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Organometallic Sulfur Complexes. 1. Syntheses, Structures, and Characterizations of Organoiron Sulfane Complexes $(\mu\text{-}S_x)[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (x = 1–4)

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A series of binuclear, sulfur- or polysulfur-bridged organoiron complexes $(\mu\text{-}S_x)[CpFe(CO)_2]_2$, x = 1–4 (Cp = $\eta^5\text{-}C_5H_5$), were prepared by substitution reactions involving either organoiron or sulfur nucleophiles or redox reactions. The structures of $(\mu\text{-}S_3)[CpFe(CO)_2]_2$ (III) and $(\mu\text{-}S_4)[CpFe(CO)_2]_2$ (IV) were determined by single-crystal X-ray diffraction. Compound III: space group $P2_1$; a = 6.645 (3), b = 12.113 (5), c = 10.753 (4) Å; β = 91.86 (5)°; V = 865.1 (6) Å^3; Z = 2; d_{calcd} = 1.040 (2) g/cm^3; 2728 reflections in final refinement on F; R = 0.062, R_w = 0.064; GOF = 1.56. Compound IV: space group $I2/c$; a = 22.72 (5), b = 11.37 (6), c = 7.14 (5) Å; β = 98.9 (2)°; V = 1822 (16) Å^3; Z = 4; d_{calcd} = 1.059 (9) g/cm^3; 877 reflections in final refinement on F; R = 0.069, R_w = 0.079; GOF = 2.17. In both molecules two $CpFe(CO)_2$ groups are joined by a bidentate sulfane bridge. Analogous structures of $(\mu\text{-}S)[CpFe(CO)_2]_2$ (I) and $(\mu\text{-}S_2)[CpFe(CO)_2]_2$ (II) were inferred from their desulfuration reactions with triphenylphosphine.

Introduction

Because of the diverse bonding modes displayed by sulfur and polysulfide, its ligation in metal complexes is of interest in several contexts. In biochemistry, inorganic sulfide and possibly polysulfide appear as critical ligands in metalloenzymes such as ferredoxin, nitrogenase, and the xanthine oxidases, primarily in association with iron or molybdenum.[1] In the context of industrial technology, inorganic sulfur (from feedstocks) is among the more common and troublesome catalyst poisons;[2] and as greater effort is directed toward the utilization of oil tars and sludges, catalytic desulfurization and removal of metal ions possibly complexed with sulfide or polysulfide will become an increasingly significant problem.[3] Additionally, in the broad area of metal-cluster chemistry sulfur ligands have proven very versatile in the construction of transition-metal cluster complexes, including heteronuclear clusters of potential catalytic utility.[4–6]

The coordination chemistry of polysulfides, S_x^{2-} (x = 2, 3, 4, ...), is of particular interest because of their large variety of modes of coordination.[6] The majority of transition-metal complexes of polysulfide reported to date fall into two classes:[4,7,8] (i) mononuclear complexes with chelating, bidentate polysulfide such as Cp_2TiS_6 (Cp = $\eta^5\text{-}C_5H_5$),[9] Cp_2VS_5,[10] and $(NH_4)_4PtS_{15}$;[11] (ii) polynuclear complexes in which the polysulfide exceeds bidenticity as in the commonly encountered bridging tetradentate S_2^{2-}, for instance in $Fe_2(CO)_6(S_2)$.[12] Simple binuclear complexes in which polysulfide serves as a bidentate, bridging ligand are infrequent, and the few examples "have been obtained accidentally".[6]

Hence, we undertook the rational synthesis of the disulfur-bridged iron complex $(\mu\text{-}S_2)[CpFe(CO)_2]_2$ (II). We chose this target because the chemistry of $CpFe(CO)_2$, or Fp, compounds is relatively well understood[13] and the Fp moiety provides reliable ^{1}H NMR and IR spectral features. We anticipated that such a complex could exemplify some of the compounds that contaminate heavy oil sludges, might be employable in the formation of interesting organometallic cluster complexes by further complexation of the disulfur ligand, and could provide a model for the bonding of O_2 in oxygen-transport metalloenzymes such as hemerythrin and hemocyanin.[14] In the course of our investigations we obtained complexes $(\mu\text{-}S_x)[CpFe(CO)_2]_2$ for x = 1–4. The syntheses, structures, characterizations, and chemistries of these complexes are reported here.

Experimental Section

Materials. All reactions were conducted under a nitrogen atmosphere with Schlenk glassware.[15] Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Methylene chloride was vacuum transferred from P_4O_{10}. Petroleum ether was purified by vacuum transfer from $LiAlH_4$. Deuterated NMR solvents, acetone-d_6 and chloroform-d_1, were dried over activated 4-Å molecular sieves and vacuum distilled. Sulfur dichloride (SCl_2) was twice distilled in the presence of a small amount of PCl_3, the fraction boiling at 55–61 °C being redistilled in the presence of PCl_3. The fraction collected at 58–61 °C was retained. A few drops of PCl_3 were added to inhibit decomposition. Sulfur monochloride (S_2Cl_2) was purified by distillation from a mixture containing sulfur (ca. 2%). The fraction distilling at 137–139 °C was retained and used within a few minutes after distillation. FpBr, $CpFe(CO)_2Br$, was prepared by reacting $[CpFe(CO)_2]_2$ with Br_2 in CCl_4.[16] Anhydrous THF solutions of stoichiometry Li_2S, Li_2S_2, and Li_2S_4 were prepared by reacting $LiHBEt_3$ and elemental sulfur as described by Gladysz.[17] Other reagents were used as purchased without further treatment.

