

Reaction of Mixed-Ligand Iron–Sulfur Cluster $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2)]$ ($Cp^* = C_5Me_5$) with Methyl Iodide. Synthesis, Structure, and Redox Behavior of $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2Me)]$

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The reaction of the mixed-ligand iron–sulfur cluster $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2)]$ ([**3**]) ($Cp^* = C_5Me_5$) with iodomethane gave a methylated cluster, $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2Me)]I$ ([**4**]I), in 60% yield. The anion exchange of [**4**]I with KPF_6 gave [**4**]PF_6 as a pure sample. A similar treatment of [**3**] using iodoethane afforded an ethylated cluster, $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2Et)]I$ ([**5**]I), and oxidized parent cluster [**3**]I. The reaction of [**3**] with 2-iodopropane did not give an alkylated cluster. An unreacted cluster [**3**] was recovered with a small amount of oxidized cluster [**3**]I. The molecular structure of $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2Me)]$ ([**4**]), which was obtained by the reduction of [**4**]PF_6 with cobaltocene, was determined by an X-ray diffraction study. Crystallographic data are: Monoclinic, $P2_1/a$, $a = 21.707(2)$ Å, $b = 21.382(2)$ Å, $c = 11.433(1)$ Å, $\beta = 98.98(1)^\circ$, $V = 5241.5(9)$ Å^3, $Z = 4$, and $R = 0.067$ for 7412 reflections with $|F_o| > 3\sigma(F_o)$. The methyl group transferred from MeI is located on the singly ligating sulfur atom in the disulfide ligand of the parent cluster [**3**]. A cyclic voltammogram of [**4**]PF_6 in 0.1 mol dm^{-3} tetrabutylammonium tetrafluoroborate–CH_3CN showed five reversible one-electron redox waves at $E_{1/2} = +1.42$ V, +0.92 V, +0.41 V, −0.38 V, and −1.22 V vs SCE, corresponding to 4+/3+, 3+/2+, 2+/1+, 1+/0, and 0/1− charged cluster couples, respectively. An irreversible two-electron reduction wave was also observed at $E_{pc} = -1.97$ V vs SCE.

It has been demonstrated that the disulfide ligands in iron sulfur clusters act as Lewis bases.[1] For instance, $[Fe_4(Cp)_4(\mu_3\text{-}S)_2(\mu_3\text{-}S_2)_2]$ ([**1**]) and $[Fe_4(Cp)_4(\mu_3\text{-}S)_3(\mu_3\text{-}S_2)$ ([**2**]) form adducts with SO_2 to give [**1**]·$2SO_2$ and [**2**]·$2SO_2$, respectively.[2–4] Cluster [**1**] reacts with Ag^+ to give $[[\mathbf{1}]_2Ag]^{3+}$, in which four sulfur atoms of disulfide ligands in [**1**] are coordinated to the silver ion.[2,5] Similarly, [**1**]·$Mo(CO)_4$, [**1**]·$Mo(Br)(CH_3CN)(CO)_2$,[6] [**1**]·$M(X)(Y)(CO)_3$ (M = Mo, W; X, Y = I, thiolate),[7] and $[Fe_4(MeC_5H_4)_4S_6]$·$Cr(CO)_4$[4] were synthesized by the reactions of [**1**] or its MeC_5H_4 derivative with carbonyl complexes of Group 6 metals. However, the alkylation of disulfide ligands has not been reported, except for only one paper by van der Linden et al.[8] They reported that [**1**] and $[Fe_4(RC_5H_4)_4(\mu_3\text{-}S)_2(\mu_3\text{-}S_2)_2]$ (R = H, Me) reacted with CH_2X_2 (X = Cl, I) and CH_3I to give alkylated products.

We isolated and characterized a mixed-ligand tetrairon cluster $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2)]$ ([**3**]) from the reaction of $[Fe_2(Cp^*)_2(CO)_4]$ with elemental sulfur and PhC≡CPh, where Cp^* denotes the pentamethylcyclopentadienyl ligand.[9] The cluster contains four iron atoms, three μ_3-S ligands and one μ_3-S_2 ligand. The latter ligand is located on the opposite side of the Fe_4S_5 core from the $Ph_2C_2S_2$ ligand. One of the S_2 sulfur atoms is bonded to two iron atoms (doubly ligating sulfur atom) and the other is bonded to the third iron atom (singly ligating sulfur atom). Compound [**3**] is the first mixed-ligand cluster having an Fe_4S_5 core, and possesses nineteen cluster electrons.

