Iron–Sulfur Clusters with SiMe₂-Bridged Cyclopentadienyl Ligands: 
[Me₂Si(η⁵-C₅H₄)₂]Fe₄S₁₂, [Me₂Si(η⁵-C₅H₄)₂]Fe₄S₆, and [Me₂Si(η⁵-C₅H₄)₂]Fe₄S₆(CO)

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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(η⁵-C₅H₄)₂Fe₄(CO)₄ (1) with S₈ yields the tetranuclear cubane-type cluster compound [Me₂Si(η⁵-C₅H₄)₂]₂Fe₄S₆ (4) and the pentanuclear cluster compound [Me₂Si(η⁵-C₅H₄)₂]₃Fe₅S₇ (3) in high yields. The photochemical reaction of 1 with S₈ yields the tetranuclear cluster compound [Me₂Si(η⁵-C₅H₄)₂]₂Fe₄S₆(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, a = 23.480(13) Å, b = 11.192 (4) Å, c = 17.84 (3) Å, β = 118.58 (9)°, V = 4118.7(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 Fe₅S₇ 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 CpFe₄S₈. However, 4 shows a markedly enhanced thermal stability compared to CpFe₄S₆. In their cyclic voltammograms, 4 and 5 exhibit electrochemical behavior typical of cubane-type Cp₄–iron–sulfur clusters, whereas the cyclic voltammogram of 3 is quite different. The νCO mode of 5 has been measured for four different oxidation states of the cluster by means of IR spectroelectrochemical methods. The Mössbauer spectra of 3 and 4 are in accordance with their pentanuclear structure.

Introduction

Dicyclopentadienyl ligands, C₅H₄–X–C₅H₄, e.g. with X = SiMe₃, impose geometrical constraints on dinuclear metal complexes. As a result, substantial changes in structures and properties can occur for these complexes when compared to their counterparts with nonbridged cyclopentadienyl groups. In our studies on cubane-like tetrairon–sulfur cluster compounds Cp₄Fe₄S₄ (x = 4–6), the use of the dicyclopentadienyl ligand C₅H₄–SiMe₂–C₅H₄ instead of isolated cyclopentadienyl (Cp) ligands resulted in the hitherto unknown Fe₅S₇ cluster compound [Me₂Si(η⁵-C₅H₄)₂]₃Fe₅S₇(CO) (1), for which we recently reported the crystal and molecular structure. This compound formed during prolonged (8 weeks) crystallization from dichloromethane/hexane of a reaction product that was recently reported the crystal and molecular structure.2 This work was dedicated to Prof. Dr. M. Herberhold on the occasion of his 60th birthday.

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 under 10⁻³ mbar pressure for 3 days. Fe(CO)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.³ Tetraethylammonium hexafluorophosphate (TBAH, Fluka) and P(C₆H₅)₃ (3, 3(PF)), were used as received. S₈ (Interchim) was sublimed under reduced pressure. [Fe]PF₆ and Me₂Si(C₅H₄)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 ¹D 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)) and by Dipl. Chem. S. Bieber at the University of Hamburg, Germany, using a conventional ⁵⁷Fe Mössbauer equipment (4, 4(PF₆)). Powder samples were either dispersed in boron nitride (3, 3(PF₆)) or sealed in Tetrabutylammonium hexafluorophosphate (TBAH, Fluka) and P(C₆H₅)₃ (3, 3(PF₆)) were used as received.

Notes:

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 Universitäts Hamburg.


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-F FTIR spectrometer. EPR spectra were recorded on a Bruker ESP 300 spectrometer and a Bruker ER-220D-LR spectrometer. Cyclic voltammetry and differential-pulse voltammetry measurements were performed using an EG&G Princeton Applied Research Model 273 galvanostat/potentiosstat. 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/AgI reference electrode (grain of AgI (Fluka)), 0.02 M Bu4NI (Janssen), and 0.1 M TBAB was employed. Spectro-electrochemical measurements with the OTTLE cell 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.