Methods. Chromatographic separations were achieved by elution of silica columns or preparative thin-layer plates (TLC) with petroleum ether/diethyl ether mixtures. The characteristic R_f values[42] for the dimeric iron complexes on 60 F_{254} silica gel TLC plates eluted with 50% diethyl ether in petroleum ether are given in Table VI. ^{1}H NMR spectra were recorded on a Varian EM-360 or a Varian T-60. A Varian CFT-20 was employed for (20-MHz) ^{13}C NMR. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer with NaCl cells for solution samples and CsI plates for Nujol mulls. Visible–near-ultraviolet absorption spectra were recorded on a Varian Super Scan 3 with diethyl ether as solvent in 1-cm quartz cells. Melting points were determined on a capillary melting point apparatus

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and are uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI. Physical properties and spectral characteristics are reported on Table VI.

Procedures. Reaction of Na[CpFe(CO)$_2$] with SCl$_2$. A 0.2 M THF solution of Na[CpFe(CO)$_2$], NaFp, was prepared by reducing [CpFe(CO)$_2$]$_2$ (5.31 g, 15 mmol) in 150 mL of THF with 1% sodium amalgam by established procedure.[18] Although at room temperature NaFp with sulfur chlorides yields primarily sulfur and Fp$_2$, at lower temperature substitution is favored over electron transfer. Slow addition (10 min) of a solution of SCl$_2$ (0.95 mL, 15 mmol) in 15 mL of THF to a rapidly stirred 150-mL portion of 0.2 M NaFp (30 mmol) cooled to −78 °C resulted in a dark red-brown solution. The solution was stirred an additional 2 h at −78 °C and warmed to room temperature. After the solvent was removed in vacuo, the residue was extracted with diethyl ether (200 mL). The extracts were filtered, reduced in vacuo to ca. 30 mL, and column chromatographed. Elution with petroleum ether and 17% diethyl ether in petroleum ether removed sulfur and Fp$_2$. Further elution with 33% diethyl ether in petroleum ether separated a deep red-brown band, which was collected under nitrogen, stripped of solvent in vacuo, and recrystallized from diethyl ether/petroleum ether, giving deep red crystals of (μ-S$_3$)[CpFe(CO)$_2$]$_2$ (III) (2.36 g, 35% yield). Anal. Calcd for $C_{14}H_{10}Fe_2O_4S_3$: C, 37.37; H, 2.24; Fe, 24.83; S, 21.33. Found: C, 37.03; H, 2.31; Fe, 25.11; S, 21.3.

Reaction of Na[CpFe(CO)$_2$] with S$_2$Cl$_2$. Slow addition (10 min) of a solution of S$_2$Cl$_2$ (1.2 mL, 15 mmol) in 20 mL of THF to a rapidly stirred 150-mL portion of 0.2 M NaFp (30 mmol) at −78 °C yielded a deep red-brown solution. The reaction mixture was stirred an additional 2 h at −78 °C, warmed to room temperature, and desolvented in vacuo. The residue was extracted with diethyl ether (200 mL). The extracts were filtered, reduced to ca. 30 mL in vacuo, and column chromatographed. Elemental sulfur and Fp$_2$ were removed by elution with petroleum ether followed by 17% diethyl ether in petroleum ether. Subsequent elution with 33% diethyl ether in petroleum ether afforded a deep red-brown band, which was collected under nitrogen. TLC examination of this eluate indicated two compounds with R_f values (50% diethyl ether in petroleum ether) of 0.32 and 0.26. These products could be separated by preparative TLC or by fractional crystallization. The first, with R_f of 0.32 (1.55 g, 23% yield), proved to be III. The second compound with R_f of 0.26 was recrystallized from diethyl ether/petroleum ether, giving bright red crystals of (μ-S$_4$)[CpFe(CO)$_2$]$_2$ (IV) (0.94 g, 13% yield). Anal. Calcd for $C_{14}H_{10}Fe_2O_4S_4$: C, 34.86; H, 2.07; Fe, 23.17; S, 26.61. Found: C, 34.96; H, 2.24; Fe, 23.65; S, 25.66.

Reaction of Na[CpFe(CO)$_2$] with SOCl$_2$. A solution of (1.09 mL, 15 mmol) SOCl$_2$ in 20 mL of THF was allowed to react with 150 mL of 0.2 M NaCp solution at −78 °C, analogously with reactions above. After chromatographic separation and recrystallization this reaction afforded III (2.7 g, 40% yield).

Reaction of [CpFe(CO)$_2$]$_2$ with Sulfur. A solution prepared from Fp$_2$ (0.708 g, 2 mmol), sulfur (1.024 g, 4 mmol), and 65 mL of THF was heated at 45–50 °C under nitrogen for 4 h. The color changed from dark red to deep red-brown. The reaction mixture was cooled to room temperature, and solvent was removed in vacuo. The oily residue was extracted with 50 mL of diethyl ether, and the extracts were filtered under nitrogen and reduced in volume in vacuo. Column chromatography (33% diethyl ether in petroleum ether) afforded a deep red-brown band. TLC examination (50% diethyl ether in petroleum ether) indicated that the band was a mixture of compounds with R_f 0.32, 0.25, and 0.21. The mixture exhibited ^{1}H NMR resonances (acetone-d_6) at δ 5.4, 5.35, and 5.32. The IR spectrum (CH$_2$Cl$_2$) contained ν_{CO} bands at 2030 and 1990 cm^{-1}. Preparative TLC allowed separation of the R_f 0.32 component. After recrystallization from diethyl ether/petroleum ether this was identified as III by ^{1}H NMR and IR spectra.

Reaction of CpFe(CO)$_2$Br with Li$_2$S. A 50-mL portion of a THF solution of Li$_2$S (0.367 g, 8 mmol) was added slowly under nitrogen to a rapidly stirred solution of FpBr (5.0 g, 19.4 mmol) in 150 mL of THF at room temperature. The reaction mixture changed from light brown to deep red-brown. It was stirred overnight, solvent was stripped in vacuo, and the oily residue was extracted with 200 mL of diethyl ether, filtered under nitrogen, and reduced to 30 mL in vacuo. Column chromatography (20% diethyl ether in petroleum ether) afforded a red-brown band, which was collected under nitrogen. Further elution with diethyl ether provided a red band identified spectrally (IR and NMR) as unreacted FpBr. TLC investigation of the red-brown band (50% diethyl ether in petroleum ether) indicated two compounds, of R_f 0.44 and 0.41. The latter was identified as Fp$_2$ by comparison with an authentic sample. The ^{1}H NMR spectrum of the mixture showed a singlet at δ 5.2 in addition to a singlet at δ 4.97 due to Fp$_2$. We were unable to separate the compounds.