This paper describes the reactivity of [**3**] toward alkyl iodides RI (R = Me, Et, ^{i}Pr). A methylated cluster, $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2Me)]$, was isolated and fully characterized by ^{1}H NMR, IR, and mass spectroscopy, elemental analysis, and X-ray crystallography. Structural and electrochemical investigations for this cluster supply some new findings.

Experimental

The iron–sulfur cluster $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2)]$ ([**3**])[9] and cobaltocene[10] were prepared according to literature methods. Tetrahydrofuran (THF), diethyl ether, and hexane were distilled from sodium benzophenone ketyl. Toluene was distilled from sodium. Acetone was distilled from anhydrous calcium sulfate. Dichloromethane was distilled from calcium hydride. Acetonitrile was distilled from P_2O_5 (twice) and then from calcium hydride. Iodomethane (MeI), iodoethane (EtI), and 2-iodopropane (^{i}PrI) were washed with an aqueous solution containing 10% $Na_2S_2O_3$, then distilled from P_2O_5. Tetrabutylammonium tetrafluoroborate (TBAB) was purchased from Tokyo Chemical Industry Co., and recrystallized from a mixed solvent of benzene and ethyl acetate (9:1). Potassium hexafluorophosphate was used without further purification.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-300 or a JEOL GX-400. Mass spectra were recorded on a JEOL JMS HX-110 mass spectrometer. Infrared spectra were recorded on a Horiba FT-200.

Electrochemical measurements were performed with a Fuso Model 311 potentiostat and a Model 321 function generator. Cyclic voltammograms were measured at room temperature using a standard three-electrode system consisting of a platinum rod as a working electrode, a coiled platinum wire as a counter electrode, and an aqueous saturated calomel electrode (SCE) as a reference elec-

Published on the web June 9, 2004; DOI 10.1246/bcsj.77.1161

trode. TBAB was used as a supporting electrolyte, and was dissolved in acetonitrile to make 0.1 M solutions (1 M = 1 mol dm^{-3}).

Reaction of [Fe$_4$(Cp*)$_3$(Ph$_2$C$_2$S$_2$)(μ_3-S)$_3$(μ_3-S$_2$)] ([3]) with MeI. To diethyl ether solution (30 mL) containing [Fe$_4$(Cp*)$_3$(Ph$_2$C$_2$S$_2$)(μ_3-S)$_3$(μ_3-S$_2$)] ([**3**]) (53 mg, 5.1×10^{-5} mol) was added 1.0 mL of 0.16 M MeI–THF solution (1.6×10^{-4} mol). The reaction mixture was stirred at room temperature for 20 h under a nitrogen atmosphere. After filtration, the collected dark-green precipitate was extracted with 10 mL of acetonitrile. The removal of volatiles afforded [Fe$_4$(Cp*)$_3$(Ph$_2$C$_2$S$_2$)(μ_3-S)$_3$(μ_3-S$_2$Me)]I ([**4**]I) as a green solid. The crystalline sample was obtained from an acetone solution of [**4**]I, which was layered with hexane. Yield 36 mg (60%). ^{1}H NMR ($CDCl_3$, 300 MHz) −5.9 (br, 15H, Me, $W_{1/2} = 960$ Hz), 3.7 (br, 30H, Me, $W_{1/2} = 190$ Hz), 5.5–6.9, 7.5–8.1 (m, 10H, Ph). No methyl signal of the S_2Me ligand was observed. IR (KBr pellet) 1655w, 1637w, 1618w, 1460w, 1425m, 1400w, 1375m, 1155w, 1109w, 1076w, 1020w, 991w, 872w, 748w, 698w, 617w, 602w, 420m cm^{-1}; MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe): *m*/*z* (% rel intensity) 1046 (M$^+$, 100), 999 (M$^+$ − SMe, 19), 911 (M$^+$ − Cp*, 23), 622 (M$^+$ − SMe − Cp* − Ph$_2$C$_2$S$_2$, 13), 487 (M$^+$ − SMe − 2Cp* − Ph$_2$C$_2$S$_2$, 53). Anal. Found: C, 44.69; H, 4.90; I, 10.55%. Calcd for $C_{45}H_{58}Fe_4IS_7$: C, 46.05; H, 4.98; I, 10.88%. The cluster [**4**]I (363 mg, 3.09×10^{-4} mol) was treated with an excess amount of KPF_6 in acetonitrile (20 mL). After evaporation of the solvent, the remaining solid was washed with 100 mL of water. The same treatment was repeated twice. The obtained solid was dried and recrystallized from acetone (15 mL) layered with hexane (50 mL) which afforded [Fe$_4$(Cp*)$_3$(Ph$_2$C$_2$S$_2$)(μ_3-S)$_3$(μ_3-S$_2$Me)](PF$_6$) ([**4**]PF$_6$). Yield 201 mg (55%). ^{1}H NMR ($CDCl_3$, 300 MHz) −6.3 (br, 15H, Me, $W_{1/2} = 880$ Hz), 3.7 (br, 30H, Me, $W_{1/2} = 200$ Hz), 5.5–6.9, 7.5–8.1 (m, 10H, Ph). No methyl signal of the S_2Me ligand was observed. IR (KBr pellet) 2970w, 2895w, 2842w, 1635w, 1454m, 1425m, 1375m, 1160w, 1020w, 872w, 840vs (νPF$_6$), 696w, 557s (δPF$_6$), 459w cm^{-1}; MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe): *m*/*z* (% rel intensity) 1046 (M$^+$, 100), 1031 (M$^+$ − Me, 6.8), 999 (M$^+$ − SMe, 18), 911 (M$^+$ − Cp*, 23), 669 (M$^+$ − Cp* − Ph$_2$C$_2$S$_2$, 6.3). Anal. Found: C, 45.48; H, 4.99%. Calcd for $C_{45}H_{58}F_6Fe_4PS_7$: C, 45.35; H, 4.91%.

