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Syntheses of *closo*-$Cp'_2(CO)_3Fe_2MS_2$ Clusters ($Cp' = \eta^5$-C_5Me_5; M = Fe, Ru) and Molecular Structure of $Cp'_2(CO)_3Fe_3S_2$

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Reactions of $Cp'_2Fe_2S_4$ (**1**) with iron carbonyls ($Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$) gave $Cp'_2(CO)_3Fe_3S_2$ (**2**), and that with $Ru_3(CO)_{12}$, $Cp'_2(CO)_3Fe_2RuS_2$ (**3**). An X-ray crystal structure analysis of **2** revealed that the $\{Fe_3S_2\}$ core has a trigonal bipyramidal configuration in which the three iron atoms form a slightly distorted triangle with two μ_3-S ligands occupying apical positions. Two of the iron atoms bear an η^5-Cp′ ligand, and the third iron atom is coordinated by three terminal carbonyl ligands. Clusters **2** and **3** are the first examples of *closo* clusters having $\{Fe_2MS_2\}$ cores (M = Fe, Ru). Crystallographic data for $Cp'_2(CO)_3Fe_3S_2$ (**2**) are as follows: $C_{23}H_{30}Fe_3O_3S_2$, monoclinic, space group $P2_1/a$, $a = 18.174(2)$ Å, $b = 10.1159$ (9) Å, $c = 14.417(1)$ Å, $\beta = 106.42(1)°$, $V = 2542.4(4)$ Å^3, $Z = 4$, and $R = 0.060$ for 6221 reflections with $|F_o| > 3\sigma(F_o)$.

Introduction

The syntheses of a number of dinuclear transition metal complexes $Cp^*_2M_2S_4$[1] have been reported, the structures of which show a surprisingly wide variety depending on the nature of the metals.[2] The complexes are excellent starting materials for constructing clusters using the nucleophilicity of sulfur ligands: For instance, the reaction of $(MeCp)_2V_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ with $Fe(CO)_5$ in the presence of Me_3NO gave a trinuclear cluster $(MeCp)_2V_2(\mu\text{-}S_2)(\mu_3\text{-}S)_2Fe(CO)_3$ in which an $Fe(CO)_3$ fragment was included.[3] Photoreaction of $Cp'_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ with $Fe(CO)_5$ ultimately gave a mixed-metal cubane cluster $Cp'_2(CO)_4Mo_2Fe_2S_4$ through the formation of a trinuclear cluster $Cp'_2Mo_2(\mu\text{-}S_2)(\mu_3\text{-}S)_2Fe(CO)_2$.[4] On the other hand, photoreaction of $(MeCp)_2Mo_2(\mu\text{-}SH)_2(\mu\text{-}S)_2$ with $Fe(CO)_5$ gave a tetranuclear cluster $(MeCp)_2(CO)_6Mo_2Fe_2S_4$ with an {Fe−Mo−Mo−Fe} zigzag chain.[5]

Among the $Cp^*_2M_2S_4$ complexes, the reactions of $Cp'_2Fe_2(\mu\text{-}S_2)_2$ with other metal complexes have not been investigated. This paper describes the reactions of $Cp'_2Fe_2S_4$ with iron and ruthenium carbonyls as the first example of cluster synthesis using $Cp'_2Fe_2S_4$.

Experimental Section

Materials. $Cp'_2Fe_2S_4$ (**1**) was prepared by the method reported by Brunner et al.[6] Iron pentacarbonyl was purchased from Aldrich Chemical Co., Ltd. Diiron nonacarbonyl,[7] triiron dodecacarbonyl,[8] and triruthenium dodecacarbonyl[9] were prepared according to literature methods. Tetrahydrofuran (THF) and hexane were distilled over sodium benzophenone ketyl. Toluene was distilled over sodium. All reactions were carried out under a dinitrogen atmosphere.