Reaction of CpFe(CO)$_2$Br with Li$_2$S$_2$. Fifty milliliters of THF solution of Li$_2$S$_2$ (8 mmol) was added slowly to a rapidly stirred 150-mL THF solution of FpBr (5.0 g, 19.4 mmol) at room temperature under nitrogen. The reaction mixture was stirred overnight, and after the usual workup (see above), products were separated by column chromatography. Elution with 50% diethyl ether in petroleum ether afforded a brown band; with 15% diethyl ether, a second brown band; and, finally, with diethyl ether, a red band identified spectrally as unreacted FpBr. Removal of solvent from the first brown band left an oily red-brown material. Numerous attempts to recrystallize this oily material were unsuccessful. Its identification as (μ-S$_2$)[CpFe(CO)$_2$]$_2$ (II) is discussed below. The second brown band yielded deep red-brown crystals of III, identified spectrally.

Reaction of CpFe(CO)$_2$Br with Li$_2$S$_4$. Slow addition under nitrogen of a 75-mL THF solution of Li$_2$S$_4$ (8 mmol) to a 100-mL THF solution of FpBr (5.0 g, 19.4 mmol) resulted in a reaction mixture that after 12 h of stirring at 35 °C yielded III and IV to the usual workup. The products were identified by melting point and ^{1}H NMR.

Reaction of CpFe(CO)$_2$Br with H$_2$S and Base. A solution of FpBr (1.28 g, 5 mmol) and triethylamine (2.78 mL, 20 mmol) in 150 mL of diethyl ether was heated to 35 °C, and H$_2$S was bubbled through the solution for ca 1.5 h. The reaction mixture was then stirred 12 h. at room temperature and filtered under nitrogen. Solvent was removed in vacuo and the residue washed with 100 mL of diethyl ether and refiltered under nitrogen. The solution was extracted with water and the ether phase separated and reduced to 10 mL in vacuo. Chromatographic separation as before yielded III (0.15 g, 20% yield), identified spectrally.

Thermolysis of (μ-S$_3$)[CpFe(CO)$_2$]$_2$ (III). A solution of III (0.9 g, 2 mmol) in toluene (40 mL) was heated to reflux under nitrogen for 8 h. The solution was cooled and the black, microcrystalline product collected by filtration. It was washed with diethyl ether and recrystallized from hot bromobenzene to give (CpFeS)$_4$ (0.46 g, 75% yield), identified by its reported IR spectrum (Nujol).[19] Anal. Calcd for C_5H_5FeS: C, 39.2; H, 3.3; Fe, 36.2; S, 21.0. Found: C, 39.39; H, 3.34; Fe, 35.23; S, 20.31.

"Titration" of Sulfur. Reactions of III and II with Triphenylphosphine. A series of reactions of compounds III and II were monitored by ^{1}H NMR spectroscopy. Typically, an NMR tube was charged with trisulfane III (0.028 g, 0.062 mmol), triphenylphosphine (0.016 g, 0.062 mmol), and 0.4 mL of acetone-d_6 and sealed under nitrogen. Subsequent reaction was monitored by ^{1}H NMR. Reactions involving III and triphenylphosphine in 1:2 and 1:3 molar ratios and II and triphenylphosphine in 1:1 and 1:2 ratios were conducted similarly (see Results and Discussion). The NMR data indicating formation of a new iron monosulfane complex, (μ-S)[CpFe(CO)$_2$]$_2$ (I), and confirming the identifications of the tri- and disulfane complexes III and II are discussed below. In each of these reactions dichloromethane extraction of the residue insoluble in diethyl ether afforded triphenylphosphine sulfide, identified by its reported IR spectrum and melting point (163–164 °C).[20]

X-ray Study

Single-crystal specimens suitable for X-ray study (several of III, but after arduous efforts only one of IV) were obtained from solution in dry, deoxygenated diethyl ether by slow evaporation in darkness under dry nitrogen (in several hours at room temperature for III; more rapidly at 5–10 °C for IV because its solution decomposes).

Methods: precession and Weissenberg photographs; diffractometry (FACS-1 Picker) with Nb(0.003-in.)-filtered Mo Kα radiation (λ = 0.71069 Å); θ–2θ scans at 2° in 2θ/min from $2\theta(\alpha_1) - 0.8$ to $2\theta(\alpha_2) + 0.8°$; 20-s background counts fore and aft; cell constants by the

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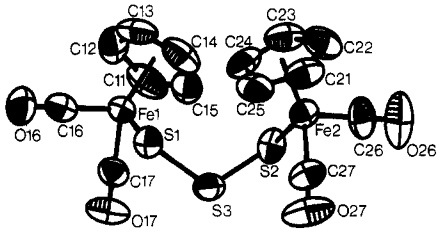

Figure 1. Molecule of compound III.

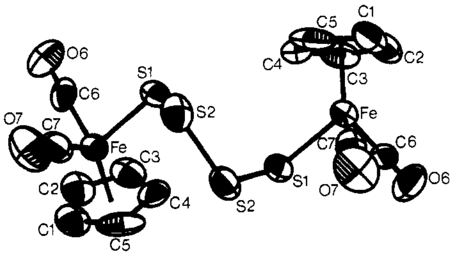

Figure 2. Molecule of compound IV.