Synthesis of [Fe$_4$(Cp*)$_3$(Ph$_2$C$_2$S$_2$)(μ_3-S)$_3$(μ_3-S$_2$Me)] ([4]). To an acetonitrile solution (60 mL) of [Fe$_4$(Cp*)$_3$(Ph$_2$C$_2$S$_2$)(μ_3-S)$_3$(μ_3-S$_2$Me)]I ([**4**]I) (126 mg, 1.07×10^{-4} mol) was added cobaltocene (50 mg, 2.7×10^{-4} mol) and the reaction mixture was stirred at room temperature for 5 h. The resulting precipitate was collected by filtration and extracted with 60 mL of THF. After removal of any volatiles, the remaining solid was recrystallized by layering hexane (40 mL) on a THF solution of the product to give [Fe$_4$(Cp*)$_3$(Ph$_2$C$_2$S$_2$)(μ_3-S)$_3$(μ_3-S$_2$Me)]·THF ([**4**]·THF). Yield 60 mg (55%). ^{1}H NMR (CD_2Cl_2, 400 MHz, −70 °C) 0.67 (s, 3H, SMe), 1.33 (s, 15H, Me), 1.59 (s, 15H, Me), 1.67 (s, 15H, Me), 6.9–7.1, 7.1–7.4 (m, 10H, Ph); IR (KBr pellet) 2924w, 2868w, 2837w, 1621m, 1579m, 1468m, 1431m, 1373m, 1166w, 1024m, 846m, 696m, 632m, 602m, 580m cm^{-1}; MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe): *m*/*z* (% rel intensity) 1046 (M$^+$, 100), 999 (M$^+$ − SMe, 18), 911 (M$^+$ − Cp*, 23), 622 (M$^+$ − SMe − Cp* − Ph$_2$C$_2$S$_2$, 13). Anal. Found: C, 52.67; H, 5.89%. Calcd for $C_{49}H_{66}Fe_4OS_7$: C, 52.60; H, 5.95%.