**[Me6]n{Si(3-C6H4)2}2Fe2(CO)4 (1)**. A mixture of 1.6 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 crystallized from toluene/hexane mixtures. Yield: 5.56 g (50%). IR and 1H NMR analyses are in accordance with the literature.

**[Me6]n{Si(3-C6H4)2}2Fe2(CO)4 (3) and [Me6]n{Si(5-C6H4)2}2Fe2(CO)4 (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 product 4. The yield after crystallization was 0.73 g (0.926 mmol, 47%). Anal. Calc.: found for 3-C6H4Cl2: C, 56.77 (56.69); H, 2.70 (2.71); S, 34.30 (34.65). Anal. Calc.: found for 4: C, 56.36 (56.39); H, 3.58 (3.56); S, 24.40 (24.06). FAB MS for 4, m/z: 805 ([M + OH]+), 788 (M+; 88%), 756 (M-52; 18%), 724 (M-28; 52%). FD MS for 3, m/z: 1035 (M+ - 1). [Me6]n[Si(3-C6H4)2]2Fe2S2CO (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 color 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 fraction proved 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 structures were determined 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 measurements were stopped. Therefore, 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 (DIRDIF2). 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 NH4PF6 was added. This mixture was heated to 20 °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.

[3]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 electrolysis unit, with a solution of Fe(dtc)2 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 with 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 heptane, 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 acetonitrile/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 1H NMR 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=S 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.

Table 1. Crystallographic Data for

\[
\begin{align*}
&M\text{e}_2\text{Si}(\eta^5-\text{C}_5\text{H}_5)\text{H}_2\text{Fe}_2\text{S}_2\text{Cl}_2(3-\text{CH}_2\text{Cl}_2)\text{ and} \\
&M\text{e}_2\text{Si}(\eta^5-\text{C}_5\text{H}_5)\text{H}_2\text{Fe}_2\text{S}_2(4)
\end{align*}
\]

\[
\begin{array}{llll}
\text{empirical formula} & \text{C}_2\text{H}_2\text{Cl}_2\text{Fe}_2\text{S}_2\text{Si}_2 & \text{C}_2\text{H}_2\text{Fe}_2\text{S}_2\text{Si}_2 \\
\text{fw} & 1121.54 & 788.40 \\
\text{space group} & \text{C}2/c (\text{No. } 15) & \text{P}1 (\text{No. } 2) \\
\text{T (K)} & 293(2) & 293(2) \\
\alpha (\text{deg}) & 23.840(13) & 78.877(4) \\
\beta (\text{deg}) & 11.192 (4) & 12.9648(9) \\
\gamma (\text{deg}) & 17.84 (3) & 13.4990(9) \\
\text{no. of indep reflns} & 10311 & 10311 \\
\text{no. of refns collected} & 2082(2) & 2082(2) \\
\text{Rmerge (on } F^2 \text{ values}) & 0.0196(4) & 0.0196(4) \\
\text{no. of indep reflns} & 1924 (3610) & 1924 (3610) \\
\text{R} & 0.0789(1728) & 0.0447(3607) \\
\text{wR} & 0.1595(3740) & 0.2303(3750) \\
\text{GOF} & 1.15(1.604) & 1.098(1.585) \\
\end{array}
\]

\[a - 2 \sigma(F_2) ; F_0 > 4 \sigma(F_0)\]

Methods on \( F^2 \) values using SHELXL with anisotropic parameters for the non-hydrogen atoms. Hydrogen atoms were included at calculated positions (H in C-H in riding mode, H in CH3 as rigid groups). The solvent molecules (CH3Cl) were found at the initial stages of the analysis. Their presence was verified with the "bypass" procedure using the program PLATON. The large anisotropy of the solvent molecules is ascribed to disorder. We were able to split the atomic positions of dichloromethane into the positions for two disordered molecules of idealized geometry. These molecules were refined as rigid groups. The refinement was continued using geometrical restraints for the cyclopentadienyl fragments (maintaining \textit{mm2} (\textit{C}_{2h}) symmetry). The refinement converged to an \textit{R} value of 0.0789 on \( F^2 \) values for 1924 observed reflections, with 209 parameters and 31 restraints. The function minimized was \( \text{GOF} = \Sigma w(F_2 - F_0)^2 / (n - p) \).