FACS–Vanderbilt least-squares program; integrated-intensity esd's by $\sigma^2(F_o) = S + t^2B + p^2I^2$, p, the "instability constant", being estimated from the excess variance of straight-line fits to the standards; all subsequent calculations by the system X-RAY-76[21] with atomic scattering factors for non-hydrogen atoms from ref 22 (for hydrogens from ref 23) and the anomalous dispersion terms f' and f'' for Fe and S from ref 24; final least-squares refinements anisotropic for all non-hydrogens (hydrogens not refined), on F with $1/\sigma^2(F_o)$ weights and rejection of $3\sigma(F_o)$ "LTLT" less-thans (both F_o and $F_c < 3\sigma(F_o)$). The final coordinates and U_{eq}'s are given in Tables I (III) and II (IV), and the atom designations in Figures 1 and 2. Tables of F_o, F_c, $\sigma(F_o)$, and U_{ij} are available as supplementary material.

Trisulfane III: red; equant rhombohedron; about 0.52 × 0.52 × 0.78 mm, mounted along a; monoclinic; absences $0k0$, k odd, indicating space group $P2_1$ or $P2_1/m$ ($P2_1$ established by the structure). Unit cell: 30 reflections centered only at $+2\theta$ gave $a = 6.645$ (3) Å, $b = 12.113$ (5) Å, $c = 10.753$ (4) Å, $\beta = 91.86$ (5)°, $V = 865.1$ (6) Å^3, $Z = 2$, and $d_{calcd} = 1.040$ (2) g/cm^3. We believe a, b, and c are too small, because of the strong absorption and comparatively large size of the specimen, but by less than 0.1%. Intensities: 2841 inequivalent reflections counted in the range $5° < 2\theta < 60°$ ($+h$, $+k$, $\pm l$); 5 standards monitored every 150 reflections (no trends, $p = 1\%$); absorption corrections by program ABSCOR ($\mu_c = 2.08$ mm^{-1}).

All non-H's were located on difference maps after the iron and sulfur atoms had been found from the Patterson; isotropic ($U = 0.12$ Å^2) H's were placed in the Cp planes at C–H = 0.98 Å with equal H–C–C angles. Final statistics: 2728 contributing reflections; GOF = 1.56; less-thans rejected 55, included 316 (GTLT's); 58 rejected out-liers with X-RAY "WDF" (labeled and described in X-RAY as $(F_o - |F_c|)/\sigma(F_c)$ but actually this multiplied by the F_{rel} scale factor) > 5.8 (13.9 corrected for F_{rel} scale factor = 0.417, and 8.9 = 13.9/1.56 if adjusted for GOF); $R = 0.062$ and $R_w = 0.064$ ($R_w^2 = \sum w(F_o - |F_c|)^2/\sum w(F_o)^2$); last-cycle shift/error average for all the variables 0.11, maximum 0.45; maximum excursion, final difference map, 0.7 e/Å^3 near an iron atom, 0.5 otherwise. The "rejected" out-liers were retained both in the R values and in the difference map.

Tetrasulfane IV: small red crystal, 0.25 × 0.25 × 0.3 mm, mounted approximately along b; monoclinic; systematic absences hkl, $h + k + l$ odd, and $h0l$, l odd, indicating space group Ic or $I2/c$ (actual group $I2/c$). Fifteen reflections, centered at both $\pm 2\theta$ gave $a = 22.72$ (5) Å, $b = 11.37$ (6) Å, $c = 7.14$ (5) Å, $\beta = 98.9$ (2)°, $V = 1822$ (16) Å^3, $Z = 4$, and $d_{calcd} = 1.059$ (9) g/cm^3. Intensity measurements: 1196 inequivalent reflections ($\pm h$, $+k$, $+l$) in the range $2° < 2\theta < 45°$; 3 standards every 200 reflections ($p = 0.7\%$, no trends). We had intended to make more intensity measurements after finding the structure, but by then, 1.5 months later, the crystal had deteriorated hopelessly.

The early chemical evidence and analyses seemed to indicate that substance IV was an isomer of III. This and taking the space group to be Ic, rather than Ic or $I2/c$, were confusing, but the Patterson and trial density maps eventually showed that the molecule has four sulfur atoms and led to the correct general structure in Ic. The structure was refined in both space groups. The agreement with the observed intensities was a trifle better for the acentric, but the centric is shown to be correct by the much more regular (and reasonable) bond lengths and angles it affords. The acentric combinations of the deviations of the acentric from the centric structure were large but the centric combinations were small, in the pattern described by Marsh and Schomaker.[26] (Many substantially different acentric "solutions" could no doubt be found, all agreeing on the centric averages and all wrong.) For the final refinement, the hydrogens were placed as before, but at C–H = 0.99 Å with $U = 0.10$ Å^2. Final details: 877 contributing reflections; GOF = 2.17; less-thans excluded 112, included 128 (GTLT's); 207 rejected out-liers with "WDF" > 6.0 (6.1 corrected

Table I. Table of Coordinates for III

	x	y	z	10^2U_{eq},[a] Å^2
Fe1	0.24054 (11)	0.0000	0.47214 (6)	4.93
Fe2	0.38833 (11)	0.26703 (51)	0.02196 (7)	5.52
S1	0.32126 (23)	0.17732 (12)	0.42171 (13)	5.79
S2	0.52810 (22)	0.13132 (12)	0.14362 (12)	6.27
S3	0.57843 (21)	0.18340 (14)	0.32282 (13)	6.59
O16	0.0489 (7)	0.0837 (4)	0.6932 (4)	9.52
O17	0.6275 (7)	−0.0244 (4)	0.6045 (4)	9.46
O26	0.5933 (10)	0.1614 (5)	−0.1799 (4)	13.32
O27	0.7046 (7)	0.4219 (4)	0.0900 (6)	11.54
C11	0.2420 (13)	−0.1623 (5)	0.4051 (7)	8.50
C12	0.0418 (14)	−0.1305 (7)	0.4455 (6)	9.95
C13	−0.0193 (11)	−0.0425 (6)	0.3674 (9)	8.64
C14	0.1270 (16)	−0.0253 (6)	0.2870 (6)	9.13
C15	0.2869 (11)	−0.0926 (6)	0.3104 (6)	8.10
C16	0.1246 (10)	0.0529 (5)	0.6049 (6)	6.64
C17	0.4776 (9)	−0.0138 (5)	0.5528 (5)	6.36
C21	0.1776 (9)	0.3884 (5)	−0.0309 (7)	7.68
C22	0.1306 (11)	0.2892 (6)	−0.0895 (6)	8.62
C23	0.0923 (9)	0.2101 (6)	0.0014 (8)	8.67
C24	0.1129 (8)	0.2580 (7)	0.1149 (7)	7.85
C25	0.1723 (9)	0.3703 (7)	0.1004 (7)	8.63
C26	0.5137 (12)	0.2049 (6)	−0.1009 (6)	8.26
C27	0.5857 (9)	0.3598 (5)	0.0626 (6)	7.14

[a] Esd's for the U_{eq} are of the order of 10%.

