Inorg. Chem. **1994,** *33,* 5337−5342

Syntheses and Structures of Mixed-Ligand Tetrairon−Sulfur Clusters: $Cp^*_2(Ph(R)C_2S_2)_2Fe_4S_4$ (Cp^* = Cp, R = Ph, Et; Cp^* = C_5Me_5, R = Ph, Me, Et) and $(C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5$

Shinji Inomata, Kunimasa Hiyama, Hiromi Tobita, and Hiroshi Ogino*

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980-77, Japan

Received February 15, 1994⊗

Mixed-ligand tetrairon−sulfur clusters $(C_5Me_5)_2(Ph_2C_2S_2)_2Fe_4S_4$ (**1**) and $(C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5$ (**2**) were synthesized by refluxing a mixture of $(C_5Me_5)_2Fe_2(CO)_4$, elemental sulfur, and PhC≡CPh in mesitylene. Similar treatments using PhC≡CMe and PhC≡CEt instead of PhC≡CPh afforded clusters corresponding to **1**, namely $(C_5Me_5)_2(Ph(Me)C_2S_2)_2Fe_4S_4$ (**3**) and $(C_5Me_5)_2(Ph(Et)C_2S_2)_2Fe_4S_4$ (**4**). The reactions of $Cp_2Fe_2(CO)_4$ with elemental sulfur and alkynes (PhC≡CPh and PhC≡CEt) afforded mixed-ligand clusters $Cp_2(Ph_2C_2S_2)_2Fe_4S_4$ (**5**) and $Cp_2(Ph(Et)C_2S_2)_2Fe_4S_4$ (**6**), respectively, as well as the cubane cluster $Cp_4Fe_4S_4$. The structures of clusters **1** and **2** were determined by X-ray structural analyses. Cluster **1** bears two C_5Me_5 and two diphenyldithiolene ligands on the four iron atoms, and there are three Fe−Fe bonds, so that Fe_4S_4 core is highly distorted. The Fe−Fe bonding distances are 2.711(1), 2.717(1), and 2.789(1) Å. The remaining three distances are 3.400(1), 3.255(1), and 3.270(1) Å. Cluster **2** contains an Fe_4S_5 core which consists of four iron atoms, three μ_3-S ligands, and one μ_3-S_2 ligand. Three iron atoms in the Fe_4S_5 core have C_5Me_5 ligands and the fourth iron atom is coordinated by a diphenyldithiolene ligand. The μ_3-S_2 ligand is located on the opposite side of the fourth iron atom. There are two Fe−Fe bonds, the lengths of which are 2.716(1) and 2.725(1) Å. The other four distances are long, ranging from 3.300(1) to 3.769(1) Å. Crystals of $\mathbf{1}\cdot CH_2Cl_2$ ($C_{49}H_{52}Cl_2Fe_4S_8$) belong to the monoclinic space group $P2_1/a$ with a = 20.679(3) Å, b = 20.130(3) Å, c = 12.742(2) Å, β = 104.97(2)°, V = 5124(1) Å^3, Z = 4, and $R(F_o)$ = 0.069 for 9193 reflections with $|F_o| \geq 3\sigma(F_o)$; those of $\mathbf{2}\cdot$THF ($C_{48}H_{63}Fe_4OS_7$) belong to the monoclinic space group $P2_1/c$ with a = 17.302(3) Å, b = 17.639(2) Å, c = 17.099(3) Å, β = 102.99(3)°, V = 5058(1) Å^3, Z = 4 and $R(F_o)$ = 0.058 for 8164 reflections with $|F_o| \geq 3\sigma(F_o)$.

Introduction

Recently, we reported that the reaction of $(C_5Me_5)_2Fe_2(CO)_4$ with elemental sulfur and PhC≡CPh gives mixed-ligand tetrairon-sulfur clusters $(C_5Me_5)_2(Ph_2C_2S_2)_2Fe_4S_4$ (**1**) and $(C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5$ (**2**).[1,2] Cluster **1** is the first example of a cubane cluster containing two octahedral metals (C_5Me_5 ligand is considered to occupy three coordination sites) and two five-coordinate metals,[3] and possesses 18 metal electrons. Compound **2** is the first mixed-ligand cluster having an Fe_4S_5 core and consists of three octahedral metals and one five-coordinate metal. Nineteen metal electrons can be allocated for this cluster.

Only a limited number of mixed-ligand tetrairon−sulfur clusters have been prepared and structurally characterized.[4−8] It is therefore important to establish the synthetic methods of these types of clusters. This paper describes the detailed results on the syntheses and structures of clusters **1** and **2**. Furthermore, the synthetic techniques developed here are also extended to other systems: the reactions of $(C_5Me_5)_2Fe_2(CO)_4$ with sulfur and PhC≡CR (R = Me, Et) and the reactions of $Cp_2Fe_2(CO)_4$ with sulfur and PhC≡CR (R = Ph, Et).

Experimental Section

General Procedures. All manipulations were carried out under a nitrogen atmosphere. Pentane, hexane, tetrahydrofuran (THF), and diethyl ether were freshly distilled from sodium benzophenone ketyl. Mesitylene, xylene, and toluene were distilled from sodium prior to use. Dichloromethane was purified by distillation from calcium hydride. $Cp_2Fe_2(CO)_4$,[9] $(C_5Me_5)_2Fe_2(CO)_4$,[10] and $(C_5Me_5)_2Fe_2S_4$[11] were prepared according to literature methods. Silica gel flash chromatography was performed under a nitrogen atmosphere. Silica gel used for the separation of **1** and **2** was deactivated by stirring it in acetone overnight at room temperature. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-200 Fourier transform spectrometer. Mass spectra were recorded using a JEOL JMS HX-110 mass spectrometer. Solution magnetic susceptibility measurements of **2** were performed by the Evans method[12] in $CDCl_3$ containing 3% $CHCl_3$ on a Varian XL-200 Fourier transform spectrometer. The concentration of **2** was 0.0320 mol dm^{-3}.

Synthesis of $(C_5Me_5)_2(Ph_2C_2S_2)_2Fe_4S_4$ (1) and $(C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5$ (2). A solution of $(C_5Me_5)_2Fe_2(CO)_4$ (1.78 g, 3.61 mmol), elemental sulfur (470 mg, 1.83 mmol), and PhC≡CPh (648 mg, 3.64 mmol) in 60 mL of mesitylene[13] was refluxed. Silica gel TLC analysis (solvent, toluene) showed a spot assignable to $(C_5Me_5)_2Fe_2S_4$ (R_f = 0.59) after 5 min from the beginning of the refluxing. After 30 min another two spots corresponding to **1** (R_f = 0.80) and **2** (R_f = 0.40) appeared on the TLC. When the solution was refluxed for 12 h, the spot of $(C_5Me_5)_2Fe_2S_4$ completely disappeared. At this point, the solution was cooled to room temperature. After removal by filtration

---

⊗ Abstract published in *Advance ACS Abstracts,* October 1, 1994.