Synthesis of $Cp'_2(CO)_3Fe_3S_2$ (2). Method A. A THF solution (15 mL) containing $Cp'_2Fe_2S_4$ (100 mg, 0.20 mmol) and $Fe_2(CO)_9$ (142 mg, 0.39 mmol) or $Fe_3(CO)_{12}$ (98 mg, 0.19 mmol) was refluxed for 15 min with stirring. After filtration, volatiles were evaporated. The residue was subjected to flash column chromatography (silica gel; eluent toluene/hexane = 1/1). Elution and concentration of the fractions afforded $Cp'_2(CO)_3Fe_3S_2$ (**2**) (yellowish brown crystals, 49 mg, 44%), a reddish brown solid,[10] and a brown solid in this order.[11] Data for **2** are as follows. ^1H NMR ($CDCl_3$, 90 MHz): δ 1.51 (CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz): δ 11.3 [$C_5(CH_3)_5$], 89.9 [$C_5(CH_3)_5$], 211.3 (CO). IR (hexane, cm^{-1}): 2017, 1966, 1956 (ν_{C-O}). MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix): *m/z* 586 (25, M$^+$), 530 (19, M$^+$ − 2CO), 502 (100, M$^+$ − 3CO). Anal. Calcd for $C_{23}H_{30}Fe_3O_3S_2$: C, 47.13; H, 5.16. Found: C, 47.10; H, 5.21.

Method B. A mixture of $Cp'_2Fe_2S_4$ (100 mg, 0.196 mmol), $Fe(CO)_5$ (0.12 mL, 0.87 mmol), and Me_3NO (120 mg, 1.60 mmol) in THF (15 mL) was stirred for 22 h at room temperature. Silica gel flash column chromatographic separation of the yellowish brown fraction afforded **2**. Yield: 42 mg (37%).

Method C. A THF solution (20 mL) containing $Cp'_2Fe_2S_4$ (100 mg, 0.196 mmol) and $Fe(CO)_5$ (0.09 mL, 0.7 mmol) was placed in a Pyrex glass tube (i.d. 1.6 cm × 20 cm) and irradiated with an Ushio UM-452 450 W medium-pressure mercury lamp for 11 h at 0 °C. Silica gel flash column chromatographic separation of the yellowish brown fraction afforded **2**. Yield: 32 mg (28%).

Synthesis of $Cp'_2(CO)_3Fe_2RuS_2$ (3). A THF solution (15 mL) containing $Cp'_2Fe_2S_4$ (100 mg, 0.196 mmol) and $Ru_3(CO)_{12}$ (98 mg, 0.19 mmol) was refluxed for 100 min. After filtration, volatiles were evaporated and then the residue was chromatographed on a silica gel flash column (eluent: hexane). Elution and concentration of the fractions afforded $Ru_3(CO)_{12}$ (5 mg) and reddish brown crystals of $Cp'_2(CO)_3Fe_2RuS_2$ (**3**) (19 mg, 31%) in this order. Data for **3** are as follows. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.55 (CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 11.6 [$C_5(CH_3)_5$], 87.8 [$C_5(CH_3)_5$], 197.29 (CO). IR (hexane, cm^{-1}): 2036, 1979, 1970 (ν_{C-O}). MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix): *m/z* 632 (100, M$^+$), 604 (73, M$^+$ − CO), 576 (16, M$^+$ − 2CO), 548 (75, M$^+$ − 3CO). Anal. Calcd for $C_{23}H_{30}Fe_2O_3RuS_2$: C, 43.75; H, 4.79. Found: C, 43.88; H, 4.73.

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(1) Abbreviations: MeCp = C_5H_4Me, Cp′ = C_5Me_5, and Cp* = general expression for substituted and nonsubstituted cyclopentadienyl ligands.

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(10) The mass spectrum and its fragmentation pattern suggest that the solid is $Cp'_3(CO)_6Fe_6S_6$: MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix) *m/z* 1101 (36, M$^+$), 933 (100, $Cp'_3Fe_6S_6$), 798 (77, $Cp'_2Fe_6S_6$), 663 (32, $Cp'Fe_6S_6$), 528 (31, Fe_6S_6), 496 (26, Fe_6S_5), 464 (9.1, Fe_6S_4), 408 (5.5, Fe_5S_4), 352 (5.2, Fe_4S_4).

(11) The solid was not characterized.

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Table 1. Crystallographic Data for Cp′$_2$(CO)$_3$Fe$_3$S$_2$ (**2**)

formula	$C_{23}H_{30}Fe_3O_3S_2$	space group	$P2_1/a$ (variant of No. 14)
a, Å	18.174(2)	T, °C	20
b, Å	10.1159(9)	λ, Å	0.71073
c, Å	14.417(1)	ϱ_{calcd}, g cm^{-3}	1.53
β, deg	106.42(1)	μ(Mo Kα), cm^{-1}	19.1
V, Å^3	2542.4(4)	R^a	0.060
Z	4	$R_w{}^b$	0.095
fw	586.16		

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = [\sigma^2(|F_o|) + aF_o{}^2]^{-1}$, $w = 0.007$.

