for the $[Fe_4S_4(Cp)_4]^z$ compounds (Figure 3a). We therefore propose a small adjustment of this scheme.

The geometries observed for the iron-sulfur clusters in $Fe_4S_4(MeCp)_4$ and $[Fe_4S_4(MeCp)_4](PF_6)$ can again be understood by a qualitative MO scheme (Figure 3b), if it is assumed that in comparison with the $[Fe_4S_4(Cp)_4]^z$ compounds the e and b_2 levels have been reversed. This could be caused by a slightly different mixing up of the antibonding tetrairon cluster orbitals and the iron-cyclopentadienyl orbitals. Interchanging the e and b_2 levels does not affect the symmetries predicted for the neutral and the dicationic cluster species. It does have consequences, however, for the monocation. Since both in the compressed and in the elongated D_{2d} configuration, the partially occupied orbitals are nondegenerate, no symmetry lowering due to the Jahn-Teller effect occurs. Apparently the compressed form is energetically the most stable. In comparison with $[Fe_4S_4(MeCp)_4]^{2+}$ the additional electron occupies a b_2 orbital, which has antibonding character with respect to the interactions between the pairs of irons 1 and 3, 2 and 4, 2 and 3, and 1 and 4 (denoted as (13,24,23,14) in Figure 3. Therefore these four Fe-Fe distances are longer in $[Fe_4S_4(MeCp)_4]^+$ than in $[Fe_4S_4(Cp)_4]^{2+}$ (2.90 and 2.83 Å, respectively).

In summary, the X-ray structure determinations of $Fe_4S_4(MeCp)_4$ and $[Fe_4S_4(MeCp)_4](PF_6)$ have yielded some interesting new data. The limited number of X-ray structures for cluster compounds with 19 excess electrons has been extended. It appears that the geometries of these compounds are not only determined by the number of excess electrons but also by quite subtle differences in the electronic structure of the terminal ligand. After a small adjustment the qualitative MO scheme proposed by Dahl's group can be used to describe the bonding in the $[Fe_4S_4(MeCp)_4]^z$ compounds.

A similar effect has recently been reported for Co_3S_2Cp'' clusters, which for $n = 0$ and $n = +1$ show slightly different structures when Cp is substituted by MeCp.[38]

Acknowledgment. We thank W. P. Bosman for valuable assistance with the X-ray work. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO) and by the Centre National de la Recherche Scientifique-DRCI.

Supplementary Material Available: Tables A-D, listing crystallographic data and experimental details, atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, and anisotropic thermal parameters for $Fe_4S_4(MeCp)_4$ and $[Fe_4S_4(MeCp)_4](PF_6)$ (6 pages); tables of calculated and observed structure factors (25 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of the Iron-Sulfur Cluster Compounds $[Fe_4S_5(MeCp)_4](PF_6)_y$ (y = 0-2). X-ray Structure Determination of $[Fe_4S_5(MeCp)_4](PF_6)$

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The series of iron-sulfur cluster compounds $[Fe_4S_5(MeCp)_4](PF_6)_y$ (y = 0-2) is readily prepared by reaction of $[Fe(MeCp)(CO)_2]_2$ with an excess of sulfur in refluxing toluene followed by a number of suitable synthesis and purification steps. The structure of $[Fe_4S_5(MeCp)_4](PF_6)$ was determined crystallographically. $[Fe_4S_5(MeCp)_4](PF_6)$ crystallizes in the triclinic system, space group $P\bar{1}$, with cell dimensions a = 9.876 (1) Å, b = 10.683 (1) Å, c = 14.642 (1) Å, α = 87.86 (3)°, β = 108.67 (2)°, γ = 90.66 (2)°, V = 1462.4 (5) Å^3, and Z = 2. Refinement of 388 parameters on 5127 "observed" reflections gave a final R value of 0.054 (R_w = 0.078). The structure consists of an asymmetric Fe_4S_5 core with each iron involved in three Fe-S bonds. The disulfur group in the iron-sulfur core is μ_3-bonded with one sulfur atom coordinating to two iron atoms and the other sulfur atom to a third iron atom. This coordination mode differs from coordination mode of the S_2 group in the related compound $[Fe_4S_5(Cp)_4][MoOCl_4(THF)]$, which is side-on bonded to one iron atom and end-on bonded to two iron atoms. From ^1H NMR spectra recorded at several temperatures in the range 208-302 K and ^1H COSY spectra recorded at 208 K it is concluded that in acetone-d_6 solution the iron-sulfur core of the $[Fe_4S_5(MeCp)_4]^{2+}$ ion is rigid with the disulfur group coordinating two neighboring iron atoms in an equivalent way and a third iron atom in a unique way. The ^1H NMR spectrum of $[Fe_4S_5(MeCp)_4]^0$ recorded in $CDCl_3$ at 319 K indicates that the iron-sulfur cluster is fluxional with the S_2 group rotating around a pseudo-3-fold axis. The electrochemical behavior of the compounds $[Fe_4S_4(MeCp)_4](PF_6)$, $[Fe_4S_5(MeCp)_4](PF_6)_2$, and $Fe_4S_6(MeCp)_4$ is very similar to the electrochemical behavior of the related compounds $[Fe_4S_4(Cp)_4](PF_6)$, $[Fe_4S_5(Cp)_4](PF_6)_2$, and $Fe_4S_6(Cp)_4$. As expected because of the electron-releasing properties of the methyl groups, the redox potentials have shifted slightly in negative direction.

Introduction

The structural properties of the compounds $[M_4(\mu_3\text{-}A)_4(\eta^5\text{-}L)_4]$, where M is a d-transition metal, A an element from group 15 or 16 of the periodic table, and L a cyclopentadienyl (Cp) or a substituted cyclopentadienyl ligand (MeCp, *i*-PrCp, Me_5Cp), have been extensively studied.[1-5] The central theme in these studies is the relation between structure and electron count.[6-8] The related compounds $[Fe_4S_5(Cp)_4]^z$ (z = 0, 1+, 2+) and $Fe_4S_6(Cp)_4$ also possesses a number of interesting structural properties in the solid state as well as in solution.[9-13] In these compounds both μ_3-

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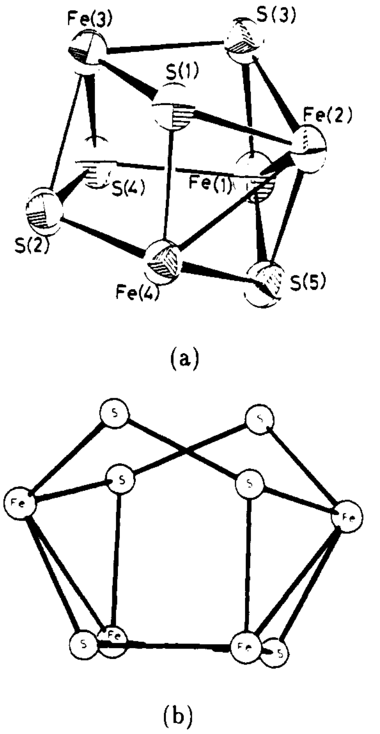

Figure 1. X-ray molecular structures of (a) $[Fe_4S_5(Cp)_4][MoOCl_4(THF)]$ and (b) $Fe_4S_6(Cp)_4$. Only the iron-sulfur cluster part is shown.

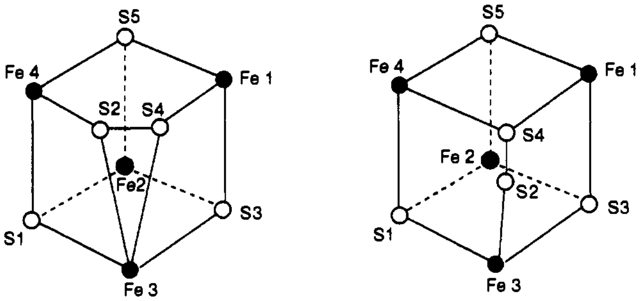

Figure 2. Two possible structures of the cluster species $[Fe_4S_5(Cp)_4]^z$, drawn as seen along the pseudo-3-fold axis through the disulfur group and iron atom 2.

bridging sulfur atoms and μ_3-bridging disulfur groups are present.

