carbonyls, the National Science Foundation for a grant in support of this research, and the University of California at Berkeley Mass Spectrometric Facility for mass spectrometric data. We also thank the Miller Institute for Basic Research in Science for a grant in the form of a Miller Professorship (to E.L.M.).

Registry No. H_2, 1333-74-0; CO, 630-08-0; $Os_3(CO)_{12}$, 15696-40-9; BBr_3, 10294-33-4; BCl_3, 10294-34-5; CH_3Br, 74-83-9; C_2H_5Br, 74-96-4; $Os_2(CO)_6Br_4$, 17731-88-3; $Os(CO)_3Br_2(NCCH_3)$, 77590-16-0; $Os_3(CO)_{10}Cl_2$, 28109-18-4; $Os_2(CO)_6Cl_4$, 17633-40-8; CH_4, 74-82-8; C_2H_4, 74-85-1; C_2H_6, 74-84-0; C_3H_8, 74-98-6; *i*-C_4H_{10}, 75-28-5; *neo*-C_5H_{12}, 463-82-1.

Supplementary Material Available: Figures 1–3, the mass spectra of $Os_2(CO)_6Br_4$, $Os_2(CO)_6Cl_4$, and $Os_3(CO)_{10}Cl_2$ (3 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Reactions of Iron–Sulfur Clusters Containing the S_2 Ligand: $[Cp_2Fe_2(S_2)(SR)_2]^{0,1+}$, $[Cp_4Fe_4S_5]^{0,1+,2+}$, and $[Cp_4Fe_4S_6]$

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Syntheses of the following disulfide-containing dinuclear and tetranuclear organoiron compounds are described: $[Cp_2Fe_2(S_2)(SR)_2]^{0,1+}$, $[Cp_4Fe_4S_5]^{0,1+,2+}$, and $[Cp_4Fe_4S_6]$ (Cp = η^5-C_5H_5). The compounds have been characterized by spectroscopic, electrochemical, and chemical properties. Temperature-dependent ^1H NMR spectroscopy indicates fluxionality of the triply bridging disulfide ligand in $Cp_4Fe_4S_5{}^n$ (n = 0 and 2+). The cluster products resulting when these disulfide-containing complexes are chemically or electrochemically oxidized, including $[CpFe(SR)(NCMe)]_2{}^{2+}$, and adducts formed with other metals via the electron-rich disulfide ligands are discussed.

Introduction

The extreme versatility of sulfur as a ligand has been well established. A variety of complexes containing elemental sulfur (S, S_2, S_5, etc.) have been reported, and new modes of bonding have recently been characterized.[1] One reason for our interest in such systems is the potential for a rich and extensive redox chemistry and the differences in structure observable for pairs of a redox couple. Structural studies of the members of a reversible redox couple can lead to a better understanding of the bonding of these materials as well as their physical and chemical properties. Previous studies have shown that the structural features observed to vary upon changing the molecular oxidation state of transition-metal clusters usually involve metal–metal interactions.[2] This has been demonstrated, for example, in the case of $[Cp_2Fe_2(SEt)_2(S_2)]$,[3] which possesses an unprecendented planar FeSSFe geometry (Figure 1).[4] There are several features which we have found interesting in this and other disulfide-containing species. Among these are the following: (1) they undergo several electron oxidation state changes without complete structural change; (2) the disulfur ligands are electron rich and have the ability to form donor–acceptor complexes; (3) an understanding of the reactivity of these coordinated ligands could lead to an understanding of the mechanisms of some processes involving metal clusters, such as catalysis.

In part, a motivation behind these studies resides in the considerable interest in new modes of cluster configurations as potential models for the active sites in complex metalloenzymes, nature's catalysts. Obviously, a better understanding of the relationship between the structure of the metal centers in complex biochemical systems and their function could lead to new materials for energy storage, energy transfer, and catalysis . Although we feel it is premature to attempt a direct comparison of the configurations demonstrated by the compounds reported here and specific biochemical species, we feel that disulfur-containing clusters should not be ruled out as being involved in some active sites of metalloenzymes.

We have directed our efforts to the synthesis and characterization of dinuclear and tetranuclear organoiron-containing cluster compounds which feature bridging disulfur (S_2) ligands. Resulting compounds reported here include the dinuclear species $[Cp_2Fe_2(S_2)(SR)_2]^n$ [R = Me (**1a**), Et (**1b**), Bzl (**1c**); n = 0, 1+; Cp = η-C_5H_5] and the tetranuclear species $[Cp_4Fe_4S_5]^n$ (**5**; n = 0, 1+, 2+) and $[Cp_4Fe_4S_6]$ (**6**). Some chemical and electrochemical properties of these compounds are described as well. We also report variable-temperature ^1H NMR evidence for fluxionality in the bonding of the triply bridging disulfide ligand in **5** and its corresponding dication $[\mathbf{5}]^{2+}$.

Experimental Section

Materials and Methods. $[CpFe(CO)_2]_2$ was obtained from Strem Chemical Co. or Pressure Chemical Co. and was recrystallized from CH_2Cl_2–hexane under nitrogen before use. $[CpFe(CO)_2]_2$ is nearly black when purified in this manner, and its solutions are slightly air sensitive. Preparations of $[CpFe(CO)(SR)]_2$ were based on the literature methods.[5] Except as noted, all commercially purchased solvents and chemicals were used as received. PF_6^- and SbF_6^- salts were obtained from the Ozark-Mahoning Co.

The reactions described below have been carried out at an altitude of 7100 ft (atmospheric pressure ~590 mmHg) except for those involving Et_2S_x. The boiling points of solvents (hence reflux temperatures) are lower than the values at standard pressure. All reactions and manipulations of solutions were performed in a nitrogen atmosphere, except where noted.

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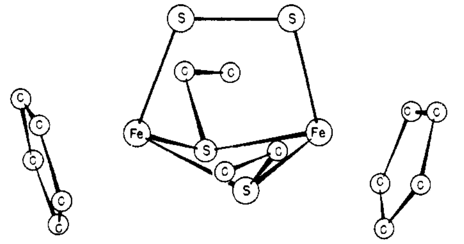

Figure 1. Molecular structure of **1b**, as reported in ref 4.

Physical Measurements. Elemental analyses were performed by Galbraith Laboratories and are given in Table I along with conductivity data which were measured with a Barnstead Model PM 70CB conductivity bridge. Proton NMR and infrared spectra were recorded on Varian A-60, EM-360, and EM-390 and Perkin-Elmer 521 spectrometers and are given in Table II. The UV-vis spectra were taken on a Cary 14 instrument, and the corresponding data are given in Table III. Mass spectra were obtained by using a CED 21-110 instrument with the sample introduced via a heated direct-introduction probe at 160 °C. Electrochemical experiments were carried out on a Princeton Applied Research Model 170 electrochemistry system with conventional three-electrode configurations.

Preparation of Ethyl Polysulfides. The method used by Bloomfield[6] for preparing diethyl tetrasulfide was followed. A solution of 32 mL (0.4 mol) of sulfur monochloride (Research Organic Chemicals) in 250 mL of CS_2 was slowly added to a solution of 62 mL (0.84 mol) of ethanethiol (Alrich Chemical Co.) in 550 mL of CS_2. As soon as the brisk evolution of HCl had subsided, the solution was gently boiled for 30 min under reflux. The solvent was removed under reduced pressure, and the residue was vacuum distilled at approximately 0.2 torr. The first 6 mL of distillate was discarded, the next 35 mL were collected in the boiling range 62–72 °C, and a final 12-mL fraction boiled at 72–74 °C. Elemental analysis indicated that the 62–72 °C fraction (sp gr 1.15 g/mL) consisted of approximately 70% Et_2S_3 and 30% Et_2S_4, while the 72–74 °C fraction was presumably nearly pure Et_2S_4. These compounds possess strong, persistent stenches and should be manipulated entirely within a fume hood.

Syntheses. In many cases a given reaction sequence describes the isolation of one or more compounds which were later found to be produced by more convenient rational synthetic routes, resulting in higher yields. In some instances it was found that some of the compounds could be readily interconverted. These are noted where appropriate.

Reaction of Et_2S_x with $[CpFe(CO)_2]_2$. Formation and Isolation of Iron–Sulfur Clusters. When 8 mL (9.2 g) of the polysulfide mixture containing primarily Et_2S_3, $[CpFe(CO)_2]_2$ (14 g, 41 mmol), and 170 mL of methylcyclohexane were refluxed for 11 h (or benzene for 23 h) with magnetic stirring, a dark green solution was produced, and a black precipitate formed. The reaction mixture was cooled and filtered.

The solution was chromatographed on a 3 × 70 cm alumina column. Development with benzene saturated with nitrogen produced two closely spaced broad bands: a deep blue band containing $Cp_2Fe_2(S_2)(SEt)_2$ (**1b**) followed by a green band due to $Cp_3Fe_3S_2(SEt)$ (**3**). The compounds were isolated by the following sequence of operations: removal of solvent from the benzene eluates, dissolution of the resulting black residue in 20 mL of CS_2, filtration, partial solvent removal, addition of 25 mL of hexane, and reduction of volume to ~10 mL. The yields based on $[CpFe(CO)_2]_2$ were 0.5 g (3%) for **1b** (mp 154–56 °C) and 0.4 g (3%) for **3** (mp 185 °C dec). These complexes are soluble in most organic solvents, especially CS_2 and CH_2Cl_2, and give green solutions which slowly decompose in the presence of air. They are air stable in the solid state, and large, well-formed single crystals of **1b** can easily be grown by slow cooling of CS_2–hexane solutions under nitrogen. When the above-described reaction in benzene was stopped after 12 h, the reaction mixture was found to contain $[CpFe(CO)(SEt)]_2$ as identified by infrared and NMR[5b] spectroscopy.