Table II. Atomic Coordinates for IV

	x	y	z	10^2U_{eq},[a] Å^2
Fe	−0.13895 (4)	0.26600 (9)	−0.00202 (13)	4.76
S1	−0.07961 (8)	0.26419 (20)	0.28565 (23)	5.70
S2	−0.03411 (9)	0.11156 (21)	0.33306 (27)	6.73
O6	−0.2307 (3)	0.3666 (6)	0.1871 (9)	9.70
O7	−0.1743 (3)	0.0229 (6)	0.0492 (9)	9.71
C1	−0.1471 (4)	0.2530 (10)	−0.2976 (11)	7.73
C2	−0.1636 (4)	0.3654 (10)	−0.2493 (11)	7.72
C3	−0.1121 (5)	0.4184 (8)	−0.1376 (10)	7.63
C4	−0.0657 (4)	0.3316 (10)	−0.1183 (11)	7.28
C5	−0.0865 (5)	0.2331 (10)	−0.2179 (11)	9.15
C6	−0.1943 (3)	0.3195 (9)	0.1100 (11)	7.19
C7	−0.1604 (3)	0.1188 (9)	0.0334 (10)	6.58

[a] Esd's for the U_{eq} are of the order of 10%.

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Table III. Bond Lengths (Å) and Angles (deg) for III

Fe1-C11	2.094 (7)	Fe2-C21	2.096 (7)
Fe1-C12	2.074 (9)	Fe2-C22	2.076 (7)
Fe1-C13	2.095 (8)	Fe2-C23	2.090 (7)
Fe1-C14	2.128 (7)	Fe2-C24	2.117 (6)
Fe1-C15	2.100 (7)	Fe2-C25	2.101 (7)
av	2.098 (19, 9)[a]	av	2.096 (15, 7)
av of 10	2.097 (16, 5)		
Fe1-C16	1.765 (6)	Fe2-C26	1.755 (7)
Fe1-C17	1.781 (6)	Fe2-C27	1.771 (6)
av	1.773 (19, 9)	av	1.763 (11, 8)
av of 4	1.768 (11, 5)		
Fe1-S1	2.283 (2)	Fe2-S2	2.280 (2)
av of 2	2.282 (2)		
S1-S3	2.043 (2)	S2-S3	2.045 (2)
av of 2	2.044 (1, 1)		
C16-O16	1.150 (8)	C26-O26	1.144 (9)
C17-O17	1.132 (7)	C27-O27	1.124 (8)
av	1.141 (13, 9)	av	1.134 (14, 10)
av of 4	1.138 (14, 10)		
C11-C12	1.465 (13)	C21-C22	1.388 (10)
C12-C13	1.409 (12)	C22-C23	1.398 (11)
C13-C14	1.338 (12)	C23-C24	1.354 (11)
C14-C15	1.357 (12)	C24-C25	1.426 (12)
C15-C11	1.364 (10)	C25-C21	1.430 (11)
av	1.387 (51, 23)	av	1.399 (31, 14)
av of 10	1.398 (36, 11)		
Fe1-C16-O16	177.6 (6)	Fe2-C26-O26	178.0 (7)
Fe1-C17-O17	178.8 (6)	Fe2-C27-O27	176.9 (6)
av	178.2 (8, 6)	av	177.4 (8, 6)
av of 4	177.8 (8, 4)		
Fe1-S1-S3	111.37 (9)	Fe2-S2-S3	111.68 (9)
av of 2	111.52 (21, 16)		
C16-Fe1-C17	92.4 (3)	C26-Fe2-C27	95.3 (3)
av of 2	93.8 (21, 14)		
S1-Fe1-C16	87.9 (2)	S2-Fe2-C26	85.9 (2)
S1-Fe1-C17	89.6 (2)	S2-Fe2-C27	91.8 (2)
av	88.8 (12, 8)	av	88.8 (42, 30)
av of 4	88.8 (25, 18)		
S1-S3-S2	111.43 (9)		
C15-C11-C12	106.3 (6)	C25-C21-C22	107.6 (6)
C11-C12-C13	105.6 (7)	C21-C22-C23	108.7 (6)
C12-C13-C14	107.6 (7)	C22-C23-C24	108.7 (7)
C13-C14-C15	111.6 (7)	C23-C24-C25	109.3 (7)
C14-C15-C11	108.8 (7)	C24-C25-C21	105.7 (6)
av	108.0 (24, 11)	av	108.0 (14, 6)
av of 10	108.0 (18, 8)		
C16-Fe1-S1-S3	151.3 (2)	C26-Fe2-S2-S3	149.9 (3)
av of 2	150.6 (10, 7)		
C17-Fe1-S1-S3	58.8 (2)	C27-Fe2-S2-S3	54.7 (2)
av of 2	56.7 (30, 21)		
Fe1-S1-S3-S2	74.47 (11)	Fe2-S2-S3-S1	80.52 (11)
av of 2	77.5 (43, 30)		

[a] For the averages in this table and Table IV the esd's are for a single value, $\sigma_1{}^2 = \Sigma(\nu_i - \langle\nu\rangle)^2/(n-1)$, and the average itself, $\sigma_n = \sigma_1/n^{1/2}$.