In the solid state two different ways of coordination have been observed for the disulfur ligands. The molecular structures of $[Fe_4S_5(Cp)_4][MoOCl_4(THF)]$ and $[Fe_4S_5(Cp)_4](PF_6)_2$ contain a disulfur group that is side-on bonded to one iron atom and end-on to two other iron atoms (Figure 1a).[10-12] In $Fe_4S_6(Cp)_4$ on the other hand, one of the sulfur atoms of each disulfur ligand is coordinated to two iron atoms and the other to a third iron atom (Figure 1b).[9,13] So far no explanation has been offered for these different coordination modes of the S_2 ligand.

In solution the iron-sulfur cores of the compounds $[Fe_4S_5(Cp)_4]^z$ (z = 0, 2+) show a temperature-dependent fluxionality.[9] In effect, the NMR spectrum of $[Fe_4S_5(Cp)_4]^0$ in $CDCl_3$ shows a 3:1 pattern at temperatures above 6 °C, which indicates that the disulfur group is equivalently bonded to the three neighboring iron atoms and thus rotates around the pseudo-3-fold axis (Figure 2). At temperatures below −40 °C, however, a 2:1:1 pattern is observed, which is consistent with a rigid iron-sulfur core and a disulfur group that coordinates equivalently to two iron atoms and uniquely to the third iron atom. By making use of proton NMR and a chiral shift reagent, Edidin et al. have shown that in $CDCl_3$ solution and at room temperature $Fe_4S_6(Cp)_4$ has a rigid iron-sulfur framework with the same chiral structure as in the solid state (Figure 1b).[14]

As part of our continuing interest in iron-sulfur-cyclopentadienyl cluster chemistry and in order to examine the influence of the terminal ligand on the properties of these compounds in the solid state as well as in solution, we have prepared and characterized the series $[Fe_4S_5(MeCp)_4](PF_6)_y$ (y = 0–2) and $Fe_4S_6(MeCp)_4$. Here we present the results including the X-ray crystal and molecular structure of $[Fe_4S_5(MeCp)_4](PF_6)$ and a ^1H COSY NMR study of $[Fe_4S_5(MeCp)_4](PF_6)_2$ in acetone-d_6 solution. The spectroscopic and electrochemical characterization of the series of compounds $[Fe_4S_4(MeCp)_4](PF_6)_y$ (y = 0–2), of which the preparation is reported elsewhere,[15] is also described.

Experimental Section

General Methods. All operations and manipulations were performed under a dinitrogen atmosphere unless indicated otherwise. $[Fe(MeCp)(CO)_2]_2$ (Alfa Products), $NaBH_4$ (Merck pa), $(Bu_4N)(PF_6)$ (TBAH; Janssen Chimica pa), and NH_4PF_6 (Janssen Chimica pa) were used as received. Elemental sulfur was purified by sublimation under reduced pressure. Ferrocene (Aldrich analyzed) was sublimed before use. Acetonitrile (Janssen Chimica pa) was distilled from CaH_2. Dichloromethane (Merck reinst) was washed with concentrated H_2SO_4, water, a 5% solution of Na_2CO_3 in water, and water, predried over $CaCl_2$, and distilled from CaH_2. Diethyl ether (Merck pa or Boom technical grade) was washed with a solution of 6 g of $FeSO_4$ and 6 mL of concentrated H_2SO_4 in 100 mL of water, predried over $CaCl_2$, and distilled from sodium. Hexane (Merck reinst) was washed with concentrated H_2SO_4, predried over $CaCl_2$, and distilled from sodium. Toluene (Merck pa) was distilled from sodium. Acetone (Merck pa) was used as received. All solvents were degassed before use by the pump-freeze-thaw method.

The elemental analysis of the compound $[Fe_4S_6(MeCp)_4](FeCl_4)$ was carried out by Analytische Laboratorien GMBH, Gummersbach, FRG. All other analyses were carried out in the microanalytical department of the University of Nijmegen.

Synthesis of $[Fe_4S_5(MeCp)_4](PF_6)_2$. A solution of 8.42 g of $[Fe(MeCp)(CO)_2]_2$ (44.1 mmol of Fe) and 2.47 g of S_8 (77.0 mmol of S) in 200 mL of toluene was refluxed for 1 h. The reaction mixture was filtered and the filtrate evaporated to dryness. The crude product obtained was washed with diethyl ether, suspended in acetonitrile, and air-oxidized in the presence of 3.60 g (22.1 mmol) of NH_4PF_6 for 48 h. The solution was then filtered and the solvent evaporated to almost dryness. According to cyclic and differential pulse voltammograms recorded at this stage, the mixture of cluster compounds consisted of about 30% $[Fe_4S_4(MeCp)_4](PF_6)$ and 70% $[Fe_4S_5(MeCp)_4](PF_6)_2$. About 100 mL of dichloromethane was added, and the solution was filtered. After addition of about 100 mL of hexane the product was collected by filtration and washed with dichloromethane and diethyl ether. This procedure was sufficient to yield 3.0 g (27%) of the desired product containing only a few percent of $[Fe_4S_4(MeCp)_4](PF_6)$. $[Fe_4S_5(MeCp)_4](PF_6)_2$ is extremely soluble in polar organic solvents, like acetone and acetonitrile, but almost insoluble in dichloromethane. Anal. Calcd for $[Fe_4S_5(MeCp)_4](PF_6)_2$: C, 29.12; H, 2.85; S, 16.19. Found: C, 29.48; H, 2.75; S, 16.68.

Synthesis of $Fe_4S_5(MeCp)_4$. To a solution of 0.46 g (0.465 mmol) of $[Fe_4S_5(MeCp)_4](PF_6)_2$ in 25 mL of acetonitrile was added 80 mg (2.11 mmol) of solid $NaBH_4$. This solution was stirred for 6 h and then stored at −20 °C overnight. After filtration and recrystallization from dichloromethane-acetonitrile 100 mg (31%) of pure product was obtained. Anal. Calcd for $Fe_4S_5(MeCp)_4$: C, 41.17; H, 4.03; S, 22.89. Found: C, 41.69; H, 3.70; S, 23.72.

Synthesis of $[Fe_4S_5(MeCp)_4](PF_6)$. To a solution of 220 mg (0.22 mmol) of $[Fe_4S_5(MeCp)_4](PF_6)_2$ in 25 mL of acetonitrile was added 160 mg (0.23 mmol) of $Fe_4S_5(MeCp)_4$. After being stirred for 8 h, the solution was filtered and 125 mL of diethyl ether was added. After storage of the solution at −20 °C the product was collected by filtration and washed with a 1:3 mixture of acetonitrile and diethyl ether and then with pure diethyl ether. The yield was 160 mg (43%). Anal. Calcd for

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$[Fe_4S_5(MeCp)_4](PF_6)$: C, 34.11; H, 3.34; S, 18.97. Found: C, 35.12; H, 3.30; S, 18.85.