The black precipitate that formed in a reaction of $[CpFe(CO)_2]_2$ (7 g) and ethyl polysulfide (16 mL) in refluxing benzene (70 mL) for 19 h was extracted with 50 mL of chloroform. Removal of solvent yielded a black solid (0.5 g, 8% yield), the infrared spectrum of which

Table I. Analytical and Conductivity Data[a]

compd	% C	% H	% Fe	% S	% N	% halide	% other	molar conductivity[b]
$Et_2S_{3,3}$ [c]	29.3 (29.3)	6.2 (6.3)		64.5 (64.5)				
Et_2S_4 [d]	26.1 (25.8)	5.3 (5.3)		68.6 (68.9)				
$Cp_2Fe_2(S_2)(SMe)_2$ (**1a**)	36.1 (36.0)	4.1 (4.0)	27.6 (27.9)	32.1 (32.1)				
$Cp_2Fe_2(S_2)(SEt)_2$ (**1b**)	39.4 (39.3)	4.8 (4.7)	26.0 (26.1)	29.9 (29.9)				
$Cp_2Fe_2(S_2)(SBzl)_2$ (**1c**)	50.8 (52.2)	4.4 (4.4)	18.0 (20.2)	22.9 (23.2)				
$[CpFe(NCCH_3)(SMe)]_2[PF_6]_2$ (**2a**)	27.4 (27.1)	3.3 (3.1)	15.7 (15.7)	9.6 (9.0)	4.0 (3.9)		8.7 (8.7)[e]	
$[CpFe(NCCH_3)(SEt)]_2[PF_6]_2$ (**2b**)	29.3 (29.4)	3.6 (3.6)	15.0 (15.2)	8.7 (8.7)	3.8 (3.8)	30.8 (31.0)	8.5 (8.4)[e]	316
$Cp_3Fe_3S_2(SEt)$ (**3**)	41.4 (41.8)	4.0 (4.1)	34.5 (34.3)	20.3 (19.7)				
$Cp_4Fe_4S_5\cdot 0.5CH_2Cl_2$ (**5**)	35.9 (35.9)	3.0 (3.1)	31.7 (32.5)	22.6 (23.3)		4.9 (5.2)		
$Cp_4Fe_4S_6$ (**6**)	35.2 (35.5)	3.2 (3.0)	32.2 (33.0)	26.0 (28.4)				
$[Cp_2Fe_2(S_2)(SEt)_2Ag_2(NCCH_3)_4][SbF_6]_2$	20.3 (20.6)	2.3 (2.5)	9.2 (8.7)	10.5 (10.0)	4.3 (4.4)	15.1 (17.8)	16.9 (16.9)[f]	295
$[(Cp_4Fe_4S_6)_2Ag][SbF_6]_3$	23.2 (22.2)	2.1 (1.9)	19.3 (20.6)	16.8 (17.7)		14.5 (15.8)	4.5 (5.0)[f]	451
$[Cp_4Fe_4S_5][PF_6]$	30.8 (30.4)	2.7 (2.6)	26.8 (28.3)	18.7 (20.3)			3.5 (3.9)[e]	
$[Cp_4Fe_4S_5][PF_6]_2\cdot CH_3CN$	26.6 (27.1)	2.4 (2.4)	23.4 (22.9)	16.4 (16.4)			6.3 (6.4)[e]	309
$Cp_4Fe_4S_5\cdot 2SO_2\cdot 0.1CH_2Cl_2$	31.3 (30.9)	2.8 (2.6)	28.5 (28.6)	28.3 (28.7)		0.9 (0.9)		
$Cp_4Fe_4S_6\cdot 2SO_2\cdot 0.25CH_2Cl_2$	30.0 (29.5)	2.6 (2.5)	27.6 (27.1)	31.5 (31.1)		2.7 (2.1)		

[a] Elemental analyses performed by Galbraith Laboratories. The numbers in parentheses are the theoretical percentages. [b] Λ_M/Ω^{-1} cm^2 mol^{-1}, measured for 10^{-4}–10^{-3} M solutions in CH_3CN. [c] Distillate fraction with 62–72 °C boiling range. [d] Distillate fraction with 72–74 °C boiling range. [e] Percent P. [f] Percent Ag.

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Table II. Infrared and Proton NMR Data

	IR,[a] cm^{-1}			NMR,[b] τ		
compd	S-S	S-R	other	Cp	R	rel intens[c]
1a	513	1294[d]		5.29 (s)	10.05 (s, CH_3)	5:3
1b	507	1249[e]		5.27 (s)	9.87 (m, C_2H_5)	1:1
1c	516	1227[e]		5.67 (s)	3.02 (m), 3.44 (m, C_6H_5), 8.68 (s, CH_2)	5:5:2
2a			2301[g]	4.62 (s)	7.74 (s, CH_3)[f]	5:3
2b			2299[g]	4.62 (s)	7.51 (q, 7.3, CH_2), 8.25 (t, 7.3, CH_3)[f]	5:2:3
2c			2290[g]	4.68 (s)	2.40 (m, C_6H_5), 6.23 (s, CH_2)[f]	5:5:2
3		1249[e]		5.45 (s), 6.30 (s)	9.0 (m, C_2H_5)	1:2:1
5	525			5.12 (s), 5.57 (s)		1:3
5$\cdot 2SO_2$	484		1263, 1096, 536[h]	5.90 (s), 5.48 (s)		1:3
6	497, 509			5.18 (s), 5.67 (s)		1:1
6$\cdot 2SO_2$	470, 483		1250, 1090, 533[h]	5.15 (s), 5.65 (s)		1:1
$[Cp_2Fe_2(S_2)(SEt)_2][SbF_6]$	543	1249[e]				
$[Cp_2Fe_2(S_2)(SEt)_2Ag_2(NCCH_3)_4][SbF_6]_2$	493	1254[e]	2272[g]			
$[Cp_4Fe_4S_5][PF_6]_2\cdot CH_3CN$	466		2255[g]	4.15 (s), 4.20 (s), 4.83 (s)		2:1:1
$[(Cp_4Fe_4S_6)_2Ag][SbF_6]_3$	470, 487					
$[CpFe(CO)(SEt)]_2[SbF_6]_2$		1258[e]	2056[i]	3.93 (s)	6.55 (m, CH_2), 8.23 (t, 7.3, CH_3)	5:2:3
$[Cp_4Fe_4S_5][PF_6]$	520					

[a] For Nujol mulls between CsBr plates. [b] s = singlet, t = triplet, q = quartet, and m = multiplet; multiplicities, coupling constants (in hertz), and assignments are given in parentheses; reference Me_4Si. Solvents: CS_2 for **1a-1c** and **3**; $CDCl_3$ for **5**, **6**, **5**$\cdot 2SO_2$, and **6**$\cdot 2SO_2$; CD_3CN for the rest. [c] ^1H NMR signal ratios. [d] S-CH_3 symmetric deformation. [e] S-CH_2wag. [f] ^1H NMR signals due to coordinated CH_3CN occur at τ 7.93, 7.90, and 7.80, respectively, for **2a-c**. [g] ν(CN). [h] ν(SO). [i] ν(CO).

Table III. Electronic Spectral Data

compd	concn,[a] M	maxima,[b] nm
1a	6.7×10^{-4}	235 (25), 305 (11), 475 (2.4), 601 (2.0), 837 (3.5)
1b	7.0×10^{-4}	233 (28), 309 (12), 479 (2.8), 600 (2.1), 840 (4.4)
2b	4.1×10^{-4}	247 (24), 286 (10), 337 (12), 402 (6.1)
$[CpFe(CO)(SEt)]_2$	7.1×10^{-4}	319 (13), 460 (2.4) sh
$[Cp_2Fe_2(S_2)(SEt)_2][PF_6]$	8.4×10^{-3}	660 (2.7)
$[Cp_4Fe_4S_5][PF_6]_2$	1.6×10^{-2}	436 (4.4) sh, 660 (0.8) sh

[a] Acetonitrile solution. [b] Numbers in parentheses are ϵ/1000; sh = shoulder.

displayed no carbonyl stretching frequencies. However, its NMR spectrum in $CDCl_3$ showed four peaks in the cyclopentadienyl region, which were found to correspond to approximately equal amounts of $Cp_4Fe_4S_5$ (**5**) and $Cp_4Fe_4S_6$ (**6**). Isolation of **6** was effected by extraction of the black solid with acetone in a Soxhlet extractor for 2 days. The NMR spectrum of the resulting precipitate exhibited two sharp peaks of equal intensity at τ 5.18 and 5.67 due to **6** and weak peaks at τ 5.12 and 5.57 due to **5**. The composition of **6** was also substantiated by single-crystal X-ray diffraction methods.[1c,7] The undissolved solid remaining after chloroform extraction was treated with about 100 mL of boiling bromobenzene. Upon being cooled to 0 °C and allowed to stand for several days, the filtered bromobenzene solution deposited a black solid which was shown to be $[CpFeS]_4$ (**4**) by infrared spectroscopy.

Reaction of the polysulfide fraction containing primarily Et_2S_4 with $[CpFe(CO)_2]_2$ in refluxing benzene for 23 h gave only barely detectable amounts of **1b** and **3**.

