 g, 2.0 mmol) and NaI (0.60 g, 4.0 mmol) in 20 mL of acetonitrile was refluxed for 6 h. The solvent was removed under reduced pressure, the residue was extracted with 40 mL of CH_2Cl_2, and the mixture was filtered. Addition of 30 mL of hexane followed by slow evaporation gave dark brown crystals of $Cp_2Fe_2(CO)_2(I)(CSMe)$ (0.48 g, 91%). A sample for analysis was obtained from 1:1 acetone/hexane at −20 °C. Anal. Calcd for $C_{14}H_{13}Fe_2IO_2S$: C, 34.75; H, 2.71; S, 6.63. Found: C, 34.43; H, 2.84; S, 5.90.

Substitution of EtI for MeI in the above reaction gave dark brown $Cp_2Fe_2(CO)_2(I)(CSEt)$ (0.48 g, 88%). This reaction required 18 h.

$[Cp_2Fe_2(CO)(MeNC)(Me_2NC)CSMe](PF_6)_2$ and $[Cp_2Fe_2(CO)(MeNC)_2CSMe]PF_6$. To a solution of the bridge-terminal isomer of $Cp_2Fe_2(CO)(MeNC)_2CS$ (0.10 g, 0.25 mmol) in 30 mL of CH_2Cl_2 was added $MeOSO_2F$ (0.10 mL, 0.14 g, 1.3 mmol), and the reaction mixture was stirred for 9 h. The greenish precipitate that formed was filtered off, washed five times with 20 mL of CH_2Cl_2, dissolved in 20 mL of acetone, and eluted through a PF_6^- ion-exchange column. Addition of heptane followed by slow evaporation gave a brown solid, which was filtered off and dried in vacuo. The crude product was extracted four times with 10 mL of water, and the resulting solution was cooled at 0–5 °C for 2 days to give small brown needles of the N,S-dimethylated complex $[Cp_2Fe_2(CO)(MeNC)(Me_2NC)CSMe](PF_6)_2$. The product was filtered off, washed once with 5 mL of cold (10 °C) water, and dried in vacuo (0.10 g, 56%). Molar conductivity in nitromethane $\Lambda = 177\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Calcd for $C_{18}H_{22}F_{12}Fe_2N_2OP_2S$: C, 30.19; H, 3.10. Found: C, 30.21; H, 3.13.

Reaction of the bis isocyanide complex (0.10 g, 0.25 mmol) with MeI (0.10 mL, 0.23 g, 1.6 mmol) at room temperature in 15 mL of CH_2Cl_2 for 30 min gave the *S*-methyl derivative of the bis-terminal isomer. The product was precipitated with 50 mL of Et_2O and filtered off. Anion exchange in acetone followed by crystallization from 1:1 acetone/Et_2O at −78 °C gave brown crystals of $[Cp_2Fe_2(CO)(MeNC)_2CSMe]PF_6$ (0.090 g, 65%). Anal. Calcd for $C_{17}H_{19}F_6Fe_2N_2OPS$: C, 36.72; H, 3.44; N, 5.04. Found: C, 36.77; H, 3.20; N, 4.98.

Results and Discussion

Substitution Reactions of $Cp_2Fe_2(CO)_3CS$. This thiocarbonyl complex undergoes thermal carbonyl substitution by PEt_3, PMe_2Ph, $PMePh_2$, and $P(OMe)_3$ to give the monosubstituted derivatives $Cp_2Fe_2(CO)_2(PR_3)CS$, which are dark green or brown, slightly air-sensitive crystalline solids (eq 1).

$$Cp_2Fe_2(CO)_3CS + PR_3 \xrightarrow[\text{reflux}]{CH_3CN} Cp_2Fe_2(CO)_2(PR_3)CS + CO \quad (1)$$

The compounds dissolve to some extent in all common organic solvents, forming deep green solutions, and in solution are somewhat more susceptible to air oxidation and thermal decomposition than is the parent thiocarbonyl complex.

Substitution proceeds rapidly and cleanly in refluxing acetonitrile. However, no reaction occurs in refluxing hexane, benzene, acetone, dimethoxyethane, or THF. In decalin at 115 °C, the reaction is slow and accompanied by decomposition to ferrocene and unidentified insoluble products. In contrast to the slow reactivity of $Cp_2Fe_2(CO)_3CS$ in these latter solvents, $Cp_2Fe_2(CO)_4$ reacts readily in refluxing benzene with phosphines,[11] phosphites,[11] and amines[12] to give the corresponding $Cp_2Fe_2(CO)_3L$ complexes. The thiocarbonyl complex, unlike $Cp_2Fe_2(CO)_4$,[13] also fails to undergo ^{13}CO exchange at room temperature in acetonitrile.

Rate studies of the reaction of $Cp_2Fe_2(CO)_3CS$ with PMe_2Ph in *n*-butyronitrile solvent at 85 °C show a 20–30 min induction period followed by a very fast reaction to yield the product. The qualitative order of reactivity in CH_3CN is $PEt_3 \approx PMe_2Ph > P(OMe)_3 \gg PMePh_2$. Extended reflux results in decomposition rather than further substitution. Other phosphines and phosphites either do not react (PPh_3, $P(OPh)_3$, 1,2-bis(diphenylphosphino)ethane) or give thermally unstable products (PBu_3). The thiocarbonyl complex is also unreactive toward amines (*n*-$PrNH_2$, Et_2NH, Et_3N, or pyridine) in refluxing acetonitrile. In view of the known reaction[5,14-16] of primary amines with terminal thiocarbonyl ligands in certain thiocarbonyl complexes to yield CNR ligands, as well as the reaction of organic thioketones with RNH_2 to give imines,[17,18] it seemed possible that the bridging CS group in $Cp_2Fe_2(CO)_3CS$ might be converted into a *n*-PrNC ligand in the reaction with *n*-$PrNH_2$; however, this did not occur.

Infrared spectra (Table I) of the PEt_3 and PMe_2Ph complexes in the carbonyl region (hexane solution) display a strong terminal ν(CO) band and a strong bridging ν(CO) absorption. Except for minor shifts in the positions of the two bands, spectra of these complexes were the same in CS_2 and CH_2Cl_2 solvents. In the CS region, the position of the ν(CS) band (CS_2 solution) indicates that the thiocarbonyl ligand remains bridging in these substituted derivatives; this CS absorption is somewhat more intense relative to the ν(CO) bands than that of $Cp_2Fe_2(CO)_3CS$. All of the bands occur at lower frequencies than in the parent compound, as would be expected after replacement of CO by a better donor ligand.