Synthesis of $Fe_4S_6(MeCp)_4$. In a number of experiments 5–10 g of $[Fe(MeCp)(CO)_2]_2$ was refluxed with an excess of sulfur in 150 mL of toluene. Both the ratio of the reactants and the reaction time were varied. The reaction mixtures were filtered and evaporated to dryness. The relative amounts of $Fe_4S_4(MeCp)_4$, $Fe_4S_5(MeCp)_4$, and $Fe_4S_6(MeCp)_4$ in these products were determined by recording a cyclic voltammogram in dichloromethane (vide infra). The optimal reaction time for $Fe_4S_6(MeCp)_4$ turned out to be 1 hour, and the optimal excess of sulfur, 15–20%. Larger amounts of sulfur did not increase the yield of $Fe_4S_6(MeCp)_4$. The crude product obtained with a reaction time of about 1 hour and at least a 15% excess of sulfur typically consisted for more than 50% $Fe_4S_6(MeCp)_4$. Efforts for purification of $Fe_4S_6(MeCp)_4$ by repeated recrystallization were not successful. Usually dichloromethane was used as solvent, which turned out to be an unsuitable choice. An attempt to purify $Fe_4S_6(MeCp)_4$ by bulk electrochemical oxidation of a mixture of about 0.75 g of $Fe_4S_4(MeCp)_4$, 1.5 g of $Fe_4S_5(MeCp)_4$, and 1.5 g (2.05 mmol) of $Fe_4S_6(MeCp)_4$ to $[Fe_4S_4(MeCp)_4](PF_6)$, $[Fe_4S_5(MeCp)_4](PF_6)$, and $Fe_4S_6(MeCp)_4$ followed by recrystallization from dichloromethane–acetonitrile did not yield pure $Fe_4S_6(MeCp)_4$. Instead, during the electrolysis 0.70 g (0.69 mmol) of an unknown compound crystallized from the dichloromethane solution. Surprisingly the synthesis of this compound, to which we tentatively assign the molecular formula $[Fe_4S_6(MeCp)_4](FeCl_4)\cdot xCH_2Cl_2$, could be successfully repeated, although with a lower yield (10%), by just storing a solution of a mixture of $Fe_4S_4(MeCp)_4$, $Fe_4S_5(MeCp)_4$, and $Fe_4S_6(MeCp)_4$ in dichloromethane for 4 days. The new compound is soluble in DMF and DMSO but not in CH_2Cl_2 and CH_3CN. Anal. Calcd for $[Fe_4S_6(MeCp)_4](FeCl_4)$: C, 31.00; H, 3.03; Cl, 15.25; Fe, 30.03; S, 20.69. Found: C, 30.78; H, 2.93; Cl, 14.40; Fe, 28.50; S, 19.52. Spectroscopic and electrochemical characterizations of $Fe_4S_6(MeCp)_4$ were done on only partially purified samples.

Measurements. Cyclic voltammetric measurements were made by using a PAR Model 173 potentiostat equipped with a PAR Model 176 I/E converter and coupled to a PAR Model 175 universal programmer. Pulse voltammograms and differential pulse voltammograms were obtained with a PAR Model 174A polarographic analyzer at a scan rate of 5 or 10 mV/s with a pulse frequency of 2.0 pulse/s. The recording device was either a Kipp BD30 or a Kipp BD90 XY recorder. Platinum working and auxiliary electrodes were used. A Ag^+/Ag (0.1 mol dm^{-3} $AgNO_3$) reference electrode in acetonitrile was employed. The half-wave potential of a 10^{-3} mol dm^{-3} solution of ferrocene was measured under the same experimental conditions: $E_{1/2} = 0.050$ V. A Ag/AgI reference electrode (0.05 M Bu_4NI and 0.4 M Bu_4NClO_4)[16] was used for the measurements in dichloromethane ($E_{1/2}(Fc^+/Fc) = 0.657$ V).

Electron spin resonance experiments were carried out on a Bruker ESP 300 spectrometer. To obtain an EPR spectrum of $[Fe_4S_4(MeCp)_4]^{3+}$ in frozen acetonitrile solution, a controlled-potential electrolysis was performed. The equipment consisted of a Wenking LB 75M potentiostat and a Birtley electronic integrator. The electrolysis was made on an approximately 1 mM solution of $[Fe_4S_4(MeCp)_4](PF_6)$ at a potential 115 mV beyond the half-wave potential of the 3+/2+ couple. After the electrolysis had been completed ($n = 1.94$ at 3% residual current) a sample was transferred under nitrogen into an EPR tube and then stored in liquid nitrogen until the EPR spectrum was recorded.

^1H NMR spectra of $Fe_4S_4(MeCp)_4$, $Fe_4S_5(MeCp)_4$, and $Fe_4S_6(MeCp)_4$ were recorded in $CDCl_3$ solution on a Bruker WM-200 spectrometer. The spectra of $Fe_4S_4(MeCp)_4$ and $Fe_4S_6(MeCp)_4$ were measured at 298 K. The spectra of $Fe_4S_5(MeCp)_4$ were recorded at 298 and 319 K. ^1H NMR spectra of the charged cluster compound $[Fe_4S_5(MeCp)_4](PF_6)_2$ were measured in acetone-d_6 solution in the temperature range 188–302 K on a Bruker AM-500 spectrometer. A phase-sensitive ^1H COSY spectrum with double-quantum filtering[17] of the compound $[Fe_4S_5(MeCp)_4](PF_6)_2$ was recorded in acetone-d_6 solution at 208 K. The 2-D spectrum was measured on a Bruker AM-500 spectrometer. A total of 256 FID's were recorded with a sweep width of 716 Hz and a time domain of 256 data points. A relaxation delay of 1.0 s was used, and prior to acquisition two dummy scans were applied. After zero filling to 1024 times 1024 data points, and multiplication by a squared sine filter, the free induction decays were Fourier transformed to yield a two-dimensional spectrum. Subsequently the spectrum was symmetrized.

In addition, a triple-quantum-filtered ^1H COSY spectrum was recorded.[17] A total of 256 FID's were measured with a time domain of 256 data points and a sweep width of 716 Hz. After zero filling to 1024 times 1024 data points, the FID's were Fourier transformed.

Table I. Crystal Data and Experimental Details for the X-ray Diffraction Study of $[Fe_4(\mu_3\text{-}S_2)(\mu_3\text{-}S)_3(MeCp)_4](PF_6)$

chem formula	$C_{24}H_{28}F_6Fe_4PS_5$	V, Å^3	1462.4 (5)
fw	845.1	Z	2
a, Å	9.876 (1)	space group	$P\bar{1}$ (No. 2)
b, Å	10.683 (1)	ρ(calcd), g·cm^{-3}	1.92
c, Å	14.642 (4)	λ, Å	0.71073 Å
α, deg	87.86 (3)	μ(Mo Kα), cm^{-1}	23.99
β, deg	108.67 (2)	R	0.054
γ, deg	90.66 (2)	R_w[a]	0.078

[a] $R_w = (\sum w(F_0 - |F_c|)^2/\sum wF_0^2)^{1/2}$.

Structure Determination of $[Fe_4S_5(MeCp)_4](PF_6)$. Black crystals were grown from a solution of $[Fe_4(\mu_3\text{-}S_2)(\mu_3\text{-}S)_3(MeCp)_4](PF_6)$ in a mixture of acetonitrile and diethyl ether. The unit cell dimensions were calculated from the setting angles of 23 reflections in the range $17° \leq 2\theta \leq 20°$. The crystal data and the experimental details are listed in Table I. A profile analysis was performed on all reflections.[18,19] After correction for Lorentz and polarization effects and after an empirical absorption correction using the program EMPABS[20] (correction factors ranging from 0.93 to 1.06), the equivalent reflections were averaged ($R_{av} = \sum(|F_o - \bar{F}_o|)/\sum F_o = 0.039$, including all reflections). No extinction correction was applied.

The structure was solved using the program DIRDIF[21,22] by expansion of a trial structure consisting of one single Fe atom in the origin in space group $P1$, which gave the relative positions of all heavy atoms. The origin was shifted to the apparent center of symmetry between the two Fe_4S_5 clusters. The light atoms were located by DIRDIF and Fourier methods. A second empirical absorption correction (DIFABS)[23] was applied with correction factors ranging from 0.88 to 1.22 and $R_{av} = 0.039$. The structure was refined by full-matrix least-squares methods (SHELX).[24] The positions and anisotropic temperature factors of the Fe, S, and MeCp groups at the Fe(1), Fe(2), and Fe(3) atoms were refined. The MeCp group at the Fe(4) atom appeared to be disordered about two distinct positions: the positions and isotropic temperature factors of two MeCp groups, each about half-weight, were refined with correlated occupancy. The PF_6 anion appeared to be strongly disordered. In a difference electron-density map we observed peaks and streaks of electron density around the P atom. We located the F atoms of one anion from the largest peaks and refined the occupancy factor of the group and the positions and anisotropic temperature factors of the individual atoms. To interpret the remaining electron density, we put six F atoms in an ideal octahedral coordination (P–F = 1.52 Å) and refined them as a group with restraint geometry and an overall isotropic temperature factor. The occupancy of the first and the second PF_6 group refined to 0.83 and 0.17, respectively. The refinement converged at $R = 0.054$ with shift/esd's < 0.17 for all atoms except for the F atoms of the second PF_6 group with shift/esd's < 0.58. Geometrical calculations were done with PARST.[25] Plots were made with PLUTO[26] and ORTEP.[27]

Positional and thermal parameters of the Fe_4S_5 cluster core are given in Table II, and selected interatomic distances and bond angles, in Table III.