Reaction of [Fe$_4$(Cp*)$_3$(Ph$_2$C$_2$S$_2$)(μ_3-S)$_3$(μ_3-S$_2$)] ([3]) with EtI. To a diethyl ether solution (20 mL) of [**3**] (50 mg, 4.9×10^{-5} mol) was added 0.6 mL of 0.25 M EtI–Et$_2$O solution (1.5×10^{-4} mol); the mixture was stirred at room temperature for 20 h under a nitrogen atmosphere. Evaporation of the solvent yielded a green solid. Acetonitrile (10 mL) was added to the solid and the suspension was filtered to collect an insoluble cluster [**3**]. Recovered [**3**] was 20 mg. Removal of the solvent from the filtrate gave a mixture of a monocationic cluster, [Fe$_4$(Cp*)$_3$(Ph$_2$C$_2$S$_2$)(μ_3-S)$_3$(μ_3-S$_2$)]I ([**3**]I), and an ethylated cluster, [Fe$_4$(Cp*)$_3$(Ph$_2$C$_2$S$_2$)(μ_3-S)$_3$(μ_3-S$_2$Et)]I ([**5**]I). Combined yield of [**3**]I and [**5**]I 18 mg. MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe): *m*/*z* (% rel intensity) 1060 ([**5**]$^+$, 100), 1031 ([**3**]$^+$, 69), 999 ([**5**]$^+$ − SEt and [**3**]$^+$ − S, 23), 925 ([**5**]$^+$ − Cp*, 22), 896 ([**3**]$^+$ − Cp*, 13), 864 ([Fe$_4$(Cp*)$_2$(Ph$_2$C$_2$S$_2$)(S)$_4$]$^+$, 7.7), 819 ([Fe$_4$(Cp*)$_3$(S)$_3$(S$_2$C$_2$H$_5$)]$^+$, 10), 655 ([Fe$_4$(Cp*)$_2$(S)$_5$]$^+$, 13), 622 ([Fe$_4$(Cp*)$_2$(S)$_4$]$^+$, 16).

Reaction of [Fe$_4$(Cp*)$_3$(Ph$_2$C$_2$S$_2$)(μ_3-S)$_3$(μ_3-S$_2$)] ([3]) with ^{i}PrI. Cluster [**3**] (44 mg, 4.3×10^{-5} mol) was dissolved in 25 mL of diethyl ether and to this solution was added 0.7 mL of a 0.20 M ^{i}PrI–Et$_2$O solution (1.4×10^{-4} mol); the mixture was stirred under a nitrogen for 20 h. After removal of the solvent, the remaining solid was extracted with 10 mL of acetonitrile. The removal of volatiles from the extract afforded [**3**]I. Yield 3 mg (6%). The residue, which was insoluble in acetonitrile, was found to be the starting cluster [**3**] (20 mg).

X-ray Structural Analysis of [Fe$_4$(Cp*)$_3$(Ph$_2$C$_2$S$_2$)(μ_3-S)$_3$(μ_3-S$_2$Me)]·THF ([4]·THF). Diffraction data were collected on a Rigaku AFC-6A four-circle diffractometer with monochromated Mo Kα radiation using the ω-scan technique. Crystallographic data are listed in Table 1. The reflection data were corrected for Lorentz and polarization factors. No correction was applied for absorption. The unit cell parameters were determined by the least-squares method using 100 reflections in the range of $25° < 2\theta < 30°$.

The structure was solved by a direct method (RANTAN81).[11] The parameters were refined by a block-diagonal least-squares method. Anisotropic temperature factors were applied for the non-hydrogen atoms in the cluster molecule. The position of the THF molecule was deduced from a difference Fourier map, and isotropically refined. Hydrogen atoms on two Ph groups were located by a calculation (d(C–H) = 1.08 Å). The isotropic thermal

Table 1. Crystallographic Data for [Fe$_4$(Cp*)$_3$(Ph$_2$C$_2$S$_2$)(μ_3-S)$_3$(μ_3-S$_2$Me)]·THF ([**4**]·THF)

Formula	$C_{49}H_{66}Fe_4OS_7$
Formula weight	1118.9
Crystal system	Monoclinic
Space group	$P2_1/a$ (variant of No. 14)
a/Å	21.707(2)
b/Å	21.382(2)
c/Å	11.433(1)
β/deg	98.98(1)
V/Å^3	5241.5(9)
Z	4
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
T/°C	21
D_{calcd}/g cm^{-3}	1.42
μ(Mo Kα)/cm^{-1}	14.1
No. of reflcns measd	16456
No. of reflcns used with $\|F_o\| > 3\sigma(F_o)$	7412
R[a]	0.067
R_w[b]	0.093

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = [\sigma^2(|F_o|) + aF_o^2]^{-1}$, where $a = 0.003$.