(1) Inomata, S.; Tobita, H.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 6145.
(2) Inomata, S.; Tobita, H.; Ogino, H. *Inorg. Chem.* **1992**, *31*, 722.
(3) Harris, S. *Polyhedron* **1989**, *88*, 2843.
(4) Kanatzidis, M. G.; Baenziger, N. C.; Coucouvanis, D.; Simopoulos, A.; Kostikas, A. *J. Am. Chem. Soc.* **1984**, *106*, 4500.
(5) Stack, T. D. P.; Holm, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2484.
(6) Kanatzidis, M. G.; Coucouvanis, D.; Simopoulos, A.; Kostikas, A.; Papaefthymiou, V. *J. Am. Chem. Soc.* **1985**, *107*, 4925.
(7) Holm, R. H.; Ciurli, S.; Weigel, J. A. *Prog. Inorg. Chem.* **1990**, *38*, 1.
(8) Weigel, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 4184.
(9) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 110.
(10) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287.
(11) Brunner, H.; Janietz, N.; Meier, W.; Sergeson, G.; Wachter, J.; Zahn, T.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1060.
(12) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.
(13) Refluxing mesitylene can be replaced by refluxing xylene, though the prolonged heating time is needed in the latter solvent because of lower boiling point.

0020-1669/94/1333-5337$04.50/0

of a precipitate (582 mg) which was not identified, mesitylene was evaporated under reduced pressure and the residue was placed on a column of silica gel (deactivated, 6 × 40 cm). The first violet band was eluted with toluene. Evaporation of the solvent afforded $(C_5Me_5)_2(Ph_2C_2S_2)_2Fe_4S_4$ (**1**) as a violet powder. Yield: 827 mg (41%). Pure crystals of $(C_5Me_5)_2(Ph_2C_2S_2)_2Fe_4S_4{\cdot}CH_2Cl_2$ (**1**$\cdot CH_2Cl_2$) suitable for X-ray analysis were obtained by layering a CH_2Cl_2 solution of **1** with diethyl ether. ^1H NMR ($CDCl_3$): δ 1.48 (30H, s, C_5Me_5), 5.32 (2H, s, CH_2Cl_2), 7.2–7.3, 7.4–7.5 (20H, m, Ph). ^{13}C NMR ($CDCl_3$) δ 10.6 ($C_5(\mathit{C}H_3)_5$), 53.4 (CH_2Cl_2), 101.7 (C_5Me_5), 127.2, 127.8, 129.8, 141.7 (C_6H_5), 174.1 ($S{=}\mathit{C}Ph$). MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe): *m/z* 1106 (M^+). Anal. Calcd for $C_{49}H_{52}Cl_2Fe_4S_8$: C, 49.38; H, 4.40. Found: C, 49.30; H, 4.49.

The second, dark green, band was eluted with ether. Evaporation of the solvent afforded the dark green oil of $(C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5$ (**2**). Yield: 454 mg (24%). This product was purified and crystallized from pentane/ether at −2 °C. ^1H NMR ($CDCl_3$): δ 7.5 (6H, br, $W_{1/2}$ = 9 Hz, Ph), 6.8 (4H, br, $W_{1/2}$ = 10 Hz, Ph), 2.8 (30H, br, $W_{1/2}$ = 21 Hz, Me), −0.5 (15H, br, $W_{1/2}$ = 46 Hz, Me). MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe): *m/z* 1031(M^+). Anal. Calcd for $C_{44}H_{55}Fe_4S_7$: C, 51.22; H, 5.37. Found: C, 51.27; H, 5.34. Crystals of $(C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5{\cdot}THF$ (**2**·THF) suitable for X-ray analysis were obtained by layering a THF solution of **2** with hexane. Solution magnetic susceptibility measurements of **2** gave an effective magnetic moment of 1.46 μ_B at 21 °C.

Reaction of $(C_5Me_5)_2Fe_2S_4$ with $PhC{\equiv}CPh$. A solution containing $(C_5Me_5)_2Fe_2S_4$ (0.308 g, 0.600 mmol) and $PhC{\equiv}CPh$ (0.219 g, 1.20 mmol) in mesitylene (18 mL)[13] was refluxed for 14 h. After 30 min from the beginning of the refluxing, silica gel TLC analysis (solvent, toluene) showed two spots corresponding to **1** (R_f = 0.80) and **2** (R_f = 0.40). The spot of $(C_5Me_5)_2Fe_2S_4$ completely disappeared after 14 h.

Synthesis of $(C_5Me_5)_2(Ph(Me)C_2S_2)_2Fe_4S_4$ (3). A solution containing $(C_5Me_5)_2Fe_2(CO)_4$ (0.492 g, 1.00 mmol), sulfur (0.128 g, 0.500 mmol), and $PhC{\equiv}CMe$ (0.116 g, 1.00 mmol) in mesitylene[13] (30 mL) was refluxed for 12 h. After removal of the precipitate (220 mg) by filtration, mesitylene was evaporated under reduced pressure and the residue was placed on a column of silica gel (4 × 40 cm). A violet band was eluted with toluene. Evaporation of the solvent afforded solid $(C_5Me_5)_2(Ph(Me)C_2S_2)_2Fe_4S_4$ (**3**). Crystals of **3** were obtained from the CH_2Cl_2/ether (ca. 3:8 v/v) solution. Yield: 48 mg (10%). ^1H NMR ($CDCl_3$): δ 1.36 (30H, s, $C_5\mathit{Me}_5$), 2.86 (6H, s, $Ph(\mathit{Me})C_2S_2$), 7.2–7.6 (10H, m, Ph). ^{13}C NMR ($CDCl_3$): δ 10.4 ($C_5(\mathit{C}H_3)_5$), 24.3 ($Ph(\mathit{Me})C_2S_2$), 107.2 (C_5Me_5), 127.3, 127.9, 129.1, 142.3 (C_6H_5), 172.6, 174.2 ($S{=}\mathit{C}Ph$). MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe): *m/z* 982 (M^+). Anal. Calcd for $C_{38}H_{46}Fe_4S_8$: C, 46.45; H, 4.72. Found: C, 45.98; H, 4.55.

