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Iron–Sulfur Clusters with SiMe₄-Bridged Cyclopentadienyl Ligands: [Me₂Si(η⁻⁵-C₅H₅)₂Fe₅S₁₂, [Me₂Si(η⁻⁵-C₅H₄)₂Fe₄S₆, and [Me₂Si(η⁻⁵-C₅H₄)₂Fe₄S₆(CO)]‡

Wouter van den Berg,† Lianne Boot,‡ Helma Joosen,§ Johannes G. M. van der Linden,|| Wil P. Bosman,‡ Jan M. M. Smits,‡ René de Gelder,§ Paul T. Beurskens,* Jürgen Heck,*§ and Anton W. Gal*,‡

Department of Inorganic Chemistry, Nijmegen SON Research Center, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands, and Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Martin-Luther-King-Plat 6, 20146 Hamburg, Germany

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The synthesis and characterization of iron–sulfur clusters stabilized by dimethylsilyl-bridged cyclopentadienyl groups are reported. The thermal reaction of Me₂Si(η⁻⁵-C₅H₅)₂Fe₅(CO)₄ (1) with S₈ yields the tetranuclear cubane-type cluster compound [Me₂Si(η⁻⁵-C₅H₅)₂Fe₅S₆ (4) and the pentanuclear cluster compound [Me₂Si(η⁻⁵-C₅H₅)₂Fe₅S₆] (3) in high yields. The photochemical reaction of 1 with S₈ yields the tetranuclear cluster compound [Me₂Si(η⁻⁵-C₅H₅)₂Fe₅S₆(CO)] (5), which contains one residual terminal carbonyl. The crystal structures of 3 and 4 have been determined. Crystal data: 3·CH₂Cl₂, monoclinic, C2/c, α = 23.480(13) Å, b = 11.192 (4) Å, c = 17.84 (3) Å, β = 118.58(9)°, V = 4118(7) Å³, Z = 4, R = 0.078; 4, triclinic, P1, a = 8.4787(7) Å, b = 12.9648(9) Å, c = 13.4990(9) Å, α = 79.857(8)°, β = 75.293(8)°, γ = 74.041(11)°, V = 1370.9(2) Å³, Z = 2, R = 0.0447. The Fe₅S₁₂ core of 3 has a bowtie structure in which a central iron atom is octahedrally coordinated by six sulfur atoms from one tetrasulfido and four disulfido groups. The structure of 4 resembles the structure of the known iron–sulfur cluster Cp₂Fe₅S₆. However, 4 shows a markedly enhanced thermal stability compared to Cp₂Fe₅S₆. In their cyclic voltammograms, 4 and 5 exhibit electrochemical behavior typical of cubane-type Cp₉ iron–sulfur clusters, whereas the cyclic voltammogram of 3 is quite different. The μCO mode of 5 has been measured for four different oxidation states of the cluster by means of IR spectrophotometric methods. The Mössbauer spectra of 3 and 4 in are in accordance with their pentanuclear structure.

Introduction

Cyclopentadienyl ligands, C₅H₅, are known for their wide range of applications in chemistry, as well as their incorporation in metal complexes. These ligands are used in a wide range of applications, from catalysts to pharmaceuticals. The use of cyclopentadienyl ligands in metal complexes has been studied extensively due to their unique electronic and structural properties. These ligands can act as both ligands and as part of the metal framework, allowing for a wide range of applications.

In this paper, we show that the neutral cluster compound [Me₂Si(η⁻⁵-C₅H₅)₂Fe₅S₁₂] (3) is a product from the thermal reaction of Me₂Si(η⁻⁵-C₅H₅)₂Fe₅(CO)₄ (1) with elemental sulfur. In this reaction, [Me₂Si(η⁻⁵-C₅H₅)₂Fe₅S₆(CO)₄] (4) is also formed.

1 Cooperative Effects in π-Ligand-Bridged Dinuclear Complexes. 18. Dedicated to Prof. Dr. M. Herberhold on the occasion of his 60th birthday.

2 University of Nijmegen.

3 Universität Hamburg.


The photochemical reaction of 1 with elemental sulfur generates the Fe₅S₁₂ cluster compound [Me₂Si(η⁻⁵-C₅H₅)₂Fe₅S₆(CO)] (5), in which one terminal CO ligand is still present.

Experimental Section

General Methods. All manipulations were carried out under a purified N₂ atmosphere, using standard Schlenk techniques, unless indicated otherwise. Al₂O₃ (aluminum oxide 90, neutral, activity III, Merck) was heated at 200 °C under 10⁻³ mbar pressure for 3 days and subsequently deactivated with 5% (w/w) H₂O saturated with N₂. SiO₂ (100, Merck) was evacuated at 10⁻³ mbar pressure for 3 days. Fe(O₃)₅ was filtered and bubbled with N₂ prior to use. The solvents were dried and subsequently distilled under N₂ atmosphere according to standard literature procedures.

Tetrabutylammonium hexafluorophosphate (TBAB, Fluka) and P(C₆H₅)₃(OH) were used as received. S₈ (Interpharm) was sublimed under reduced pressure. [FeCP₄]₄ and Me₂Si(C₅H₅)₂ were prepared by published procedures.

