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Cluster synthesis by the reactions of [$Cp'_2M_2S_4$] with metal complexes ($Cp' = Cp$ and substituted cyclopentadienyl ligands, $M = Fe$, Ru)

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Contents

Abstract

Dinuclear transition-metal sulfur complexes of the type [$Cp'_2M_2S_4$] ($Cp' = Cp$ and substituted cyclopentadienyl ligands) have been used as excellent starting materials for building up multinuclear transition-metal sulfur clusters. However, little is known about the versatility of the iron- and ruthenium-containing complexes. This urged us to examine the nature of $Cp'_2M_2S_4$ ($M = Fe$, Ru). The present review describes the research on homo- and heteronuclear cluster synthesis by the reactions of $Cp'_2M_2S_4$ ($M = Fe$, Ru) with various transition-metal complexes. © 2000 Elsevier Science S.A. All rights reserved.

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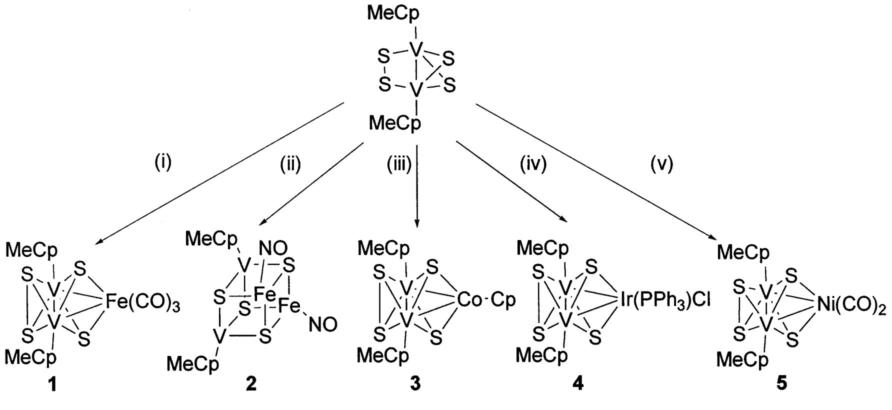
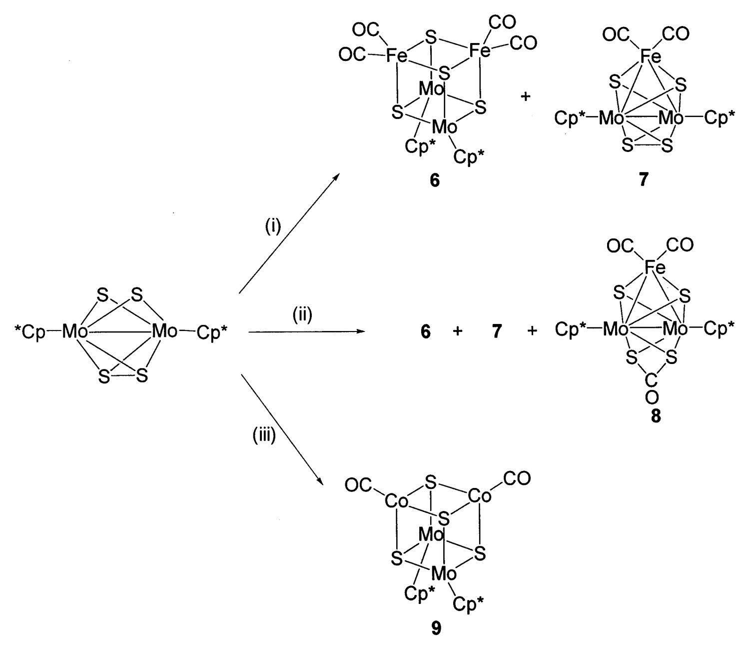
1. Introduction