Synthesis of $(C_5Me_5)_2(Ph(Et)C_2S_2)_2Fe_4S_4$ (4). The synthesis of **4** was almost identical with that of **3** except for the use of $PhC{\equiv}CEt$ instead of $PhC{\equiv}CMe$. From the reaction mixture of $(C_5Me_5)_2Fe_2(CO)_4$ (0.494 g, 1.00 mmol), sulfur (0.128 g, 0.500 mmol), and $PhC{\equiv}CEt$ (0.260 g, 2.00 mmol), product **4** was obtained in 15% yield (76 mg). ^1H NMR ($CDCl_3$) δ 1.38 (6H, t, *J* = 8 Hz, $CH_2C\mathit{H}_3$), 1.42 (30H, s, $C_5\mathit{Me}_5$), 3.16 (4H, q, *J* = 8 Hz, $C\mathit{H}_2CH_3$), 7.3–7.6 (10H, m, Ph). ^{13}C NMR ($CDCl_3$): δ 10.4 ($C_5\mathit{Me}_5$), 16.7 ($CH_2\mathit{C}H_3$), 30.7 ($\mathit{C}H_2CH_3$), 101.4 (C_5Me_5), 127.3, 127.8, 129.1, 142.4 (C_6H_5), 174.1, 179.8 ($Ph(Et)\mathit{C}_2S_2$); MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe): *m/z* 1011 ($(M + H)^+$). Anal. Calcd for $C_{40}H_{50}Fe_4S_8$: C, 47.53; H, 4.99. Found: C, 47.12; H, 4.93.

Synthesis of $Cp_2(Ph_2C_2S_2)_2Fe_4S_4$ (5). A xylene solution (60 mL)[14] containing $Cp_2Fe_2(CO)_4$ (0.709 g, 2.00 mmol), sulfur (0.262 g, 1.00 mmol), and $PhC{\equiv}CPh$ (0.801 g, 4.50 mmol) was refluxed for 11 h. After the solution was cooled to room temperature, a black powder (414 mg) was removed by filtration. The powder was identified as the known cubane cluster $Cp_4Fe_4S_4$ by mass and ^1H NMR spectroscopy. The isolation of $Cp_2(Ph_2C_2S_2)_2Fe_4S_4$ (**5**) was carried out by silica gel chromatography (4 × 40 cm). After $PhC{\equiv}CPh$ was removed by eluting with a mixed solvent system of toluene–hexane (4:3 v/v), the violet band of **5** was eluted with toluene. Removal of solvent by a rotary evaporator afforded the solid of **5**. Yield: 310 mg (32%). Crystals of **5** were obtained from CH_2Cl_2/ether (ca. 1:1 v/v). ^1H NMR ($CDCl_3$): δ 4.96 (10H, s, C_5H_5), 7.2–7.3, 7.4–7.5 (20H, m, Ph). ^{13}C NMR ($CDCl_3$): δ 89.3 (C_5H_5), 127.86, 127.92, 129.6, 141.6 (C_6H_5), 179.0 ($S{=}\mathit{C}Ph$). MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe): *m/z* 966 (M^+). Anal. Calcd for $C_{39}H_{32}Cl_2Fe_4S_8$: C, 44.55; H, 3.07. Found: C, 44.11; H, 3.36.

Table 1. Crystallographic Data for $(C_5Me_5)_2(Ph_2C_2S_2)_2Fe_4S_4{\cdot}CH_2Cl_2$ (**1**$\cdot CH_2Cl_2$) and $(C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5{\cdot}THF$ (**2**·THF)

	1$\cdot CH_2Cl_2$	**2**·THF
formula	$C_{49}H_{52}Cl_2Fe_4S_8$	$C_{48}H_{63}Fe_4OS_7$
a, Å	20.679(3)	17.302(3)
b, Å	20.130(3)	17.639(2)
c, Å	12.742(2)	17.099(3)
β, deg	104.97(2)	102.99(3)
V, Å^3	5124(1)	5085(1)
Z	4	4
fw	1191.61	1103.88
space group	$P2_1/a$ (variant of No. 14)	$P2_1/c$ (No. 14)
T, °C	21	21
λ, Å	0.710 73	0.710 73
ϱ_{obsd}, g cm^{-3}	1.54	1.44
ϱ_{calcd}, g cm^{-3}	1.55	1.44
μ (Mo Kα), cm^{-1}	15.9	14.6
R^a	0.069	0.058
$R_w{}^b$	0.102	0.087

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = [\sigma^2(|F_o|) + aF_o{}^2]^{-1}$, where a = 0.005 for **1**$\cdot CH_2Cl_2$ and 0.003 for **2**·THF.

Synthesis of $Cp_2(Ph(Et)C_2S_2)_2Fe_4S_4$ (6). The synthesis of **6** was almost identical with that of **5** except for the use of $PhC{\equiv}CEt$ instead of $PhC{\equiv}CPh$: A mesitylene solution (25 mL)[13] containing $Cp_2Fe_2(CO)_4$ (0.353 g, 1.00 mmol), sulfur (0.128 g, 0.500 mmol), and $PhC{\equiv}CEt$ (0.259 g, 2.00 mmol) was refluxed for 4 h. A black precipitate of $Cp_4Fe_4S_4$ (183 mg) was removed by filtration. From the filtrate purple crystals of **6** were separated by column chromatography (4 × 40 cm). Yield: 80 mg (18%). ^1H NMR ($CDCl_3$): δ 1.38 (6H, t, *J* = 8 Hz, $CH_2C\mathit{H}_3$), 3.21 (4H, q, *J* = 8 Hz, $C\mathit{H}_2CH_3$), 4.88 (10H, s, Cp) 7.4–7.6 (10H, m, Ph). ^{13}C NMR ($CDCl_3$) δ 16.8 ($CH_2\mathit{C}H_3$), 31.3 ($\mathit{C}H_2CH_3$), 89.0 (Cp), 127.9, 128.1, 129.0, 142.0 (C_6H_5), 178.8, 184.5 ($Ph(Et)C_2S_2$). MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe): *m/z* 870 (M^+). Anal. Calcd for $C_{30}H_{30}Fe_4S_8$: C, 41.39; H, 3.47. Found: C, 41.04; H, 3.77.

X-ray Crystal Structural Determination of $(C_5Me_5)_2(Ph_2C_2S_2)_2Fe_4S_4{\cdot}CH_2Cl_2$ (1·CH_2Cl_2) and $(C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5{\cdot}THF$ (2·THF). Diffraction data for **1**$\cdot CH_2Cl_2$ and **2**·THF were collected on a Rigaku AFC-6A four-circle diffractometer with graphite-monochromated Mo Kα radiation using the $\omega-2\theta$ scan technique. Crystallographic data for clusters **1**$\cdot CH_2Cl_2$ and **2**·THF are listed in Table 1. The reflection data were collected in the range $3 < 2\theta < 60°$ ($\pm h$, $+k$, $+l$), and were corrected for Lorentz and polarization factors. No correction was applied for absorption.