Structure Determination of 4. Suitable crystals of 4 were grown from THF/hexane mixtures at approximately 30 °C. A crystal (0.40 x 0.20 x 0.03 mm) was mounted on a glass fiber, coated with Mo Kα radiation. Crystal data are given in Table 1. A detailed description of the data collection and reduction procedures is given elsewhere. The structure was solved by the program system DIRDIF using the program PATTY to locate the heavy atoms. The hydrogen atoms of the methyl groups were refined as rigid rotors with idealized sp3 hybridization and a C-H bond length of 0.97 Å. Crystal data are given in Table 1. A detailed description of the data collection and reduction procedures is given elsewhere.

Results and Discussion

Thermal Synthesis of \[\text{Me}_2\text{Si}(\eta^5-\text{C}_5\text{H}_5)\text{H}_2\text{Fe}_2\text{S}_2(3)\] and \[\text{Me}_2\text{Si}(\eta^5-\text{C}_5\text{H}_5)\text{H}_2\text{Fe}_2\text{S}_2(4)\]. Compound 1 was synthesized by a modified literature procedure. The thermal reaction of 1 with \( \text{S}_8 \) (Scheme 1) was followed by means of IR spectroscopy. The results of these reactions are shown in Table 1. The CO vibrations of 1 gradually disappeared, and no intermediates were observed. The IR spectrum of 2 revealed the expected values (788 amu) for the parent peak. The isotope distribution around the parent peak and the decomposition pattern point to a product with composition \[\text{Me}_2\text{Si}(\eta^5-\text{C}_5\text{H}_5)\text{H}_2\text{Fe}_2\text{S}_2.\]

Photocatalytic Synthesis of \[\text{Me}_2\text{Si}(\eta^5-\text{C}_5\text{H}_5)\text{H}_2\text{Fe}_2\text{S}_2(5)\]. A mixture of 1 and an excess of \( \text{S}_8 \) in toluene was irradiated for 10 h with a high-pressure mercury lamp (Scheme 2). The resulting 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 \( \delta = 220.7 \) 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 \( M^+ = 816 \) amu, although its intensity is only about 20% of the \( [\text{M} - \text{CO}]^+ \) 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 thermal analysis. After heating of 5 in toluene, the only product identified was 4, in virtually 100% yield. This confirms that 5 is an Fe2S8 cluster with an additional CO ligand. Further evidence for the presence of a terminal carbonyl ligand was obtained from IR spectroelectrochemical measurements (vide infra). The photoreaction of \[\text{Me}_2\text{Si}(\eta^5-\text{C}_5\text{H}_5)\text{H}_2\text{Fe}_2\text{S}_2(4)\] with \( \text{S}_8 \) in methanol has been reported to give \( \eta^5-\text{C}_5\text{H}_5\text{R} \) \( \text{Fe}_2\text{S}_8(\text{CO})_4 \), \( \eta^5-\text{C}_5\text{H}_5\text{R} \) \( \text{Fe}_2\text{S}_6(\text{CO})_4 \), and \( \eta^5-\text{C}_5\text{H}_5\text{R} \) \( \text{Fe}_2\text{S}_4 \) as consecutive products.

Molecular Structures. a. \[\text{Me}_2\text{Si}(\eta^5-\text{C}_5\text{H}_5)\text{H}_2\text{Fe}_2\text{S}_2(3)\]. 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


at elevated temperatures over a longer period (8 weeks) had resulted in oxidative decomposition of 3, yielding 3\(^+\)FeC\(_4\)S\(_4\).\(^2\)

The geometry of 3 (Figure 1, Tables 2 and 3) differs only slightly from the geometry of 3\(^+\), as reported to date\(^1\). The unit cell of 3 consists of a central iron atom range from 2.23 to 2.28 Å and are well within the iron-sulfur clusters only.\(^1\) A few examples of such a shape have been reported.\(^2\) The occurrence of the tetrasulfido group is unprecedented for iron-sulfur clusters. Sulfur is known to form catenanes, including the S\(_4^2\) anion, in a large number of compounds.\(^3\) Thus far, no S\(_4^2\)-iron-sulfur clusters with S\(_4\) groups, \(n > 2\), have been reported.