Physical Measurements. FAB mass spectra were recorded on a VG 7070 mass spectrometer. FD mass spectra were recorded on a JEOL JMS-SX/SX102A at the University of Amsterdam, The Netherlands. ¹H and ¹³C NMR and ¹H 2D COSY NMR spectra were recorded on a Bruker AC 100 MHz FT spectrometer, a Bruker WM 200 FT spectrometer, a Varian Gemini 200 BB spectrometer, and a Bruker AM 300 MHz FT spectrometer. Mössbauer spectra were recorded by Dr. Mulder at the Kamerlingh Onnes Institute of the University of Leiden, The Netherlands, using a constant-acceleration spectrometer equipped with a ⁵⁷Co source in a Rh matrix (3, 3[PF₆]₃) and by Dipl. Chem. S. Bieber at the University of Hamburg, Germany, using a conventional ⁵⁷Fe Mössbauer equipment (4, 4[PF₆]₃). Powder samples were either dispersed in boron nitride (3, 3[PF₆]₃) or sealed in a Rh matrix (3, 3[PF₆]₃).
brass rings with Kapton windows, and studied at 77 K or used neat (4, [4]PF6), transferred to a small Schlenk flask with Mylar foil windows, and studied at room temperature. Isomer shifts are reported relative to Fe metal at 298 K in both cases. IR spectra were recorded on a Perkin-Elmer 1720-X FTIR spectrometer. EPR spectra were recorded on a Bruker ESP 300 spectrometer and a Bruker ER-220DL-LR spectrometer. Cyclic voltammetry and differential-pulse voltammetry measurements were performed using an EG&G Princeton Applied Research Model 273 galvanostat/potentiostat. A conventional three-electrode cell, with Pt working and auxiliary electrodes and 0.1 M TBAB electrolyte, was used. The working electrode was cleaned by polishing with 0.3 mm aluminum oxide, followed by sonication, prior to use. In CH2Cl2, an Ag/Ag reference electrode (grain of Agl (Fluka), 0.02 M Bu4N (Janssen), and 0.1 M TBAB) was employed. Spectro-electrochemical measurements with the OTTLE cell6 were performed in CH2Cl2 with 0.1 M TBAB by Dr. F. Hartl, University of Amsterdam. Elemental analyses (C, H, S) were carried out on a Carlo Erba NCSO analyzer by the microanalytical department of this university.

[MeSn(η^5-C5H5)2Fe(CO)3] (1) can be prepared either photochemically or thermally.7 Thermal route: A 10.4 g (53.3 mmol) sample of Fe(CO)5 and 5.0 g (26.9 mmol) of (CsH5)2SnMe2 was dissolved in 400 mL of toluene, and the mixture was refluxed for 6 h. The solvent was removed in vacuo, and the resulting red oil with red crystalline material was purified by column chromatography (alumina, 5% H2O; toluene/hexane (2:1:1)). The first yellow band was discarded. The broad red band was collected, the solvent was removed in vacuo, and the resulting residue was dried in vacuo and crystallized from toluene/hexane mixtures. Yield: 5.56 g (50%). IR and 1H NMR analyses are in accordance with the literature.

[MeSn(η^5-C5H5)2Fe2S2] (3) and [MeSn(η^5-C5H5)2Fe2S4] (4). A mixture of 1.60 g of 1 (3.90 mmol) and 1.13 g of Sg (4.41 mmol) in 400 mL of toluene was refluxed for 69 h. During the reaction, the color changed from dark red to black and a black precipitate was formed. The mixture was filtered, and the residue was extracted with dichloromethane to give product 3 after evaporation of the solvent. The yield after crystallization from dichloromethane/hexane was 0.76 g (0.734 mmol, 47% based on Fe). The filtrate from the reaction mixture was dried in vacuo, and the residue was recrystallized from a dichloromethane/hexane mixture to give the black product 4. The yield after crystallization was 0.73 g (0.926 mmol, 47%). Anal. Calcd (found) for 3: C 26.77 (27.73); H 2.70 (2.71); S 34.30 (34.65). Anal. Calcd (found) for 4: C 35.56 (36.39); H 3.58 (3.56); S 24.40 (24.05). FAB MS for 4, m/z: 805 ([M + 2H]+, 4%); 788 (M+, 88%); 756 (M - S)18%; 742 (M - 2S), 32%). FD MS for 3, m/z: 1085 (M, 1%)

[MeSn(η^5-C5H5)2Fe2S4] (5) A mixture of 0.95 g of 1 (2.32 mmol) and 0.84 g of Sg (3.28 mmol) in 400 mL of toluene was cooled to 0 °C and irradiated with a high-pressure mercury lamp for 10 h. The reaction mixture slowly changed from dark red to black, and an insoluble precipitate formed on the lamp. The mixture was filtered to remove any insoluble material. The filtrate was evaporated to dryness, and the resulting black solid was purified by column chromatography (alumina, 5% H2O; toluene/hexane (1:1)). The first eluted, dark red band contained the starting material 1; then pure toluene was used as eluent and a second, black band was collected, evaporated to dryness, and recrystallized from CH2Cl2/hexane. Yield: 0.4 g (0.55 mmol, 40%). Anal. Calcd (found) for 5: C 34.65 (34.35); H 3.35 (3.70); S 21.14 (21.40). FAB MS for 5, m/z: 788 (M - CO)*, 2%; 756 (M - S - CO)*, 28%; 724 (M - 2S - CO)*, 19%; 692 (M - 3S - CO)*, 7%). FD MS for 5, m/z: 816 (M*, 100%); 788 (M - CO)*, 20%; 756 (M - S - CO)*, 10%).