The structure of **1**$\cdot CH_2Cl_2$ was solved by the direct method (MULTAN), which afforded the positions of the four iron atoms and eight sulfur atoms. All remaining non-hydrogen atoms except for the CH_2Cl_2 molecule were refined by the block-diagonal least-squares method with anisotropic thermal parameters. The CH_2Cl_2 molecule was disordered. The equivalent thermal values of three carbon atoms of one Ph group in **1** (C(39), C(40), and (41)) were very large because of the influence of the disordered CH_2Cl_2 molecule. The coordinates of the hydrogen atoms, excluding those on C_5Me_5 ligands and those on the Ph group with large equivalent thermal values, were deduced from difference Fourier maps and refined using isotropic temperature factors.

The structure of **2**·THF was solved by the heavy atom method which provided the positions of the four iron atoms and seven sulfur atoms. All remaining non-hydrogen atoms were refined by the block-diagonal least-squares method with anisotropic thermal parameters. Hydrogen atoms on two Ph groups were located by calculation (d(C–H) = 1.08 Å). The isotropic thermal parameters of hydrogen atoms were fixed at 1.5 times the equivalent thermal parameters of the carbon atoms to which they are covalently bonded.

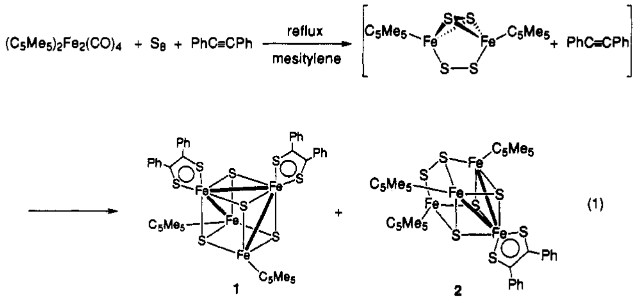
---

(14) Xylene can be replaced by mesitylene.

Values for the atomic scattering factors of non-hydrogen and hydrogen atoms were those in refs 15 and 16, respectively. Calculations were performed on a Nippon Electric Co. ACOS-2000 computer at Tohoku University Computer Center using the Universal Computation Program System UNICS III.[17]

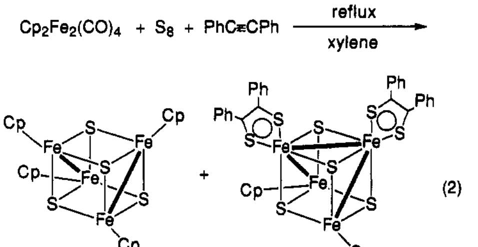
Results and Discussion

Synthesis of Tetrairon-Sulfur Clusters. The reaction of $(C_5Me_5)_2Fe_2(CO)_4$ with elemental sulfur and PhC≡CPh was found to give the mixed-ligand tetrairon–sulfur clusters $(C_5Me_5)_2(Ph_2C_2S_2)_2Fe_4S_4$ (**1**) and $(C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5$ (**2**). Cluster **2** was less stable than **1** and was unstable on commercially available silica gel. Isolation of **2** was successfully achieved by the use of silica gel deactivated with acetone. The reaction of $(C_5Me_5)_2Fe_2(CO)_4$ with sulfur and PhC≡CPh was followed by TLC: $(C_5Me_5)_2Fe_2S_4$ was formed at an early stage of the reaction and then disappeared with time. $(C_5Me_5)_2Fe_2S_4$ is thus considered to be one of the reaction intermediates (eq 1). In fact, the reaction of $(C_5Me_5)_2Fe_2S_4$ with PhC≡CPh in refluxing mesitylene gave **1** and **2** (see Experimental Section). In reaction 1, when PhC≡CMe and PhC≡CEt were used instead of PhC≡CPh, clusters **3** and **4** respectively, which correspond to **1**, were formed. The formation of clusters corresponding to **2** was not confirmed.



(1)

The reaction of $Cp_2Fe_2(CO)_4$ with elemental sulfur and PhC≡CPh gave $Cp_4Fe_4S_4$[18] and a mixed-ligand cluster $Cp_2(Ph_2C_2S_2)_2Fe_4S_4$ (**5**) which corresponds to **1** (eq 2). In this reaction, a cluster containing an Fe_4S_5 core which corresponds to **2** was not obtained. The reaction using PhC≡CEt instead of PhC≡CPh also gave clusters $Cp_4Fe_4S_4$ and $Cp_2(Ph(Et)C_2S_2)_2Fe_4S_4$ (**6**).



(2)

The reactions of various metal carbonyls with elemental sulfur and PhC≡CPh have been reported: With $M(CO)_6$ (M = Cr, Mo, W), monomeric dithiolene complexes $M(S_2C_2Ph_2)_3$ were obtained;[19] the reaction of $Ni(CO)_4$ with sulfur and PhC≡CPh afforded $Ni(S_2C_2Ph_2)_2$;[20] and reactions of $CpCo(CO)_2$ or CpCo(cod) (cod = cyclooctadiene) with sulfur and alkynes gave the monomeric complexes CpCo(dithiolene).[21] In contrast to these, however, the reaction of $Fe(CO)_5$ with sulfur and PhC≡CPh gave a complex $(Ph_2C_2S_2)_4Fe_4S_4$ which was believed to have a cubane-type structure.[22]

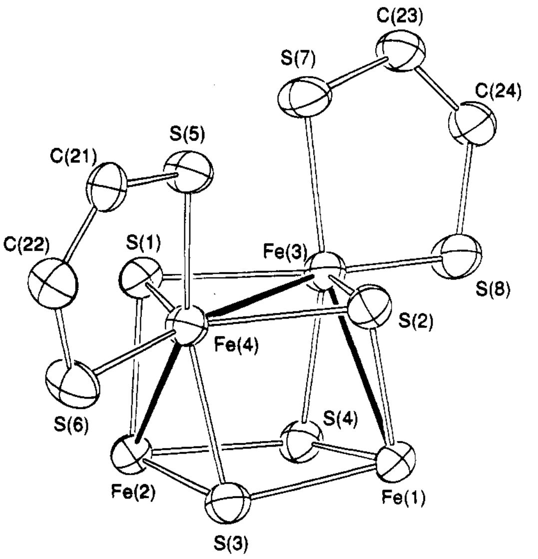


Figure 1. ORTEP drawing of Fe_4S_4 core of **1** with two dithiolene chelate rings.