Results and Discussion

Synthesis of the Compounds $[Fe_4S_5(MeCp)_4](PF_6)_y$ ($y = 0$–2). Reaction of $[Fe(MeCp)(CO)_2]_2$ with elemental sulfur in refluxing

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Table II. Fractional Positional and Thermal Parameters (Å^2) for the Fe_4S_5 Moiety of $[Fe_4(\mu_3\text{-}S_2)(\mu_3\text{-}S)_3(MeCp)_4](PF_6)$ (with Esd's)

atom	x	y	z	$100U_{eq}$[a]
Fe(1)	0.01494 (9)	0.46219 (6)	−0.23223 (6)	3.59 (3)
Fe(2)	0.00475 (8)	0.16640 (7)	−0.30131 (5)	3.11 (2)
Fe(3)	0.13925 (8)	0.14565 (6)	−0.11195 (5)	3.03 (2)
Fe(4)	−0.20149 (8)	0.31102 (7)	−0.23344 (6)	3.75 (3)
S(1)	−0.09057 (14)	0.12294 (11)	−0.18843 (10)	3.37 (4)
S(2)	0.0884 (2)	0.28307 (13)	−0.01733 (10)	4.09 (4)
S(3)	0.16799 (13)	0.29636 (11)	−0.21176 (9)	3.11 (4)
S(4)	−0.05085 (15)	0.04369 (12)	−0.10896 (10)	3.76 (4)
S(5)	−0.1087 (2)	0.34745 (13)	−0.34795 (10)	4.08 (4)
C(11)	0.1143 (9)	0.58496 (6)	−0.3066 (6)	6.93 (13)
C(12)	0.1844 (8)	0.5948 (6)	−0.2081 (6)	6.18 (12)
C(13)	0.0883 (9)	0.6336 (6)	−0.1636 (6)	6.82 (13)
C(14)	−0.0424 (9)	0.6531 (6)	−0.2294 (7)	7.01 (13)
C(15)	−0.0291 (10)	0.6225 (6)	−0.3213 (6)	8.92 (13)
C(111)	0.1906 (14)	0.5452 (10)	−0.3756 (8)	13.19 (14)
C(21)	0.1084 (6)	0.1213 (6)	−0.4083 (4)	4.51 (11)
C(22)	−0.0404 (7)	0.1474 (6)	−0.4532 (4)	5.08 (12)
C(23)	−0.1204 (7)	0.0601 (7)	−0.4179 (5)	5.92 (12)
C(24)	−0.0208 (8)	−0.0209 (5)	−0.3495 (5)	5.57 (12)
C(25)	0.1162 (7)	0.0164 (6)	−0.3441 (4)	5.12 (12)
C(211)	0.2320 (9)	0.1902 (8)	−0.4255 (6)	7.53 (13)
C(31)	0.3533 (7)	0.1149 (6)	−0.0219 (5)	5.11 (12)
C(32)	0.2576 (6)	0.0609 (6)	0.0248 (4)	4.60 (11)
C(33)	0.1766 (7)	−0.0311 (5)	−0.0312 (4)	4.78 (12)
C(34)	0.2175 (7)	−0.0377 (5)	−0.1155 (5)	5.05 (12)
C(35)	0.3266 (7)	0.0510 (6)	−0.1085 (5)	4.86 (12)
C(311)	0.4567 (7)	0.2197 (7)	0.0174 (6)	6.91 (13)
C(41)[b]	−0.3777 (12)	0.3902 (11)	−0.1975 (9)	4.9 (2)
C(42)	−0.3934 (12)	0.4230 (12)	−0.2939 (10)	5.6 (2)
C(43)	−0.4072 (13)	0.3198 (12)	−0.3482 (11)	6.5 (2)
C(44)	−0.4000 (12)	0.2184 (11)	−0.2811 (9)	5.2 (2)
C(45)	−0.3747 (11)	0.2599 (10)	−0.1854 (9)	4.7 (2)
C(411)[b]	−0.3706 (15)	0.4678 (14)	−0.1136 (12)	8.8 (2)
C(51)[c]	−0.4051 (13)	0.3730 (13)	−0.3301 (10)	5.2 (2)
C(52)	−0.3795 (12)	0.4325 (12)	−0.2442 (10)	4.8 (2)
C(53)	−0.3656 (14)	0.3458 (13)	−0.1668 (12)	6.1 (2)
C(54)	−0.3861 (13)	0.2284 (13)	−0.2185 (11)	5.2 (2)
C(55)	−0.4019 (13)	0.2395 (12)	−0.3189 (10)	5.2 (2)
C(511)[c]	−0.448 (2)	0.434 (2)	−0.4275 (14)	10.5 (2)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j a^*_i a^*_j a_i a_j U_{ij}$. [b] Occupation factor for C(41), C(411): 0.534 (2). [c] Occupation factor for C(51), C(511): 0.466 (2).

toluene produces a mixture of $Fe_4S_4(MeCp)_4$, $Fe_4S_5(MeCp)_4$, and $Fe_4S_6(MeCp)_4$. These clusters, in contrast with their non-methylated analogues $Fe_4S_x(Cp)_4$ (x = 4–6), show an excellent solubility in toluene. In comparison with the reaction of $[Fe(Cp)(CO)_2]_2$ with sulfur, shorter reaction times are needed due to the higher reactivity of the methylated starting dimer. In order to have an idea of the composition of the product mixture after filtration and evaporation of the toluene, a cyclic voltammogram of a sample of every batch was recorded. The interpretation was straightforward, since these clusters show the same redox behavior as their non-methylated counterparts with only slightly different potentials. Regardless of the excess of sulfur used, long reaction times gave mixtures consisting for almost 100% $Fe_4S_4(MeCp)_4$. It appears thus that $Fe_4S_5(MeCp)_4$ and $Fe_4S_6(MeCp)_4$ are thermally unstable and are converted into $Fe_4S_4(MeCp)_4$ in refluxing toluene. On the other hand, with a reaction time of about 1 hour and an excess of at least 15% sulfur, a mixture consisting for more than 50% $Fe_4S_6(MeCp)_4$ was obtained. A convenient route to the pure $[Fe_4S_5(MeCp)_4]^z$ cluster compounds proceeds via the air oxidation of the neutral clusters in the presence of excess NH_4PF_6. A mixture of $[Fe_4S_4(MeCp)_4](PF_6)$ and $[Fe_4S_5(MeCp)_4](PF_6)_2$ is thus obtained. Apparently, upon air oxidation of $Fe_4S_6(MeCp)_4$, sulfur is expelled and $[Fe_4S_5(MeCp)_4](PF_6)_2$ is formed. $[Fe_4S_5(MeCp)_4](PF_6)_2$ and $[Fe_4S_4(MeCp)_4](PF_6)$ can easily be separated by recrystallization from nonpolar solvents like dichloromethane because of the large difference in solubility.

