Cluster Core Expansion through Incorporation of Transition-metal Fragments or an Alkyne Molecule into an Incomplete Cubane-type Fe_2RuS_4 Cluster

Masaaki Okazaki,* Atsushi Sakuma, Hiromi Tobita,* and Hiroshi Ogino[†]
Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578
[†]*Miyagi Study Center, University of the Air, Sendai 980-8577*

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Treatment of $Cp^{S2}{}_2Fe_2S_4$ ($Cp^{S2} = 1,3\text{-}C_5H_3(SiMe_3)_2$) with $[CpRu(MeCN)_3]^+$ in acetonitrile at room temperature led to the formation of an incomplete cubane-type cluster $[(Cp^{S2}Fe)_2(CpRu)S_4]^+$ (**1**). Further treatment of **1** with $[Cp'Ru(MeCN)_3]^+$ ($Cp' = Cp, Cp^*$) produced $[(Cp^{S2}Fe)_2(CpRu)(Cp'Ru)S_4]^{2+}$. Cluster **1** reacted with DMAD to give the 1:1 adduct through formation of three sulfur–carbon bonds.

Dinuclear transition-metal sulfido complexes of the type $Cp'_2M_2S_4$ (Cp' = Cp and substituted Cp) have been recognized as useful building blocks for the rational synthesis of transition metal sulfido clusters,[1] which are important because of their potential use for the biological and industrial catalytic processes.[2] Our research has focused on the cluster construction starting from $Cp'_2Fe_2S_4$.[3] Reactions of $Cp^*{}_2Fe_2S_4$ with iron and ruthenium carbonyls gave *closo*-$(Cp^*Fe)_2M(CO)_3(\mu_3\text{-}S)_2$ clusters.[3a] In the reaction with $[Cp^*Ru(MeCN)_3](PF_6)$, cubane-type $[Cp^*{}_4Fe_2Ru_2S_4](PF_6)_2$ was formed. Introduction of bulkier Cp^{S2} ligands ($Cp^{S2} = 1,3\text{-}C_5H_3(SiMe_3)_2$) onto the iron centers allowed the isolation of the intermediate, $[(Cp^{S2}Fe)_2(Cp^*Ru)S_4](PF_6)$.[3b] Existence of three bulky substituted Cp ligands, however, led to the poor reactivity of the cluster. This paper describes the synthesis and structure of sterically less crowded $[(Cp^{S2}Fe)_2(CpRu)S_4]^+$, and the reactions of this trinuclear cluster with $[Cp'Ru(MeCN)_3]^+$ ($Cp' = Cp, Cp^*$) or an alkyne molecule resulting in cluster core expansion.

An acetonitrile solution of $Cp^{S2}{}_2Fe_2S_4$ and 1 equiv. of $[CpRu(MeCN)_3](TFPB)$ (TFPB = tetrakis{3,5-bis(trifluoromethyl)phenyl}borate) was stirred for 2 h at room temperature (Scheme 1). Volatiles were removed under reduced pressure and recrystallization of the residue from CH_2Cl_2/hexane at −10 °C gave dark brown crystals of $[(Cp^{S2}Fe)_2(CpRu)S_4](TFPB)$ (**1**) in 74% yield.[4] ORTEP drawing of the cationic part in **1** is depicted in Figure 1.[5] The structural feature of **1** resembles that of $[(Cp^{S2}Fe)_2(Cp^*Ru)S_4](PF_6)$ we previously reported.[3b] Thus, the cluster possesses an Fe_2Ru core with $\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2$ and $\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2$ disulfido groups. The bond lengths of Ru–Fe1 (2.7627(6) Å) and Ru–Fe2 (2.7791(6) Å) are in the normal range expected for the ruthenium–iron single bonds. The distance between two iron atoms is 3.4814(7), indicating the absence of a direct bond between them. Cluster **1** can be best described as a "CpRu"-fragment-capped "$Cp^{S2}{}_2Fe_2S_4$", in which the "$Cp^{S2}{}_2Fe_2S_4$" fragment is bound to the ruthenium center in κ^5(Fe1,Fe2,S1,S3,S4) fashion. Rauchfuss et al. reported formation of $[Cp^*{}_3Ru_3S_4](PF_6)$ by the reaction of $Cp^*{}_2Ru_2S_4$ with $[Cp^*Ru(MeCN)_3](PF_6)$, of which the SO_2 adduct has been characterized by X-ray diffraction study.[6]