The additional ν(CO) bands in the spectra of the $PMePh_2$ and $P(OMe)_3$ derivatives in hexane solution, and a shoulder on the ν(CS) band in all of the spectra, suggest the presence of cis and trans isomers of $Cp_2Fe_2(CO)_2(PR_3)CS$ in solution, with one isomer predominant in most cases. (In this and in all subsequent discussion, the designations cis and trans refer to the positions of the cyclopentadienyl groups in relation to the Fe–Fe bond.) However, in the more polar CH_2Cl_2 solvent, spectra of the $PMePh_2$ (1953 vs, 1745 s) and $P(OMe)_3$ (1959 vs, 1755 s) complexes show only two ν(CO) absorptions, suggesting that one isomer predominates; their spectra in $CHCl_3$ are very similar. Previously it had been concluded that the cis isomer of $Cp_2Fe_2(CO)_3(CS)$ is favored in polar solvents.[5] It thus appears likely that the cis isomer of the $Cp_2Fe_2(CO)_2(L)CS$ complexes is the major form in CH_2Cl_2 and $CHCl_3$.

Proton NMR spectra of the complexes in $CDCl_3$ (Table II) all show two sharp cyclopentadienyl resonances (one split by ^{31}P coupling). Since the infrared spectra of these complexes in chloroform are all very similar and show only single bands for the bridging and terminal carbonyls, it appears that only one isomer is present in this solvent. (Satisfactory NMR spectra in less polar solvents were not obtained owing to the much lower solubility of the complexes in such media.) The ^{13}C NMR data (Table III) for $Cp_2Fe_2(CO)_2(PEt_3)CS$ in $CDCl_3$ also indicate only one isomer and show that substitution

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Table I. Infrared Data for the Complexes

compd[a]	ν(CO),[b] cm⁻¹	ν(CS),[c] cm⁻¹
$Cp_2Fe_2(CO)_3CS$	2012 vs, 1972 vs, 1813 s	1130 m
$Cp_2Fe_2(CO)_3CS$[d]	1999 vs, 1962 w, 1803 m	1120 m
$Cp_2Fe_2(CO)_2(L)CS$		
L = PEt_3	1945 vs, 1760 s	1102 m[e]
L = PMe_2Ph	1950 vs, 1758 s	1104 m[e]
L = $PMePh_2$	1970 vs, 1951 s, 1764 m (sh), 1757 s	1100 m[e]
L = $P(OMe)_3$	1972 vs, 1952 m, 1783 w (sh), 1765 s	1108 m[e]
L = MeNC	2150 m-s,[f] 2005 m, 1973 m (sh), 1965 vs, 1794 s, 1743 w[f]	1119 s, 1113 s
$Cp_2Fe_2(CO)(MeNC)_2CS$[g]	2143 s,[f] 1960 s, 1951 vs, 1723 s,[f] 1717 m (sh)[f]	1119 s, 1111 s
$Cp_2Fe_2(CO)(MeNC)_2CS$[h]	2154 vs,[f] 1751 s	1101 m-s
$[Cp_2Fe_2(CO)_3CSMe]FSO_3$	2038 s, 2001 w, 1854 m	
$[Cp_2Fe_2(CO)_3CSEt]BF_4$	2037 s, 2007 w, 1854 m	
$[Cp_2Fe_2(CO)_3CSR]PF_6$		
R = Me	2040 s, 2012 w, 1856 m	1028 w
R = Et	2040 s, 2009 w, 1855 m	1024 w
R = *n*-Pr	2039 s, 2008 w, 1855 m	1022 w
R = *n*-Bu	2039 s, 2009 w, 1855 m	1024 w
R = All	2040 s, 2010 w, 1856 m	1017 w
R = Bz	2039 s, 2011 w, 1857 m	1023 w
$[Cp_2Fe_2(CO)_2(L)CSMe]PF_6$		
L = PEt_3	1985 vs, 1818 s	1004 m
L = PMe_2Ph	1991 vs, 1816 s	1008 m
L = $PMePh_2$	2003 vs, 1811 s	1008 m
L = $P(OMe)_3$	2004 vs, 1812 s	
L = MeNC	2196 s,[f] 2006 vs, 1834 s	1019 m
$[Cp_2Fe_2(CO)(MeNC)_2CSMe]PF_6$	2190 vs,[f] 1815 s	1014 m
$[Cp_2Fe_2(CO)(MeNC)(Me_2NC)CSMe](PF_6)_2$[i]	2223 s,[f] 2030 vs, 1620 s[f]	1043 m
$[Cp_2Fe_2(CO)_2(PEt_3)CSBz]PF_6$	1979 vs, 1809 s	998 m
$Cp_2Fe_2(CO)_2(I)CSR$[j]		
R = Me	1992 vs, 1807 s	1011 m
R = Et	1991 vs, 1807 s	1009 m

[a] Abbreviations: Me = methyl, Et = ethyl, Pr = *n*-propyl, Bu = *n*-butyl, All = allyl, Bz = benzyl, Ph = phenyl; s = strong, m = medium, w = weak, sh = shoulder, v = very. [b] In hexane solution for neutral compounds; in CH_2Cl_2 solution for ionic compounds (except where noted). [c] In CS_2 solution for neutral compounds; in CH_2Cl_2 solution for ionic compounds (except where noted). [d] In acetonitrile. [e] w-m shoulder at ~1120 cm⁻¹. [f] ν(CN) frequency. [g] Bridge-terminal isomer. [h] Bis-terminal isomer; in CH_2Cl_2. [i] In KBr wafer. [j] In CH_2Cl_2.