In the Me\(_2\)Si(S\(_5\)C\(_5\)H\(_5\))\(_2\)Fe\(_2\) units, each iron is coordinated by three sulfur atoms and one C\(_\text{H}_5\) ring. The angle between the least-squares planes of the C\(_\text{H}_5\) rings is 99°. This is almost identical to the value in the starting material 1 (97°), which suggests that the strain in the bridging Me\(_2\)Si(S\(_5\)C\(_5\)H\(_5\)) ligand does not increase on going from 1 to 3. The Fe(2)–Fe(3) distance (2.55 Å) is short compared to the distances in known cyclopentadienyl iron-sulfur cluster compounds with a C-p Fe-S distance (2.62 and 2.63 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 [Me\(_2\)Si(S\(_5\)C\(_5\)H\(_5\))Fe] units range from 2.17 to 2.29 Å and are normal values for Fe–S distance in iron-sulfur cluster compounds.\(^4\)–\(^6\)

The structure of 4 is very similar to that of C\(_p\)Fe\(_2\)S\(_4\).\(^33\)\(^,\)\(^34\) The Fe(1)–Fe(2) and Fe(3)–Fe(4) distances are 2.62 and 2.63 Å. The occurrence of the tetrasulfido group is unprecedented for iron-sulfur clusters. Sulfur is known to form catenanes, including the S\(_4^2\) anion, in a large number of compounds. Thus far, no S\(_4^2\)-iron-sulfur clusters with S\(_4\) groups, \(n > 2\), have been reported.

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For 3, the sixteen C₄H₄ protons provide eight signals with equal intensities and the six protons of the Me₂Si groups give rise to two signals with triple intensities. The number of C₄H₄ resonances reflects the C₂ symmetry of the molecule, in agreement with the X-ray structure analysis.

In accordance with the pseudo-C₂ symmetry of the crystal structure, 4 has six resonance signals with equal intensities and one signal with double intensity for the sixteen C₄H₄ protons. 2D COSY ¹H NMR analysis of 4 shows a clear correlation between two sets of C₄H₄ proton signals, ascribed to the two sets of equivalent C₄H₄ moieties. Upon brief contact of a CDCl₃ solution of 4 with air, three of the C₄H₄ proton signals (one having double intensity) in the ¹H NMR spectrum broaden (see Figure 3a). When a sample of 4 in CDCl₃ is exposed to air for days or when a mixture of 4 and 4(PF₆) is dissolved in CDCl₃ (Figure 3b), the initially broadened C₄H₄ signals in the ¹H NMR spectrum broaden further and shift.

Comparison with the 2D COSY ¹H NMR of 4 reveals that the sharp signals belong to one C₄H₄ ring and the broadened signals to the other C₄H₄ ring of the Me₂Si(η⁴-C₅H₄)₂ 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 Fe₅S₅ cluster. This conclusion is in accordance with Kubas’ result, which showed that, upon oxidation of Cp₅-Fe₅S₅, the electron is taken from an antibonding orbital localized at the iron atoms Fe(1) and Fe(3).³⁰

In the ¹H NMR spectrum of 5, thirteen signals with equal intensities and one signal with triple intensity are observed for the C₄H₄ protons and four signals with triple intensities are observed for the methyl protons. In the 2D COSY ¹H NMR spectrum, a correlation was found between four sets of ¹H resonances. Thus four different C₄H₄ moieties are present in this molecule, in accordance with its lack of symmetry. This lack of symmetry is also confirmed by the ¹³C 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 CDCl₃ (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 fragment.