[4]PF6. Method A. A sample of 0.15 g (0.19 mmol) of 4 was dissolved in 30 mL of dichloromethane, and the solution was cooled to 0 °C. Then 0.07 g (0.19 mmol) of [Fe]PF6 was added, and the reaction mixture was allowed to warm to room temperature, and was stirred for 24 h. Subsequently, 10 mL of hexane was added, and the resulting black precipitate was filtered off, washed with hexane, and dried in vacuo. CV showed the product to be pure [4]PF6.

[4]PF6 can be prepared in the same way as [4]PF6, but also by controlled-potential bulk electrolysis. In a typical experiment, 38.5 mg of 3 was dissolved in dichloromethane, and the solution was placed in a standard electrolysing unit, with a solution of Fe(dtc)3 in the counter electrode compartment in order to lower the cell potential. The potential of the working electrode was just above the first oxidation potential, and the passed charge was measured until the anodic current was less than 1% of its initial value. The calculated molecular mass of 3 was 1050 ± 50 amu (theoretical value 1036 amu).

[4]PF6. A sample of 84 mg (0.107 mmol) of 4 was dissolved in 35 mL of dichloromethane, and the solution was cooled to 0 °C. Approximately 30 mL (0.6 mmol) of Br2 was added in a syringe, and the reaction mixture was stirred for 5 min. A brown precipitate formed, which was filtered off in air, washed with CH2Cl2 and hexane, and dried in air. CV in acetonitrile showed it to be a mixture of [4]Br2 and impurities. Yield: 80 mg (80%). The brown powder was dissolved in demineralized water, the mixture was filtered, and the filtrate was added to a saturated KPF6 solution in water. Within 1 min, a brown precipitate was formed. This was filtered off, washed with water and diethyl ether, and dried in air. Crystallization of crude [4]PF6 from an acetone/diethyl ether mixture in air yielded [4]PF6.

Conversion of 5 to 4. A sample of 56.6 mg (0.0693 mmol) of 5 was dissolved in 50 mL of toluene, and the solution was refluxed for 8 h. The solvent was removed in vacuo, and the resulting black solid was crystallized from CH2Cl2. After filtration, the mother liquor was evaporated to dryness (fraction 1). The residue was redissolved in a small amount of CH2Cl2, and a large amount of hexane was added. The resulting precipitate was filtered off and dried in vacuo (fraction 2). Both fractions proved to be pure 4 according to CV and 1H NMR spectroscopy. The combined yield was quantitative. The conversion of 5 to 4 can be followed by 1HNMR spectroscopy in a sealed NMR tube at 100 °C.

Attempted Reaction of 4 with PPh3. A 53.4 mg sample of 4 (0.068 mmol) and (03 mg of PPh3 (0.39 mmol) were dissolved in 50 mL of toluene. This solution was refluxed for 32 h, after which the solvent was removed in vacuo. The only product identified (1H NMR) was 4. The reaction was followed with IR spectroscopy. No P=SP4 vibration was observed throughout the experiment.

Structure Determination of 3. Crystals of 3-CH2Cl2 were grown from dichloromethane/hexane mixtures. The black crystals were of poor quality. After thorough inspection, only one crystal was considered to be useful. The crystal (0.12 x 0.26 x 0.24 mm) was mounted in a glass capillary (sealed under N2 atmosphere) to prevent decomposition and loss of solvent molecules and used to measure a full sphere of reflection data. The unit cell dimensions were determined from the setting angles of 25 reflections in the range 15° < 2θ < 25°. Crystal data are given in Table 1.

There was no decomposition during the time of the measurements until, after 10 713 reflections were measured, the crystal cracked and the measurement was stopped. It was not possible to further optimize the cell parameters afterward. The Fe and S atoms were found from an automatic Patterson interpretation (PATTY), followed by a phase refinement procedure to expand the fragment (DIRDIF®). A Fourier map showed the presence of a dichloromethane molecule. The structure was refined by full-matrix least-squares.

Method B. A sample of 0.05 g (0.063 mmol) of 4 was slurried in acetonitrile, and 0.06 g (0.38 mmol) of NLHFP, was added. This mixture was then heated to 70 °C and was stirred for 24 h, during which the compound slowly dissolved. After addition of 25 mL of dichloromethane, the mixture was filtered to yield a white residue and a black filtrate. The filtrate was evaporated to dryness. The resulting black solid was pure [4]PF6 according to CV.
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Table 1. Crystallographic Data for [Me₃Si(η⁵-C₅H₅)₂]Fe₂S₂(C₂H₅Cl) (3-CH₂Cl₂) and [Me₃Si(η⁵-C₅H₅)₂]FeS₄ (4)

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<tr>
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* F² = 2σ(F₂); F₁ > 4σ(F₁). All data. ¹ R = Σ||F₁|| - ||F₀||/Σ||F₀||. ² R = Σσ(F₁ — F₀)²/Σσ(F₁)². ³ GOF = (Σw(F₀² — F₁²)²/n — p)¹/². ⁴ n = total number of reflections and p = total number of parameters.