Table II. ^1H NMR Data for the Complexes[a]

compd[b]	δ(Cp)[c]	δ(R)[c]
$Cp_2Fe_2(CO)_3CS$	4.79, 4.85 (2:5)	
$Cp_2Fe_2(CO)_3CS$[d]	5.01	
$Cp_2Fe_2(CO)_2(L)CS$		
L = PEt_3	4.53 (d),[e] 4.80	0.70-1.60 (m, Et)
L = PMe_2Ph	4.25 (d),[e] 4.79	0.91 (d, Me),[f] 1.45 (d, Me),[f] 7.30-7.90 (m, Ph)
L = $PMePh_2$	4.24 (d),[e] 4.61	1.70 (d, Me),[f] 7.20-7.60 (m, Ph)
L = $P(OMe)_3$	4.59 (d),[g] 4.74	3.58 (d, Me)[h]
L = MeNC	4.70, 4.82	3.03 (Me)
$Cp_2Fe_2(CO)(MeNC)_2CS$[i]	4.67, 4.83	2.96 (Me),[j] 3.72 (Me)[k]
$Cp_2Fe_2(CO)(MeNC)_2CS$[l]	4.60	3.05 (Me)[j]
$[Cp_2Fe_2(CO)_3CSR]PF_6$		
R = Me	5.65 (br)	3.77 (Me)
R = Et	5.58	1.69 (t, CH_3), 4.30 (br, q, CH_2)
R = *n*-Pr	5.75 (br)	1.20 (t, CH_3), 1.90-2.40 (m, CH_2), 4.35 (br, q, CH_2)
R = *n*-Bu	5.73 (br)	1.05 (br, t, CH_3), 1.34-2.10 (br, m, CH_2CH_2), 4.36 (br, q, CH_2)
R = All	5.62	4.93 (br, t, CH_2), 5.30-6.50 (m, $CH{=}CH_2$)
R = Bz	5.60, 5.72	5.43 (br, CH_2), 7.48 (m, Ph)
$[Cp_2Fe_2(CO)_2(L)CSMe]PF_6$		
L = PEt_3	5.23 (d),[e] 5.43	0.80-1.80 (m, Et), 3.60 (Me)
L = PMe_2Ph	5.12 (d),[e] 5.46	1.43 (d, Me),[m] 1.68 (d, Me),[m] 3.58 (Me), 7.51 (m, Ph)
L = $PMePh_2$	5.14 (d),[e] 5.38	2.14 (d, Me),[m] 3.53 (Me), 7.10-7.50 (br, m, Ph)
L = $P(OMe)_3$	5.27, 5.39	3.67 (d, Me and CSMe)
L = MeNC	5.33, 5.42	3.22 (Me),[j] 3.67 (Me)
$[Cp_2Fe_2(CO)_2(PEt_3)CSBz]PF_6$[n]	5.06 (d),[g] 5.22	0.60-1.60 (m, Et), 7.60 (m, Ph)
$[Cp_2Fe_2(CO)(MeNC)(Me_2NC)CSMe](PF_6)_2$	5.83, 5.92	3.28 (Me),[j] 3.77 (Me), 4.28 (Me),[o] 4.34 (Me)[o]
$[Cp_2Fe_2(CO)(MeNC)_2CSMe]PF_6$	5.07	3.22 (Me),[j] 3.57 (Me)
$Cp_2Fe_2(CO)_2(I)CSEt$	4.82, 4.87	1.67 (t, CH_3), 4.30 (br, CH_2)

[a] $CDCl_3$ solution for neutral compounds, acetone-d_6 solution for ionic compounds (except where noted). [b] See Table I, note *a*. [c] Abbreviations: d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. [d] In acetone-d_6. [e] J_{PFeCH} = 1.8 Hz. [f] J_{PCH} = 9.0 Hz. [g] J_{PFeCH} = 1.0 Hz. [h] J_{POCH} = 11 Hz. [i] Bridge-terminal isomer. [j] Terminal isocyanide. [k] Bridging isocyanide. [l] Bis-terminal isomer. [m] J_{PCH} = 10 Hz. [n] CD_3CN solution. [o] Bridging Me_2NC^+ ligand.

of a donor ligand for CO in $Cp_2Fe_2(CO)_3CS$ results in a downfield shift of the bridging thiocarbonyl carbon resonance; ^{31}P coupling is observed to the CS and CO bridging ligands.

Infrared spectra of the complexes in various solvents do not change with time, which suggests that upon dissolution cis-trans isomerization is rapid. The isomerization of $[CpFe(CO)_2]_2$[19-23] and some of its substituted derivatives[13,24,25] has been studied in detail, and a reasonable mechanism for this process has been proposed by Adams and Cotton;[25] this mechanism also satisfactorily accounts for the cis-trans isomerization of $Cp_2Fe_2(CO)_3CS$.[5] Interconversion of *cis*- and *trans*-$Cp_2Fe_2(CO)_2(PR_3)CS$ may also occur by the Adams-Cotton mechanism, as shown in eq 2, provided that the CS and PR_3 ligands are on the same Fe atom in the nonbridged intermediate. The other possible intermediate would seem less favorable, since the best π-acceptor ligand (CS)[26] and the donor ligand would be on different Fe atoms; in any case this

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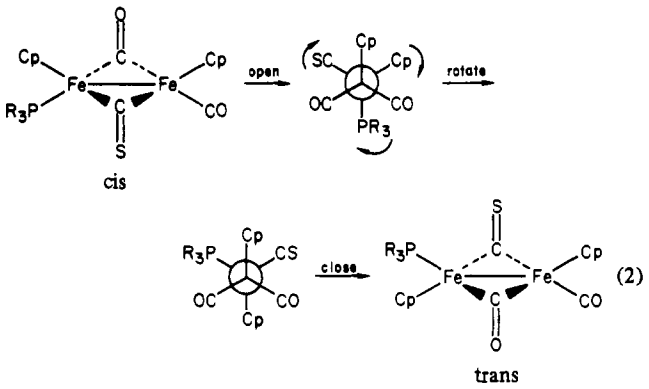
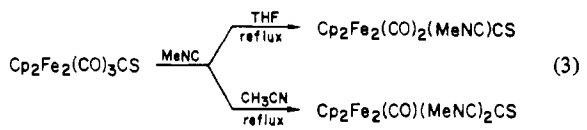


(2)

intermediate would lead to an isomer without a briding CS, for which there is no evidence.