Physical Measurements. NMR spectra were recorded on JEOL FX-90Q, Varian XL-200, and Bruker ARX 300 spectrometers. IR spectra were recorded on Horiba FT-200 and Bruker IFS66V spectrophotometers. Mass spectra were recorded on a JEOL JMS-HX110 spectrometer.

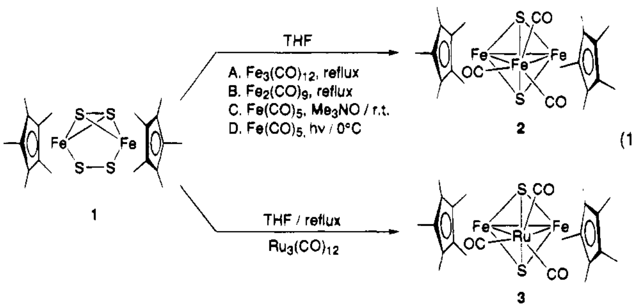
X-ray Crystal Structural Determination of 2. Single crystals of **2** were obtained by cooling a hexane solution of **2** at −30 °C. Diffraction data were collected on a Rigaku AFC-6A four-circle diffractometer with graphite-monochromated Mo Kα radiation using the $\omega-2\theta$ scan technique. Crystallographic parameters are listed in Table 1. The reflection data were corrected for Lorentz and polarization factors. No correction was applied for absorption.

The structure was solved by the heavy atom method, which provided the positions of the three iron and two sulfur atoms. All remaining non-hydrogen atoms were refined by the block-diagonal least squares method with anisotropic thermal parameters. None of the hydrogen atoms could be located from the difference Fourier map.

Values for the atomic scattering factors of non-hydrogen atoms were those in ref 12. Calculations were performed on a Nippon Electric Co. ACOS-3900 computer at Tohoku University Computer Center using the Universal Computation Program System UNICS III.[13]

Results and Discussion

Synthesis. Triiron cluster **2** was formed in the reactions of Cp′$_2$Fe$_2$S$_4$ (**1**) with three kinds of iron carbonyls (eq 1) and isolated as yellowish brown crystals. The reaction of **1** with Fe$_2$(CO)$_9$ or Fe$_3$(CO)$_{12}$ proceeds smoothly in refluxing THF. However, no reaction of **1** with Fe(CO)$_5$ occurred even in a refluxing toluene solution. In order to obtain **2** from this system, the addition of Me$_3$NO (well-known as a decarbonylation reagent[14]) was necessary. Photolysis of a THF solution containing **1** and Fe(CO)$_5$ also afforded **2**. These findings indicate that the generation of the coordinatively unsaturated complex Fe(CO)$_4$ is crucial for the formation of **2**.



(1)

The mixed-metal trinuclear cluster Cp′$_2$(CO)$_3$Fe$_2$RuS$_2$ (**3**) was formed in the reaction of complex **1** with Ru$_3$(CO)$_{12}$ in refluxing THF. This indicates that the thermal generation of the coordinatively unsaturated complex Ru(CO)$_4$ from Ru$_3$(CO)$_{12}$ is again crucial for driving the reaction to give **3**. Clusters **2** and **3** are very soluble in organic solvents such as hexane, benzene, and dichloromethane and air-stable in the solid state but slowly decompose in air-exposed solution.

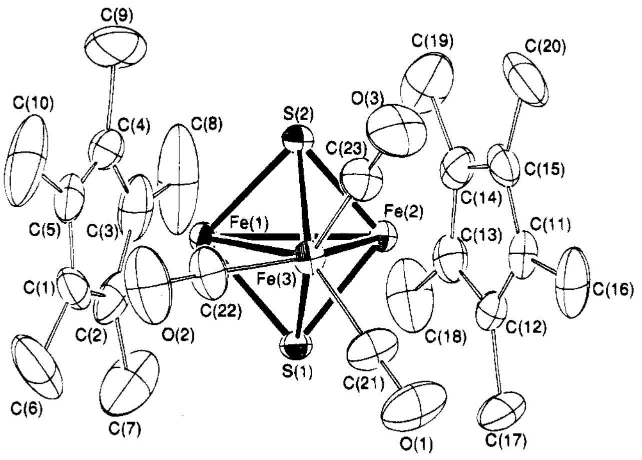


Figure 1. ORTEP drawing of Cp′$_2$(CO)$_3$Fe$_3$S$_2$ (**2**).