Table IV. Bond Lengths (Å) and Angles (deg) for IV

Fe-C1	2.095 (8)	C1-C5	1.426 (14)
Fe-C2	2.099 (9)	C2-C1	1.390 (16)
Fe-C3	2.120 (9)	C3-C2	1.442 (12)
Fe-C4	2.109 (9)	C4-C3	1.436 (14)
Fe-C5	2.124 (10)	C5-C4	1.372 (15)
av	2.109 (13, 6)[a]	av	1.413 (31, 14)
Fe-C6	1.705 (9)	C6-O6	1.189 (11)
Fe-C7	1.772 (11)	C7-O7	1.146 (13)
av	1.738 (48, 34)	av	1.168 (30, 22)
Fe-S1	2.276 (2)	S1-S2	2.022 (3)
		S2-S2	2.093 (3)
C5-C1-C2	109.1 (9)	S1-S2-S2	108.03 (13)
C1-C2-C3	107.2 (8)	C6-Fe-S1	87.5 (3)
C2-C3-C4	106.7 (8)	C7-Fe-S1	90.0 (2)
C3-C4-C5	108.8 (8)	av	88.8 (18, 12)
C4-C5-C1	108.1 (10)	C6-Fe-S1-S2	133.68 (36)
av	107.98 (102, 46)	C7-Fe-S1-S2	41.90 (30)
Fe-C6-O6	174.0 (9)	Fe-S1-S2-S2	74.16 (14)
Fe-C7-O7	177.4 (7)	S1-S2-S2-S1	50.95 (14)
av	175.7 (24, 17)		
C6-Fe-C7	91.8 (4)		
Fe-S1-S2	112.02 (11)		

[a] See footnote *a* in Table III.

for F_{rel} scale factor = 0.981; 2.8 if adjusted for GOF); R = 0.069 and R_w = 0.079; last-cycle shift/error average for all variables 0.16, maximum 0.72; maximum excursion, final difference map, 0.8 e/Å^3. The rejected out-liers were retained in the R values and the difference map. No absorption corrections (μ_c = 2.08 mm^{-1}; range of A for small 2θ about 0.54–0.59).

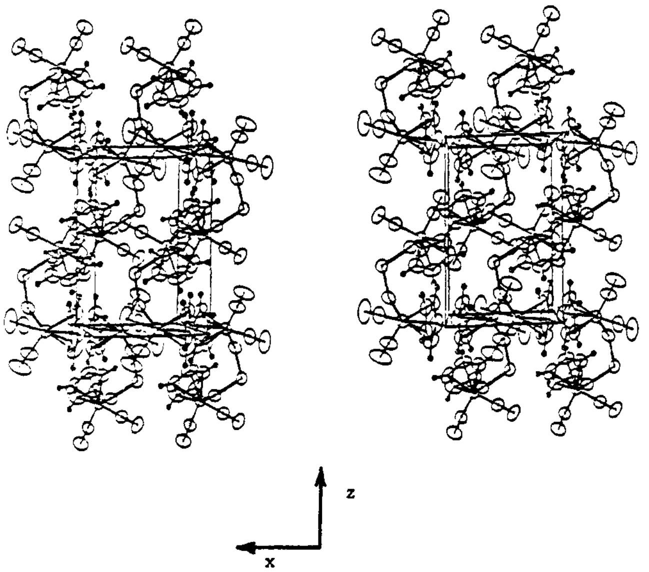

Figure 3. Stereoview of the unit cell and packing of III.

Discussion of the Structures. By and large the details of the two molecular structures agree very well (see Tables III and IV and Figures 1 and 2, where corresponding C's and O's have analogous numbers) and are fairly conventional, as can be gathered from the sample comparisons afforded by Table V. The approximate 2-fold symmetry of the molecule of III includes the orientations of the Cp's (which lie trans to each other, each with a C approximately cis to adjacent S) as well as the bond angles and bond lengths and even much of the deviation from perfect local 2-fold or 5-fold symmetry in the CpFe(CO)$_2$ groups, although the irregularities of the intraring C–C and C–C–C values do not conform. The agreement of the halves of III with IV, which has crystallographic 2-fold symmetry, includes the FeSSS torsion angle, the orientation of the Cp, and even, it seems a considerable part of the irregularities of the Cp's and CO's. What may be both extraordinary and lacking of explanation are the small SSSS torsion angle and differing S–S lengths in IV. IV packs differently from III (Figures 3 and 4), the interior sulfurs forming tight columns about the glide plane along c, each being in rather close contact (3.66 Å) with one other across the glide plane in such a way as would squeeze down the torsion angle if the short contact were sufficiently repulsive. This is doubtful, because intermolecular contacts as short as about 3.35 Å occur in several forms of elemental sulfur, but hardly impossible in view of the wide range of contact distances in such simple nominally molecular crystals as Cl$_2$, Br$_2$, I$_2$, and the allotropes of sulfur.[29] In any case, the torsion angle is unusually small,

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Table V. Comparisons of Distance (Å) and Angle (deg) Averages

	X-S[a]	S-S	XSS	SSS	XSSS	SSSS	Fe-Cp	C-C	Fe-CO	C-O	Fe-CO
III	2.282	2.042	111.5	111.5	77.5		2.097	1.398	1.768	1.138	177.8
IV	2.276	2.021, 2.093	112	108	74.2	51.2	2.109	1.413	1.74	1.17	176
Na_2S_4[b]		2.074, 2.061		109.8		97.8					
$Ba_2S_4 \cdot H_2O$[c]		2.074, 2.062		104.1		76.4					
S_8, orthorhombic[d]		2.060		108.0		98.7					
S_6, rhombohedral[d]		2.057		102.2		74.5					
S_{12}[d]		2.053		106.5		86.1					
S[d]		2.066		106.0		85.3					
$FeCpSnCl_3$[e]							2.092	1.409	1.785	1.130	176.5
$Cp_2Fe_2(S_2)_2(CO)$[f]	2.27	1.99	114				2.12[n]	1.44[n]	1.70	1.12	173
$[CH_3SFe_2(CO)_6]_2S$[g]	2.274, 2.248								1.74	1.18	176
2,2-$(ICH_2CH_2)_2S_3$[h]	1.86	2.05	98	113	82						
$(CH_3)_2S_3$[i]	1.78	2.04	104	104	93						
$[(SO_3)_2S_3]^{-2}$[j]	2.14	2.04	103	106	110						
$(C_5(CH_3)_5)_2TiS_3$[k]	2.413	2.041	76.3	105.3	49						
$(CH_3C_5H_4)_4Ti_2S_6$[l]	2.425	2.056	115.4	109.1	64.6						
$(SO_3)_2S_4^{-2}$[m]	2.10	2.04, 2.04	101	111	107	91					