Structure of $(C_5Me_5)_2(Ph_2C_2S_2)_2Fe_4S_4$ (1). The structure of the Fe_4S_4 core moiety with two dithiolene chelate rings in **1** is shown in Figure 1. Final atomic coordinates and selected interatomic distances and angles are listed in Tables 2 and 3, respectively. Cluster **1** is a mixed-ligand cubane cluster containing an Fe_4S_4 core with two C_5Me_5 ligands and two diphenyldithiolene ligands. The arrangement of the dithiolene ligands adopts distorted square-pyramidal configuration around the iron atoms (Fe(3), Fe(4)), which locate on ca. 0.6 Å above the mean basal planes (S(1)–S(4)–S(8)–S(7) for Fe(3) and S(2)–S(3)–S(6)–S(5) for Fe(4)).

The X-ray crystal structure of **1** shows that two phenyl groups of each dithiolene ligand are nonequivalent. However, the ^{13}C NMR spectrum (see Experimental Section) indicates that they are equivalent and fluxional.[23]

The Fe_4S_4 core in **1** has three Fe–Fe bonds in the sequence Fe(1)–Fe(3)–Fe(4)–Fe(2). The distances Fe(1)–Fe(3), Fe(3)–Fe(4), and Fe(4)–Fe(2) are 2.711(1), 2.789(1), and 2.717(1) Å, respectively—values which are somewhat larger than those for Fe–Fe single bonds observed in $Cp_4Fe_4S_4$ (2.65 Å),[18] $(ON)_4Fe_4S_4$ (2.65 Å),[24] and $(C_5H_4Me)_4Fe_4S_4$ (2.61 Å).[25] The remaining three distances Fe(1)–Fe(2), Fe(1)–Fe(4), and Fe(2)–Fe(3) are 3.400(1), 3.255(1), and 3.270(1) Å, suggesting no Fe–Fe bond.

The metal fragment orbital model[3] and qualitative MO bonding scheme developed by the Dahl group[26] predict that a

---

(15) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2A, pp 72–98, and Table 2.3.1, pp 149–150.

(16) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(17) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyuusho Houkoku* **1979**, *55*, 69.

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

(19) Schrauzer, G. N.; Finck, H. W.; Mayweg, V. *Z. Naturforsch.* **1964**, *19b*, 1080.

(20) Schrauzer, G. N.; Mayweg, V. *J. Am. Chem. Soc.* **1962**, *84*, 3221.

(21) Kajitani, M.; Ochiai, R.; Kobayashi, N.; Akiyama, T.; Sugimori, A. *Chem. Lett.* **1987**, 245.

(22) Balch, A. L. *J. Am. Chem. Soc.* **1969**, *91*, 6962.

(23) The fluxional behavior will be reported elsewhere.

(24) (a) Gall, R. S.; Connelly, N. G.; Dahl, L. F. *J. Am. Chem. Soc.* **1974**, *96*, 4019. (b) Chu, C. T.-W.; Lo, F. Y.-K; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 3409.

(25) Blonk, H. L.; van der Linden, J. G. M.; Steggerda, J. J.; Geleyn, R. P.; Smits, J. M. M.; Beurskens, G.; Beurskens, P. T.; Jordanov, J. *Inorg. Chem.* **1992**, *31*, 957.

Table 2. Final Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors for $(C_5Me_5)_2(Ph_2C_2S_2)_2Fe_4S_4 \cdot CH_2Cl_2$ (**1**$\cdot CH_2Cl_2$)

atom	*x*	*y*	*z*	B_{eqv},[a] Å^2
Fe(1)	1393.5(4)	1943.3(4)	5011(1)	2.3
Fe(2)	2529.5(4)	3147.1(4)	4914(1)	2.3
Fe(3)	2152.7(4)	1748.1(4)	3593(1)	2.3
Fe(4)	3022.4(4)	1933.7(4)	5644(1)	2.3
S(1)	3050(1)	2423(1)	4152(1)	2.5
S(2)	2174(1)	1205(1)	5057(1)	2.6
S(3)	2211(1)	2539(1)	6122(1)	2.5
S(4)	1596(1)	2681(1)	3858(1)	2.4
S(5)	3681(1)	1077(1)	5699(1)	2.8
S(6)	3650(1)	2211(1)	7214(1)	3.3
S(7)	2765(1)	1199(1)	2728(1)	3.4
S(8)	1315(1)	1547(1)	2233(1)	3.2
C(1)	489(4)	2318(4)	5268(7)	4.3
C(2)	807(4)	1913(4)	6164(6)	4.3
C(3)	856(3)	1275(4)	5780(6)	4.2
C(4)	571(3)	1256(4)	4643(6)	3.6
C(5)	330(3)	1908(4)	4323(6)	4.1
C(6)	2263(4)	4108(3)	4233(6)	3.6
C(7)	2934(4)	3959(3)	4190(6)	4.0
C(8)	3330(3)	3860(3)	5268(6)	3.8
C(9)	2926(3)	3953(3)	5988(6)	3.5
C(10)	2262(3)	4110(3)	5347(5)	3.2
C(11)	287(5)	3017(5)	5353(12)	8.3
C(12)	1017(6)	2109(7)	7354(8)	8.4
C(13)	1130(5)	658(5)	6474(10)	7.0
C(14)	483(5)	648(5)	3938(9)	7.1
C(15)	−53(4)	2125(7)	3217(8)	7.1
C(16)	1685(5)	4288(4)	3289(7)	5.7
C(17)	3164(7)	3935(5)	3156(9)	7.1
C(18)	4075(4)	3702(4)	5573(10)	6.2
C(19)	3138(5)	3948(4)	7221(7)	5.3
C(20)	1675(4)	4295(4)	5783(7)	4.9
C(21)	4269(3)	1091(3)	6931(4)	2.5
C(22)	4262(3)	1611(3)	7626(5)	2.8
C(23)	2246(3)	950(3)	1495(5)	3.0
C(24)	1579(3)	1089(3)	1290(4)	2.8
C(25)	4706(3)	500(3)	7209(5)	2.5
C(26)	5034(3)	236(4)	6470(6)	3.6
C(27)	5410(4)	−343(4)	6699(7)	4.4
C(28)	5457(4)	−667(4)	7681(7)	4.5
C(29)	5128(4)	−420(4)	8418(7)	4.5
C(30)	4760(3)	162(3)	8182(5)	3.3
C(31)	4716(4)	1715(3)	8718(5)	3.6
C(32)	4475(5)	1912(4)	9573(6)	5.4
C(33)	4880(7)	2017(5)	10613(7)	7.4
C(34)	5526(6)	1944(4)	10794(7)	7.2
C(35)	5802(6)	1748(5)	9986(9)	7.8
C(36)	5408(4)	1629(5)	8902(7)	5.4
C(37)	2579(4)	650(5)	718(7)	5.8
C(38)	2474(6)	941(10)	−306(8)	10.8
C(39)	2860(10)	674(13)	−1102(11)	17.4
C(40)	3210(7)	98(13)	−639(13)	16.5
C(41)	3333(6)	−221(11)	345(15)	15.4
C(42)	3002(5)	99(7)	1023(12)	10.1
C(43)	1063(3)	870(3)	323(5)	3.1
C(44)	547(4)	1319(4)	−193(6)	4.0
C(45)	43(4)	1098(5)	−1078(6)	5.1
C(46)	20(4)	479(5)	−1456(6)	4.8
C(47)	529(4)	40(4)	−969(6)	4.6
C(48)	1046(4)	233(4)	−103(6)	4.1