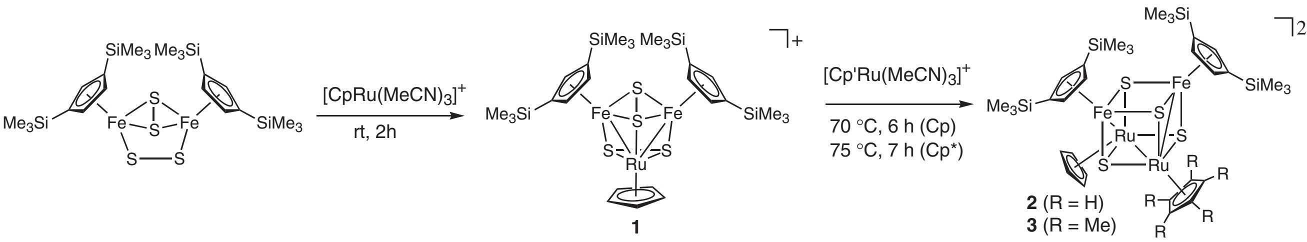
Cluster **1** can be considered as an incomplete cubane-type Fe_2RuS_4 cluster, which could provide a direct route to the cubane-type cluster through incorporation of one metal fragment.[7] The thermal reaction of **1** with $[CpRu(MeCN)_3](TFPB)$ in acetonitrile was carried out at 70 °C for 6 h (Scheme 1). Volatiles were removed under reduced pressure and recrystallization of the residue from CH_2Cl_2/hexane at −10 °C afforded a dark brown solid of $[(Cp^{S2}Fe)_2(CpRu)_2S_4](TFPB)_2$ (**2**) in 65% yield.[8] The results of the elemental analysis and mass spectrum are in good agreement with the formula of **2**. We have not been able to make single crystals of **2** suitable for X-ray diffraction study.

Thermolysis of **1** and bulkier $[Cp^*Ru(MeCN)_3](PF_6)$ under the slightly severer conditions (75 °C, 7 h), followed by treatment with NH_4PF_6, gave $[(Cp^{S2}Fe)_2(CpRu)(Cp^*Ru)S_4](PF_6)_2$ (**3**) in 25% yield (Scheme 1).[9] Recrystallization of the evaporated reaction mixture residue from acetonitrile/diethyl ether gave single crystals suitable for X-ray diffraction study. An ORTEP drawing of the cationic part in **3** is depicted in Figure 1.[5] Complex **3** has an $Fe_2Ru_2S_4$ cubane-type core with Cp, Cp*, and two Cp^{S2} ligands. The Fe_2Ru_2 core is distorted from the ideal tetrahedral structure. The distances of Ru1–Ru2 (2.8206(11) Å), Ru1–Fe1 (2.7313(16) Å), and Ru2–Fe2 (2.7452(17) Å) indicate the presence of each metal–metal single bond, while the distances of Ru1–Fe2 (3.3889(17) Å), Ru2–Fe1 (3.3884(16) Å), and Fe1–Fe2 (3.4154(19) Å) indicate no bond between them. Assuming that one μ_3-sulfido ligand donates four electrons to the core, cluster **3** can be recognized as a 66e species. This electron count is consistent with the existence of three metal–metal bonds as an electron-precise cluster. Compound **3** is the first $Fe_2Ru_2S_4$ cubane-type cluster that is X-ray characterized.

We succeeded in the synthesis of the transition-metal sulfido cubane-type cluster **3** having three different metal fragments, by means of the stepwise incorporation of two different metal fragments into $Cp^{S2}{}_2Fe_2S_4$. Such a synthetic methodology has not been well established.[10] In 1995, Kunchen and his co-workers succeeded for the first time in the stepwise construction of the Mo_2WCuS_4 cubane-type clusters by reacting $Mo_2S_4(R_2PS_2)_2$ with $W(CO)_3(MeCN)_3$ and then with CuI.[10a] Hidai et al. nicely developed this method and synthesized a variety of cubane-type heterometallic sulfido clusters.[10b]

Heating an acetonitrile solution of **2** with dimethyl acetylenedicarboxylate (DMAD) at 75 °C for 5 h led to quantitative formation of **4** (Eq 1). Recrystallization of the evaporated reaction mixture residue from diethyl ether/hexane at −10 °C afforded dark brown crystals of **4** in 88% yield.[11] The results of elemental analysis and mass spectrum indicate that cluster **4** makes the adduct with DMAD in the ratio of 1:1.

Shibahara et al. reported the reaction of an incomplete cubane-type cluster $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ with acetylene to form the adduct $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)(\mu_3\text{-}S_2C_2H_2)]^{4+}$.[12] The alkenedithiolate ligand bridges over two molybdenum atoms symmetrically, in which the two molybdenum centers and the pro-



Scheme 1.