Table 2. Final Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors for Cp′$_2$(CO)$_3$Fe$_3$S$_2$ (**2**)

atom	x	y	z	B_{eqv},^{a} Å^2
Fe(1)	2837.3(3)	530.1(5)	2341.5(4)	2.8
Fe(2)	1457.5(3)	818.2(5)	2682.6(4)	2.8
Fe(3)	1980.3(3)	−1529.9(5)	2493.8(4)	3.2
S(1)	2504.8(5)	63.6(10)	3613.4(6)	3.2
S(2)	1713.8(5)	165.3(10)	1401.7(6)	3.2
O(1)	1664(4)	−2917(5)	4113(4)	9.6
O(2)	3241(3)	−3165(5)	2311(6)	10.4
O(3)	751(3)	−2928(5)	1107(4)	9.1
C(1)	4022(3)	410(6)	2658(4)	5.3
C(2)	3823(4)	1626(7)	2975(4)	6.6
C(3)	3343(4)	2274(6)	2120(6)	7.5
C(4)	3302(3)	1430(8)	1333(4)	6.7
C(5)	3710(3)	314(6)	1663(4)	5.4
C(6)	4549(4)	−602(11)	3314(9)	12.2
C(7)	4054(6)	2164(13)	3990(6)	13.7
C(8)	2986(7)	3654(8)	2056(13)	16.9
C(9)	2868(6)	1784(15)	302(7)	16.1
C(10)	3843(6)	−818(11)	1043(9)	14.4
C(11)	440(3)	599(5)	3099(4)	5.0
C(12)	945(3)	1424(6)	3749(4)	4.9
C(13)	1122(3)	2530(5)	3252(4)	5.1
C(14)	716(3)	2375(6)	2262(4)	5.4
C(15)	285(3)	1168(6)	2166(4)	5.3
C(16)	89(4)	−672(8)	3329(8)	9.1
C(17)	1239(5)	1234(11)	4828(5)	9.1
C(18)	1636(5)	3700(7)	3722(8)	9.5
C(19)	682(6)	3340(10)	1417(7)	11.8
C(20)	−237(4)	635(11)	1220(6)	10.2
C(21)	1794(4)	−2365(5)	3492(4)	5.8
C(22)	2763(3)	−2486(5)	2371(5)	5.8
C(23)	1234(3)	−2369(5)	1637(4)	5.3

[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 $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$.

X-ray Crystal Structure of 2. An ORTEP drawing of **2** with atom-numbering scheme is shown in Figure 1. Positional and selected interatomic distances and angles are summarized in Tables 2 and 3. The {Fe$_3$S$_2$} core of **2** adopts a trigonal bipyramidal configuration: The three Fe atoms form a slightly distorted triangle which is bicapped by two μ_3-S ligands. Each of the Fe(1) and Fe(2) atoms bears an η^5-Cp′ ligand in a mutually staggered configuration, while the Fe(3) atom has three terminal carbonyl ligands. The three Fe−Fe interatomic distances Fe(1)−Fe(2) (2.704(1) Å), Fe(1)−Fe(3) (2.648(1) Å),

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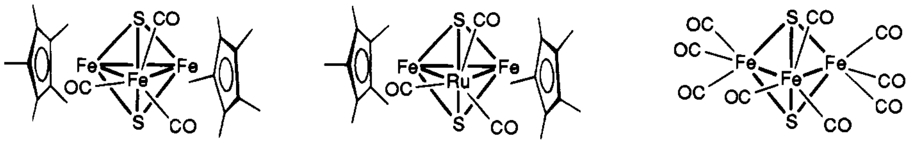
Chart 1. Structural Comparison among the Clusters with an $\{Fe_2MS_2\}$ Core



2 **3** **4**

Table 3. Interatomic Distances (Å) and Angles (deg) for $Cp'_2(CO)_3Fe_3S_2$ (**2**)