$Cp_2Fe_2(CO)_2(MeNC)CS$ and $Cp_2Fe_2(CO)(MeNC)_2CS$. Methyl isocyanide reacts with $Cp_2Fe_2(CO)_3CS$ in refluxing THF or cyclohexane to form the red-brown monosubstituted complex $Cp_2Fe_2(CO)_2(MeNC)CS$. If this reaction is carried out in refluxing acetonitrile, however, the purple disubstituted compound $Cp_2Fe_2(CO)(MeNC)_2CS$ is obtained. In both cases a brown, tarry decomposition product is also formed, but there is no evidence for a trisubstituted derivative. The reaction of $Cp_2Fe_2(CO)_4$ with MeNC in refluxing THF gives a mixture of mono-, di-, and trisubstituted complexes, all of which have been characterized.[24,27] Phenyl isocyanide does not react with $Cp_2Fe_2(CO)_3CS$ under the conditions shown in eq 3, also in contrast to $[CpFe(CO)_2]_2$ which reacts with PhNC at room temperature.[28]



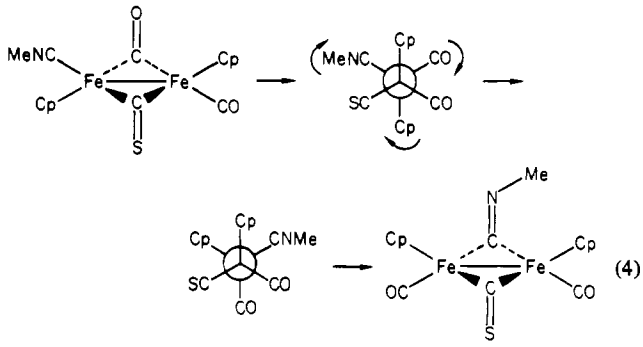
(3)

The stability and solubility of the isocyanide complexes are similar to those of the phosphine-substituted compounds. Solutions of $Cp_2Fe_2(CO)_2(MeNC)CS$ vary in color from green (CS_2) to gray (C_6H_6) to greenish brown (CH_3CN); the disubstituted complex is green in nonpolar media and purple in polar solvents. An analogue of the monosubstituted compound, $Cp_2Fe_2(CO)_2(t\text{-BuNC})CS$, was mentioned recently in a report.[29]

The infrared spectrum of $Cp_2Fe_2(CO)_2(MeNC)CS$ in hexane shows strong bands at 2150, 1965, and 1794 cm^{-1} indicative of a terminal isocyanide ligand, a terminal carbonyl, and a bridging carbonyl, respectively. These bands arise from the predominant isomer, in which the MeNC ligand is terminal; two strong bands in the bridging thiocarbonyl region suggest that cis and trans forms of this isomer are present in comparable amounts; apparently the ν(CO) and ν(CN) frequencies of the two isomers are virtually the same. Weaker infrared absorptions at 2005, 1973, and 1743 cm^{-1} may be assigned to a small amount of another isomer (or pair of cis–trans isomers) in which both CS and MeNC are bridging ligands. The observation of two terminal ν(CO) bands indicates the presence of at least the cis isomer and probably also the trans, as found in related systems.[3,5,19] There is no evidence for an isomer with a terminal CS ligand. The analogous carbonyl complex $Cp_2Fe_2(CO)_3(MeNC)$[24] also exists in terminal and bridging isocyanide forms, but, in contrast to $Cp_2Fe_2(CO)_2(MeNC)CS$, the two isomers are present in about equal amounts.

The ^1H NMR spectrum of $Cp_2Fe_2(CO)_2(MeNC)CS$ taken in $CDCl_3$ shows low-intensity peaks which may be assigned to the equivalent Cp ligands (δ 4.94) and the briding MeNC ligand (δ 3.73) of the MeNC-bridged form. The three major peaks in the spectrum (Table II) correspond to the terminal MeNC ligand and the nonequivalent Cp groups of the predominant terminal MeNC form. If both cis and trans isomers are present as suggested by the ν(CS) infrared region, then either the cis–trans isomerization must be rapid on the NMR time scale at the ambient temperature of the measurements or the chemical shifts of the two isomers are coincident. On the basis of NMR studies[19-23] of other $Cp_2Fe_2(CO)_4$ derivatives, the latter possibility seems unlikely; therefore, the rapid cis–trans isomerization probably proceeds via a terminal CS-containing intermediate stabilized by the MeNC on the same Fe as the CS, as shown in eq 2. Since this cis–trans isomerization occurs more rapidly than that of $Cp_2Fe_2(CO)_3CS$, it appears that the MeNC accelerates it, perhaps by stabilization of the nonbridged intermediate.

If the mechanism in eq 2 is modified by requiring the bridging CS to move to the Fe atom bearing the CO ligand as shown in eq 4, rotation around the Fe–Fe bond followed



(4)

by CS and MeNC bridge closure will yield the MeNC-bridged compound. This terminal-to-bridge MeNC interconversion is also accompanied by trans to cis isomerization of the Cp rings. Because of the high π-bonding capability[30] of the terminal CS group, the intermediate in eq 2 with the CS group on the Fe atom bearing the MeNC ligand would probably be of lower energy than that in eq 4; therefore, one might predict that cis–trans isomerization of the MeNC terminal isomer would be faster than MeNC terminal-bridging interconversion. Although further studies are required, this prediction appears to be borne out by the ^1H NMR spectrum which shows separate resonances for the MeNC terminal and bridging forms but only time-averaged signals for the cis and trans isomers of the MeNC terminal form. The rapid cis–trans isomerization is supported by studies of the t-BuNC terminal $Cp_2Fe_2(CO)_3(t\text{-BuNC})$ complex which shows time-averaged Cp resonances even at −120 °C.[31]

The disubstituted derivative $Cp_2Fe_2(CO)(MeNC)_2CS$ also exists in two isomeric forms, which in this case may be separated chromatographically. Absorptions in the infrared spectrum (Table I) of the major isomer in hexane may be attributed to a terminal isocyanide (2143 cm^{-1}), a terminal CO (1960, 1951 cm^{-1}), and a bridging isocyanide (1723, 1717 cm^{-1}).