[a] "X" stands for "Fe" or the other atom at the end of a sulfane chain. [b] Reference 27. [c] Reference 28. [d] Reference 29. [e] Reference 30. [f] Reference 31. [g] Reference 32. [h] Reference 33. [i] Reference 34. [j] Reference 35. [k] Reference 36. [l] Reference 8. [m] Reference 37. [n] One $C_5H_4CH_3$ disordered, not included.

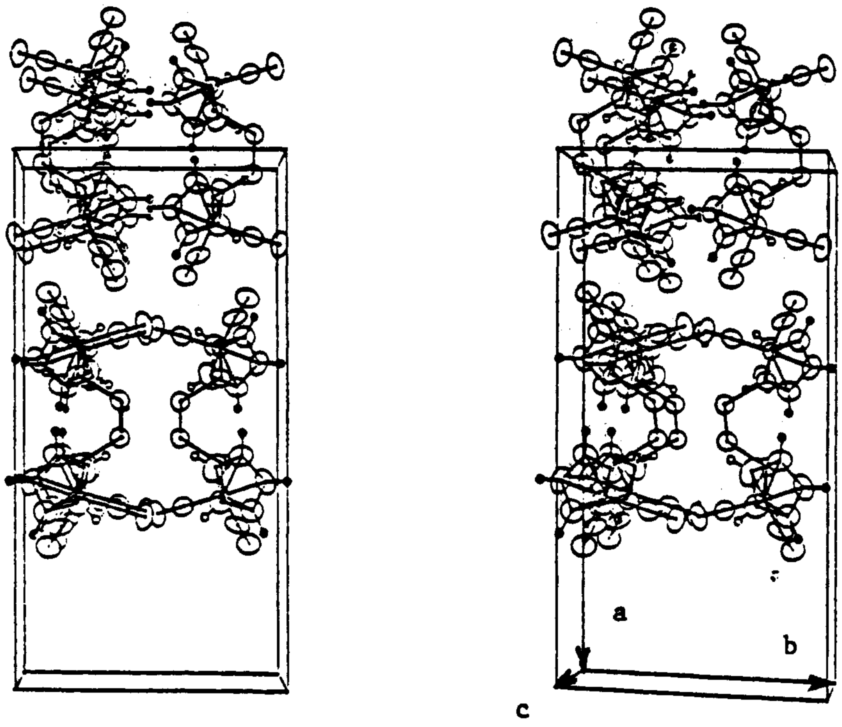

Figure 4. Stereoview of the unit cell and packing of IV.

whereas the S–S difference, though many times its esd, is perhaps not beyond doubt. It is, it happens, in pretty good agreement with Hordvik's[38] curve of S–S vs. XSSY angle, from which we read off 2.04 Å for S1–S2 and 2.08 Å for S2–S2. Unfortunately, the extensive citations of Hordvik's curve, though largely accepting it, show that it cannot be taken as the last word on S–S distances.

Results and Discussion

In light of the well-known tendency of sulfur to catenate[39] (particularly under reducing conditions), it should not have been a surprise that products were formed that contained numbers of sulfur atoms different from those of the reagents. The most commonly encountered sulfane product was the three-sulfur-bridged complex III. This was the major product of reaction NaFp with SCl_2, S_2Cl_2, or even $SOCl_2$. Reactions of the sulfur nucleophiles Li_2S_2 and Li_2S_4 with FpBr also gave III, as did reaction of H_2S with FpBr in the presence of triethylamine. The trisulfane complex, III, was the only sulfane product isolable from the redox reaction of Fp_2 with sulfur.

The three-sulfur-bridged complex, III, readily crystallizes from petroleum ether solutions as red-brown crystals. It is fairly stable as a solid but in solution is sensitive to both air and light. It and the other organoiron sulfanes encountered in this study can be easily distinguished by their characteristic ^1H NMR spectra and chromatographic behavior; see Table VI. Its ready crystallization may in part account for its isolation from so many different reaction procedures, but III does appear to be more stable than the other sulfanes. At elevated temperature (110 °C for 8 h), III is converted almost

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Table VI

(a) Properties of the Bis(cyclopentadienyliron dicarbonyl) Sulfanes

compd	color	R_f[a]	mp, °C	IR ν_{CO}, cm^{-1}		visible λ,[d] nm
				b	*c*	
IV	bright red	0.26	79–80	2033 1992	2022 1995 1960	389 283 (sh)
III	deep red	0.32	104–105	2028 1987	2039 2020 1993 1974	450
II	red-brown	0.44		2025 1984	2015[e] 1987 1975	400

(b) ^{1}H NMR and ^{13}C NMR Spectra of the Bis(cyclopentadienyliron dicarbonyl) Sulfanes

compd	solvent	^{1}H NMR δ	^{13}C NMR[f] δ
IV	acetone-d_6	5.35 (Cp, s)	
	chloroform-d_1	5.19 (Cp, s)	86.48 (Cp, s), 212.74 (CO, s)
III	acetone-d_6	5.4 (Cp, s)	
	chloroform-d_1	5.18 (Cp, s)	86.11 (Cp, s), 213.11 (CO, s)
II	acetone-d_6	5.2 (Cp, s)	
	chloroform-d_1		86.36 (Cp, s), 212.47 (CO, s)
I	acetone-d_6	5.1 (Cp, s)	

[a] 50% diethyl ether in petroleum ether used as eluent. [b] CH_2Cl_2. [c] Nujol mull. [d] In diethyl ether. [e] Thin film. [f] ^{1}H decoupled.

quantitatively to $(CpFeS)_4$, a molecule featuring an iron–sulfur cube reminiscent of the "box" in ferredoxin and related enzymes. $(CpFeS)_4$ has been previously prepared by reacting Fp_2 with propylene sulfide[19a] and by prolonged thermolysis of Fp_2 with sulfur.[19b] In light of our results it is reasonable to conclude that organoiron sulfanes such as III were probably intermediates in these syntheses of $(CpFeS)_4$.