[a] The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eqv} = {}^4/_3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac\cos\beta)$. The B_{ij}'s are defined by $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $(C_5Me_5)_2(Ph_2C_2S_2)_2Fe_4S_4 \cdot CH_2Cl_2$ (**1**$\cdot CH_2Cl_2$)

	Distances		
Fe(1)···Fe(2)	3.400(1)	Fe(1)−Fe(3)	2.711(1)
Fe(1)···Fe(4)	3.255(1)	Fe(2)···Fe(3)	3.270(1)
Fe(2)−Fe(4)	2.717(1)	Fe(3)−Fe(4)	2.789(1)
Fe(1)−S(2)	2.185(2)	Fe(1)−S(3)	2.250(2)
Fe(1)−S(4)	2.204(2)	Fe(2)−S(1)	2.183(2)
Fe(2)−S(3)	2.197(2)	Fe(2)−S(4)	2.254(2)
Fe(3)−S(1)	2.262(2)	Fe(3)−S(2)	2.153(2)
Fe(3)−S(4)	2.273(2)	Fe(3)−S(7)	2.182(2)
Fe(3)−S(8)	2.149(2)	Fe(4)−S(1)	2.155(2)
Fe(4)−S(2)	2.260(2)	Fe(4)−S(3)	2.280(2)
Fe(4)−S(5)	2.187(2)	Fe(4)−S(6)	2.158(2)
S(5)−C(21)	1.721(6)	S(6)−C(22)	1.729(6)
S(7)−C(23)	1.733(6)	S(8)−C(24)	1.713(7)
C(21)−C(22)	1.374(9)	C(23)−C(24)	1.363(9)
	Angles		
S(2)−Fe(1)−S(4)	102.11(7)	S(2)−Fe(1)−S(3)	85.17(6)
S(3)−Fe(1)−S(4)	79.60(6)	S(1)−Fe(2)−S(4)	84.35(6)
S(1)−Fe(2)−S(3)	102.18(7)	S(3)−Fe(2)−S(4)	79.65(6)
S(1)−Fe(3)−S(4)	82.13(6)	S(1)−Fe(3)−S(2)	101.55(7)
S(2)−Fe(3)−S(4)	100.89(7)	S(7)−Fe(3)−S(8)	87.12(7)
S(1)−Fe(4)−S(2)	101.52(6)	S(1)−Fe(4)−S(3)	100.40(7)
S(2)−Fe(4)−S(3)	82.75(6)	S(5)−Fe(4)−S(6)	87.38(7)
Fe(2)−S(1)−Fe(3)	94.73(7)	Fe(2)−S(1)−Fe(4)	77.56(7)
Fe(3)−S(1)−Fe(4)	78.27(6)	Fe(1)−S(2)−Fe(3)	77.38(6)
Fe(1)−S(2)−Fe(4)	94.13(6)	Fe(3)−S(2)−Fe(4)	78.35(6)
Fe(1)−S(3)−Fe(4)	91.86(6)	Fe(1)−S(3)−Fe(2)	99.70(7)
Fe(2)−S(3)−Fe(4)	74.69(6)	Fe(1)−S(4)−Fe(2)	99.40(7)
Fe(2)−S(4)−Fe(3)	92.50(6)	Fe(3)−S(4)−Fe(1)	74.54(5)
Fe(4)−S(5)−C(21)	107.7(2)	Fe(4)−S(6)−C(22)	108.5(2)
Fe(3)−S(7)−C(23)	107.5(2)	Fe(3)−S(8)−C(24)	109.3(3)
S(5)−C(21)−C(22)	118.5(5)	S(6)−C(22)−C(21)	117.8(5)
S(7)−C(23)−C(24)	118.2(5)	S(8)−C(24)−C(23)	117.8(5)

cubane cluster with 18 metal electrons has a total Fe−Fe bond order of 3: twelve electrons occupy the six metal−metal bonding orbitals and the remaining six electrons occupy the metal−metal antibonding orbitals. The core structure of **1** with three Fe−Fe single bonds is consistent with this prediction. As $[Cp_4Fe_4S_4]^{2+}$ [26] and $[\{(CF_3)_2C_2S_2\}_4Fe_4S_4]^{2-}$ [27] are also clusters with 18 metal electrons, it is expected that each cluster has a total bond order of 3. However, these clusters adopt D_{2d} symmetry and have four equivalent Fe−Fe bonds. Therefore, each Fe−Fe bond corresponds to a bond order of $^3/_4$. The localization of the three Fe−Fe bonds in **1** may be due to the lower symmetry of the cluster; two C_5Me_5 ligands and two dithiolene ligands coordinate to the four iron atoms in **1**. However, it should be noted that the "homoleptic clusters", $[(C_5H_4Me)_4Ru_4S_4]^{2+}$ [28] and $[\{C_5H_4(SiMe_3)\}_4Ru_4S_4]^{2+}$,[28,29] also have three localized metal−metal bonds.

The 12 Fe−S bonding distances in the Fe_4S_4 core range from 2.153(2) to 2.280(2) Å. The mean value of the distances is 2.22 Å, which is almost identical with those of $Cp_4Fe_4S_4$ (2.22 Å),[18] $(C_5H_4Me)_4Fe_4S_4$ (2.22 Å),[25] $[Cp_4Fe_4S_4]^+$ (2.21 Å),[30] $[(C_5H_4Me)_4Fe_4S_4]^+$ (2.19 Å),[25] $[Cp_4Fe_4S_4]^{2+}$ (2.19 Å),[26] and $[\{(CF_3)_2C_2S_2\}_4Fe_4S_4]^{2-}$ (2.22 Å).[27] On the other hand, the distances between the iron and sulfur atoms in the dithiolene chelate rings 2.149(2)−2.187(2) Å (average 2.17 Å) are shorter than those in the Fe_4S_4 core. This suggests that the Fe-S(dithiolene) bonds have some unsaturated bonding character. The averaged bond distance is quite similar to those in $[\{(CF_3)_2C_2S_2\}_4Fe_4S_4]^{2-}$ (2.17 Å),[27] $[Fe_2\{S_2C_2(CF_3)_2\}_4]^-$ (2.18

---

(26) Trinh-Toan; Teo, B. K.; Ferguson, J. A.; Meyer, T. J.; Dahl, L. F. *J. Am. Chem. Soc.* **1977**, *99*, 408.