The presence of two bands for each of these latter modes indicates that this isomer exists in solution in two forms, possibly cis and trans or the two structures (syn and anti) resulting from different orientations of the CH_3 group in the bent bridging $CNCH_3$ ligand. This latter type of isomerism has been reported previously in $Cp_2Fe_2(CO)_2(CNMe)_2$ and is very rapid.[32] In other solvents (C_6H_6, CS_2, CH_2Cl_2, and

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Table III. ^{13}C NMR Data[a]

compd	δ(Cp)	δ(R)	δ(CO)	δ(CS)
$Cp_2Fe_2(CO)_3CS$	92.1		211.4,[b] 268.1[c]	380.8
$Cp_2Fe_2(CO)_2(PEt_3)CS$[d]	88.5, 89.7[e]	7.17 (Et), 17.3 (d, Et)[f]	216.8,[b] 278.3 (d)[c,g]	396.2 (d)[g]
$[Cp_2Fe_2(CO)_3CSBz]PF_6$	92.3, 92.9	60.7, (CH_2), 129.6, 130.2, 133.9 (Ph)	207.4,[b] 251.6[c]	403.1
$[Cp_2Fe_2(CO)_2(PEt_3)CSMe]PF_6$	88.3[e,h]	5.70 (Et), 17.1 (d, Et)[i]	213.4,[b] 256.4 (d)[c,j]	407.9 (d)[j]

[a] Shifts in ppm downfield from Me_4Si; acetone-d_6 solution (except where noted). [b] Terminal CO. [c] Bridging CO. [d] $CDCl_3$ solution. [e] J_{PFeC} not observed. [f] J_{PC} = 23.8 Hz. [g] J_{PFeC} = 14.9 Hz. [h] Center of two peaks, which apparently obscure signal from *S*-methyl carbon. [i] J_{PCH} = 28.3 Hz. [j] J_{PFeC} not obtained.

CH_3CN), only single bands are observed for each of these modes, probably due to broadening and overlapping of the two similar absorptions. However, two ν(CS) bridging bands remain in all of these solvents, suggesting that both cis and trans isomers are present.

The infrared spectrum (Table I) of the minor isomer in CH_2Cl_2 exhibits one terminal isocyanide band (2154 cm^{-1}), one bridging CO band (1751 cm^{-1}), and a bridging CS absorption (1110 cm^{-1}). The observation of single bands for each of these ligands suggests that only one isomer of this bis-terminal isocyanide form is present.

The ^1H NMR spectrum (Table II) of $Cp_2Fe_2(CO)(MeNC)_2CS$ in $CDCl_3$ shows strong, sharp singlets for the two Cp groups (δ 4.67, 4.83), the terminal MeNC group (δ 2.96), and the bridging MeNC (δ 3.72) for the bridge-terminal isomer and two less intense peaks for Cp (δ 4.60) and MeNC (δ 3.05) of the bis-terminal isomer. NMR spectra in other solvents (acetone-d_6, CS_2, and C_6D_6) are similar, though the proportion of the bis-terminal isomer is somewhat greater in the more polar solvents. The isomeric forms of $Cp_2Fe_2(CO)(MeNC)_2CS$ contrast with those of $Cp_2Fe_2(CO)_2(MeNC)_2$[25] which exists in solution as the trans bridge-terminal and the cis bis bridging isocyanide isomers in comparable amounts. The presence of the strongly bridging CS group in $Cp_2Fe_2(CO)(MeNC)_2CS$ excludes the formation of the bis bridging isocyanide isomer.

Infrared spectra of solutions of the bridge-terminal isomer of $Cp_2Fe_2(CO)(MeNC)_2CS$ seem to indicate the presence of cis–trans or syn–anti forms which interconvert rapidly as shown by its ^1H NMR spectrum. However, the bridge-terminal and bis-terminal forms interconvert much more slowly. These isomerization processes may occur by bridge opening followed by rotation around the Fe–Fe bond and closure to form the isomeric product.

Alkylated Thiocarbonyl Complexes, $[Cp_2Fe_2(CO)_2(L)CSR]^+$. The sulfur atom of the bridging thiocarbonyl ligand in $Cp_2Fe_2(CO)_3CS$ is readily alkylated at room temperature to give the *S*-alkyl derivatives $[Cp_2Fe_2(CO)_3CSR]^+$ (eq 5).

$$Cp_2Fe_2(CO)_3CS \xrightarrow[CH_2Cl_2]{MeOSO_2F} [Cp_2Fe_2(CO)_3CSMe]FSO_3$$
$$\xrightarrow[CH_2Cl_2]{[Et_3O]BF_4} [Cp_2Fe_2(CO)_3CSEt]BF_4$$
$$\xrightarrow{neatPrI} [Cp_2Fe_2(CO)_3CSPr]I \xrightarrow[exchange]{PF_6^-} [Cp_2Fe_2(CO)_3CSPr]PF_6 \quad (5)$$

Alkyl fluorosulfonates, trialkyloxonium salts, and primary alkyl iodides react, as do certain unusually reactive primary alkyl bromides (e.g., benzyl).

Alkyl chlorides, most alkyl bromides, and secondary and tertiary alkyl iodides do not react under the same conditions. For alkylating agents that give *S*-alkyl compounds, the order of reactivity is $ROSO_2F$, $[R_3O]BF_4 \gg$ BzBr, AllBr > MeI > EtI > *n*-PrI, *n*-BuI. The alkyl halide reactions are rather slow in solution and are best carried out with the halide itself as the solvent. Conversion to the hexafluorophosphate salts is easily accomplished and generally is desirable, since PF_6^- has no infrared absorptions in the bridging thiocarbonyl region. This step is necessary for the benzyl and allyl derivatives, because in these cases the alkylation is reversible; the reverse reaction occurs slowly even in the solid state (eq 6).

$$Cp_2Fe_2(CO)_3CS + RBr \rightleftharpoons [Cp_2Fe_2(CO)_3CSR]Br \quad R = Bz, All \quad (6)$$

The *S*-alkyl complexes $[Cp_2Fe_2(CO)_3CSR]PF_6$ are red, microcrystalline solids which are air stable both in the solid state and in solution. The methyl and ethyl derivatives are slightly water soluble, sparingly soluble in CH_2Cl_2, but fairly soluble in acetone and acetonitrile; compounds with larger R groups, particularly the benzyl and allyl complexes, are much more soluble in polar organic solvents. Their solutions have a characteristic deep red color. Conductivity measurements indicate that the compounds are 1:1 electrolytes in nitromethane.[33]

The monosubstituted complexes $Cp_2Fe_2(CO)_2(L)CS$ (L = PR_3 or MeNC) undergo S-alkylation more rapidly than $Cp_2Fe_2(CO)_3CS$, but, in general, the $[Cp_2Fe_2(CO)_2(L)CSR]^+$ compounds are best prepared by reaction of the $[Cp_2Fe_2(CO)_3CSR]^+$ complexes with L (see below).