Preparation of 1 by Reaction of $[CpFe(CO)(SR)]_2$ with S_8. A magnetically stirred mixture of $[CpFe(CO)_2]_2$ (30 g, 84 mmol), Et_2S_2 (51 g, 320 mmol), and methylcyclohexane (350 mL) was refluxed for 16 h. The resulting solution of $[CpFe(CO)(SEt)]_2$ was cooled, filtered to remove a black precipitate (pyrophoric when dry), and refluxed with S_8 (13.2 g, 51 mmol) for 3.5 h. After the reaction mixture was allowed to cool to about 40 °C, it was filtered to remove a black precipitate (which was later found to contain small amounts of **4**-**6**) and placed onto an alumina column (4 × 45 cm). Elution with deoxygenated benzene gave an initial yellow band of ferrocene, which was discarded, closely followed by the characteristic deep blue band of **1b**. No green band due to **3** was observed. The benzene eluate containing **1b** was collected, and the solvent was removed in vacuo. The residue was dissolved in about 30 mL of CS_2 and filtered. After partial solvent removal, 40 mL of ethanol was added, and the volume of the solution was reduced to 30-40 mL. The black crystalline precipitate of **1b** was collected on a frit, washed with a small amount of hexane, and air-dried. This material weighed 2.7 g (8% yield based on $[CpFe(CO)_2]_2$). **1a** and **1c** were prepared in an identical fashion. **1c** was difficult to separate from unreacted Bzl_2S_2, even with the use of chromatography. A pure sample of **1c** was obtained by oxidation of the crude material to $[CpFe(NCCH_3)(SBz)]_2[PF_6]_2$ (**2c**) and reaction of the latter with aqueous polysulfide (see below).

The products of the reactions of $[CpFe(CO)(SPh)]_2$ and $[CpFe(CO)(SeEt)]_2$[8] with S_8 were intractable.

Improved Preparation of 1. Better yields of **1** were obtained by a procedure which utilizes **2** (see below) as starting material. The example given is for **1b**.

A mixture of 20 mL of ammonium polysulfide solution (J. T. Baker, 20% "$(NH_4)_2S$") and 20 mL of methanol was added dropwise to a vigorously stirred solution of **2b** (7.36 g) in CH_3CN (300 mL). The solution was stirred an additional 30 min, during which time it became gray-green and deposited a brown precipitate. After all solvent was removed in vacuo, the residue was extracted with 150 mL of CS_2. Solvent removal from the filtered extract afforded 3.2 g of crude **1b**, which was purified by chromatography on alumina (4 × 20 cm). The compound, dissolved in a minimum amount of CS_2, was placed onto the column and eluted with deoxygenated benzene. The yield of **1b**, which was isolated from the eluate as described above, was 2.7 g (63%).

Aqueous sodium sulfide can be used instead of ammonium polysulfide in the preparation, but the resulting yield of **1** is lower (40%) unless the Na_2S solution contains some dissolved sulfur ($\sim 1/8$ mol of S_8/mol of Na_2S). Addition of a 2:1 molar ratio of "Na_2S_2" to **2** gave a 61% yield in the case of **1b** and a 44% yield in the case of **1c**. Reaction of **2** with aqueous Na_2Se gave an intractable product.

Preparation of $[CpFe(NCCH_3)(SR)]_2[PF_6]_2$ (2) from $[CpFe(CO)(SR)]_2$. Examples are given here for a large-scale preparation of **2b** and a small-scale preparation of **2a**. A magnetically stirred mixture of 49.4 g of $[CpFe(CO)_2]_2$, 85 mL of Et_2S_2, and 600 mL of

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(8) Rosenbuch, P.; Welcman, N. *J. Chem. Soc. A* **1972**, 1963.

methylcyclohexane was refluxed for 16 h. The reaction mixture was cooled and filtered (**Caution**: the precipitate removed here is pyrophoric when dry), and all volatiles were removed in vacuo (0.1 torr). The residue (52.7 g), containing $[CpFe(CO)(SEt)]_2$, was placed into a polyethylene container[9] along with 100 g of NH_4PF_6 (99.5%) and 1500 mL of CH_3CN (Eastman, <0.1% H_2O). The solution was saturated with oxygen and then stirred magnetically while exposed to air for 2 weeks. The solution volume was maintained at 1000–1500 mL by replenishment with CH_3CN. The carbonyl complex was initially oxidized to its deep blue-green monocation, which slowly underwent a second oxidation and subsequent displacement of carbonyl by CH_3CN, resulting in further solution color changes to green and finally to deep red. NH_3 (resulting from proton removal from NH_4^+) was slowly evolved from the reaction mixture. Reduction of solution volume to 200 mL followed by addition of 1300 mL of H_2O precipitated **2b** as a microcrystalline brown solid, which was collected on a medium-porosity frit, washed thoroughly with H_2O, and dried. Extraction of the precipitate through the frit with CH_3CN (1300–1500 mL), followed by slow evaporation of the extract to ~100 mL, yielded large, well-formed, brown-black crystals of **2b**. A large excess of CH_2Cl_2 was added to precipitate most of the dication still left in solution. The product was filtered off, washed with CH_2Cl_2, and dried. The total yield was 51.34 g (50% based on $[CpFe(CO)_2]_2$). **2** can be readily recrystallized from CH_3CN–CH_2Cl_2.

The preparation of **2a** is analogous, except that care must be exercised in monitoring its formation from $[CpFe(CO)(SMe)]_2^{2+}$. Whereas **2b** is reasonably stable to air and moisture in the reaction mixture, **2a** apparently is less stable, and if the reaction mixture is allowed to stir longer than necessary, decomposition to an insoluble fine brown precipitate occurs. The reaction of 1.3 g of $[CpFe(CO)(SMe)]_2$ with air in 150 mL of CH_3CN containing 2 g of NH_4PF_6 for 3 days yielded 1.05 g of **2a** (45% based on $[CpFe(CO)(SMe)]_2$).

The synthesis of **2c** is complicated by the nonvolatility of the unreacted Bzl_2S_2 in the preparation of $[CpFe(CO)(SBzl)]_2$, which results in the formation of an oily residue upon solvent removal. It is best to use this oil in the oxidation step and remove the Bzl_2S_2 later.

Elemental analysis (Table I) of **2** gave excellent agreement with theory. **2** is insoluble in water and nonpolar solvents and was recrystallized from and characterized in acetonitrile. **2** is air stable both in solution and in the solid state.

Preparation of 2b from $[CpFe(CO)(SEt)]_2[PF_6]_2$. $[CpFe(CO)(SEt)]_2[PF_6]_2$[10] (0.71 g) and NH_4PF_6 (0.5 g) were refluxed in CH_3CN (25 mL) for 4 h in a flask open to the atmosphere. The resulting solution was cooled, reduced in volume to 3 mL, and treated with 15 mL of H_2O to precipitate **2b**. The latter was washed with H_2O, dried, and recrystallized by dissolution in 20 mL of CH_3CN, reduction of the solution volume to 5 mL, and addition of CH_2Cl_2 (20 mL). The yield of black, microcrystalline **2b** was 0.505 g (69%).

Preparation of 2 by Oxidation of 1 with $NOPF_6$. Into a 100-mL flask were placed 3.6 mmol of **1** and 20 mL of acetonitrile. The solution–slurry was magnetically stirred in a bath of cold water while 2.2 g (12.6 mmol) of solid $NOPF_6$ was added. After a brisk evolution of nitric oxide, during which the solution became deep red-brown and no undissolved solids remained, 100 mL of diethyl ether was added from a dropping funnel over a 2–3-min period. The resulting brown precipitate of **2** was collected on a medium-porosity frit, washed with diethyl ether, and redissolved in 50 mL of acetonitrile. After this solution was filtered and reduced in volume to 15 mL, 100 mL of water was added from a dropping funnel over a 5-min period. The precipitate was collected on a frit and washed with water, 5 mL of ethanol, and diethyl ether. The yield of **2** was ~70%.

Air Oxidation of 1 to 2. A mixture of **1b** and excess NH_4PF_6 in acetonitrile was exposed to air for several days. Intermittent passage of oxygen through the solution hastened the oxidation, which could easily be followed by the color change from green to red. The solution was concentrated, and a fivefold excess of water was added to precipitate the product, which was identified as **2b**.

Reaction of 1b with $AgSbF_6$. Formation of $[Cp_2Fe_2(S_2)(SEt)_2Ag_2(NCCH_3)_4](SbF_6)_2$. When an acetonitrile solution of $AgSbF_6$ and a slurry of **1b** in acetonitrile were mixed in 1:2 ratio, no color change occurred, but the solid dissolved. Addition of excess ether to the above solution precipitated a dark gray-green solid which, unlike **1b**, is insoluble in nonpolar solvents. Although its UV–vis spectrum (Table III) is very similar to that of **1b**, its infrared spectrum (Table II) conclusively shows that both CH_3CN and SbF_6^- groups are present. This, along with analytical data (Table I), indicated that the stoichiometry of the precipitate is $[Cp_2Fe_2(S_2)(SEt)_2Ag_2(NCCH_3)_4][SbF_6]_2$. The complex is not stable in solution for more than 1 h or so at room temperature, even under nitrogen, and the solid is also unstable over long periods of time.

Reaction of $[CpFe(CO)_2]_2$ with S_8. Identification of Cubane Cluster Products, $Cp_4Fe_4S_x$ (x = 4–6). A series of reactions of $[CpFe(CO)_2]_2$ (10 g, 28.4 mmol) with S_8 (5 g, 19.5 mmol) in refluxing toluene (175–250 mL) were carried out. Reaction times were varied from 3 to 22 h. In all cases, the resulting black precipitates were collected from the cooled reaction mixtures and extracted with CH_2Cl_2 (100 mL). Partial solvent removal from the filtered extracts and treatment with hexane yielded black solids. These were shown by NMR to consist primarily of $Cp_4Fe_4S_6$ (**6**) with small amounts (5–10% each) of $Cp_4Fe_4S_4$ (**4**) and $Cp_4Fe_4S_5$ (**5**). The undissolved material from the extraction process was found to contain **4**, S_8, and insoluble decomposition products. About 0.7 g of **4** was recovered by extraction with hot bromobenzene (250 mL) and identified by infrared and NMR spectroscopy. The yields of crude **6** were found to be highly dependent on reaction time, increasing from ca. 1 to 4 g as the length of reaction was reduced from 22 to 3 h. Purification of **6** from residual amounts of **4** could not be accomplished either by repeated recrystallization from CH_2Cl_2 or $CHCl_3$ or by column chromatography. However, as will be shown below, pure **6** can be obtained by means of complexation with SO_2.