(27) Lemmen, T. H.; Kocal, J. A.; Lo, F. Y.-K.; Chen, M. W.; Dahl, L. F. *J. Am. Chem. Soc.* **1981**, *103*, 1932.

(28) Houser, E. J.; Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 7440.

(29) Houser, E. J.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1993**, *32*, 4069.

(30) (a) Trinh-Toan; Fehlhammer, W. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1977**, *99*, 402. (b) Ferguson, J. A.; Meyer, T. *J. Chem. Commun.* **1971**, 623.

Table 4. Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors for $(C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5$·THF (**2**·THF)

atom	x	y	z	B_{eqv},[a] Å^2
Fe(1)	3465.0(4)	−961.8(4)	1585.8(4)	2.6
Fe(2)	3575.9(4)	903.8(4)	1706.2(4)	2.6
Fe(3)	2428.6(4)	115.2(4)	−256.1(4)	2.8
Fe(4)	2268.7(4)	21.8(4)	1632.6(5)	2.9
S(1)	2494.5(7)	910.4(7)	752.3(7)	2.9
S(2)	2396.6(8)	−790.8(7)	636.8(7)	2.9
S(3)	3404.0(8)	−58.5(7)	2459.1(7)	2.9
S(4)	3711.6(8)	48.6(7)	−122.1(8)	3.1
S(5)	4124.5(7)	−29.1(6)	1114.4(7)	2.7
S(6)	1584.9(8)	867.9(7)	2116.3(9)	3.5
S(7)	1521.7(9)	−824.0(7)	2024.8(9)	3.7
C(1)	3172(4)	−2137(3)	1728(4)	4.0
C(2)	3600(4)	−1830(3)	2463(3)	4.2
C(3)	4363(4)	−1582(3)	2361(4)	4.7
C(4)	4405(4)	−1744(3)	1553(4)	4.5
C(5)	3661(4)	−2063(3)	1159(4)	4.1
C(6)	2373(5)	−2526(4)	1574(5)	6.7
C(7)	3325(6)	−1822(4)	3244(4)	6.8
C(8)	5039(5)	−1243(5)	2964(5)	8.1
C(9)	5106(5)	−1626(4)	1167(6)	7.4
C(10)	3469(6)	−2328(4)	298(4)	7.0
C(11)	3414(3)	2088(3)	1910(3)	3.5
C(12)	3943(4)	1989(3)	1375(4)	4.1
C(13)	4619(4)	1586(3)	1810(4)	5.0
C(14)	4497(4)	1403(3)	2582(4)	4.7
C(15)	3744(3)	1721(3)	2644(3)	3.7
C(16)	2659(4)	2551(3)	1723(4)	4.9
C(17)	3831(6)	2290(4)	532(4)	6.7
C(18)	5353(5)	1401(5)	1505(7)	8.8
C(19)	5089(5)	1020(5)	3252(6)	8.1
C(20)	3390(5)	1696(4)	3383(4)	5.2
C(21)	2268(4)	262(4)	−1513(3)	4.9
C(22)	1875(4)	−426(4)	−1361(4)	4.5
C(23)	1261(3)	−210(3)	−963(3)	4.0
C(24)	1284(3)	576(3)	−871(3)	3.9
C(25)	1906(4)	878(4)	−1197(3)	4.3
C(26)	2900(5)	329(7)	−1991(5)	8.6
C(27)	2056(6)	−1215(5)	−1614(5)	8.9
C(28)	666(5)	−721(5)	−724(5)	7.4
C(29)	718(5)	1066(6)	−509(5)	7.6
C(30)	2113(6)	1720(5)	−1240(5)	7.8
C(31)	967(3)	399(3)	2639(3)	3.1
C(32)	944(3)	−367(3)	2592(3)	3.3
C(33)	546(3)	892(3)	3117(3)	3.3
C(34)	448(4)	660(4)	3868(4)	4.8
C(35)	63(5)	1129(4)	4316(4)	6.0
C(36)	−226(5)	1813(4)	4017(4)	6.1
C(37)	−145(4)	2046(4)	3263(4)	5.5
C(38)	246(4)	1597(3)	2821(4)	4.1
C(39)	462(3)	−882(3)	2985(3)	3.3
C(40)	816(4)	−1496(3)	3439(4)	4.4
C(41)	364(5)	−1975(4)	3800(4)	5.6
C(42)	−429(5)	−1873(4)	3698(4)	6.1
C(43)	−791(4)	−1274(5)	3237(4)	5.7
C(44)	−354(4)	−782(4)	2881(4)	4.7

[a] The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eqv} = {}^4/_3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac\cos\beta)$. The B_{ij}'s are defined by $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$.

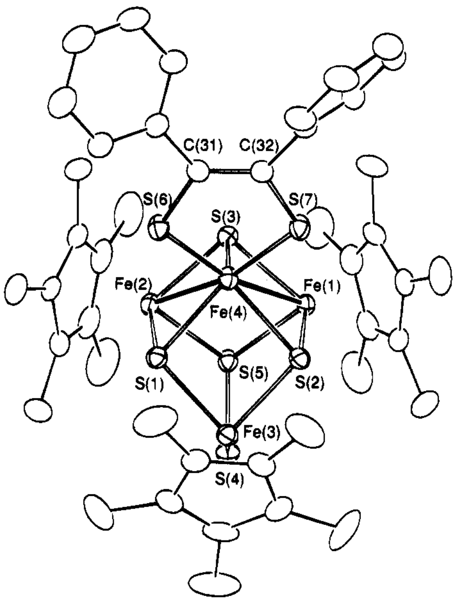


Figure 2. ORTEP drawing of **2**. Thermal ellipsoids are at 30% probability.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for $(C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5$·THF (**2**·THF)