Infrared spectra of the $[Cp_2Fe_2(CO)_3CSR]^+$ compounds in the carbonyl region resemble the spectrum of $Cp_2Fe_2(CO)_3CS$ in acetonitrile (Table I), except that the three bands occur at higher frequencies, as expected. The band pattern is very similar to that of the cis isomer of $Cp_2Fe_2(CO)_3CS$ which indicates that the complexes exist only as cis isomers; this structure has been verified by X-ray crystallography for $[Cp_2Fe_2(CO)_3CSEt]BF_4$.[4] The CS stretching absorption appears as a weak, rather broad band, characteristically about 100 cm^{-1} lower than the ν(CS) band of $Cp_2Fe_2(CO)_3CS$.

Proton NMR spectra (Table II) of the complexes show the expected alkyl resonances and, in most cases, a single fairly broad Cp resonance. An exception is the spectrum of $[Cp_2Fe_2(CO)_3CSBz]PF_6$, which shows two distinct Cp peaks. The ^{13}C NMR spectrum (Table III) of this derivative also shows two Cp resonances, and the alkylated bridging CS carbon (δ 403.1) is downfield from that in $Cp_2Fe_2(CO)_3CS$ (δ 380.8).

The crystal structure of $[Cp_2Fe_2(CO)_3CSEt]BF_4$[4] shows that the bridging C–S–Et group is nonlinear. Thus, the cyclopentadienyl groups in $[Cp_2Fe_2(CO)_3CSR]^+$ complexes are nonequivalent and should give separate NMR signals, as do the Cp ligands of the similar *S*-alkyl complex $[Cp_2Fe_2(CO)_2(CS)CSMe]FSO_3$.[1] The observation of a single, somewhat broad Cp resonance for most of the *S*-alkyl derivatives of $Cp_2Fe_2(CO)_3CS$ can be attributed to rapid inversion at the sulfur atom or possibly rotation around the C–S bond, which results in equivalence of the Cp groups on the NMR time scale (eq 7). Evidently this process is fairly rapid at room temperature for all of the *S*-alkyl complexes except the *S*-

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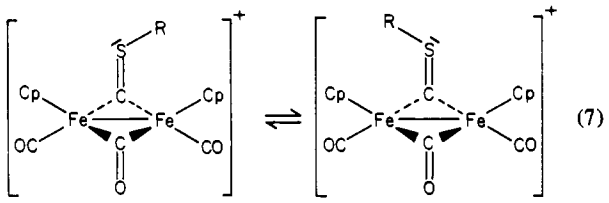
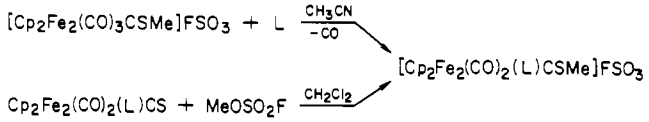


(7)

benzyl derivative, whose two Cp resonances coalesce at 48 °C in CD_3CN solvent.

The *S*-methyl thiocarbonyl complex, $[Cp_2Fe_2(CO)_3CSMe]^+$, undergoes CO substitution, in most cases, somewhat more readily than does the parent thiocarbonyl compound. Reaction with PEt_3 or PMe_2Ph in polar solvents (acetonitrile, acetone or nitromethane) occurs rapidly at room temperature to give the monosubstituted complexes $[Cp_2Fe_2(CO)_2(PR_3)CSMe]FSO_3$. Ligands such as $PMePh_2$, $P(OMe)_3$, and MeNC give analogous products, but these reactions require heating. In general, higher overall yields (based on $Cp_2Fe_2(CO)_3CS$) of $[Cp_2Fe_2(CO)_2(L)CSMe]FSO_3$ are obtained by this method than by the alternative route (eq 8) involving alkylation of the



(8)

$Cp_2Fe_2(CO)_2(L)CS$ complexes. The hexafluorophosphate salt of $[Cp_2Fe_2(CO)_3CSMe]^+$ reacts somewhat faster than the fluorosulfonate salt, but the latter is a more convenient starting material; ion exchange to give the PF_6^- form, if desired, is more easily accomplished after ligand substitution, owing to the greater solubility of the substituted derivatives. The phosphine and phosphite complexes are brown, slightly air-sensitive solids which dissolve in polar organic solvents to give yellow-green solutions; the red-brown MeNC derivative exhibits similar solubility and stability.

Most ligands that do not react with $Cp_2Fe_2(CO)_3CS$ such as PPh_3 and $P(OPh)_3$ also fail to give substituted derivatives of the *S*-methyl thiocarbonyl compound. Extended heating of $[Cp_2Fe_2(CO)_3CSMe]FSO_3$ in acetonitrile with the ligands that react results only in decomposition to unidentified products.

Reaction of $[Cp_2Fe_2(CO)_3CSMe]^+$ with NaI in refluxing acetonitrile gives the dark brown iodide-substituted complex $Cp_2Fe_2(CO)_2(I)(CSMe)$, which has a bridging CSMe group and a terminal I^- ligand. This compound is more conveniently obtained directly from $Cp_2Fe_2(CO)_3CS$ (eq 9); the ethyl analogue is prepared similarly.

$$Cp_2Fe_2(CO)_3CS + MeI \xrightarrow[CH_3CN,\ reflux]{NaI} Cp_2Fe_2(CO)_2(I)(CSMe) + CO \quad (9)$$

The other *S*-alkyl complexes $[Cp_2Fe_2(CO)_3CSR]PF_6$ also undergo the above substitution reactions (eq 8), though somewhat more slowly, if R = Et, *n*-Pr, or *n*-Bu. However, reaction of the benzyl and allyl derivatives with donor ligands results in dealkylation to give $Cp_2Fe_2(CO)_3CS$ rather than substitution. Substituted *S*-alkyl complexes with these alkyl groups must therefore be prepared by alkylation of $Cp_2Fe_2(CO)_2(L)CS$.