Table III. Interatomic Distances (in Å, with Esd's) and Angles (deg, with Esd's) for the Fe_4S_5 Moiety of $[Fe_4(\mu_3\text{-}S_2)(\mu_3\text{-}S)_3(MeCp)_4](PF_6)$

Fe(1)···S(2)	3.494 (2)	Fe(1)–S(3)	2.290 (2)
Fe(1)–S(4)	2.174 (2)	Fe(1)–S(5)	2.159 (2)
Fe(2)–S(1)	2.182 (2)	Fe(2)–S(3)	2.231 (2)
Fe(2)–S(5)	2.219 (2)	Fe(3)–S(1)	2.201 (2)
Fe(3)–S(2)	2.223 (2)	Fe(3)–S(3)	2.211 (2)
Fe(3)···S(4)	3.362 (2)	Fe(4)–S(1)	2.272 (2)
Fe(4)···S(2)	3.528 (2)	Fe(4)–S(4)	2.209 (2)
Fe(4)–S(5)	2.175 (2)	S(2)–S(4)	2.020 (2)
Fe(1)···Fe(2)	3.344 (1)	Fe(1)···Fe(3)	3.783 (1)
Fe(1)–Fe(4)	2.660 (1)	Fe(2)–Fe(3)	2.665 (1)
Fe(2)···Fe(4)	3.001 (1)	Fe(3)···Fe(4)	3.698 (1)
S(1)···S(2)	3.121 (2)	S(1)···S(3)	3.236 (2)
S(1)···S(4)	3.232 (2)	S(1)···S(5)	3.250 (2)
S(2)···S(3)	3.184 (2)	S(4)···S(5)	3.435 (2)
S(3)···S(4)	3.243 (2)	S(3)···S(5)	2.864 (2)
Fe(1)–C(11)	2.101 (9)	Fe(1)–C(12)	2.130 (7)
Fe(1)–C(13)	2.128 (7)	Fe(1)–C(14)	2.129 (7)
Fe(1)–C(15)	2.076 (8)	Fe(2)–C(21)	2.197 (7)
Fe(2)–C(22)	2.141 (6)	Fe(2)–C(23)	2.120 (6)
Fe(2)–C(24)	2.132 (6)	Fe(2)–C(25)	2.174 (7)
Fe(3)–C(31)	2.124 (6)	Fe(3)–C(32)	2.141 (6)
Fe(3)–C(33)	2.160 (6)	Fe(3)–C(34)	2.123 (6)
Fe(3)–C(35)	2.104 (7)	Fe(4)–C(41)	2.161 (13)
Fe(4)–C(42)	2.169 (12)	Fe(4)–C(43)	2.183 (11)
Fe(4)–C(44)	2.107 (11)	Fe(4)–C(45)	2.106 (13)
Fe(4)–C(51)	2.150 (12)	Fe(4)–C(52)	2.159 (13)
Fe(4)–C(53)	2.18 (2)	Fe(4)–C(54)	2.087 (14)
Fe(4)–C(55)	2.126 (12)		

S(3)–Fe(1)–S(4)	93.15 (6)	S(3)–Fe(1)–S(5)	80.10 (6)
S(4)–Fe(1)–S(5)	104.90 (7)	S(1)–Fe(2)–S(3)	94.32 (6)
S(1)–Fe(2)–S(5)	95.20 (7)	S(3)–Fe(2)–S(5)	80.14 (6)
S(1)–Fe(3)–S(2)	89.76 (7)	S(1)–Fe(3)–S(3)	94.36 (6)
S(2)–Fe(3)–S(3)	91.83 (6)	S(1)–Fe(4)–S(4)	92.31 (6)
S(1)–Fe(4)–S(5)	93.91 (7)	S(4)–Fe(4)–S(5)	103.19 (7)
Fe(2)–S(1)–Fe(3)	74.90 (6)	Fe(2)–S(1)–Fe(4)	84.69 (6)
Fe(3)–S(1)–Fe(4)	111.55 (7)	Fe(3)–S(2)–S(4)	104.72 (8)
Fe(1)–S(3)–Fe(2)	95.41 (6)	Fe(1)–S(3)–Fe(3)	114.36 (7)
Fe(2)–S(3)–Fe(3)	73.75 (5)	Fe(1)–S(4)–Fe(4)	74.72 (6)
Fe(1)–S(4)–S(2)	112.76 (9)	Fe(4)–S(4)–S(2)	112.98 (8)
Fe(1)–S(5)–Fe(2)	99.62 (7)	Fe(1)–S(5)–Fe(4)	75.73 (6)
Fe(2)–S(5)–Fe(4)	86.16 (6)		

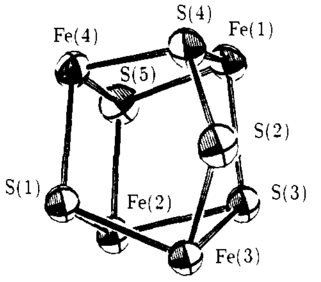

Figure 3. ORTEP drawing of the structure of $[Fe_4(\mu_3\text{-}S_2)(\mu_3\text{-}S)_3(MeCp)_4]^+$, together with the atomic labeling scheme. Only the iron–sulfur part is shown. The projection is on the plane through iron atoms 1, 3, and 4. For clarity, only one of the disordered molecules is shown.

During attempts to purify $Fe_4S_6(MeCp)_4$ it turned out that dichloromethane is reactive toward this cluster compound. Reactivity of dichloromethane toward organometallic compounds has been observed before.[28,29] Analytical, spectroscopic, electrochemical, and structural information obtained from single crystals of poor quality[30] show that a new compound has been formed with a most probable composition of $[Fe_4S_6(MeCp)_4](FeCl_4)\cdot xCH_2Cl_2$.

Description of the Structure of $[Fe_4(\mu_3\text{-}S_2)(\mu_3\text{-}S)_3(MeCp)_4](PF_6)$. Crystalline $[Fe_4(\mu_3\text{-}S_2)(\mu_3\text{-}S)_3(MeCp)_4](PF_6)$ is built from discrete $[Fe_4(\mu_3\text{-}S_2)(\mu_3\text{-}S)_3(MeCp)_4]^+$ and $(PF_6)^-$ ions. The molecular structure of $[Fe_4(\mu_3\text{-}S_2)(\mu_3\text{-}S)_3(MeCp)_4]^+$ is shown in

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(28) Szmanda, C. R. Ph.D. Thesis, University of Wisconsin—Madison, 1979.

(29) Agaskar, P. A.; Cotton, F. A.; Dunbar, K. R.; Falvello, F. R.; O'Connor, C. J. *Inorg. Chem.* **1987**, *26*, 4051.

(30) The space group is probably monoclinic with cell dimensions a = 9.365 Å, b = 17.369 Å, c = 21.631 Å, and β = 89.5°: Smits, J. M. M.; Bosman, W. P.; Beurskens, P. T. Unpublished results.

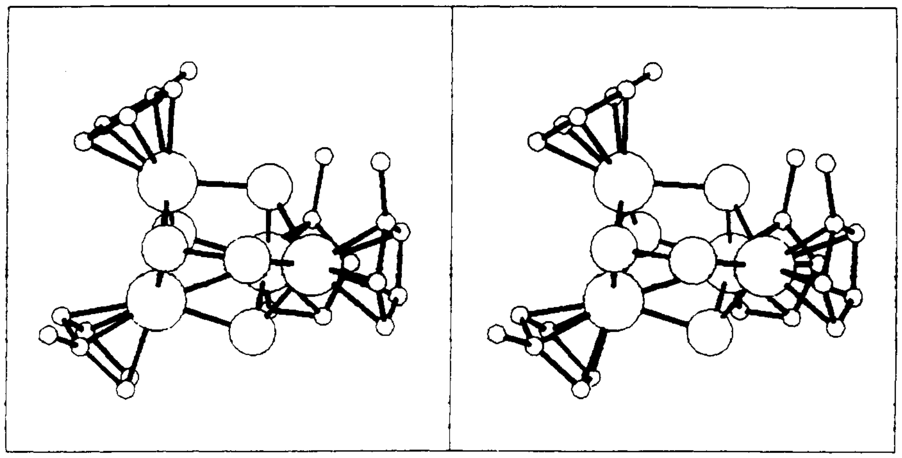

Figure 4. Stereoplot of the molecular structure of $[Fe_4(\mu_3\text{-}S_2)(\mu_3\text{-}S)_3(MeCp)_4]^+$. For clarity, only one of the disordered molecules is shown.