The infrared spectrum shows an absorption band at 1923 cm⁻¹, and the ¹³C NMR spectrum contains a resonance signal at δ = 220.7 ppm. These spectroscopic data strongly point to the presence of a terminal CO ligand in the cluster compound. The FD mass spectrum of 5 shows the expected parent ion peak M^+ at 816 amu, although its intensity is only about 20% of the (M — CO)^+ peak at 788 amu. Unfortunately, attempts to obtain suitable crystals for X-ray structure analysis have failed thus far. The composition of 5 was however confirmed by thermoanalysis. After heating of 5 in toluene, the color of the reaction mixture slowly changed from dark red to black, and a black precipitate (3) was formed. Compound 4 was obtained from the deeply colored filtrate. Compounds 3 and 4 were obtained as pure black crystalline compounds by recrystallization from dichloromethane/hexane.

The results and discussion are summarized in the following sections.

Results and Discussion

Thermal Synthesis of [Me₃Si(η⁵-C₅H₅)₂]Fe₂S₂ (3) and [Me₃Si(η⁵-C₅H₅)₂]FeS₄ (4). Compound 1 was synthesized by a modified literature procedure.⁶ The thermal reaction of 1 with S₄ (Scheme 1) was followed by means of IR spectroscopy. The CO vibrations of 1 gradually disappeared, and no intermediate carbonyl-containing product could be detected. During the reaction, the color of the reaction mixture slowly changed from dark red to black, and a black precipitate (3) was formed.

Compound 4 was obtained from the deeply colored filtrate. Compounds 3 and 4 were obtained as pure black crystalline compounds by recrystallization from dichloromethane/hexane.

In the FD mass spectrum, a parent ion peak for 3 is found at 1035 amu (M^+ — 1). The FAB mass spectrum of 4 revealed the expected value (788 amu) for the parent peak. The isotope distribution around the parent peak and the decomposition pattern point to a product with composition [Me₃Si(η⁵-C₅H₅)₂]Fe₃S₄.

Photocatalytic Synthesis of [Me₃Si(η⁵-C₅H₅)₂]Fe₂S₂(CO) (5). A mixture of 1 and an excess of S₄ in toluene was irradiated for 10 h with a high-pressure mercury lamp (Scheme 2). The resulting reaction mixture was filtered and the solvent of the filtrate was removed. After purification of the black residue by column chromatography and subsequent crystallization, the new iron—sulfur cluster compound 5 was obtained.

The infrared spectrum shows an absorption band at 1923 cm⁻¹, and the ¹³C NMR spectrum contains a resonance signal at δ = 220.7 ppm. These spectroscopic data strongly point to the presence of a terminal CO ligand in the cluster compound. The FD mass spectrum of 5 shows the expected parent ion peak M^+ at 816 amu, although its intensity is only about 20% of the (M — CO)^+ peak at 788 amu. Unfortunately, attempts to obtain suitable crystals for X-ray structure analysis have failed thus far. The composition of 5 was however confirmed by thermoanalysis. After heating of 5 in toluene, the only product identified was 4, in virtually 100% yield. This confirms that 5 is an Fe₃S₄ cluster with an additional CO ligand. Further evidence for the presence of a terminal carbonyl ligand was obtained from IR spectrophotometric measurements (vide infra). The photocatalytic reaction of (η⁵-C₅H₅R)₂Fe₂S₄(CO)₄ with S₄ in methanol has been reported to give (η⁵-C₅H₅R)₄Fe₃S₄(CO), (η⁵-C₅H₅R)₂Fe₂S₄(CO), and (η⁵-C₅H₅R)₂FeS₄ as consecutive products.¹⁴

Molecular Structures. a. [Me₃Si(η⁵-C₅H₅)₂]Fe₃S₂ (12). Crystals of 3-CH₂Cl₂ suitable for X-ray structure analysis were obtained by slow diffusion of hexane into a dichloromethane solution during a short period (1 week at room temperature). Earlier attempts to crystallize 3 from CH₂Cl₂/hexane mixtures.

two Me₂S(η⁵-C₅H₅)Fe₂ moieties (Figure 1). The tetrasulfido ligand bridges the central iron atom and the Me₂S(η⁵-C₅H₅)₂-Fe₂ moieties in a μ₂-μ₂-bonding mode.

The central iron atom is almost ideally octahedrally coordinated by six sulfur atoms. The Fe—S bond lengths of the central iron atom range from 2.23 to 2.28 Å and are well within the range observed for other Fe—S distances in octahedral complexes in which Fe has a formal oxidation state of II.²⁻²⁵ Although small, the structural deviations on going from 3 to 3⁺ are the largest for the Fe₅θ cores, thus indicating Fe(1) as the formal Fe(III) center in 3⁺.

The S—S distances in the tetrasulfido group are in the range 2.02—2.10 Å. This dispersion has been found for other tetrasulfido ligands.²⁶

The occurrence of the tetrasulfido group is unprecedented for iron—sulfur clusters. Sulfur is known to form catenanes, including the S₅²⁻ anion, in a large number of compounds.²⁷⁻²² Thus far, no η⁵-C₅Fe iron—sulfur clusters with S₅ groups, x > 2, have been reported.