The single terminal and single bridging $\nu(CO)$ absorptions in infrared spectra (Table I) of the $[Cp_2Fe_2(CO)_2(L)CSMe]^+$ complexes are consistent with a structure in which a CO and the $CSMe^+$ ligand are bridging while L and a CO are terminal. The absence of additional $\nu(CO)$ bands indicates that only one isomer is present. Since the $[Cp_2Fe_2(CO)_3CSR]^+$ complexes have the cis geometry, these substituted derivatives are presumably also cis. Their proton NMR spectra (Table II) exhibit singlets for the two Cp groups which also supports this structure. The lack of further splitting or broadening of these resonances indicates that the *S*-methyl group is either oriented in only one direction or rapidly moves back and forth as indicated in eq 7. The ^{13}C NMR spectrum (Table III) of $[Cp_2Fe_2(CO)_2(PEt_3)CSMe]PF_6$ is consistent with these conclusions.

Alkylation of $Cp_2Fe_2(CO)(CNMe)_2CS$. While $Cp_2Fe_2(CO)_2(MeNC)CS$ reacts with $MeOSO_2F$ or MeI to give $Cp_2Fe_2(CO)_2(MeNC)CSMe^+$ according to eq 8, alkylation of $Cp_2Fe_2(CO)(CNMe)_2CS$ yields products which depend upon the alkylating agent (eq 10). Methyl iodide gives the

$$Cp_2Fe_2(CO)(MeNC)_2CS \xrightarrow[CH_2Cl_2]{MeI} [Cp_2Fe_2(CO)(MeNC)_2CSMe]^+$$
$$\xrightarrow[CH_2Cl_2]{MeOSO_2F} [Cp_2Fe_2(CO)(MeNC)(Me_2NC)CSMe]^{2+} \quad (10)$$

S-methyl compound with two terminal MeNC groups, whereas the stronger alkylating $MeOSO_2F$ gives the dimethylated product in which bridging CS and MeNC groups are alkylated. This pattern of reactivity suggests that the bridge-terminal isomer of $Cp_2Fe_2(CO)(MeNC)_2CS$ is less nucleophilic than the bis-terminal isomer and so rearranges to the latter form before reacting with the weaker electrophile MeI, whereas the stronger alkylating agent $MeOSO_2F$ reacts immediately at either S or N and thus locks the molecule into a form which can undergo a second alkylation. It might be noted that in all of these reactions, the bridging CS group is alkylated, which contrasts with related reactions of the carbonyl analogues $Cp_2Fe_2(CO)_3CNR$ and $Cp_2Fe_2(CO)_2(CNR)_2$ that yield bridging CNR alkylated products.[34]

The infrared spectrum (Table I) of $[Cp_2Fe_2(CO)(MeNC)(Me_2NC)CSMe]^{2+}$ shows $\nu(CN)$ bands for the terminal MeNC (2223 cm^{-1}) and bridging $CNMe_2^+$ (1620 cm^{-1}) groups, a $\nu(CO)$ band for the terminal CO (2030 cm^{-1}), and a $\nu(CS)$ absorption for the $CSMe^+$ group (1043 cm^{-1}). Supporting this structure is its ^1H NMR spectrum (Table II) which shows singlets for the two Cp rings, for the two different Me groups of the bridging $CNMe_2^+$ ligand, for the bridging CSMe group, and for the terminal CNMe ligand. The lack of splitting of the Cp or Me resonances suggests that the Me group is either fixed in one orientation or rapidly moves back and forth as indicated in eq 7. The spectra do not establish whether the Cp groups are cis or trans to each other.

The infrared spectrum of the monomethylated product $Cp_2Fe_2(CO)(MeNC)_2CSMe^+$ shows a single $\nu(CN)$ band (2190 cm^{-1}) for the two terminal MeNC ligands, a bridging $\nu(CO)$ band (1815 cm^{-1}), and the $\nu(CS)$ band of the bridging $CSMe^+$ ligand. Singlets in its ^1H NMR spectrum for the equivalent Cp rings, the equivalent terminal MeNC ligands, and the $CSMe^+$ group are consistent with the structure indicated by the infrared results. The lack of splitting of the Cp and MeNC resonances indicates that the Me of the $CSMe^+$ rapidly moves back and forth. There is no evidence for more than one isomer of the complex.

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Registry No. $Cp_2Fe_2(CO)_3CS$, 67113-80-8; $Cp_2Fe_2(CO)_2(PEt_3)CS$, 76157-14-7; $Cp_2Fe_2(CO)_2(PMe_2Ph)CS$, 76157-15-8; $Cp_2Fe_2(CO)_2(PMePh_2)CS$, 76157-16-9; $Cp_2Fe_2(CO)_2\{P(OMe)_3\}CS$, 76157-17-0; $Cp_2Fe_2(CO)_2(MeNC)CS$ (terminal isomer), 76157-18-1; $Cp_2Fe_2(CO)(MeNC)_2CS$ (bridge-terminal isomer), 76157-19-2; Cp_2Fe_2-

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$(CO)(MeNC)_2CS$ (bis-terminal isomer), 76157-20-5; $[Cp_2Fe_2(CO)_3CSMe]FSO_3$, 76157-22-7; $[Cp_2Fe_2(CO)_3CSEt]BF_4$, 66540-79-2; $[Cp_2Fe_2(CO)_3CSMe]PF_6$, 76189-80-5; $[Cp_2Fe_2(CO)_3CSEt]PF_6$, 76157-24-9; $[Cp_2Fe_2(CO)_3CSPr]PF_6$, 76157-26-1; $[Cp_2Fe_2(CO)_3CSBu]PF_6$, 76157-28-3; $[Cp_2Fe_2(CO)_3CSBz]PF_6$, 76157-30-7; $[Cp_2Fe_2(CO)_3CSAll]PF_6$, 76157-32-9; $[Cp_2Fe_2(CO)_2(PEt_3)CSMe]PF_6$, 76157-34-1; $[Cp_2Fe_2(CO)_2(PMe_2Ph)CSMe]PF_6$, 76157-36-3; $[Cp_2Fe_2(CO)_2(PMePh_2)CSMe]PF_6$, 76157-38-5; $[Cp_2Fe_2(CO)_2(P(OMe)_3)CSMe]PF_6$, 76157-40-9; $[Cp_2Fe_2(CO)_2(MeNC)CSMe]PF_6$, 76157-42-1; $[Cp_2Fe_2(CO)_2(PEt_3)CSBz]PF_6$, 76157-44-3; $Cp_2Fe_2(CO)_2(I)(CSMe)$, 76157-45-4; $Cp_2Fe_2(CO)_2(I)(CSEt)$, 76157-46-5; $[Cp_2Fe_2(CO)(MeNC)(Me_2NC)CSMe](PF_6)_2$, 76172-96-8; $[Cp_2Fe_2(CO)(MeNC)_2CSMe]PF_6$, 76157-48-7; $MeOSO_2F$, 421-20-5; $[Et_3O]BF_4$, 368-39-8; MeI, 74-88-4; EtI, 75-03-6; *n*-PrI, 107-08-4; *n*-BuI, 542-69-8; BzBr, 100-39-0; AllBr, 106-95-6; $Cp_2Fe_2(CO)_2(MeNC)CS$ (bridge isomer), 76172-97-9.