The tetrasulfane complex IV can also be crystallized from petroleum ether solution. It forms bright red-brown crystals, which slowly decompose in air. In solution at room temperature it gradually converts to III. Compound IV could be isolated from reactions of NaFp with S_2Cl_2 or from reactions of Li_2S_4 with FpBr. It was also detected chromatographically among the products of reaction of Fp_2 with sulfur.

The original target molecule, the two-sulfur-bridged complex, II, only appeared as a product in reactions of FpBr with Li_2S or Li_2S_2. Despite numerous attempts at crystallization, II could only be isolated as a dark red-brown oil. It is moderately air sensitive and in solution even under nitrogen steadily decomposes. Fp_2 and sulfur are among its decomposition products.

Since we were unable to secure crystals of II, its structural identification was difficult. There are no readily accessible spectral features to indicate the number of sulfur atoms in the molecule. However, it proved possible to virtually titrate the number of sulfur atoms in these organoiron sulfane complexes by monitoring their reactions with triphenylphosphine by ^{1}H NMR. It has long been known that triphenylphosphine can desulfurize organic trisulfanes to give disulfides,[40] as in eq 1.

$$R{-}SSS{-}R + P(C_6H_5)_3 \rightarrow R{-}SS{-}R + S{=}P(C_6H_5)_3 \quad (1)$$

Triphenylphosphine has also been used to desulfurize organometallic clusters[41,8] as in eq 2. Thus, it was expected that

$$Cp_4Co_4S_6 + 2P(C_6H_5)_3 \rightarrow Cp_4Co_4S_4 + 2S{=}P(C_6H_5)_3 \quad (2)$$

careful quantitative reaction of triphenylphosphine with our organoiron sulfane complexes might provide an indication of the number of sulfur atoms per molecule.

In benzene-d_6 in a sealed NMR tube at room temperature the trisulfane complex reacted rapidly with 1 equiv of triphenylphosphine. However, examination by ^{1}H NMR indicated that, besides complete conversion of the triphenylphosphine to triphenylphosphine sulfide, the reaction products consisted of 0.5 equiv of unreacted III and a new organoiron complex indicated by a Cp resonance at δ 5.1. The new complex was subsequently deduced to be the monosulfane complex $(\mu\text{-}S)[CpFe(CO)_2]_2$ (I). Reacting III with 2 equiv of triphenylphosphine yielded only the new complex and 2 equiv of triphenylphosphine sulfide. Reacting III with 3 equiv of triphenylphosphine resulted in complete desulfuration of the complex, giving 1 equiv of the sulfurless dimer Fp_2 and 3 equiv of triphenylphosphine sulfide.

Thus it appears that the disulfane, II, if formed in these desulfurization reactions, is much more readily desulfurized than either the trisulfane or the monosulfane. Of course, identification of the new complex indicated by the ^{1}H NMR peak at δ 5.1 as the previously unobserved monosulfane, I, is implicit in the stoichiometries.

The red-brown oily product, tentatively identified as the disulfane, could also be titrated with triphenylphosphine. Reaction with 1 equiv of triphenylphosphine gave the monosulfane and triphenylphosphine sulfide, while reaction with 2 equiv of triphenylphosphine gave just Fp_2 and 2 equiv of triphenylphosphine sulfide. Again, the stoichiometries of these reactions along with the spectral features, Table VI, clearly confirm the identification of the oily product as the disulfane complex.

Thus, we were able to prepare and characterize either by single-crystal X-ray crystallography or by chemical inference an entire series of neutral, binuclear organometallic sulfane complexes of the form $(\mu\text{-}S_x)Fp_2$ (x = 1–4). In each of these complexes the sulfur chain is a simple bidentate, bridging ligand with other lone pairs accessible for further ligation. The complexes could be prepared by straightforward nucleophilic substitution reactions, although catenation (or decatenation) of sulfur was commonly encountered. We are presently engaged in extending the methodology to the analogous preparation of organometallic sulfanes with other metals and in attempting to produce heteronuclear cluster complexes by further ligation of the sulfurs in these organoiron sulfanes.

Acknowledgment. The work was supported by grants from the Graduate School Research Fund of the University of Washington and the M. J. Murdock Charitable Trust of the Research Corp. We also wish to thank Judy Schomaker for help in preparing the manuscript.

Registry No. I, 85202-55-7; II, 80711-20-2; III, 80711-21-3; IV, 80711-22-4; NaFp, 12152-20-4; $CpFe(CO)_2Br$, 12078-20-5; $(CpFeS)_4$, 64314-90-5; SCl_2, 10545-99-0; $SaCl_2$, 10025-67-9; $SOCl_2$, 7719-09-7; Li_2S, 12136-58-2; Li_2S_2, 51148-09-5; Li_2S_4, 74321-15-6; H_2S, 7783-06-4; sulfur, 7704-34-9.

Supplementary Material Available: Tables of F_o, F_c, $\sigma(F_o)$, U_{ij}'s, and hydrogen atom coordinates (39 pages). Ordering information is given on any current masthead page.

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(42) R_f = distance moved by compound/distance moved by solvent front.