In the Me₂S(η⁵-C₅H₅)Fe₂ units, each iron is coordinated by three sulfur atoms and one C₅H₅ ring. The angle between the least-squares planes of the C₅H₅ rings is 99°. This is almost identical to the value in the starting material 1 (97°), which suggests that the strain in the bridging Me₂S(η⁵-C₅H₅) ligand does not increase on going from 1 to 3. The Fe₁(Fe₂)Fe(3) distance (2.55 Å) is short compared to the distances in known cyclopentadienyl iron—sulfur cluster compounds without a Cp—Cp linkage (average 2.65 Å) and is close to the value in the starting material 1 (2.51 Å). The coordination geometry around the Si atom is that of a slightly distorted tetrahedron. The Fe—S distances to the [Me₂S(η⁵-C₅H₅)₂]Fe₂ units range from 2.17 to 2.29 Å and are normal values for Fe—S distances in iron—sulfur cluster compounds.²⁴⁻²⁶

b. [Me₂S(η⁵-C₅H₅)₂]Fe₂S₄ (4). Crystals of 4 suitable for X-ray diffraction were grown from THF/hexane. The molecular structure of this cluster is shown in Figure 2. The molecule exhibits almost perfect C₂ symmetry in the solid state (see Tables 4 and 5).

The structure of 4 is very similar to that of Cp₂Fe₂S₄.²³⁻³⁵ The Fe₁(Fe₂)Fe(3)—Fe(4) distances are 2.62 and 2.63

at elevated temperatures over a longer period (8 weeks) had resulted in oxidative decomposition of 3, yielding 3⁺[FeCl₄]⁻²²

The geometry of 3 (Figure 1, Tables 2 and 3) differs only slightly from the geometry of 3⁺.²²

The unit cell of 3·CH₂Cl₂ contains both enantiomers of the chiral molecule, each situated around a crystallographic 2-fold axis through the central iron atom.

The Fe₅θS₅ cores of 3 and 3⁺ have a bowtie shape.¹⁵⁻¹⁹ For iron—sulfur clusters only a few examples of such a shape have been reported to date.²⁰⁻²² Compound 3 consists of a central Fe atom linked via one tetrasulfido and four disulfido fragments.


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For 3, the sixteen \( \text{C}_2\text{H}_4 \) protons provide eight signals with equal intensities and the six protons of the \( \text{Me}_2\text{Si} \) groups give rise to two signals with triple intensities. The number of \( \text{C}_2\text{H}_4 \) resonances reflects the \( C_2 \) symmetry of the molecule, in agreement with the \( X \)-ray structure analysis.

In accordance with the pseudo-\( C_2 \) symmetry of the crystal structure, 4 has six resonance signals with equal intensities and one signal with double intensity for the sixteen \( \text{C}_2\text{H}_4 \) protons. 2D COSY \( ^1{H} \) NMR analysis of 4 shows a clear correlation within two sets of \( \text{C}_2\text{H}_4 \) proton signals, ascribed to the two sets of two equivalent \( \text{C}_2\text{H}_4 \) moieties. Upon brief contact of a \( \text{CDCl}_3 \) solution of 4 with air, three of the \( \text{C}_2\text{H}_4 \) proton signals (one having double intensity) in the \( ^1{H} \) NMR spectrum broaden (see Figure 3a). When a sample of 4 in \( \text{CDCl}_3 \) is exposed to air for days or when a mixture of 4 and \( 4(\text{PF}_6) \) is dissolved in \( \text{CDCl}_3 \) (Figure 3b), the initially broadened \( \text{C}_2\text{H}_4 \) signals in the \( ^1{H} \) NMR spectrum broaden further and shift.

Comparison with the 2D COSY \( ^1{H} \) NMR of 4 reveals that the sharp signals belong to one \( \text{C}_2\text{H}_4 \) ring and the broadened signals to the other \( \text{C}_2\text{H}_4 \) ring of the \( \text{Me}_2\text{Si}(\eta^4-\text{C}_8\text{H}_8) \) unit. The broadening can be explained by a weak paramagnetism, due to a small amount of oxidized species, which allows rapid electron exchange with the neutral complex. The preferential broadening of one set of signals indicates that the unpaired electron in 4 is predominantly localized in the Fe(1)—Fe(3) or the Fe(2)—Fe(4) pair of the \( \text{FeS}_4 \) cluster. This conclusion is in accordance with Kubas' result, which showed that, upon oxidation of \( \text{Cp}_2\text{FeS}_4 \), the electron is taken from an antibonding orbital localized at the iron atoms Fe(1) and Fe(3).

In the \( ^1{H} \) NMR spectrum of 5, thirteen signals with equal intensities and one signal with triple intensity are observed for the \( \text{C}_2\text{H}_4 \) protons and four signals with triple intensities are observed for the methyl protons. In the 2D COSY \( ^1{H} \) NMR spectrum, a correlation was found between four sets of \( ^1{H} \) resonances. Thus four different \( \text{C}_2\text{H}_4 \) moieties are present in this molecule, in accordance with its lack of symmetry. This lack of symmetry is also confirmed by the \( ^{13}C \) NMR spectrum of 5 (Table 6). Fourteen signals between 70 and 105 ppm are observed, one of which has a double intensity. One more resonance is believed to be hidden under the intense signal of \( \text{CDCl}_3 \) (77 ppm). As expected, the resonances of the ipso carbons were not observed. The four methyl signals of the two dimethylsilyl groups are found around 0 ppm. A weak signal at 221 ppm is assigned to the carbonyl group.