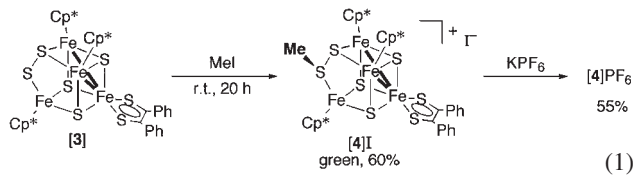
parameters of hydrogen atoms were fixed at 1.5-times the equivalent thermal parameters of the carbon atoms to which they are covalently bonded.

The values for the atomic scattering factors of non-hydrogen and hydrogen atoms were those given in Refs. 12 and 13, respectively. Calculations were performed on a Nippon Electric Co. ACOS-3000 computer system at the Tohoku University Computer Center using the Universal Crystallographic Computation Program System UNICS III.[14]

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 235380.

Results and Discussion

Reactions of $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2)]$ ([3]) with RI (R = Me, Et, ^{i}Pr). The cluster $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2)]$ ([**3**]) easily reacted with the electrophile MeI to give a methylated cluster $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2Me)]$I ([**4**]I) as a green solid in 60% yield. This salt did not give a satisfactory elemental analysis, in spite of repeated recrystallizations. Fortunately, the difficulty was solved by an anion exchange of [**4**]I with KPF_6, which gave pure salt [**4**]PF_6 (Eq. 1).

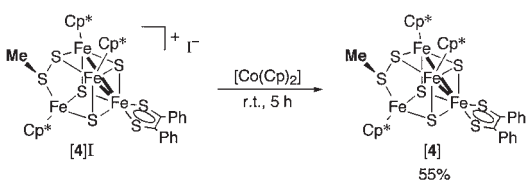


(1)

The mass spectrum of [**4**]PF_6 showed a molecular ion peak at $m/z = 1046$, indicating the formation of a methylated product of [**3**]. The ^{1}H NMR spectrum of [**4**]PF_6 showed broad signals of Cp* ligands at −6.3 and 3.7 ppm in the relative intensities of 2:1 and broad signals of Ph groups in the ranges of 5.5–6.9 and 7.5–8.1 ppm. The broadening and paramagnetic shift of the signals indicate that the cluster [**4**]PF_6 is a paramagnetic 19-electron cluster. No signal assignable to the attached methyl group was observed, which suggests that the unpaired electron localizes mainly in the vicinity of the S_2Me ligand. The ^{1}H NMR spectrum of [**4**]I was almost identical to that of [**4**]PF_6.

The reaction of cluster [**3**] with EtI gave the ethylated product $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2Et)]$I ([**5**]I) as well as the oxidized salt of the parent cluster ([**3**]I). The mass spectrum of the reaction mixture showed molecular ion peaks of both $[\mathbf{5}]^+$ and $[\mathbf{3}]^+$ at $m/z = 1060$ and 1031, respectively, and some fragmentation peaks of them. The reaction of [**3**] with ^{i}PrI did not give an alkylated cluster.

The reduction of [**4**]I with cobaltocene afforded a neutral cluster [**4**] in moderate yield (55%) (Eq. 2). The ^{1}H NMR spectrum of [**4**] showed three sharp signals assignable to Cp* ligands at 1.32, 1.59, and 1.67 ppm in the relative ratio of 1:1:1, suggesting a chiral structure of [**4**] (vide infra).



(2)

Structure of $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2Me)]\cdot$THF ([4]·THF). The position of the attached methyl group was unequivocally determined by an X-ray structure analysis for the neutral cluster $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2Me)]$ ([**4**]). The structure of [**4**] is shown in Fig. 1. Selected interatomic distances and angles are listed in Table 2. The mo-

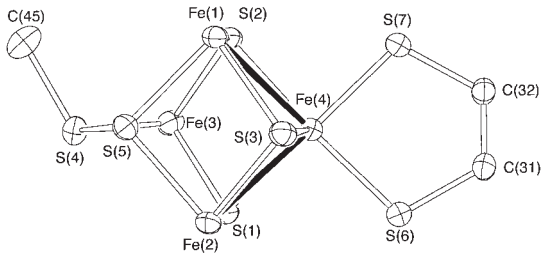


Fig. 1. ORTEP drawing of the $Fe_4(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2Me)$ moiety of [**4**]·THF. Cp* and Ph groups are omitted for clarity. Thermal ellipsoids are at 30% probability level.