	Distances		
Fe(1)···Fe(2)	3.300(1)	Fe(1)···Fe(3)	3.769(1)
Fe(1)−Fe(4)	2.716(1)	Fe(2)···Fe(3)	3.760(2)
Fe(2)−Fe(4)	2.725(1)	Fe(3)···Fe(4)	3.307(2)
Fe(1)−S(2)	2.189(2)	Fe(1)−S(3)	2.202(2)
Fe(1)−S(5)	2.252(2)	Fe(2)−S(1)	2.188(2)
Fe(2)−S(3)	2.191(2)	Fe(2)−S(5)	2.250(2)
Fe(3)−S(1)	2.206(2)	Fe(3)−S(2)	2.219(2)
Fe(3)−S(4)	2.183(2)	Fe(4)−S(1)	2.267(2)
Fe(4)−S(2)	2.274(2)	Fe(4)−S(3)	2.151(2)
Fe(4)−S(6)	2.180(2)	Fe(4)−S(7)	2.176(2)
S(4)−S(5)	2.079(2)	S(6)−C(31)	1.748(7)
S(7)−C(32)	1.740(7)	C(31)−C(32)	1.354(7)
	Angles		
S(2)−Fe(1)−S(5)	92.60(6)	S(2)−Fe(1)−S(3)	103.99(6)
S(3)−Fe(1)−S(5)	79.60(6)	S(1)−Fe(2)−S(3)	103.64(6)
S(1)−Fe(2)−S(5)	92.59(6)	S(3)−Fe(2)−S(5)	79.89(6)
S(1)−Fe(3)−S(2)	85.70(7)	S(1)−Fe(3)−S(4)	94.56(6)
S(2)−Fe(3)−S(4)	94.08(6)	S(1)−Fe(4)−S(2)	83.01(7)
S(1)−Fe(4)−S(3)	102.33(6)	S(2)−Fe(4)−S(3)	102.84(6)
S(6)−Fe(4)−S(7)	86.67(7)	Fe(3)−S(1)−Fe(4)	95.34(6)
Fe(2)−S(1)−Fe(3)	117.68(6)	Fe(2)−S(1)−Fe(4)	75.38(6)
Fe(1)−S(2)−Fe(3)	117.49(7)	Fe(1)−S(2)−Fe(4)	74.93(6)
Fe(3)−S(2)−Fe(4)	94.76(6)	Fe(1)−S(3)−Fe(2)	97.39(8)
Fe(1)−S(3)−Fe(4)	77.18(6)	Fe(2)−S(3)−Fe(4)	77.73(6)
Fe(1)−S(5)−Fe(2)	94.27(6)	Fe(2)−S(5)−S(4)	109.02(7)
Fe(1)−S(5)−S(4)	109.04(7)	Fe(4)−S(6)−C(31)	108.5(2)
Fe(4)−S(7)−C(32)	108.0(2)	S(6)−C(31)−C(32)	117.1(5)
S(7)−C(32)−C(31)	118.8(5)		

Å),[31] and $Fe\{S_2C_2(CF_3)_2\}(S_2CNEt_2)_2$ (2.20 Å).[32] The shortness of these Fe−S bonds has been attributed to metal−ligand π back-bonding.[21,31,32]

Structure of $(C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5$ (2). The structure of **2** is shown in Figure 2. Final atomic coordinates and selected interatomic distances and angles are listed in Tables 4 and 5, respectively. Cluster **2** has an Fe_4S_5 cubane like core with three C_5Me_5 ligands and one diphenyldithiolene ligand. The dithiolene ligand is coordinated to Fe(4) to make distorted square-pyramidal configuration around the iron atom, which lies ca. 0.55 Å above the mean basal plane (S(1)−S(2)−S(7)−S(6)). The Fe_4S_5 core consists of four iron atoms, three μ_3-S ligands, and one μ_3-S_2 ligand. The μ_3-S_2 ligand is located on the opposite side of the core from the dithiolene ligand. The μ_3-S_2 ligand bridges three iron atoms, in which S(5) bridges two iron atoms (Fe(1) and Fe(2)) and S(4) coordinates to only one iron atom (Fe(3)). This coordination mode of the μ_3-S_2 ligand is also found in $[(C_5H_4Me)_4Fe_4S_5]^+$,[33] while it is different from that in

---

(31) Schultz, A. J.; Eisenberg, R. *Inorg. Chem.* **1973**, *12*, 518.
(32) Johnston, D. L.; Rohrbaugh, W. L.; Horrocks, W. D., Jr. *Inorg. Chem.* **1971**, *10*, 1474.
(33) Blonk, H. L.; Mesman, J.; van der Linden, J. G. M.; Steggerda, J. J.; Smits, J. M. M.; Beurskens, G.; Beurskens, P. T.; Tonon, C.; Jordanov, *J. Inorg. Chem.* **1992**, *31*, 962.

$[Cp_4Fe_4S_5]^+$ [34] and $[Cp_4Fe_4S_5]^{2+}$.[35] In the latter complexes, the S_2 ligand coordinates to an iron atom in a "side on" manner, with each of its sulfur atoms bonded to one other iron atom.

The Fe−Fe interatomic distances in **2**, Fe(1)−Fe(4) (2.716(1) Å) and Fe(2)−Fe(4) (2.725(1) Å), are short. The remaining four distances are long and range from 3.300(1) to 3.769(1) Å, suggesting no Fe−Fe bond. Therefore, there are two Fe−Fe bonds with a V-shaped configuration. Similar V-shaped configuration of Fe−Fe bonds to this has been observed also for $[Cp_4Fe_4S_5]^+$ [34] and $[Cp_4Fe_4S_5]^{2+}$,[35] although all iron atoms in these clusters are bound to the same kind of supporting ligands, i.e. cyclopentadienyls.

Cluster **2** has 19 metal electrons. Existence of one unpaired electron is reflected in the broad ^1H NMR signals and the magnetic moment determined by the Evans method (see Experimental Section). The direct application of the metal fragment orbital model and the Dahl's MO bonding scheme indicates that cluster **2** has total bond order of 2.5. In the real cluster, only two interatomic separations Fe(1)−Fe(4) and Fe(2)−Fe(4) are short. Each Fe−Fe bond must therefore have a bond order of 1.25.

The averaged value of the 12 Fe−S bonding distances in Fe_4S_5 core is 2.21 Å and normal. On the other hand, the averaged value of Fe−S(dithiolene) distances is 2.18 Å and shorter than those in the Fe_4S_5 core. This suggests again that the Fe−S(dithiolene) bonds have some unsaturated bonding character. The S(4)−S(5) distance of the μ_3-S_2 ligand (2.079(2) Å) is comparable with those observed in the triply-bridged disulfide ligands of various metal complexes (2.01−2.07 Å).[36]

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research (No. 04241102 and No. 05209203) from the Ministry of Education, Science, and Culture.

Supplementary Material Available: Tables of crystal data, atomic positional and thermal parameters, and bond distances and bond angles for **1** and **2** (32 pages). Ordering information is given on any current masthead page.

---

(34) Dupré, N.; Hendriks, H. M. J.; Jordanov, J.; Gaillard, J.; Auric, P. *Organometallics*, **1984**, *3*, 800.

(35) Dupré, N.; Auric, P.; Hendriks, H. M. J.; Jordanov, J. *Inorg. Chem.* **1986**, *25*, 1391.

(36) Müller, A.; Jaegermann, W.; Enemark, J. H. *Coord. Chem. Rev.* **1982**, *46*, 245.