\( \text{Mössbauer Spectroscopy} \). The data for 3 and 4, \( z = 0, +1 \), are assembled in Table 7. The Mössbauer spectrum of 3 reveals a superposition of different iron sites (Figure 4a).

The best fit for 3 is obtained using a 2:2:1 iron site model according to the X-ray structure analysis (Figure 1) and to NMR spectroscopic data. The unique iron atom has an isomer shift of 0.25 mm s\(^{-1}\) and a quadrupole splitting of 0.43 mm s\(^{-1}\). The two pairs of iron atoms have very similar quadrupole splittings (1.10 and 1.11 mm s\(^{-1}\)) and slightly different isomer shifts (0.25 and 0.35 mm s\(^{-1}\)). Upon oxidation of 3 to 3\( ^+ \), the same 2:2:1 Fe site ratio is observed (Figure 4b) but all the signals have shifted. The doublet of the central iron site has shifted to a lower value, consistent with a higher relative s-electron density at the central Fe nucleus caused by the loss of a d electron.

\( ^1{H} \) NMR and \( ^{13}C \) NMR Spectroscopy. The data for 3 and 4, \( z = 0, +1 \), are assembled in Table 7. The Mössbauer spectrum of 3 reveals a superposition of different iron sites (Figure 4a).

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Table 6. 'H NMR Data for Compounds 3, 4, 5, and 4(PF6) and 13C NMR Data for Compound 5

<table>
<thead>
<tr>
<th>compd</th>
<th>'H NMR</th>
<th>13C NMR</th>
<th>Si—CH3</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>5.90 (2); 5.64 (2); 5.36 (2); 5.31 (2); 5.24 (2); 5.05 (2); 4.77 (2); 4.05 (2)</td>
<td>75.1; 74.0</td>
<td>0.32 (6); 0.25 (6)</td>
<td>-0.10 (6)</td>
</tr>
<tr>
<td>4</td>
<td>6.90 (2); 6.11 (2); 5.98 (2); 5.05 (2); 4.59 (2); 4.41 (4); 3.71 (2)</td>
<td>75.1; 74.0</td>
<td>0.29 (6); 0.15 (6)</td>
<td>-0.10 (6)</td>
</tr>
<tr>
<td>4(PF6)</td>
<td>7.96 (2); 6.72 (2); 6.58 (2); 6.19 (2); 5.68 (2); 5.08 (2); 4.97 (2); 4.62 (2)</td>
<td>75.1; 74.0</td>
<td>0.51 (3); 0.46 (3); 0.32 (3);</td>
<td>0.15 (3)</td>
</tr>
<tr>
<td>5</td>
<td>5.57 (1); 5.45 (1); 5.23 (1); 5.18 (1); 5.11 (1); 5.05 (1); 4.98 (1); 4.88 (1); 4.73 (1); 4.69 (1); 4.66 (1); 4.54 (1); 4.36 (3); 3.90 (1)</td>
<td>75.1; 74.0</td>
<td>-1.4; -1.7; -2.2; -2.9</td>
<td>220.7</td>
</tr>
</tbody>
</table>

* CDCl3 (7.29 ppm) solutions at 298 K. Integrations are given in parentheses. No clear couplings could be observed. * CD3CN (2.01 ppm) solution at 298 K. c CDCl3 (77.0 ppm) solution at 298 K. d Quaternary carbons are not observed.

Figure 3. 'H NMR spectra in CDCl3 at 200 MHz: (a) 4 after brief contact with air; (b) a mixture of 4 and 4(PF6).

Table 7. Mössbauer Data for Iron—Sulfur Cluster Compounds

<table>
<thead>
<tr>
<th>compd</th>
<th>fraction (%)</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>Γ (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>40</td>
<td>0.25</td>
<td>1.10</td>
<td>0.34</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>0.35</td>
<td>1.11</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.25</td>
<td>0.43</td>
<td>0.29</td>
</tr>
<tr>
<td>3+</td>
<td>40</td>
<td>0.22</td>
<td>1.07</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.42</td>
<td>1.09</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.16</td>
<td>1.53</td>
<td>0.29</td>
</tr>
<tr>
<td>4</td>
<td>3+</td>
<td>0.34</td>
<td>1.02</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>4+</td>
<td>0.31</td>
<td>0.96</td>
<td>0.25</td>
</tr>
</tbody>
</table>

* Vs α-Fe at room temperature.

The doublet of one of the two two-iron sites also shifts to lower values, albeit to a lesser extent, whereas the doublet of the other two-iron site shifts to higher values. The most remarkable result of the Mössbauer studies is the minor change of the quadrupole splitting of the two two-iron sites upon oxidation, whereas the QS of the central iron atom changes substantially, in accordance with the change from low-spin Fe(II) to low-spin Fe(III) in octahedral coordination.

The Mössbauer spectra for 4 and 4(PF6) are almost identical and consist of one doublet, implying that the Fe sites are identical. This is obviously not true from a structural point of view, but Mössbauer spectroscopy appears to be unable to distinguish between the various Fe sites. The spectra reported for Cp4Fe4S8 (recorded at 4 K) also show one doublet, but the data were fitted in accordance with a two-site model. The value for the IS of 4 is lower than that found for Cp4Fe4S8.

Figure 4. Mössbauer spectra of (a) 3 and (b) 3(PF6), recorded at 77 K.