Preparation of $Cp_4Fe_4S_6$ (6). A mixture of $[CpFe(CO)_2]_2$ (10 g, 28.4 mmol), S_8 (5 g, 19.5 mmol), and toluene (175 mL) was refluxed for 3 h with vigorous magnetic stirring. Foaming due to rapid CO loss occurred during initial reflux. The reaction mixture was cooled and filtered through a medium-porosity frit (inert atmosphere unnecessary). The black precipitate collected on the frit was washed with toluene (50 mL), dried in air, and extracted with CH_2Cl_2 (100 mL). The extract was filtered through a medium-porosity frit, saturated with SO_2 gas, and allowed to stand for 1 h under an SO_2 atmosphere. A crystalline black precipitate of $Cp_4Fe_4S_6\cdot 2SO_2\cdot 0.25CH_2Cl_2$ (3.39 g, 29%) deposited, allowing separation of **6** from **4**, which does not form an SO_2 adduct. The SO_2 adduct was washed with diethyl ether, air-dried, and redissolved in 200 mL of $CHCl_3$ at ~40 °C. The SO_2 was driven off by alternately briefly removing the volatiles in vacuo and reheating the solution to ~40 °C for several minutes. After several such cycles, the solution was filtered through a medium frit, and the volume of the filtrate reduced to 50–75 mL in vacuo. Heptane (120 mL) was added, the solution volume reduced to 150 mL, and the resultant precipitate was filtered off, washed with ether, and air-dried. The yield of $Cp_4Fe_4S_6\cdot xCHCl_3$ ($x < 1$) was 2.66 g (ca. 25%). This product contains a small percentage of insoluble material which can be removed by recrystallization from CH_2Cl_2 (100 mL). Addition of heptane (100 mL) to the filtered solution followed by reduction of solution volume to ~125 mL yielded 2.01 g of microcrystalline $Cp_4Fe_4S_6\cdot 0.25CH_2Cl_2$.

6 is air stable in the solid state, but solutions slowly decompose in air. It is moderately soluble in halogenated solvents and slightly soluble in benzene, CS_2, acetone, and CH_3CN. **6** is somewhat thermally unstable and should be stored in a freezer.

Oxidation of 6 with $AgSbF_6$. Isolation of $[(Cp_4Fe_4S_6)_2Ag][SbF_6]_3$. Compound **6** (0.4 g, 0.59 mmol) was stirred with $AgSbF_6$ (0.3 g, 0.87 mmol) in 5 mL CH_3CN for 10 min. Diethyl ether (25 mL) was then slowly added to precipitate the product, which was collected on a fine-porosity frit and washed with water. The air-dried precipitate was recrystallized by extraction with CH_3CN (30 mL), reduction of the resulting solution volume, and addition of ether. The recrystallization was repeated, giving 0.48 g (75%) of black microcrystalline $[(\mathbf{6})_2Ag][SbF_6]_3$, which is air stable both as a solid and in solution. It is paramagnetic and gives a strong ESR signal in the solid state.[1c] Storage in a freezer is recommended since slow decomposition takes place at room temperature.

Electrochemical Oxidation of 6 to $[Cp_4Fe_4S_5]^{2+}$. Into an electrochemical cell were placed 50 mL of a 0.1 M solution of doubly recrystallized $NaSbF_6$ in Spectrograde CH_3CN and 0.676 g (1 mmol) of **6**. The slurry was oxidized in an inert atmosphere at +0.5 V vs.

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[9] A polyethylene container was used because fluoride ion, produced by hydrolysis of PF_6^-, attacked glass vessels, leading to impure product formation.

[10] de Beer, J. A.; Haines, R. J.; Greatrex, R.; van Wyk, J. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2341.

SCE, resulting in the formation of a deep brown solution. The solution was transferred to a flask, and the solvent was removed in vacuo. The residue, after having been washed with water to remove $NaSbF_6$ and dried, weighed 0.844 g. Recrystallization of the crude product from CH_3CN–toluene gave 0.695 g (52%) of [**5**]$[SbF_6]_2$ as a black microcrystalline solid.

A PF_6 salt can be prepared in a manner similar to that described above by using NH_4PF_6 as electrolyte. Elemental analysis and conductivity measurements (Table I) confirm that the compounds are dications; the sharp resonances in their NMR spectra (Table II) indicate they are diamagnetic. A water-soluble iodide salt can also be prepared by metathesis with KI in CH_3CN solution. The salts are air stable in solution.

Preparation of $[Cp_4Fe_4S_5][PF_6]_2$ by Air Oxidation of 6 in Solution. Compound **6** (1.0 g) was stirred with 2.0 g of NH_4PF_6 in 150 mL of CH_3CN in a polyethylene beaker (or other nonglass vessel) exposed to the atmosphere. After 2 days the deep brown solution was filtered and reduced in volume to ~25 mL. CH_2Cl_2 (100 mL) was added, and the resulting precipitate was collected on a frit, washed with CH_2Cl_2, dried, and then washed with water, ethanol and hexane. The solid was redissolved in CH_3CN (60 mL), and the solution was filtered, reduced in volume to 25 mL, and treated with 100 mL of CH_2Cl_2. The brown precipitate of [**5**]$[PF_6]_2\cdot CH_3CN$ was collected, washed with CH_2Cl_2, and dried in vacuo. The yield was 0.87 g (63%). The infrared spectrum indicated the presence of CH_3CN in the crystal lattice (ν(CN) = 2255 cm^{-1}).

Preparation of 5 by Reduction of [5]$[PF_6]_2\cdot CH_3CN$ with $NaBH_4$. [**5**]$[PF_6]_2\cdot CH_3CN$ (2.5 g, 2.56 mmol) was dissolved in 150 mL of CH_3CN, and 50 mL of water was added. $NaBH_4$ (0.57 g, 15 mmol) in 25 mL of H_2O was added dropwise over a 15-min period to the above solution at 0 °C. After the reaction mixture was stirred for 1 h, the precipitate that formed was collected on a frit and washed with water, ethanol, and acetone. The crude product (1.61 g) was recrystallized by extraction with CH_2Cl_2 (120 mL), reduction of the solution volume to 20 mL, and addition of hexane (40 mL). The yield of black, platelike crystalline aggregates of **5** was 1.45 g (83%). Elemental analysis indicated that 0.5 mol of CH_2Cl_2/mol of **5** was retained in the crystal lattice. The solubility and air stability of **5** are similar to those of **6**.

Preparation of $[Cp_4Fe_4S_5][PF_6]$. A mixture of **5** (0.193 g, 0.3 mmol), [**5**]$[PF_6]_2$ (0.293 g, 0.3 mmol), and CH_3CN (12 mL) was stirred for 10 min. The resulting deep brown solution was filtered and reduced in volume to 2 mL. Ether (15 mL) was then slowly added to precipitate [**5**]$[PF_6]$ as a black solid (0.452 g, 93%). The latter is very soluble in polar solvents and moderately soluble in CH_2Cl_2.

Conversion of 6 to 4 and 5 to 4 in Refluxing Bromobenzene. A solution of **6** (0.4 g) in bromobenzene (25 mL) was refluxed for 15 min. The reaction mixture was filtered hot, and the filtrate was cooled in a freezer overnight. Black needlelike crystals of **4** (0.2 g, 57%) formed, which were collected on a frit, washed with pentane, and air-dried. A similar conversion of **5** to **4** can be carried out also.

Preparation of $Cp_4Fe_4S_x\cdot 2SO_2$ (x = 5, 6) and $Cp_2Fe_2(S_2)(SEt)_2\cdot 2SO_2$. Solutions of **5** or **6** in minimum quantities of CH_2Cl_2 or $CHCl_3$ were found to give 60–70% yields of crystalline precipitates of bis SO_2 adducts upon saturation with SO_2. Small amounts of solvent (0.1–0.3 mol/mol of adduct) were found to be retained in the crystal lattice.

The SO_2 could be removed by heating the adducts to 110–115 °C in vacuo. However, extensive decomposition of the cubane clusters took place. $CHCl_3$ solutions of the SO_2 adducts released SO_2 upon pumping in vacuo with only minor decomposition, thereby allowing recovery of pure **5** or **6** in good yield.

$Cp_2Fe_2(S_2)(SEt)_2$ (0.146 g, 0.342 mmol) was dissolved in liquid SO_2 at −63 °C. Removal of solvent at this temperature under high vacuum gave a nearly black residue which lost SO_2 upon warming to room temperature to give $Cp_2Fe_2(S_2)(SEt)_2$. SO_2 (0.690 mmol) was recovered (mmol of SO_2/mmol of complex = 2.02), indicating that the composition of the solid at −63 °C was $Cp_2Fe_2(S_2)(SEt)_2\cdot 2SO_2$.