Table 2. Selected Interatomic Distances (Å) and Angles (°) for $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2Me)]\cdot$THF ([**4**]·THF)

Fe(1)···Fe(2)	3.305(1)	Fe(1)···Fe(3)	3.828(1)
Fe(1)–Fe(4)	2.742(1)	Fe(2)···Fe(3)	3.815(1)
Fe(2)–Fe(4)	2.762(1)	Fe(3)···Fe(4)	3.206(1)
Fe(1)···S(1)	3.874(2)	Fe(1)–S(2)	2.205(2)
Fe(1)–S(3)	2.211(2)	Fe(1)···S(4)	3.593(2)
Fe(1)–S(5)	2.241(2)	Fe(2)–S(1)	2.205(2)
Fe(2)···S(2)	3.887(2)	Fe(2)–S(3)	2.205(2)
Fe(2)···S(4)	3.443(2)	Fe(2)–S(5)	2.245(2)
Fe(3)–S(1)	2.191(2)	Fe(3)–S(2)	2.192(2)
Fe(3)–S(4)	2.188(2)	Fe(3)···S(5)	3.464(2)
Fe(4)–S(1)	2.277(2)	Fe(4)–S(2)	2.306(2)
Fe(4)–S(3)	2.144(2)	Fe(4)···S(5)	3.530(2)
Fe(4)–S(6)	2.206(2)	Fe(4)–S(7)	2.184(2)
S(3)···S(5)	2.872(3)	S(4)–S(5)	2.165(3)
S(1)···S(5)	3.238(2)	S(2)···S(5)	3.215(2)
S(4)–C(45)	1.814(10)		
S(6)–C(31)	1.746(7)	S(7)–C(32)	1.748(7)
C(31)–C(32)	1.342(9)		
S(2)–Fe(1)–S(5)	92.64(7)	S(2)–Fe(1)–S(3)	103.72(7)
S(3)–Fe(1)–S(5)	80.35(7)	S(1)–Fe(2)–S(3)	102.48(8)
S(1)–Fe(2)–S(5)	93.35(7)	S(3)–Fe(2)–S(5)	80.38(7)
S(1)–Fe(3)–S(2)	89.46(8)	S(1)–Fe(3)–S(4)	88.29(7)
S(2)–Fe(3)–S(4)	92.56(8)	S(1)–Fe(4)–S(2)	84.61(7)
S(1)–Fe(4)–S(3)	102.09(8)	S(2)–Fe(4)–S(3)	102.57(7)
S(6)–Fe(4)–S(7)	86.57(7)		
Fe(3)–S(1)–Fe(4)	91.65(7)	Fe(2)–S(1)–Fe(3)	120.37(8)
Fe(2)–S(1)–Fe(4)	76.06(7)	Fe(1)–S(2)–Fe(3)	121.03(8)
Fe(1)–S(2)–Fe(4)	74.83(6)	Fe(3)–S(2)–Fe(4)	90.87(6)
Fe(1)–S(3)–Fe(2)	96.90(8)	Fe(1)–S(3)–Fe(4)	78.02(7)
Fe(2)–S(3)–Fe(4)	78.84(7)	Fe(1)–S(5)–Fe(2)	94.93(8)
Fe(2)–S(5)–S(4)	102.64(10)	Fe(1)–S(5)–S(4)	109.23(10)
S(5)–S(4)–Fe(3)	105.41(10)	Fe(3)–S(4)–C(45)	110.2(3)
S(5)–S(4)–C(45)	98.8(3)		
Fe(4)–S(6)–C(31)	108.1(2)	Fe(4)–S(7)–C(32)	108.2(2)
S(6)–C(31)–C(32)	118.0(5)	S(6)–C(31)–C(33)	117.0(5)
S(7)–C(32)–C(31)	119.0(5)	S(7)–C(32)–C(39)	114.4(5)