Table IV. Proton NMR Data for $[Fe_4S_x(MeCp)_4]^0$ (x = 4, 5) and $[Fe_4S_x(MeCp)_4]^{2+}$ (x = 4, 5) in Solution[a]

cluster species	solvent	T, K	chem shift δ, ppm: ring protons	chem shift δ, ppm: methyl protons
$[Fe_4S_4(MeCp)_4]^0$	$CDCl_3$	298	4.37 (8), 3.44 (8)	2.12 (12)
$[Fe_4S_5(MeCp)_4]^0$	$CDCl_3$	319	4.66 (2), 4.21 (6), 4.05 (2), 3.95 (6)	2.13 (3), 1.84 (9)
$[Fe_4S_6(MeCp)_4]^0$	$CDCl_3$	298	4.63 (2), 4.59 (2), 4.28 (2), 4.17 (2), 4.01 (4), 3.95 (4), 3.95 (2), 3.65 (2)	2.20 (6), 1.90 (6)
$[Fe_4S_5(MeCp)_4]^{2+}$	acetone-d_6	208	6.15 (2), 6.02 (2), 5.89 (2), 5.86 (2), 5.68 (2), 5.56 (2), 5.40 (2), 5.13 (2)	2.43 (6), 2.30 (3), 2.05 (3)
		302	5.97 (2), 5.89 (2), 5.85 (4), 5.71 (2), 5.50 (2), 5.31 (2), 5.05 (2)	2.42 (6), 2.24 (3), 1.98 (3)

[a] TMS was used as a reference. The number of protons is indicated between parentheses.

Figures 3 and 4. Selected bond lengths, some other relevant distances, and selected bond angles have been given in Table III.

As in most other Fe_4S_x cluster compounds, each iron atom is involved in three Fe–S bonds. Three types of Fe atoms can be distinguished. Fe(2) is coordinated by three μ_3-sulfido ligands. Fe(1) and Fe(4) are coordinated by two μ_3-sulfido ligands and by S(4) of the disulfur group. Finally, Fe(3) is coordinated by two μ_3-sulfido ligands and by S(2) of the disulfur group. With the exception of two bonds of 2.272 (2) and 2.290 (2) Å, all Fe–S bonds have a length between 2.159 (2) and 2.231 (2) Å. Two Fe–Fe distances of 2.660 (1) and 2.665 (1) Å are bonding, and three distances lying in the 3.34–3.78-Å range are nonbonding. A formal bond order of 0.5 can be assigned to the Fe–Fe distance of 3.001 (1) Å. This gives a total bond order of 2.5, which is equal to the bond order of $[Fe_4S_4(MeCp)_4](PF_6)$.[15] The S–S bond length of 2.020 (2) Å is shorter than the S–S distances observed in $[Fe_4S_5(Cp)_4]^+$ and $[Fe_4S_5(Cp)_4]^{2+}$ (2.067 (4) and 2.056 (3) Å, respectively). It is not sure, however, that these variations in bond length are due to different effective charges present on the disulfur ligand, since different modes of coordination are involved.[31] The overall structure of the cation is quite asymmetric, since the plane including the disulfur ligand, Fe(2), Fe(3), and S(5) is only by approximation a mirror plane.

The most striking difference between the structure of the $[Fe_4S_5(MeCp)_4]^+$ cation and the structure known for the $[Fe_4S_5(Cp)_4]^+$ cation[10] is that the S_2 ligand is no longer side-on bonded to Fe(3) (Figure 1a). As a consequence, Fe(3) is now four-coordinate, whereas it showed a unique five-coordination in the non-methylated cluster compound. Moreover, in the $[Fe_4S_5(MeCp)_4]^+$ cation each iron atom is involved in at least one Fe–Fe bond, whereas in the $[Fe_4S_5(Cp)_4]^+$ cation two Fe atoms are involved in one Fe–Fe bond, one Fe atom in two, and one Fe atom in none. So the introduction of a methyl group on the four Cp rings brings about a significant change in the geometry of the cluster. A considerable change in cluster geometry was also observed for $[Fe_4S_4(MeCp)_4]^+$ in comparison with $[Fe_4S_4(Cp)_4]^+$, which we have attributed to a subtle electronic influence of the cyclopentadienyl rings.[15] A similar electronic influence more than a steric influence could also be operative in the Fe_4S_5 compounds.

^{1}H NMR and COSY Spectra. To obtain information about the structure of the cluster compounds $[Fe_4S_4(MeCp)_4]^z$ (z = 0, 2+), $[Fe_4S_5(MeCp)_4]^z$ (z = 0, 2+), and $[Fe_4S_6(MeCp)_4]^0$ in solution, ^{1}H NMR spectra were recorded. The results are listed in Table IV.

For an interpretation of the spectra of $[Fe_4S_5(MeCp)_4]^z$ (z = 0, 2+) it is important to note that, as in $[Fe_4S_5(Cp)_4]^z$ (z = 0, 2+),[9] the disulfur group in the core may show fluxional behavior by rotating around a pseudo-3-fold symmetry axis (Figure 2). If the disulfur ligand is not fluxional, there are two possible core structures corresponding to the two likely coordination modes of the S_2 ligand. It can easily be seen, however, that in both structures two of the iron atoms are equivalent and two are unique. If the disulfur ligand shows fluxionality the three adjacent irons are, on the average, equivalently bonded to it. In that case only the fourth iron lying on the pseudo-3-fold axis through the S_2 group is unique. ^{1}H NMR spectra of $[Fe_4S_5(MeCp)_4]^{2+}$ were recorded in acetone-d_6 solution in the temperature range 188–302 K. The methyl protons give three resonance signals in the ratio 2:1:1. This provides a first indication that the iron–sulfur core is indeed rigid. The pattern of the resonance signals due to the ring protons is more complex. At 208 K eight signals of equal intensity are visible. At 302 K two of the resonances accidentally coincide. Because the NMR spectra allow different conclusions with respect to the equivalence of the methylcyclopentadienyl rings, both a phase-sensitive ^{1}H COSY spectrum with double-quantum filtering and a ^{1}H COSY spectrum with triple-quantum filtering of $[Fe_4S_5(MeCp)_4]^{2+}$ were recorded in acetone-d_6 at 208 K. The spectra are shown in Figure 5. The interpretation of these spectra is straightforward. Two methylcyclopentadienyl rings are chemical equivalent. In these rings all four ring protons are unique and are coupled to each other. Therefore cross peaks are present for these sites (A, C, D, F) in the double-quantum as well as in the triple-quantum filtered spectrum. The two other rings are unique, but in each ring there are two pairs of equivalent ring protons coupled to each other. Both sites B and E, and sites G and H, therefore show cross peaks in the double-quantum filtered but not in the triple-quantum filtered spectrum. These results imply that under the experimental conditions $[Fe_4S_5(MeCp)_4]^{2+}$ has a rigid iron–sulfur framework.

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[31] Müller, A.; Jaegermann, W.; Enemark, J. H. *Coord. Chem. Rev.* **1982**, *46*, 245.