Results and Discussion

(I) Synthesis of Iron–Sulfur Clusters. $[CpFe(CO)_2]_2$ has been found to undergo a complex reaction (eq 1) with an ethyl polysulfide mixture containing primarily Et_2S_3. Five oligomeric products containing iron and sulfur were isolated in low yield (<10% each) and characterized. Although **4** had previously been prepared and structurally characterized,[11] **1b**, **3**, **5**, and **6** are new compounds. Unlike the reaction of $[CpFe(CO)_2]_2$ with R_2S_2, which gives $[CpFe(CO)(SR)]_2$ as the major product under conditions similar to those of eq 1,[5] no carbonyl-containing complexes were recovered as final products. However, $[CpFe(CO)(SEt)]_2$ was found to be present in the reaction mixture as an intermediate product, a discovery which prompted use of this complex or its analogues as a starting material for preparation of **1** (eq 2). Although the yield of **1b** (Figure 1) from eq 2 (8%) was higher than that from eq 1 (3%), it was still low due to formation of side products. A multistep synthesis of **1** that gives a much higher overall yield based on $[CpFe(CO)_2]_2$ as the starting material has been devised and will be discussed later. Side products of eq 2 included **4**–**6** but not **3**. An R = Ph derivative could not be prepared. Thus, it is clear that reactions involving replacement of carbonyls with S_n ligands are very complex and yield many products, as has been observed previously. Even minor changes in the reactants can alter the course of the reactions unpredictably. For example, use of Et_2S_4 in the reaction shown in eq 1 resulted in significantly diminished yields of **1b** and **3**. Although **1c** was found to be a minor product of the reaction of $[CpFe(CO)_2]_2$ with Bzl_2S_2,[12] normally $[CpFe(CO)(SR)]_2$ is obtained in high yield upon use of alkyl disulfides.[5] Thus it would appear that the trisulfide Et_2S_3 is important in the formation of the Fe–S–S–Fe linkage, although from a mechanistic point of view, little can be inferred from these results.

$$[CpFe(CO)_2]_2 + Et_2S_x\ (x = 3, 4) \xrightarrow[\text{reflux, 11 h}]{\text{methylcyclohexane}} \underset{\mathbf{1b}}{Cp_2Fe_2(S_2)(SEt)_2} + \underset{\mathbf{3}}{Cp_3Fe_3S_2(SEt)} + \underset{\mathbf{4}}{Cp_4Fe_4S_4} + \underset{\mathbf{5}}{Cp_4Fe_4S_5} + \underset{\mathbf{6}}{Cp_4Fe_4S_6} \quad (1)$$

$$[CpFe(CO)(SR)]_2 + S_8 \xrightarrow[\text{reflux}]{\text{methylcyclohexane}} \underset{\substack{\mathbf{1a},\ R = Me\\ \mathbf{1b},\ R = Et\\ \mathbf{1c},\ R = Bzl}}{Cp_2Fe_2(S_2)(SR)_2} + \mathbf{4} + \mathbf{5} + \mathbf{6} \quad (2)$$

The stoichiometry of the trinuclear cluster **3** was determined by elemental analysis (Table I), NMR (Table II), and mass spectral data (parent ion peak at *m/e* 488.0; calcd mol wt of **3** 487.96). Dahl and co-workers have independently synthesized and structurally characterized $Cp_3Fe_3S_2(SMe)$,[13] which possesses a triangular array of CpFe moieties with triply bridging sulfur atoms above and below the plane of iron atoms and a methyl mercaptide ligand bridging two irons. It is probable that **3** also has this structure.

The tetranuclear species **5** was identified to be a product of eq 1 and 2. Subsequently, it has been more conveniently synthesized by reducion of $[\mathbf{5}]^{2+}$ (obtained by oxidation of **6**). This will be discussed in more detail later.

6 was initially isolated in very low yield from the black precipitate obtained according to eq 1 and was characterized by a single-crystal X-ray structure determination,[1c,7] Once the structure (Figure 2) was solved, a better synthetic route to the compound was found. Schunn and co-workers had previously obtained **4** in moderate yield by refluxing $[CpFe(CO)_2]_2$ with a small excess of sulfur (molar ratio of S/Fe of 1.44) in toluene for 16 h.[11a] We decided to invesitgate the products of a similar reaction mixture containing a larger excess of sulfur (eq 3). Compounds **4**–**6** were identified as

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[11] (a) Schunn, R. A.; Fritchie, C. J., Jr.; Prewitt, C. T. *Inorg. Chem.* **1966**, *5*, 892. (b) Wei, C. H.; Wilkes, G. R.; Treichel, P. M.; Dahl, L. F. *Ibid.* **1966**, *5*, 900.

[12] Campana, C., private communication.

[13] Sinclair, D.; Dahl, L. F., private communication.

$$[CpFe(CO)_2]_2 + S_8\ (excess) \xrightarrow[reflux]{toluene} \underset{\mathbf{4}}{Cp_4Fe_4S_4} + \underset{\mathbf{5}}{Cp_4Fe_4S_5} + \underset{\mathbf{6}}{Cp_4Fe_4S_6} \quad (3)$$

products and were separable by fractional crystallization. **5** was identified as a minor product (<2% yield) and was not isolated, but **4** and **6** were each obtained in 25–35% yields. Both **5** and **6** are thermally unstable since increasing the reflux period from 3 h to 22 h in eq 3 decreased their yields considerably. Also, both **5** and **6** can be converted to **4** in refluxing bromobenzene in 15 min, presumably by loss of sulfur (eq 4).

$$\underset{\mathbf{6}}{Cp_4Fe_4S_6} \xrightarrow[reflux]{bromobenzene} \underset{\mathbf{4}}{Cp_4Fe_4S_4} + {}^1/_4S_8 \quad (4)$$

Apparently the triply bridging S_2 ligands in **5** and **6** are susceptible to cleavage to triply-bridging S ligands and elemental sulfur. As will be shown later, oxidation of **6** to a dication also results in loss of sulfur. Even at ambient temperatures, solid **5** and **6** slowly decompose over extended periods of time.

6 cannot easily be completely freed of small amounts of the less soluble **4** solely by recrystallization. However, passage of SO_2 through solutions of the cubane clusters has been found to result in the precipitation of SO_2 adducts of **5** and **6** but not of **4** (eq 5). The SO_2 is expected to be bound to the

$$Cp_4Fe_4S_x\ (x = 5, 6) \xrightarrow[CH_2Cl_2]{SO_2} Cp_4Fe_4S_x{\cdot}2SO_2 \quad (5)$$

electron-rich S_2 ligands in a manner exemplified by the mercaptide–SO_2 interaction in $Cu(PPh_2Me)_3(SPh){\cdot}SO_2$.[14] It can be reversibly removed from the clusters, thereby facilitating separation of **6** from **4**.

Finally, regarding eq 3, a photochemical reaction of S_8 with $[CpFe(CO)_2]_2$ in methanol has recently been reported.[15] The X-ray structure of one of the products, $Cp_2Fe_2(S_2)_2(CO)$, has been determined and shows two S_2 groups bridging the irons in an asymmetric fashion.

The reactions described above and several others yet to be discussed are summarized in Figure 3.

(II) Electrochemical Properties of and Further Synthetic Routes to the Disulfur Complexes. (A) Dinuclear Species. The electrochemistry of **1** has been reported[16] and can be summarized as in eq 6 (for **1b**). Solutions of **1b** were subjected

$$\text{irrev redn prod} \xleftarrow{-1.2\ V} \underset{\mathbf{1b}}{[Cp_2Fe_2(S_2)(SEt)_2]} \xrightarrow{0.21\ V} \underset{[\mathbf{1b}]^+}{[Cp_2Fe_2(S_2)(SEt)_2]^+} \xrightarrow{0.90\ V} \underset{[\mathbf{1b}]^{2+}}{[Cp_2Fe_2(S_2)(SEt)_2]^{2+}} \xrightarrow[-S_2]{CH_3CN} \underset{\mathbf{2b}}{[CpFe(NCCH_3)(SEt)]_2{}^{2+}} \quad (6)$$

to a variety of oxidizing agents in an attempt to prepare $[\mathbf{1b}]^+$, which had been isolated previously only via electrochemical oxidation and found to contain a one-electron iron–iron bond.[1c,3,16] Silver(I) salts such as $AgSbF_6$ gave no rapid color changes which would indicate oxidation. However, a species with the stoichiometry $[Cp_2Fe_2(S_2)(SEt)_2Ag_2(NCCH_3)_4][SbF_6]_2$ was isolated. Presumably the Ag(I) atoms are coordinated by sulfur atoms in the Fe–S cluster and CH_3CN ligands. Bromine was found to possess the proper oxidation potential to take the neutral complex to its monocation (and no further), but a pure product could not be isolated. Nitrosonium salts such as $NOPF_6$ were found to oxidize **1** in CH_3CN solution with concomitant loss of S_2 (eq 7). The

$$\underset{\mathbf{1}}{Cp_2Fe_2(S_2)(SR)_2} + 2NOPF_6 \xrightarrow[-S_2]{CH_3CN} [CpFe(NCCH_3)(SR)]_2[PF_6]_2 + 2NO \quad (7)$$

2a, R = Me
2b, R = Et
2c, R = Bzl

oxidation product was identified to be the deep-red solvent-substituted dication **2**, the X-ray structure[1c,7] of which (R = Et) confirms that the bridging S_2 group has been replaced by terminal CH_3CN ligands. As can be seen from eq 6, **2** is actually produced in a stepwise fashion in eq 7. The proposed immediate precursor is $[\mathbf{1}]^{2+}$, which has thus far been detected only electrochemically. Oxidation of **1** with $NOPF_6$ in CH_2Cl_2 at ambient temperature failed to produce this elusive species, which would be expected to possess a full iron–iron bond and hence a strained geometry:

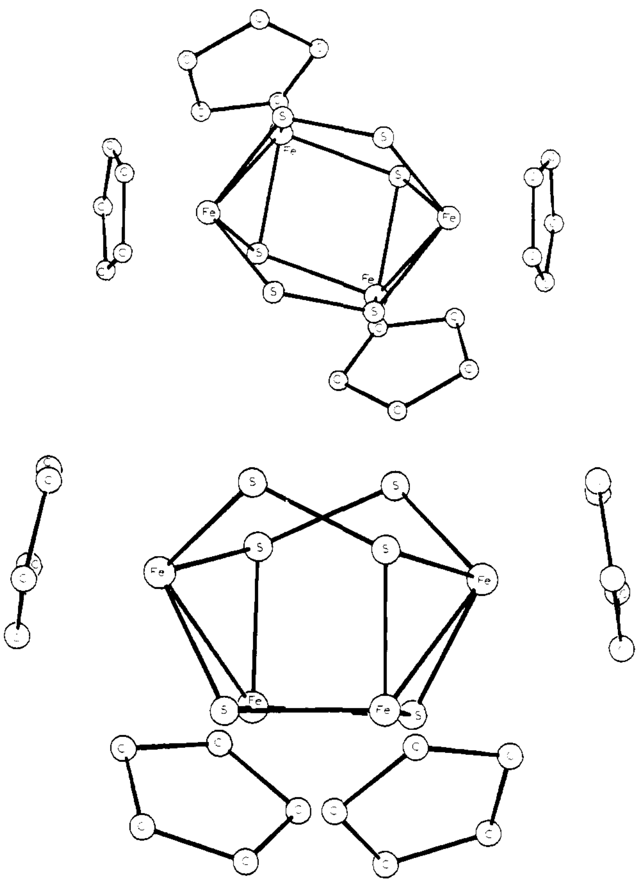

Figure 2. Molecular structure of **6**, as reported in ref 1c.

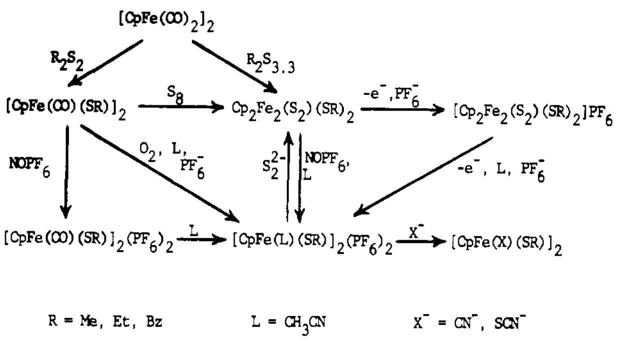

Figure 3. Reactions of dinuclear mercapto-bridged iron complexes.

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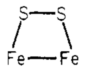
(14) Eller, P. G.; Kubas, G. J. *J. Am. Chem. Soc.* **1977**, *99*, 4346.

(15) Giannotti, C.; DuCourant, A. M.; Chanaud, H.; Chiaroni, A.; Riche, C. *J. Organomet. Chem.* **1977**, *140*, 289.

(16) Kubas, G. J.; Vergamini, P. J.; Eastman, M. P.; Prater, K. B. *J. Organomet. Chem.* **1976**, *117*, 71.



Both **1** and $[\mathbf{1}]^+$ are also oxidized by atmospheric oxygen in CH_3CN to give **2**, stabilized by large counteranions (eq 8).

$$[Cp_2Fe_2(S_2)(SR)_2]^{0,1+} \xrightarrow{O_2,\ CH_3CN,\ PF_6^-} [CpFe(NCCH_3)(SR)]_2[PF_6]_2 \quad (8)$$

2 has been found to undergo a variety of ligand-substitution reactions. The coordinated CH_3CN groups are labile and easily replaced by neutral or anionic ligands (e.g., CN^-) to give dicationic or neutral complexes (e.g., $[CpFe(CN)(SR)]_2$).[1c,17] Perhaps the most novel reaction of this type is the regeneration of **1** by interaction of **2** with aqueous polysulfide (eq 9).

$$\underset{\mathbf{2}}{[CpFe(NCCH_3)(SR)]_2[PF_6]_2} + S_2^{2-}(aq) \xrightarrow{CH_3CN} \underset{\mathbf{1}}{Cp_2Fe_2(S_2)(SR)_2} + 2PF_6^- \quad (9)$$

Yields of 44–63% were obtained when commercial ammonium polysulfide solution was utilized as the source of S_2^{2-}. Excess aqueous Na_2S also will react to give **1**, but better yields (55–61%) were obtained by using "Na_2S_2" (a nominal stoichiometry for the mixture of polysulfides obtained when Na_2S and sulfur are dissolved together in water in a 1:1 molar ratio). In order for the reaction shown in eq 9 to be useful in a preparative route to **1**, a synthesis of **2** from a starting material other than **1** was devised. We observed that the carbonyl groups in the dication $[CpFe(CO)(SR)]_2^{2+}$ [10] are weakly bound and slowly displaced at ambient temperature by CH_3CN to give **2**. Thus **2b** was found to be readily prepared by refluxing $[CpFe(CO)(SEt)]_2[PF_6]_2$ in CH_3CN for 4 h. **2** was also synthesized in good yield by sequential air oxidation of $[CpFe(CO)(SR)]_2$ to its dication and in situ carbonyl loss (eq 10). Detailed studies of this reaction have been carried out

$$[CpFe(CO)(SR)]_2 + 2NH_4PF_6 + {}^1/_2O_2 \xrightarrow[3\text{–}14\ \text{days}]{CH_3CN} [CpFe(NCCH_3)(SR)]_2[PF_6]_2 + 2CO + 2NH_3 + H_2O \quad (10)$$

$$R = Me, Et, Bzl$$

and will be reported separately.[17] The reaction pathway described in eq 9 and 10 results in an overall yield of **1b** of 32% based on the $[CpFe(CO)_2]_2$ starting material used to prepare $[CpFe(CO)(SEt)]_2$.

A comparison between the redox properties of **1** and those reported[10,18] for $[CpFe(CO)(SR)]_2$ can be made. Both complexes can be reversibly oxidized to monocations and quasi-reversibly oxidized to dications. In the case of R = Et, the respective oxidation potentials (vs. SCE) in CH_2Cl_2 for the disulfur species (0.37 and 1.04 V) are 0.5 V higher than for those of the carbonyl complexes (–0.13 and 0.54 V). We have observed that both the disulfur and carbonyl ligands in the dicationic form of the complexes are susceptible to replacement by CH_3CN solvent molecules to yield **2**. The rate of conversion of $[\mathbf{1}]^{2+}$ to **2** is much higher compared to that for the carbonyl dication.

(B) Tetranuclear "Cubane" Clusters. Compound **6** possesses the same stoichiometry as the previously known cobalt analogue, $Cp_4Co_4S_6$.[19] However, their structures differ significantly. While both have essentially a "cubane" framework of CpM, μ_3-S, and μ_3-S_2 moieties, the cobalt species contains no metal–metal interactions and no symmetry, whereas **6** has two bonding Fe–Fe distances and possesses a C_2 axis (Figure 2). In both solid and solution states, all four CpCo units are nonequivalent, but in **6**, two pairs of CpFe units are equivalent as shown by NMR (Figure 4). Cyclic voltammetry (Figure 5) indicates that **6** possesses reversible redox properties, and the electrochemistry is summarized in eq 11. The voltammetric wave at 0.367 V appears to be quasi-reversible, and $[\mathbf{6}]^{2+}$, like $[\mathbf{1}]^{2+}$, is unstable and loses sulfur to form $[\mathbf{5}]^{2+}$. The Fe_4S_5 cluster, $[\mathbf{5}]^n$, which, from infrared and NMR evidence, has a cubanelike structure with three μ_3-S and one μ_3-S_2 (ν_{S-S} = 522 cm^{-1}), also has a rich electrochemistry (eq 12). Cyclic voltammograms of $[\mathbf{5}]^{2+}$ (Figure 6), as well as **5** in CH_2Cl_2, do not exhibit a reduction wave corresponding to anion formation. Both $[\mathbf{5}]^+$ and $[\mathbf{5}]^{2+}$ have been isolated and characterized as PF_6^- salts.

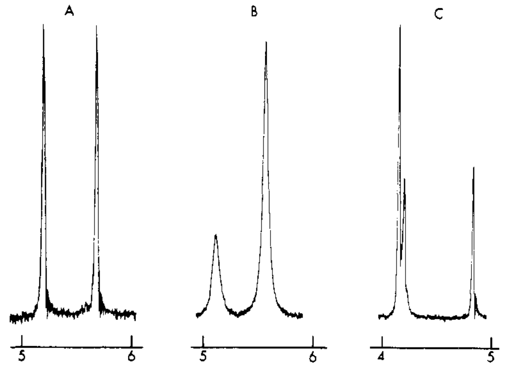


Figure 4. Proton NMR of tetranuclear species: A, **6** in $CDCl_3$; B, **5** in $CDCl_3$; C, $[\mathbf{5}][PF_6]_2$ in CD_3CN; reference Me_4Si (=τ 10).