This could be due to the different temperatures at which 4 (298 K) and Cp4Fe4S8 (4 K) have been measured. The almost negligible changes in the spectra upon going from 4 to 4+ seem to indicate that changes in electron density upon oxidation are counteracted by structural changes, as has been postulated for the Cp4Fe4S8+ series. Redox Behavior and Spectroelectrochemical Measurements. Redox potentials of 3—5 are listed in Table 8, together with those of some other iron—sulfur clusters. All potentials are quoted as the potential of the Fe/Fc+ redox couple.

Figure 8. 'W' sequence in CDCl3 at 200 MHz: (a) 4 after brief contact with air; (b) a mixture of 4 and 4(PF6).

Table 7. Mössbauer Data for Iron—Sulfur Cluster Compounds

<table>
<thead>
<tr>
<th>compd</th>
<th>fraction (%)</th>
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<th>QS (mm/s)</th>
<th>Γ (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>40</td>
<td>0.25</td>
<td>1.10</td>
<td>0.34</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>0.35</td>
<td>1.11</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.25</td>
<td>0.43</td>
<td>0.29</td>
</tr>
<tr>
<td>3+</td>
<td>40</td>
<td>0.22</td>
<td>1.07</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.42</td>
<td>1.09</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.16</td>
<td>1.53</td>
<td>0.29</td>
</tr>
<tr>
<td>4</td>
<td>3+</td>
<td>0.34</td>
<td>1.02</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>4+</td>
<td>0.31</td>
<td>0.96</td>
<td>0.25</td>
</tr>
</tbody>
</table>

* Vs α-Fe at room temperature.

The doublet of one of the two two-iron sites also shifts to lower values, albeit to a lesser extent, whereas the doublet of the other two-iron site shifts to higher values. The most remarkable result of the Mössbauer studies is the minor change of the quadrupole splitting of the two two-iron sites upon oxidation, whereas the QS of the central iron atom changes substantially, in accordance with the change from low-spin Fe(II) to low-spin Fe(III) in octahedral coordination.

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(40) An increase in the QS on going from low-spin Fe(II) to low-spin Fe(III) in an octahedral coordination is found for M,Fe(CN)6 (M = Na, K; x = 4, 3), although to a lesser extent: Drugo, R. S. Physical Methods in Chemistry; W. B. Saunders Co.: Philadelphia, PA, 1977; p 541.

Table 8. Redox Potentials for Complexes 3, 4, 5, and Related Compounds*  
<table>
<thead>
<tr>
<th>Complex</th>
<th>E_{1/2} (V) (E_a (mV))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>-1.53 (60) -0.41 (56) 0.49</td>
</tr>
<tr>
<td>4</td>
<td>-1.75 (60) -0.45 (57) 0.14 (57) 0.80 (56) 1.02</td>
</tr>
<tr>
<td>5</td>
<td>-1.62 (58) -0.38 (57) -0.01 (58) 0.80 (58)</td>
</tr>
<tr>
<td>CluPFeS6</td>
<td>-0.73</td>
</tr>
<tr>
<td>CluPFeS6d</td>
<td>-0.62</td>
</tr>
<tr>
<td>CluPFeS6d</td>
<td>-0.45</td>
</tr>
<tr>
<td>FeS6</td>
<td>-0.83</td>
</tr>
<tr>
<td>FeS6</td>
<td>-0.10</td>
</tr>
</tbody>
</table>

* CH2Cl2 solutions with 0.1 M TBAH as supporting electrolyte. Potentials versus Fe/Fe++. Peak separations are given in parentheses.  
‡ Peak potential. ‡ From literature 62,63.  
* From literature. 36,62.  
† From literature. 31.  
/ Adsorption phenomenon.

The Fe3S12 cluster compound 3 exhibits a reversible reduction (0/−1) and oxidation (0/+1) and an irreversible +1/+2 oxidation. The second oxidation occurs at approximately 900 mV higher potential than the first. This redox behavior differs somewhat from that of the Fe5S8 cubane-type clusters 4 and 5. The redox behavior of 4 and 5 is characteristic of cyclopentadienyl iron–sulfur cubane-type clusters and resembles strongly that of analogous clusters with nonbridged cyclopentadienyl groups, C5FeS5 and C5FeS5. In CH2Cl2, 4 undergoes two reversible oxidations, separated by 600 mV, two irreversible oxidations, and one irreversible reduction. Compound 5 shows three reversible oxidations and one irreversible reduction. There is a striking similarity between the redox potentials of compound 4 and its nonbridged analog, C5FeS5. Except for the second oxidation, all redox potentials of 4 are within 50 mV of those for C5FeS5. Apparently, the bridging SiMe3 group has little influence on the electronic properties of this cluster in the oxidation states −1, 0, and +1. This parallels the electronic influence of the SiMe3 group in sandwich complexes. 45 In the Fe5S8 compound [η5-C5H4SiMe3]Fe5S8, however, the SiMe3 group is believed to be electron-donating, causing a negative shift in redox potentials. 46 In compound 4, the ligand seems to be responsible for the shift of the +1/+2 transition: steric constraints within the bridging dicyclopentadienyl ligand might hamper the oxidation step +1/+2.

The redox potentials of the cluster compounds depend on the solvent used. For example, on going from CH2Cl2 to DMF, the +1/+2 transition of 4 shifts 100 mV in the negative direction, indicating an increasing cluster ion–solvent interaction.