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Mechanisms of Iron–Cobalt Bond Breaking in Tetracarbonyliron-μ-(dimethylarsenido)-tricarbonylcobalt(*Fe–Co*)[1]

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The kinetics have been examined of heterolytic fission of the Fe→Co bond in $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3$ in cyclohexane or decalin. Fission is induced by a series of P-, As-, and Sb-donor ligands that become coordinated to the Co atom, and the rates are all closely first order in the concentration of entering ligand. The variation of the second-order rate constant with the nature of the entering P-donor ligands suggests that a concerted but largely I_d process is occurring with the less nucleophilic ligands but that the reactions become more I_a in character as the ligand nucleophilicity increases.

Complexes of the type $(OC)_4Fe(\mu\text{-}AsMe_2)M$ (M = $Mn(CO)_4$, $Fe(CO)_2(NO)$, $Co(CO)_3$, $Mo(CO)_2(\eta^5\text{-}C_5H_5)$, etc.)[2-4] have been shown to react with phosphorus-donor ligands according to eq 1. This involves simple heterolytic fission of

$$(OC)_4Fe(\mu\text{-}AsMe_2)M + L \rightarrow (OC)_4Fe(\mu\text{-}AsMe_2)ML \quad (1)$$

the Fe→M bond and the addition of the ligand L to the metal atom in the group M. When M = $Co(CO)_3$[5] and $Mn(CO)_4$[6] a series of Fe→Co and Fe→Mn bond-breaking and bond-making reactions can be carried out, leading to a very extensive array of more highly substituted derivatives. The compounds with M = $Co(CO)_3$ and $Fe(CO)_2(NO)$ have been shown to act as catalysts for the dimerization of norbornadiene.[7] Quantitative kinetic studies of such reactions would be of interest in helping to define their detailed mechanisms and energetics and, possibly, in characterizing reactive intermediates. We report here the results of a kinetic study of the reactions of $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3$ with some P-, As-, and Sb-donor ligands.

Experimental Section

The complex $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3$ was prepared by Dr. H.-J. Langenbach and kindly provided for this work by Professor H. Vahrenkamp. The solvents and phosphorus-donor ligands were obtained and treated before use as described elsewhere.[8,9] Triphenylarsine and -stibine (Eastman Organic Chemicals and J. T. Baker Chemical Co., respectively) were recrystallized from methanol.

Table I. Infrared Spectra[a] of the Products of Reaction of $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3$ with L in Decalin

L	ν(Fe–CO), cm^{-1}			ν(Co–CO), cm^{-1}		
$P(C_6H_{11})_3$	2028 s	1958 vs	1926 vs	2046 w	1974 vs	1965 s
P-*n*-Bu_3	2030 m	1958 s	1927 vs	2051 w	1980 s	1969 s
$PPhEt_2$	2031 s	1959 s	1928 vs	2051 w	1984 s	1971 s
PPh_2Et	2032 s	1959 s	1928 vs	2055 w	1986 s	1974 s
$P(OMe)_3$	2036 s	1961 m	1929 vs	2063 vw	1997 s	1987 s
$P(OMe)_3$[b]	2029 s	1965 m	1931 vs	2054 vw	1996 s	1990 s
PPh_3	2032 s	1960 m	1929 vs	2054 w	1988 s	1976 s
PPh_3[b]	2027 s	1962 s	1931 vs	2048 w	1992 s	1978 s
etpb[c]	2037 s	1962 m	1930 vs	2059 vw	2013 s	1998 s
$P(OPh)_3$	2035 s	1961 m	1928 m	2060 vw	2000 vw	1988 s
$AsPh_3$[d]	2031 m	1962 m	1931 s	2056 vw	1987 s	1975 s
$SbPh_3$[d]	2036 m	1962 m	1932 s	2060 vw	1988 s	1976 vs

[a] Assignments made as in ref 4. [b] Spectra in cyclohexane of $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3L$ isolated and characterized as in ref 4. [c] $P(OCH_2)_3CEt$. [d] In cyclohexane.

Solutions of air-sensitive liquid phosphines were prepared by transferring the pure liquid under argon in a syringe to a serum-capped volumetric flask which was flushed with argon. The flask was filled to the mark with degassed solvent driven through a stainless steel needle from a Schlenk tube by a positive pressure of argon. Solid $P(C_6H_{11})_3$ was weighed into a similar flask, which was then flushed with argon and filled to the mark with degassed solvent. Solutions of the less air-sensitive ligands were made up under air and degassed in Schlenk tubes by several freeze–pump–thaw cycles. For most kinetic runs 2.5 mL of ligand solution was transferred by syringe to a serum-capped 10-mm silica cell, which was flushed with argon. The cells were then placed in the thermostated multicell cell holder of a Cary 16K spectrophotometer and left for 20 min for temperature equilibration. Reactions were initiated by rapidly injecting 0.05 mL of a concentrated, degassed solution of complex by means of a syringe and vigorously shaking the cell for a few seconds. Temperature control (±0.1 °C) was maintained by using a circulating Brinkman-Lauda Model K temperature bath, and temperatures were monitored constantly using a Minco Inc. platinum or nickel resistance thermometer. This was immersed in a water-filled cell in the cell holder and was connected to a Data Precision Model 3500 digital multimeter. When the re-

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