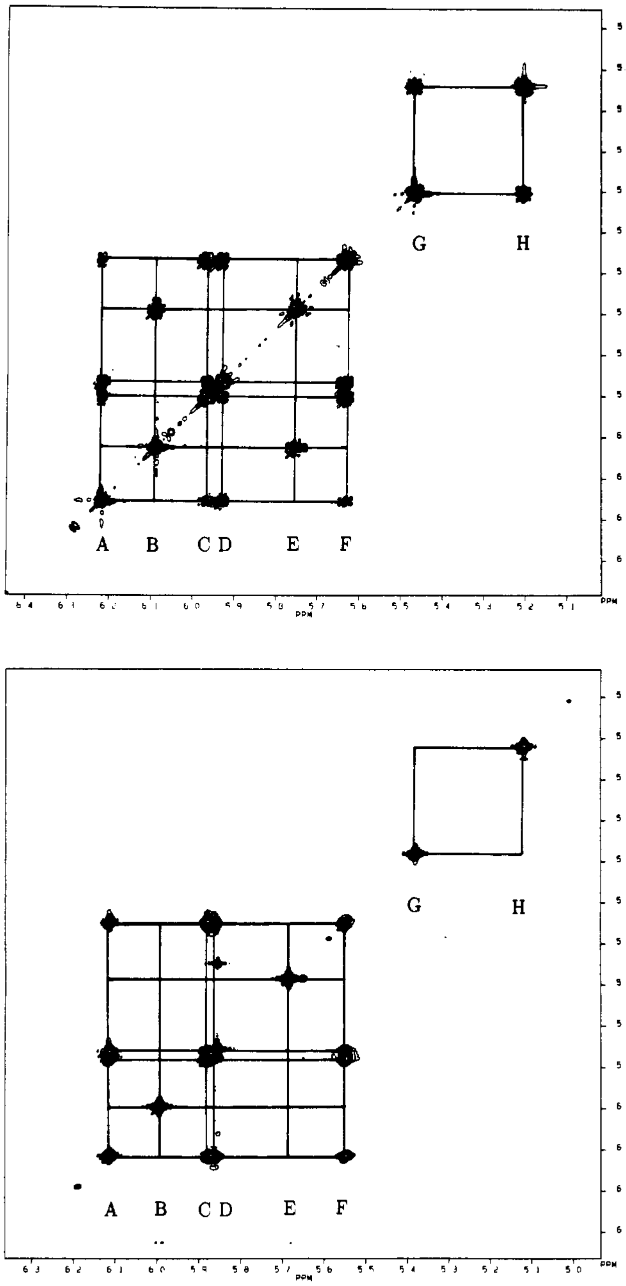

Figure 5. ^{1}H COSY spectra of $[Fe_4S_5(MeCp)_4](PF_6)_2$ in acetone-d_6 solution at 208 K: (a, top) phase-sensitive spectrum with double-quantum filtering; (b, bottom) spectrum with triple-quantum filtering.

The ^{1}H NMR spectra of $[Fe_4S_5(MeCp)_4]^0$ recorded in $CDCl_3$ at 319 K show a 3:1 pattern for both the ring and the methyl proton resonance signals. This indicates that the cluster core is fluxional with the disulfur group rotating around a pseudo-3-fold axis. The NMR spectrum recorded at 298 K shows a complicated pattern with broad resonance signals, which suggests that, like the cluster in the non-methylated compound $Fe_4S_5(Cp)_4$,[9] the cluster core of $[Fe_4S_5(MeCp)_4]^0$ loses its fluxionality at lower temperatures.

In $[Fe_4S_6(MeCp)_4]^0$ two disulfur groups are present. The proton NMR spectrum recorded at 298 K in $CDCl_3$ solution shows two methyl proton resonances of equal intensity. This is consistent both with a structure similar to the rigid chiral structure of $Fe_4S_6(Cp)_4$ and with the presence of two fluxional disulfur units. The occurrence of eight resonance signals for the ring protons proves that the iron–sulfur core is rigid. If they were fluxional, only four resonance signals would have been visible.

Table V. EPR Values for the Cluster Species $[Fe_4S_x(RC_5H_4)_4]^+$ (x = 4, 5; R = H, Me) and $[Fe_4S_4(RC_5H_4)_4]^{3+}$ (R = H, Me) As Recorded in Frozen Acetonitrile Solution at 4 K

cluster species	g_1	g_2	g_3	g_{av}
$[Fe_4S_4(MeCp)_4]^+$	2.133	2.025	1.987	2.048
$[Fe_4S_4(Cp)_4]^+$	2.125	2.014	1.968	2.036
$[Fe_4S_5(MeCp)_4]^+$	2.128	2.008	1.981	2.039
$[Fe_4S_5(Cp)_4]^{+a}$	2.118	1.999	1.968	2.028
$[Fe_4S_4(MeCp)_4]^{3+}$	2.085^c	1.983^d		2.017
$[Fe_4S_4(Cp)_4]^{3+b}$	2.072^c	1.998^d		2.023

^{a}Recorded at 40 K. ^{b}From ref 32. Recorded at 77 K. $^c g_{\parallel}$. $^d g_{\perp}$.

The spectra that have been recorded for $[Fe_4S_4(MeCp)_4]^{2+}$ in acetone-d_6 solution all show line broadening effects and a considerable upfield shift of the methyl proton resonance signal. This can probably be ascribed to partial reduction of the cluster compound to $[Fe_4S_4(MeCp)_4](PF_6)$. Recently, Ogino et al. reported that dissolving the compound $[Fe_4S_4(Cp)_4](PF_6)_3$ in various solvents caused a reduction to $[Fe_4S_4(Cp)_4](PF_6)$ or $[Fe_4S_4(Cp)_4](PF_6)_2$.[32]

The ^{1}H NMR spectrum of $[Fe_4S_4(MeCp)_4]^0$ recorded in $CDCl_3$ solution at 298 K shows three resonance signals in the ratio 2:2:3. This indicates that all four cyclopentadienyl rings are equivalent.

EPR Spectra. X-band spectra of the paramagnetic species $[Fe_4S_4(MeCp)_4]^z$ (z = 1+, 3+) and $[Fe_4S_5(MeCp)_4]^+$ were recorded in frozen acetonitrile solution at 4 K. $[Fe_4S_4(MeCp)_4]^{3+}$ was generated in solution by controlled-potential electrolysis (see Experimental Section). The EPR spectra are similar to the EPR spectra of the non-methylated analogues (Table V).[32,33] The g values are characteristic of an overall electronic spin state $S = {}^1/_2$. The signals are anisotropic, and they easily power-saturate below 25 K. For both monocations there is an increase of the average g value as compared to the non-methylated clusters. For $[Fe_4S_4(MeCp)_4]^{3+}$ on the other hand, there is a decrease of the average g value as compared to the non-methylated analogue. For both the $[Fe_4S_4(MeCp)_4]^z$ and the $[Fe_4S_4(Cp)_4]^z$ compounds the average g value decreases in the order from the monocationic to the tricationic cluster species. For the $[Fe_4S_5(Cp)_4]^z$ (z = 1−, 1+, 3+) series, on the contrary, it has been found that the average g value increases in the order from the most reduced to the most oxidized species.[33] In the case of iron–sulfur cluster thiolate compounds, an increase of the averge g value is known to indicate a decrease of the ferrous character of the iron atoms.[33] The opposite trend observed here suggests that for the cyclopentadienyl compounds there is no simple relation between the average g value and the electron density on the iron–sulfur core.

Electrochemistry. Electrochemical data for $[Fe_4S_4(MeCp)_4](PF_6)$ and $[Fe_4S_5(MeCp)_4](PF_6)_2$ in acetonitrile and for $[Fe_4S_6(MeCp)_4]^0$ in CH_2Cl_2 solution are listed in Table VI. Cyclic voltammograms of these clusters recorded at a platinum electrode in the same solvents are shown in Figure 6. In the cyclic voltammogram of $Fe_4S_6(MeCp)_4$ the two reduction waves at −1.47 and −1.75 V are attributed to a minute contamination with elemental sulfur. This was established by recording a CV of elemental sulfur under the same conditions. The oxidation of $[Fe_4S_6(MeCp)_4]^{2+}$ is accompanied by adsorption phenomena. The small reduction peak at 0.41 V is due to the reduction of $[Fe_4S_4(MeCp)_4]^{3+}$ probably formed upon decomposition of $[Fe_4S_6(MeCp)_4]^{3+}$.