**Mössbauer Spectroscopy.** The data for ³ and ⁴, z = 0, +1, are assembled in Table 7. The Mössbauer spectrum of ⁴ 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 ⁴⁺, 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 one d electron.³⁹

**References**


(39) A change in the isomer shift from a high to a low value on going from low-spin Fe(II) to low-spin Fe(III) is generally found in octahedrally coordinated Fe₅S₅ species, although the regions of IS(Fe(II)) and IS(Fe(III)) differ distinctly: Gülich, P.; Link, R.; Trustewin, A. X. Mössbauer Spectroscopy and Transition Metal Chemistry; Springer-Verlag: Berlin, 1978.
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 with the change from low-spin Fe(II) to low-spin Fe(III) in an octahedral coordination is found for M,v[Fe(CN)6]2+. The IS of Fe3+ (recorded at 4 K) also show one doublet, but the data were fitted in accordance with a two-site model. The spectra reported for Cp4Fe3S6 (recorded at 4 K) also show one doublet, but the data were fitted in accordance with a two-site model.24 The value for the IS of 4 is lower than that found for Cp4Fe3S6.

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 Cp4Fe3S6 (4 K) also show one doublet, but the data were fitted in accordance with a two-site model.24 The value for the IS of 4 is lower than that found for Cp4Fe3S6.

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Iron–Sulfur Clusters

The Fe₅S₆²⁻ 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 Fe₅S₆ cubane-type clusters 4 and 5. The redox behavior of 4 and 5 is characteristic of cyclopenta-diennyl iron–sulfur cubane-type cluster compounds and resembles strongly that of analogous clusters with nonbridged cyclopenta-diennyl groups, Cp₆FeS₆ and Cp₆FeS₆. In CH₃Cl₂, 4 undergoes two reversible oxidations, separated by 200 mV, two irreversible oxidations, and one reversible reduction. Compound 5 shows three reversible oxidations and one reversible reduction. There is a striking similarity between the redox potentials of compound 4 and its nonbridged analog, Cp₆FeS₆. Except for the second oxidation, all redox potentials of 4 are within 50 mV of those for Cp₆FeS₆. Apparently, the bridging SiMe₂ 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 SiMe₂ group in sandwich complexes. In the Fe₅S₆ compound [η⁵-C₅H₅]SiMe₂)Fe₂S₆, however, the SiMe₂ group is believed to be electron-donating, causing a negative shift in redox potentials. In compound 4, the ligand seems to be responsible for the shift of the +1/+2 transition: steric constraints within the bridging dicyclopenta-diennyl 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 CH₃Cl₂ to DMF, the +1/+2 transition of 4 shifts 100 mV in the negative direction, indicating an increasing cluster iron–solvent interaction.

The redox behavior of 5 differs from that of 4 despite the fact that both compounds contain an Fe₅S₆ core. The redox potentials of the −1/0 and 0/+1 transitions are shifted to slightly more positive values with respect to the corresponding redox processes of 4, perhaps due to the electron-withdrawing nature of bonded CO. In contrast, the redox pair +1/+2 is shifted about 150 mV in the negative direction with respect to 4. The redox wave +2/+3 shows a characteristic feature indicating adsorption phenomena of the oxidized compound on the surface of the electrode.

In infrared spectroelectrochemical measurements, the energy of the CO stretching vibration of 5 in CH₃Cl₂ was found to increase in steps of 22, 32, and 34 cm⁻¹, respectively, on passing through the cluster oxidation states −1 (1901 cm⁻¹), 0 (1923 cm⁻¹), +1 (1955 cm⁻¹), and +2 (1989 cm⁻¹). For the trication, no νCO was observed, probably because CO dissociates at this oxidation state, although the 2+/3+ redox transition was found to be reversible (vide infra). The shifts in νCO are in agreement with a strengthening of the C–O bond upon decrease of electron density available for π back-donation. The sensitivity of carbonyl ligands to (partial) electron transfer has been well documented. 47–49