lecular structure of [**4**] is very similar to those of the parent cluster [**3**] and its mono- and dications,[9,15] except for the presence of the methyl group. The methyl group transferred from iodomethane resides at the singly ligating sulfur atom in the disulfide ligand (S(4) atom in Fig. 1). The S(4) adopts a distorted tetrahedral geometry involving the lobe of the lone pair electrons, which makes S(4) atom chiral. This also explains that, as shown in the ^{1}H NMR spectrum, all three Cp* ligands in cluster [**4**] are inequivalent. The S(4)–S(5) bond distance in the S_2Me ligand (2.165(3) Å) is longer by 0.086 Å than that for [**3**] (2.079(2) Å) and indicates weakening the S–SMe bond.

The interatomic distances of Fe(1)–Fe(4) (2.742(1) Å) and Fe(2)–Fe(4) (2.762(1) Å) are shorter than the other four Fe–Fe distances, which indicate the presence of Fe–Fe bonds. These four distances (3.206(1)–3.828(1) Å) suggest no Fe–Fe bond. The averaged value of the six Fe–Fe distances of [**4**] is 3.28 Å, which is longer than that of [**3**] (3.26 Å). This is understandable, if one considers that clusters [**3**] and [**4**] have 19 and 20 skeletal electrons, respectively.[1] Total Fe–Fe bond order of [**4**] is 2. As shown above, two localized Fe–Fe bonds are observed in this cluster.

Cyclic Voltammogram of [4]PF_6. The cyclic voltammogram of [**4**]PF_6 exhibits five reversible one-electron redox waves (Fig. 2). The electrochemical data are given in Table 3,

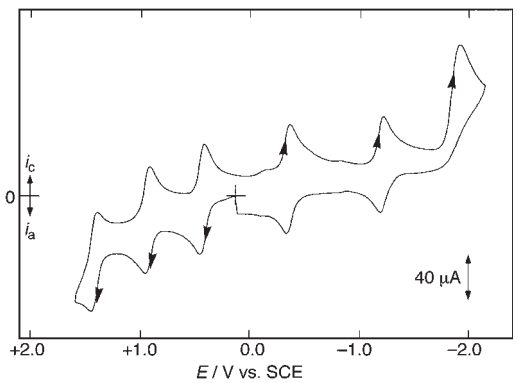


Fig. 2. Cyclic Voltammogram of $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2Me)](PF_6)$ ([**4**]PF_6) in CH_3CN containing 0.1 M TBAB. Concentration of [**4**]PF_6: 9.3×10^{-4} M. Sweep rate: 50 mV s^{-1}.

Table 3. Electrochemical Data of Clusters [**3**]PF_6 and [**4**]PF_6 in 0.1 M TBAB–CH_3CN

Cluster	Couple	$E_{1/2}$/V vs SCE	Number of skeletal electrons
3	3+/2+	+1.00	16/17
	2+/1+	+0.43	17/18
	1+/0	−0.15	18/19
	0/1−	−0.85	19/20
4	4+/3+	+1.42	16/17
	3+/2+	+0.92	17/18
	2+/1+	+0.41	18/19
	1+/0	−0.38	19/20
	0/1−	−1.22	20/21
	1− → 3−	−0.38	21/23

along with those of the parent cluster $[Fe_4(Cp^*)_3(Ph_2C_2S_2)(\mu_3\text{-}S)_3(\mu_3\text{-}S_2)]$ ([**3**]). [**3**] shows four reversible one-electron redox waves, indicating the formation of five species from a cluster having 16 skeletal electrons (+3 charged species) to a cluster having 20 skeletal electrons (−1 charged species). Its methylated cluster [**4**] shows formation of six species from the cluster having 16 skeletal electrons (+4 charged species) to a cluster having 21 skeletal electrons (−1 charged species). Furthermore, the −1 charged cluster exhibits an irreversible two-electron reduction wave at −1.97 V vs SCE (E_{pc}). This behavior has not been observed for the other clusters having a Fe_4S_5 core. The irreversible two-electron reduction of $[\mathbf{4}]^-$ suggests that the reduction is accompanied by a large structural change. One possible explanation for this behavior is the occurrence of the S–SMe bond cleavage upon reduction. The X-ray crystallography showed a consistent elongation of the S–S bond in [**4**], compared with that in [**3**].

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