Essentially identical results were obtained from the three voltammetric techniques that were applied (normal and differential pulse and cyclic voltammetry). Apart from the $[Fe_4S_6(MeCp)_4]^{2+/3+}$, the $[Fe_4S_5(MeCp)_4]^{-/2-}$, and the $[Fe_4S_4(MeCp)_4]^{0/-}$ transitions, which are irreversible, and the $[Fe_4S_5(MeCp)_4]^{0/-}$ transition, which is not entirely reversible on the CV time scale (i_b/i_f = 0.8), all transitions are reversible processes. This conclusion is reached from the commonly applied criteria in the analysis of current–voltage curves. In the cyclic voltammetric experiments peak current ratios were found to be equal to 1.0, and peak potential separations were in the range of ΔE_p = 60–70 mV. In the differential pulse voltammograms recorded

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Table VI. Half-Wave Potentials (in V vs the Fc^+/Fc Couple) for the $[Fe_4S_x(RC_5H_4)_4]^z$ (x = 4, 5; R = H, Me) Cluster Series

		redox transition					
cluster series	solvent	$-/2-$	$0/-$	$+/0$	$2+/+$	$3+/2+$	$4+/3+$
$[Fe_4S_4(MeCp)_4]^z$	CH_3CN		-2.1^a	-0.82	-0.16	0.40	0.92
$[Fe_4S_4(Cp)_4]^z$	CH_3CN		-2.1^a	-0.73	-0.10	0.43	0.94
$[Fe_4S_5(MeCp)_4]^z$	CH_3CN	-2.3^a	-1.77	-0.71	-0.38	0.72	
$[Fe_4S_5(Cp)_4]^z$	CH_3CN	-2.2^a	-1.72	-0.62	-0.33	0.79	
$[Fe_4S_6(MeCp)_4]^z$	CH_2Cl_2		-1.89	-0.57	-0.24	$0.86^{a,b}$	
$[Fe_4S_6(Cp)_4]^z$	CH_2Cl_2		-1.72	-0.45	-0.14	$0.85^{a,b}$	

[a] Peak potential. [b] Adsorption phenomena.

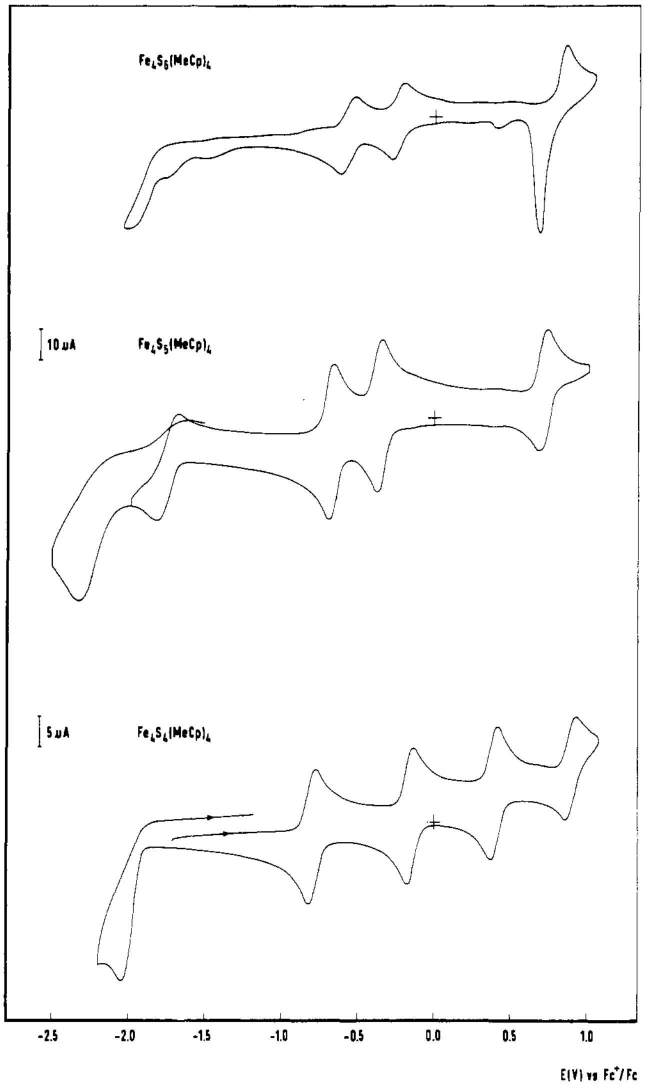

Figure 6. Cyclic voltammograms of $[Fe_4S_4(MeCp)_4](PF_6)$ and $[Fe_4S_5(MeCp)_4](PF_6)_2$ in CH_3CN (0.1 M TBAH) and of $Fe_4S_6(MeCp)_4$ in CH_2Cl_2 (0.1 M TBAH). Potentials are in volts vs the Fc^+/Fc couple.

the peak widths at half-height, $w_{1/2}$, are all equal to 100 mV.

The shapes of the cyclic voltammetric curves strongly resemble those of the non-methylated cluster compounds $[Fe_4S_x(Cp)_4]^z$ (x = 4–6),[34,35] but with the exception of the $[Fe_4S_4(MeCp)_4]^{0/-}$ and the $[Fe_4S_6(MeCp)_4]^{2+/3+}$ transition, the redox potentials of the clusters described here have shifted to more negative values. For the +/0 and 2+/+ transitions of the $[Fe_4S_4(MeCp)_4]^z$ and $[Fe_4S_4(Cp)_4]^z$ series in acetonitrile this shift is 0.09 and 0.06 V, respectively. Reaction entropy measurements made on these compounds show that the entropy contribution to $E_{1/2}$ results in a *positive* shift of 0.025 V in both cases.[36] The redox potentials for the +/0 transitions of a number of metallocenes, $M(Me_xCp)_2$ (M = Fe, x = 0, 1, 4, 5) and $M(Me_xCp)_2$ (M = Co, Ni; x = 0, 5), show a remarkably constant shift in negative direction of about 0.05 V for each methyl group substituted on the Cp rings.[37–39] Shifts of about the same magnitude have been observed for a number of dinuclear and trinuclear coordination compounds with bridging nitrosyl ligands.[40,41] Therefore it can be concluded that the introduction of a methyl group on each Cp ring of the $[Fe_4S_x(Cp)_4]^z$ (x = 4, z = 1+; x = 5, z = 2+; x = 6, z = 0) compounds causes a shift in the redox potentials that lies in the same range as observed for a number of other compounds having terminal Cp ligands.

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Registry No. $[Fe_4S_5(MeCp)_4](PF_6)_2$, 138984-29-9; $[Fe_4S_4(MeCp)_4](PF_6)$, 138984-30-2; $Fe_4S_5(MeCp)_4$, 138984-31-3; $[Fe_4S_5(MeCp)_4](PF_6)$, 138984-33-5; $Fe_4S_6(MeCp)_4$, 138984-34-6; $[Fe_4S_6(MeCp)_4](FeCl_4)$, 138984-36-8; $[Fe(MeCp)(CO)_2]_2$, 32028-30-1; $Fe_4S_4(MeCp)_4$, 138984-37-9; $[Fe_4S_4(Cp)_4]^+$, 118732-28-8; $[Fe_4S_5(Cp)_4]^+$, 89016-75-1; $[Fe_4S_4(MeCp)_4]^{3+}$, 138984-38-0; $[Fe_4S_4(MeCp)_4]^-$, 138984-39-1; $[Fe_4S_4(Cp)_4]^-$, 121380-06-1; $[Fe_4S_5(MeCp)_4]^-$, 138984-40-4; $[Fe_4S_5(Cp)_4]^-$, 108742-88-7; $[Fe_4S_6(MeCp)_4]^-$, 138984-41-5; $[Fe_4S_6(Cp)_4]^-$, 121978-13-0.

Supplementary Material Available: Tables A–D, listing crystallographic data and experimental details, atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, and anisotropic thermal parameters for $[Fe_4S_5(MeCp)_4](PF_6)$ (7 pages); a table of calculated and observed structure factors (34 pages). Ordering information is given on any current masthead page.

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