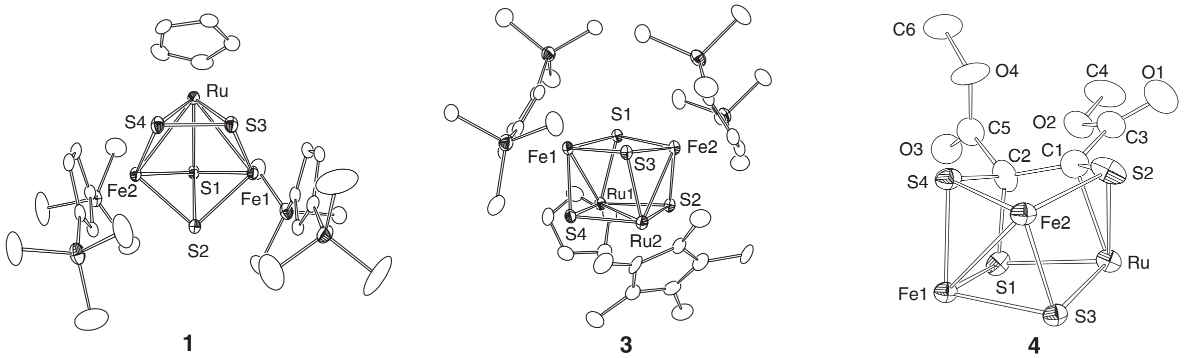
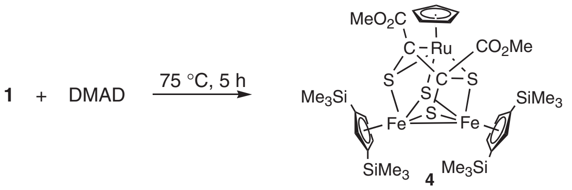


Figure 1. ORTEP drawings of **1**, **3**, and **4**. Thermal ellipsoids are shown at the 30% probability level. The counter anion and hydrogen atoms were omitted for clarity. In **4**, Cp^{S2} and Cp ligands were also omitted.

tons of the alkenedithiolate ligand are both chemically equivalent. However, this is not the case for cluster **4**. The ^1H signals of the $SiMe_3$ groups on the Cp^{S2} ligands were observed at δ 0.41, 0.46, 0.53, and 0.58, indicating the presence of two chemically inequivalent, chiral iron centers. Accordingly, the ^1H signals of two methyl groups on the DMAD fragment were observed independently at δ 3.30 and 3.89.



(1)

The structure of **4** was unequivocally determined by X-ray diffraction study (Figure 1).[5] Cluster **1** makes an adduct with one molecule of DMAD which bridges over Ru, S1, S2, and S4 atoms, in which two sulfur–sulfur bonds and two ruthenium–iron bonds were cleaved as a result of the incorporation of DMAD: The distances of S1–C2, S2–C1, and S4–C2 are 1.883(10), 1.692(7), and 1.971(9) Å, respectively, indicating the formation of three carbon–sulfur bonds. The formation of the ruthenium–carbon bond is evident from the distance of Ru–C1 (2.091(8) Å). The distance of Fe1–Fe2 (2.6524(11) Å) is in the normal range expected for the single iron–iron bonds, whereas the distances of Ru–Fe1 (3.5005(10) Å) and Ru–Fe2 (3.4597(10) Å) indicate the absence of the ruthenium–iron bond. The carbon–carbon distance in the alkenedithiolate ligand is 1.460(10), which is closer to that of ethane (1.54 Å) than to that of ethene (1.33 Å).

In conclusion, we achieved the stepwise construction of Fe_2RuS_4 (**1**) and $Fe_2Ru_2S_4$ (**2**) clusters by the reaction of $Cp^{S2}{}_2Fe_2S_4$ with $[CpRu(MeCN)_3]^+$. Further treatment of the incomplete cubane-type cluster **1** with $[Cp^*Ru(MeCN)_3]^+$ gave a cubane-type cluster **3** with three different metal fragments. One molecule of DMAD was incorporated into **1** to form **4** with an unprecedented core.

References and Notes

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4 **1**: Anal. Found: C, 42.14; H, 3.65%. Calcd for $C_{59}H_{59}BF_{24}Fe_2RuS_4Si_4$: C, 41.97; H, 3.52%. MS (FAB) *m/z* 825 (M^+, 100).

5 The crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC240682-240684).

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8 **2**: Anal. Found: C, 42.44; H, 2.75%. Calcd for $C_{96}H_{76}B_2F_{48}Fe_2Ru_2S_4Si_4$: C, 42.43; H, 2.82%. MS (FAB) *m/z* 992 (M^+, 100).

9 **3**: Anal. Found: C, 32.85; H, 4.50%. Calcd for $C_{37}H_{62}F_{12}Fe_2P_2Ru_2S_4Si_4$: C, 32.89; H, 4.62%. MS (FAB) *m/z* 1062 (M^+, 100).

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11 **4**: Anal. Found: C, 42.60; H, 3.70%. Calcd for $C_{65}H_{65}BF_{24}Fe_2O_4RuS_4Si_4$: C, 42.65; H, 3.58%. MS (FAB) *m/z* 968 (M^+, 91).

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