| Table 8. Redox Potentials for Complexes 3, 4, 5, and Related Compounds |
|----------------------|------------------|------------------|------------------|------------------|
| complex             | E₁/₂ (V)          | ΔE₉ (mV)         |                  |
| 3                   | −1.53 (60)        | −0.41 (56)       | 0.49             |
| 4                   | −1.70 (60)        | −0.45 (57)       | 0.80             |
| 5                   | −1.62 (58)        | −0.38 (57)       | 0.80 (38)        |
| Cp₆FeS₆⁺             | −0.73             | −0.00            | 0.80             |
| Cp₆FeS₆²⁻            | −1.76             | −0.62            | 0.30             |
| [Me(η⁵-C₅H₅)]₄FeS₆⁺ | −1.72             | −0.45            | 0.45             |
| [Me(η⁵-C₅H₅)]₄FeS₆²⁻| −0.83             | −0.10            | 0.86             |

a CH₃Cl₂ solutions with 0.1 M TBAH as supporting electrolyte. Potentials versus Fe/Fe⁺. Peak separations are given in parentheses. b Peak potential. c From literature. d From literature. e From literature. f Adsorption phenomenon.

| Table 9. EPR Data for 3⁺, 4⁺, and 5⁺ |
|----------------------|------------------|------------------|
| g₁                   | g₂                | g₃                |
| 3⁺                   | 2.148             | 2.123             | 1.980             |
| 4⁺                   | 2.094             | 2.003             | 1.982             |
| 5⁺                   | 2.061             | 2.037             | 1.997             |

a Obtained from CHCl₃/DMF (1/1) solutions of the PF₆ salts at T = 110K. b Obtained in situ by means of controlled-potential electrolysis in DMF, measured at 8 K. c g = ± 0.001. cm⁻¹), +1 (1955 cm⁻¹), and +2 (1989 cm⁻¹).

EPR Spectroscopy. Frozen-solution EPR spectra of 3⁺ and 4⁺ were obtained from DMF/CHCl₃ solutions of the PF₆ salts. The frozen-solution spectrum of 5⁺ was recorded after generation in situ by controlled-potential electrolysis in an EPR tube. 40 All three spectra reveal three different g values (Table 9), consistent with a rhombic g tensor of a low-spin S = 1/₂ system.

For 3⁺ and 5⁺, a small g anisotropy is found, in agreement with observations for other cubane-type [Cp₆FeS₆] radicals, 42–45 The g anisotropy of 3⁺ is considerably more pronounced. This is in accordance with the virtually octahedrally coordinated central iron atom being the paramagnetic center. 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 was freed from radical inhibitor; therefore, chlorine radicals are held responsible for the oxidation of part of 3 to 3⁺ and the decomposition of another part to yield the FeCl₄⁻ anion. The resulting salt [3]FeCl₄ precipitated.

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, Cp₆FeS₆ loses elemental sulfur upon heating, ultimately yielding Fe₅S₆FeCl₄. 33

As can be deduced from their cyclic voltammograms, compounds 3 and 4 can be oxidized to their monocations and at mild potentials. [3]PF₆ and [4]PF₆ were obtained by use of air or [FeCl]PF₆ as oxidants. The redox behavior of 4 indicates that 4 can be oxidized to the dication by a powerful oxidant. Indeed, 47–49

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 cyclopentadienyl proton signals and two dimethylsilyl proton signals (Table 6). The C₅H₄ proton signals have clearly shifted downfield with respect to those of the neutral starting material.* After crystallization that the compound had been reduced to the monocationic form of this PF₆⁻ salt from acetone/diethyl ether in air, measurement of the equilibrium potential of an acetonitrile solution revealed that the compound is a dicationic form of this complex. The proposed structure of 5 is shown in Figure 6.

Figure 5. Schematic representation of the core contraction of Fe₄S₆ 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-C₅H₄)₂]₂Fe₄S₆ (CO) (5).

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 C₅H₄ rings of the (η⁵-C₅H₄)₅—SiMe₂—(η⁵-C₅H₄) 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 C₄Fe₄S₄ (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 C₄Fe₄S₄. However, other spectroscopic properties of 4 are very similar to those of C₄Fe₄S₆.

The reaction mechanism of the reaction of [Me₂Si(η⁵-C₅H₄)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 −1/2 (tetrasulfido group). Small sulfur catenane anions are known to form from S₈ upon electron uptake.59—61 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-C₅H₄)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.

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