Distances			
Fe(1)−Fe(2)	2.704(1)	Fe(1)−S(1)	2.139(2)
Fe(1)−Fe(3)	2.648(1)	Fe(1)−S(2)	2.139(1)
Fe(2)−Fe(3)	2.601(1)	Fe(2)−S(1)	2.136(1)
Fe(3)−C(21)	1.782(9)	Fe(2)−S(2)	2.133(2)
Fe(3)−C(22)	1.770(7)	Fe(3)−S(1)	2.290(1)
Fe(3)−C(23)	1.772(6)	Fe(3)−S(2)	2.285(1)
C(21)−O(1)	1.135(12)	C(22)−O(2)	1.129(9)
C(23)−O(3)	1.138(9)	S(1)···S(2)	3.107(2)
Angles			
Fe(2)−Fe(1)−Fe(3)	58.15(2)	S(1)−Fe(1)−S(2)	93.13(6)
Fe(1)−Fe(2)−Fe(3)	59.84(2)	S(1)−Fe(2)−S(2)	93.40(6)
Fe(1)−Fe(3)−Fe(2)	62.01(2)	S(1)−Fe(3)−S(2)	85.54(5)
Fe(2)−Fe(1)−S(1)	50.71(5)	Fe(2)−Fe(1)−S(2)	50.63(3)
Fe(3)−Fe(1)−S(1)	55.94(5)	Fe(3)−Fe(1)−S(2)	55.82(3)
Fe(1)−Fe(2)−S(1)	50.82(3)	Fe(1)−Fe(2)−S(2)	50.84(5)
Fe(3)−Fe(2)−S(1)	56.80(3)	Fe(3)−Fe(2)−S(2)	56.70(5)
Fe(1)−Fe(3)−S(1)	50.72(3)	Fe(1)−Fe(3)−S(2)	50.76(4)
Fe(2)−Fe(3)−S(1)	51.31(4)	Fe(2)−Fe(3)−S(2)	51.27(4)
C(21)−Fe(3)−C(22)	99.4(4)	Fe(3)−C(21)−O(1)	178.3(9)
C(21)−Fe(3)−C(23)	93.0(4)	Fe(3)−C(22)−O(2)	175.5(7)
C(22)−Fe(3)−C(23)	98.5(3)	Fe(3)−C(23)−O(3)	178.2(6)

and Fe(2)−Fe(3) (2.601(1) Å) are in the range expected for Fe−Fe single bonds.

The bond lengths between Fe(1) and the μ_3-S ligands and between Fe(2) and the μ_3-S ligands (2.133(2)−2.139(2) Å) are shorter than the usually observed values for Fe−S single bonds (2.18−2.26 Å),[15] while those between Fe(3) and the μ_3-S ligands (2.285(1) and 2.290(1) Å) are longer than the normal values for Fe−S single bonds. The difference of the Fe−S bond lengths is apparently due to the difference between electronic environments of FeCp′ and $Fe(CO)_3$ fragments: Each FeCp′ fragment receives three electrons from two μ_3-S ligands, while $Fe(CO)_3$ fragment two electrons from the μ_3-S ligands to attain the 18-electron rule.

Cluster **2** is the first example of *closo* cluster with an $\{Fe_3S_2\}$ core. $(OC)_9Fe_3S_2$ (**4**) is the only known example of a cluster with the $\{Fe_3S_2\}$ core.[16] Its structure is compared with **2** and **3** in Chart 1. Cluster **4** has only two Fe−Fe bonds and thus corresponds to a *nido* cluster. The difference between the $\{Fe_3S_2\}$ core geometries of **2** and **4** can be easily understood by Wade's rules.[17] Only four examples of homonuclear *closo* clusters with $\{M_3S_2\}$ cores are known: $[(MeCp)_3Co_3S_2]^{2+}$,[18] $[(p\text{-cymene})_3M_3S_2]^{2+}$ (M = Ru, Os),[19] $[(OC)_9Mn_3S_2]^-$,[20] and $[Cp'_3Ir_3S_2]^{2+}$.[21]

Spectroscopic Characterization of Trinuclear Clusters $Cp'_2(CO)_3Fe_2MS_2$ (M = Fe, Ru). IR spectra of **2** and **3** show three characteristic bands in the terminal CO stretching vibrational region (2100−1900 cm^{-1}) and the absence of bridging CO ligand. ^1H and $^{13}C\{^1H\}$ NMR spectra reveal that the two Cp′ ligands in each cluster are equivalent. These observations are consistent with the X-ray crystal structure. Only one $^{13}C\{^1H\}$ NMR signal was observed for the CO ligands of each cluster. This indicates that three carbonyls in each cluster are fluxional at ambient temperature.

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Supplementary Material Available: Tables of full crystallographic data, anisotropic thermal parameters, and bond distances and angles for **2** (5 pages). Ordering information is given on any current masthead page.

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