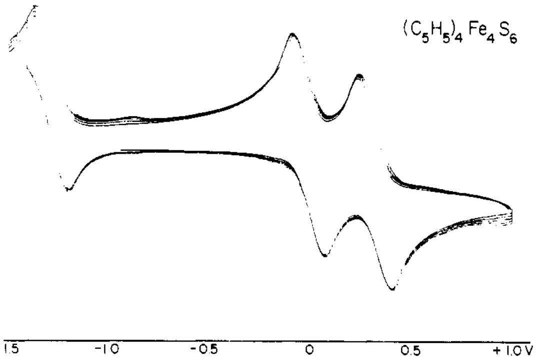


Figure 5. Cyclic voltammogram of **6** in CH_2Cl_2 (0.1 M $[Bu_4N][SbF_6]$ as supporting electrolyte; 200 mV/s scan rate; SCE reference).

$$[Cp_4Fe_4S_6]^- \xrightarrow{-1.325\ V} [Cp_4Fe_4S_6] \xrightarrow{0.06\ V} [Cp_4Fe_4S_6]^+ \xrightarrow{0.367\ V} [Cp_4Fe_4S_6]^{2+} \xrightarrow{-S} [Cp_4Fe_4S_5]^{2+} \quad (11)$$

$$[Cp_4Fe_4S_5] \xrightarrow{-0.28\ V} [Cp_4Fe_4S_5]^+ \xrightarrow{0.02\ V} [Cp_4Fe_4S_5]^{2+} \xrightarrow{1.14\ V} [Cp_4Fe_4S_5]^{3+} \quad (12)$$

Since **4** was found to oxidize to its monocation[20] upon treatment with silver salts, one would expect **6** to undergo similar oxidation. This indeed proved to be the case, but the compound that was isolated unexpectedly contained silver in addition to $[\mathbf{6}]^+$ cations (eq 13). The structure of the novel

$$\underset{\mathbf{6}}{2Cp_4Fe_4S_6} + 3AgSbF_6 \xrightarrow{CH_3CN} [(Cp_4Fe_4S_6)_2Ag][SbF_6]_3 + 2Ag \quad (13)$$

paramagnetic trication revealed that one sulfur atom from each S_2 group coordinates in essentially a tetrahedral fashion about

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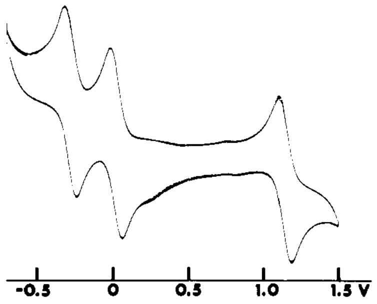


Figure 6. Cyclic voltammogram of [5][PF_6]$_2$ in CH_3CN (0.1 M NH_4PF_6 as supporting electrolyte; scan rate 200 mV/s; SCE reference).

the silver(I), with the cubane cluster essentially acting as a bidentate ligand.[1c,7] The coordination of silver to the disulfur ligands indicates that the latter retain a fair degree of basicity even in the oxidized form of **6**. In the neutral cluster, the S_2 groups are even more reactive, since the complex, on the whole, possesses more electron density. This is borne out by the moderately strong coordination of a Lewis acid, SO_2, to **6** (eq 5) as well as the ligation of **6** to molybdenum in $Mo(CO)_4(Cp_4Fe_4S_6)$.[21] Abstraction of sulfur from **6** by PPh_3 to form **5** and Ph_3PS was found to be slow, however, even in refluxing chloroform.

Attempts to isolate salts of [**6**]$^+$ by use of chemical oxidants such as iodine and oxygen resulted in conversion of **6** to [**5**]$^{2+}$ as shown in eq 14. Elemental sulfur was identified to be a

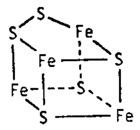
$$\underset{\mathbf{6}}{Cp_4Fe_4S_6} + {}^{1}/{}_{2}O_2 + 2NH_4PF_6 \xrightarrow{CH_3CN} [Cp_4Fe_4S_5][PF_6]_2 + {}^{1}/{}_{8}S_8 + 2NH_3 + H_2O \quad (14)$$

product of eq 14. The dicationic product [**5**][PF_6]$_2$, which crystallizes as an acetonitrile solvate and can also be prepared by bulk electrolysis of **6** at +0.5 V or by air oxidation of **5**, was identified by elemental analysis, conductivity measurements, and IR and NMR (Figure 4) spectra. A rationalization for the loss of sulfur from **6** upon oxidation is steric strain imposed within the molecule. Chemical reduction of [**5**]$^{2+}$ to **5** in 83% yield has been affected with sodium borohydride in aqueous acetonitrile. Thus, a good symthetic route to **5** is air oxidation of **6** to [**5**]$^{2+}$ followed by reduction of the latter with borohydride. Reaction of equimolar quantities of **5** and [**5**][PF_6]$_2$ in CH_3CN enabled isolation of a paramagnetic monocation, [**5**][PF_6]. The solution-state structures of both **5** and [**5**]$^{2+}$ are fluxional above −40 °C, as will be discussed in the following section on NMR spectra.

(III) NMR Studies. For diamagnetic compounds containing η-C_5H_5 groups, proton NMR is an excellent characterization tool. Cp rings give single sharp resonances which seldom overlap even in multicomponent systems. Table II gives NMR data for various Fe–S complexes. Figure 7 shows a spectral trace for **1b**. Surprisingly, the ethyl protons do not give rise to the expected triplet–quartet pattern observed, for example, in the spectrum of $[CpFe(CO)(SEt)]_2$. Instead, a multiplet near τ 10.0 must be assumed to contain the overlapping methylene and methyl resonances of the bridging ethyl mercaptide groups. This type of signal is not unprecedented, however. The NMR spectrum of $[Co(S_2CSEt)_2(SEt)]_2$ also had been observed to contain a multiplet of similar general appearance at τ 9.0 which was assigned to a bridging SEt group.[22] In this case, the large upfield shift of the methylenic protons was attributed to the influence of anisotropic residual temperature-independent paramagnetism. This is a likely rationalization for the spectrum of **1b** since **1b** also has been found to display residual TIP.[16] The NMR of **3** shows a similar broad unresolved multiplet at τ 9.0 due to C_2H_5.

NMR studies clearly indicate that the coordinated CH_3CN ligands in **2** are labile and slowly exchange with solvent molecules. When CD_3CN is used as the solvent, complete exchange occurs in 10–15 min. This exchange can be followed by observing the intensity of the signal due to coordinated CH_3CN diminish with time and the intensity of the resonance due to free CH_3CN grow.

Geometries of the tetranuclear clusters in solution can readily be studied by observing the Cp region. The spectrum of **6** (Figure 4) is consistent with two sets of two equivalent iron sites and does not change over a −40 to +100 °C temperature range. This configuration is observed in the X-ray crystal structure, and thus it is reasonable to conclude that the solution and solid-state structures are essentially the same. A recent report by Norton et al. also indicates that the chirality of this cluster is preserved in solution and it remains rigid at room temperature.[23] At first glance, the spectrum of **5** (Figure 4) may seem reasonable in that a 3:1 ratio of intensities of Cp peaks corresponds to the assumed 3:1 ratio of S to S_2 ligands. However, a close examination of the CpFe sites in the expected structure of **5** reveals that there are three chemically unique Fe atoms, hence a 1:2:1 (or 2:1:1) pattern is expected.



Proposed structure of Fe_4S_5 core (excluding Fe-Fe interactions)

Furthermore, it is readily apparent from Figure 4 that the room temperature ^1H NMR signals due to **5** are broader than those observed for [**5**]$^{2+}$, which, significantly, *are* in a 2:1:1 pattern, and **6**. Thus the possibility of exchange averaging due to *fluxional behavior* was examined and subsequently confirmed in both **5** and [**5**]$^{2+}$ by variable-temperature studies. The appearance of a 1:2:1 pattern at −40 °C for **5** (Figure 8) and the collapse of the 2:1:1 signal into a 3:1 pattern for [**5**]$^{2+}$ at 70 °C (Figure 9) indicate that an intramolecular exchange process involving the Fe_4S_5 core is occurring. The averaging of only three and not all of the CpFe sites would appear to be related to the presumed triply bridging nature of the S_2 group. It is probable that, in a structure such as that proposed for **5**, the S_2 ligand is limited, even in a dynamic situation, to bonding interactions with only three iron atoms, assuming that the S–S bond remains intact at all times. Thus a process in which the S_2 is, on the average, bound equivalently to three irons is apparently occurring above −40 °C for **5** and above 70 °C for [**5**]$^{2+}$. Interconversion of three equivalent structures is one possibility (see Scheme I). It is important to note that, if two Fe–Fe bonds are assumed to be present in **5** on the basis of the known structures of **4** and **6**, they also must be fluxional so that the three CpFe moeities attain equivalence. Similarly, the equivalent of *three* Fe–Fe single bonds would be expected in [**5**]$^{2+}$, which perhaps explains the higher temperature at which onset of dynamic behavior occurs in [**5**]$^{2+}$. Further studies, including X-ray structural determinations, will be necessary before more can be said about this unique type of rearrangement. We believe this is the first example of a dynamic process directly involving an S_n ligand and one of the few cases involving metal–metal bonding in a cluster in two

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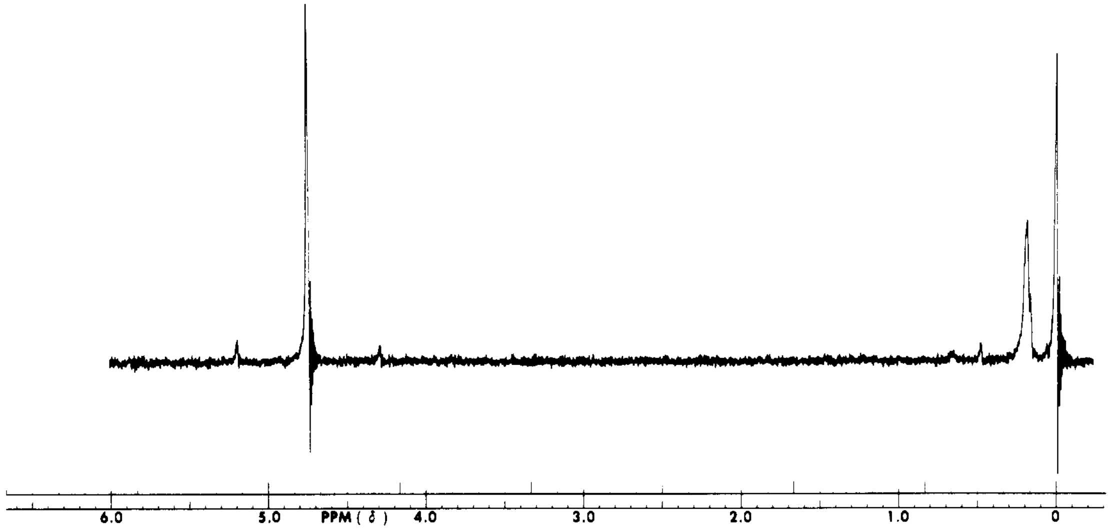


Figure 7. Proton NMR spectrum of **1b** in CS_2 solution (reference Me_4Si).