Table 9. EPR Data for 3+, 4+, and 5+  
<table>
<thead>
<tr>
<th>g1</th>
<th>g2</th>
<th>g3</th>
<th>g4</th>
</tr>
</thead>
<tbody>
<tr>
<td>3+</td>
<td>2.418</td>
<td>2.123</td>
<td>1.980</td>
</tr>
<tr>
<td>4+</td>
<td>2.094</td>
<td>2.003</td>
<td>1.982</td>
</tr>
<tr>
<td>5+</td>
<td>2.061</td>
<td>2.037</td>
<td>1.997</td>
</tr>
</tbody>
</table>

* Obtained from CHCl3/DMF (1/1) solutions of the Pf4 salts at T = 110K.  
† Obtained in situ by means of controlled-potential electrolysis in DMF, measured at 8 K.  
‡ From literature. 57–61.  
§ From literature. 57,58.  
‖ From literature. 55,56.

Reactivity. As mentioned above, 3 appeared to be reactive toward freshly distilled dichloromethane, as is well established for other sulfido group containing complexes. 57,58 The dichloromethane used was freed from radical inhibitor; therefore, chloride radicals are held responsible for the oxidation of part of 3 to 3+ and the decomposition of another part to yield the FeCl2− anion. The resulting salt [3]FeCl4 precipitated. 3

Surprisingly, 4 is thermally very stable and is recovered unchanged after refluxing in toluene for 32 h, even in the presence of an excess of triphenylphosphine. In marked contrast to 4, C5FeS5 loses elemental sulfur upon heating, ultimately yielding Fe2P2S6. 43

As can be deduced from their cyclic voltammograms, compounds 3 and 4 can be oxidized to their monocations at mild potentials. [3]Pf4 and [4]Pf4 were obtained by use of air or [Fe2P2S6] as oxidants. The redox behavior of 4 indicates that 4 can be oxidized to the dication by a powerful oxidant. Indeed, 47–49


Figure 5. Schematic representation of the core contraction of Fe₅S₆ to Fe₄S₄. Solid circles represent Fe atoms in the front plane, and dashed circles, Fe atoms in the back plane.

Figure 6. Proposed structure of [Me₂Si(η⁵-C₅H₅)₅]Fe₄S₄ (CO) (5).

upon addition of Br₂ to 4, the dication 4²⁺ was obtained. According to its cyclic voltammogram, the resulting sample contained some impurities. After anion exchange with KPF₆, the product was still impure, but upon recording an ¹H NMR spectrum, we observed eight sharp cyclopentadienyi proton signals and two dimethylsilyl proton signals (Table 6). The C₅H₅ proton signals have clearly shifted downfield with respect to those of the neutral starting material. After crystallization of this PF₆ salt from acetone/diethyl ether in air, measurement of the equilbrium potential of an acetonitrile solution revealed that the compound had been reduced to the monocationic form [4]PF₆⁶.

Conclusions. The introduction of silicon-bridged cyclopentadienyl ligands into iron—sulfur cluster chemistry provided a useful means for the preparation of new clusters, 3—5. The flexibility in relative orientation of the two C₅H₅ rings of the (η⁵-C₅H₅)—SiMe₂—(η⁵-C₅H₅) ligand is apparently limited for 4. This prevents the expulsion of one or two sulfur atoms and the associated contraction of the iron—sulfur core previously observed for Cp₄Fe₄S₄ (see Figure 5).

The increased steric strain upon cluster-core contraction also seems to be indicated by the distinct positive shift of the potential of the second oxidation step of 4 as compared to Cp₄Fe₄S₄. However, other spectroscopic properties of 4 are very similar to those of Cp₄Fe₄S₄.

The reaction mechanism of the reaction of [Me₂Si(η⁵-C₅H₅)₅]Fe₂(CO)₄ (1) with S₈ is complicated because iron is formally oxidized from +1 to +3 and sulfur is reduced from 0 to −2 (monosulfido groups), −1 (disulfido groups), or −½ (tetralsulfido group). Small sulfur catenane anions are known to form from S₈ upon electron uptake. A part of the diiron starting complex has to be destroyed completely to generate the iron atoms for the central iron site in 3. Notwithstanding this decomposition, the conversion of 1 to 3 and 4 is almost quantitative.

The photochemical reaction of [Me₂Si(η⁵-C₅H₅)₅]Fe₂(CO)₄ (1) with S₈ yielded 5 as the only identifiable compound. Compound 5 may be considered as an intermediate in the thermal reaction, very close to the end of the reaction pathway (in casu, compound 4). The proposed structure of 5 is shown in Figure 6. Compared to the case of 4, the number of valence electrons at each iron center remains unchanged and an Fe–CO bond forms instead of an Fe–S bond. This would explain the ease of transformation of 5 into 4.

Acknowledgment. We thank Mrs. A. Roelofsen (University of Nijmegen) for electrochemical measurements, Dr. F. Hartl (University of Amsterdam) for spectroelectrochemical measurements with the OTTLE cell, Dr. F. Mulder (Kamerlingh Onnes Laboratory at Leiden University) and Dipl. Chem. S. Bieber (Hamburg University) for Mössbauer measurements, and Dipl. Chem. F. Moritz for EPR measurements. We are indebted to Prof. Dr. Ir. J. J. Steggerda for his continuing interest and fruitful discussions, and we are grateful for financial support from the SON/NWO.