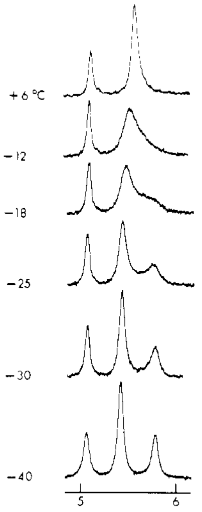


Figure 8. Variable-temperature proton NMR of **5** in $CDCl_3$ (reference Me_4Si).

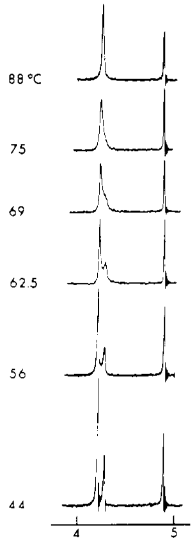
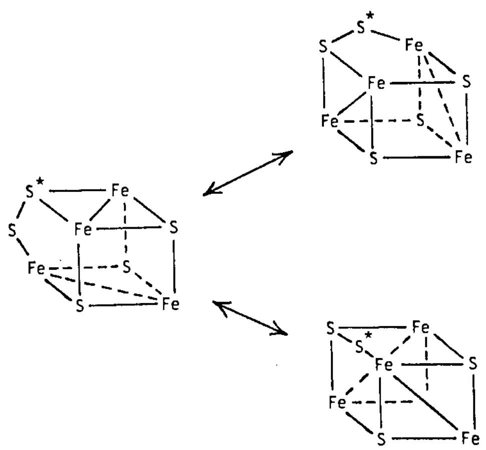


Figure 9. Variable-temperature proton NMR of [**5**][PF_6]$_2$ in CD_3NO_3 (reference Me_4Si).

different molecular oxidation states.

As far as assignments of the Cp resonances in **5** and **6** are concerned, it appears that the signals at highest field are associated with the CpFe moieties bonded to the μ_2-sulfur of the S_2 ligand. However, since this observation is based primarily on the spectra of **5**, the above can only be regarded as tentative. The Cp resonances undergo large downfield shifts (1–2 ppm) when **4**,[24] **5**, and $[CpFe(CO)(SR)]_2$ are oxidized to their respective dications.

Scheme I



(IV) Infrared Spectra. Table II lists selected observed infrared frequencies for the Fe–S complexes. Of special interest is the S–S stretch of the disulfide. Medium-intensity bands observed in the 466–543-cm^{-1} region are attributed to this mode, which generally falls within this frequency range.[1a] Another easily distinguishable absorption not due to Cp modes includes the characteristic band near 1250 cm^{-1} due to the S–CH_2 wag in mercaptide-containing compounds which is very useful for identifying SCH_2R moieties.[25] Similarly, the S–CH_3 symmetric deformation near 1300 cm^{-1} is clearly indicative of this group. Compounds containing PF_6^- or SbF_6^- anions display very intense P–F or Sb–F absorptions. The SbF_6^- anion absorbs at 655 and 287 cm^{-1}, resulting in less interference with other bands than the absorption of corresponding PF_6^- anion (845, 553 cm^{-1}). The CH_3CN groups in **2** and $[Cp_2Fe_2(S_2)(SEt)_2Ag_2(NCCH_3)_4][SbF_6]_2$ give rise to bands near 2300 cm^{-1} indicative of end-on coordinated ligand.[26] Lattice CH_3CN in [**5**][PF_6]$_2$·CH_3CN gives ab-

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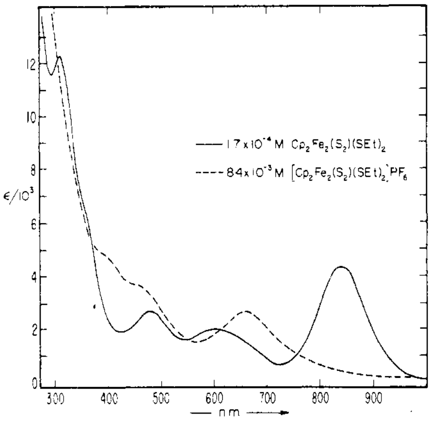

Figure 10. Electronic spectra of **1b** and [**1b**][PF_6].

sorptions at significantly lower frequencies.

(V) Electronic Spectra. The absorption spectra of **1b** and its monocation are compared in Figure 10. The neutral dimer spectrum shows five distinct maxima (a strong band at 233 nm is off scale) spread over a 600-nm range. Oxidation of the complex radically alters the spectrum; only one well-defined maximum at 660 nm and two shoulders near 400 and 470 nm remain, and no detectable peaks or shoulders could be located in the UV region. It is difficult to assign these transitions because of the complexity of the ligands. However, the disulfide-bridged ruthenium ammines, $[L_2(NH_3)_8Ru_2S_2]^{n+}$ (L = neutral or charged ligand; n = 2, 4),[27] give rise to spectra remarkably similar in appearance to that for **1**. In both cases, a strong (ϵ (2–3) × 10^4) band at 230–240 nm is present, in addition to either two or three progressively weaker absorptions in the 285–600-nm region, ending with a very symmetric band of increased intensity in the 700–840-nm region. Tentative assignment of the latter peak to a charge-transfer transition involving the disulfide is made in light of the absence of such a peak in the spectra of mercaptide-bridged iron dimers not containing the S_2 ligand (Table III). Certain iron complexes containing S^{2-} (such as $KFeS_2$) or dithiolate ligands can also give rise to bands in the 700–900-nm region, and $[Co(WS_4)_2]^{2-}$ has been reported to give a strong absorption at 820 nm (ϵ 5 × 10^3).[28] Thus, strong low-energy transitions, though not a common feature of sulfur complexes, cannot be considered to be diagnostic of M–S_2–M geometries.

The tetranuclear clusters gave strong ultraviolet absorptions tailing off into the visible region, but well-defined maxima were not observed. The spectrum of [**5**][PF_6]$_2$ exhibited shoulders at 436 and 660 nm.

Conclusions

Sulfur-rich reaction mixtures containing $[CpFe(CO)_2]_2$ have been used to synthesize cluster compounds containing doubly and triply bridging disulfide ligands. These electron-rich ligands have been shown to be very versatile (1) by virtue of their ability to bond with back-donation from S_2 to form strong bonds with metals, (2) by demonstrating a fluxional behavior while in a triply bridging configuration, and (3) by functioning as a Lewis base donor while in a triply bridging configuration.

The electrochemistry of these disulfide containing clusters is quite extensive and reversible redox processes have been consistently observed with them. The irreversible loss of sulfur upon oxidation, observed in the planar Fe_2S_2 dimer (**1**) as well as in the Fe_4S_6 cubane cluster (**6**), has been rationalized on the basis of strain induced in the molecule by changes in the metal–metal bonding.

Thus far no bonding model for bridging S_2 ligands has been quantified to the point where explicit predictions can be made regarding the synthesis of compounds containing S_2. However, since, in many compounds containing monatomic sulfur as a ligand, a disulfide ligand would bond in an electronically similar fashion, it would be expected that many known compounds containing S^{2-} could be modified to contain electron-rich disulfide ligands. Several new examples of bonding geometries for disulfide have recently been structurally characterized by Müller.[1b] In general, the S–S bond length for the disulfide ligand varies over a significant range, and no consistency has been observed for a particular geometry. It appears that this problem could prove to be a fruitful area for further study.

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy.

Registry No. **1a**, 62053-26-3; **1b**, 39796-99-1; **1b**·$2SO_2$, 77589-70-9; [(**1b**)$Ag_2(NCCH_3)_4$]$(SbF_6)_2$, 77589-72-1; [**1b**][SbF_6], 59196-35-9; [**1b**][PF_6], 59196-34-8; **1c**, 62029-06-5; **2a**, 77589-74-3; **2b**, 62029-12-3; **2c**, 77589-76-5; **3**, 77589-77-6; **4**, 12171-59-4; **5**, 77589-78-7; [**5**][SbF_6]$_2$, 77902-71-7; [**5**][PF_6]$_2$, 77924-71-1; [**5**][I]$_2$, 77743-48-7; [**5**][PF_6], 77902-72-8; **5**·$2SO_2$, 77589-79-8; **6**, 72256-41-8; **6**·$2SO_2$, 77589-80-1; [(**6**)$_2$Ag]$(SbF_6)_3$, 77904-05-3; $[CpFe(CO)(SEt)]_2[SbF_6]_2$, 77589-81-2; $[CpFe(CO)_2]_2$, 12154-95-9; $[CpFe(CO)(SEt)]_2$, 12092-25-0; $[CpFe(CO)(SMe)]_2$, 12087-63-7; $[CpFe(CO)(SBzl)]_2$, 52346-17-5; $[CpFe(CO)(SEt)]_2[PF_6]_2$, 77589-83-4; Et_2S_3, 3600-24-6; Et_2S_4, 13730-34-2; Et_2S_2, 110-81-6; S_8, 10544-50-0; ammonium polysulfide, 9080-17-5; Na_2S, 1313-82-2; $AgSbF_6$, 26042-64-8.

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