The syntheses and reactivities of dinuclear transition-metal sulfur complexes of the type $[\mathrm{Cp'_2M_2S_4}]$ (Cp′ = Cp and substituted cyclopentadienyl ligands) have been reported for various transition-metals, and their structures show a surprisingly wide variety depending on the nature of the metal centers [1]. The construction of transition-metal sulfur clusters has been a subject of research in relation to the possible relevance to biological [2] and industrial [3] catalysis. The Mo and V dimers have been employed as excellent starting materials for synthesis of homo- and heteronuclear clusters. Rauchfuss and his co-workers established the construction of the vanadium–sulfur clusters by the reaction of $\mathrm{(MeCp)_2V_2S_4}$ (MeCp = η^5-$\mathrm{C_5H_4Me}$) with various transition-metals. The dimer reacted with $\mathrm{Fe(CO)_5}$, $\mathrm{Hg[Fe(NO)(CO)_3]_2}$, $\mathrm{CpCo(CO)_2}$, $\mathrm{IrCl(N_2)(PPh_3)_2}$, and $\mathrm{Ni(CO)_4}$ to give $\mathrm{(MeCp)_2V_2S_4Fe(CO)_3}$ (**1**), $\mathrm{(MeCp)_2V_2S_4Fe_2(NO)_2}$ (**2**), $\mathrm{(MeCp)_2V_2S_4CoCp}$ (**3**), $\mathrm{(MeCp)_2V_2S_4IrCl(PPh_3)}$ (**4**), and $\mathrm{(MeCp)_2V_2S_4Ni(CO)_2}$ (**5**), respectively, as illustrated in Scheme 1 [4]. Wachter and his co-workers employed $\mathrm{Cp^*_2Mo_2S_4}$ (Cp* = η^5-$\mathrm{C_5Me_5}$) (Scheme 2). Photolysis of $\mathrm{Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2}$ and $\mathrm{Fe(CO)_5}$ gave a cubane-type cluster $\mathrm{Cp^*_2Mo_2Fe_2S_4(CO)_4}$ (**6**) and a trinuclear cluster $\mathrm{Cp^*_2Mo_2(\mu\text{-}S_2)(\mu_3\text{-}S)_2Fe(CO)_2}$ (**7**) [5]. The Mo dimer reacted with $\mathrm{Fe_2(CO)_9}$ in THF at room temperature to give not only **6** and **7** but also a trigonal-bipyramidal cluster **8** composed of one iron, two molybdenum and two sulfur atoms [5]. The $\mathrm{Mo_2Co_2S_4}$ cubane-type cluster **9** was synthesized by the reaction of the Mo dimer with $\mathrm{Co_2(CO)_8}$ via liberation of carbon monoxide [6].

Among the $\mathrm{Cp'_2M_2S_4}$ complexes, surprisingly little has been known about the reactivity of the iron and ruthenium dimers toward other transition-metals. In 1980, Gianotti et al. reported that the photolysis of $\mathrm{Cp_2Fe_2(CO)_4}$ in the presence of elemental sulfur gave an isomeric pair of $\mathrm{Cp_2Fe_2S_4}$ [7]. The structure of one isomer was solved by the single crystal X-ray analysis, in which two disulfide ligands take different coordination mode [8]: One disulfide ligand bounds to two iron centers in



Scheme 1. (i) $\mathrm{Fe(CO)_5}$ (ii) $\mathrm{Hg[Fe(NO)(CO)_3]_2}$ (iii) $\mathrm{CpCo(CO)_2}$ (iv) $\mathrm{IrCl(N_2)(PPh_3)_2}$ (v) $\mathrm{Ni(CO)_4}$.

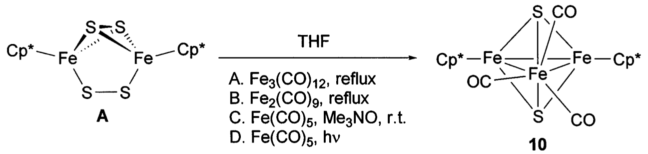


Scheme 2. (i) $Fe(CO)_5$, *hν* (ii) $Fe_2(CO)_9$ (iii) $Co_2(CO)_8$.

a μ-η^2:η^2 side-on manner, whereas the other adopts a μ-η^1:η^1 *endo*-on manner. The iron-iron distance of 3.49 Å shows no metal–metal interaction. In 1985, Wachter et al. reported that the Cp* analog, which was obtained by the thermal reaction of $Cp^*_2Fe_2(CO)_4$ with elemental sulfur, has a similar structure [9]. Rauchfuss et al. synthesized the ruthenium dimer $(C_5Me_4Et)_2Ru_2S_4$ by a thermal reaction. The structure was found to be quite similar to the iron analog [10]. The present review deals with the cluster construction by the reactions of $Cp'_2M_2S_4$ (M = Fe, Ru) with transition-metals.

2. Cluster construction by the reactions of $Cp'_2Fe_2S_4$ with transition-metals [11]

Triiron cluster **10** was synthesized by the reaction of $Cp^*_2Fe_2S_4$ (**A**) with three kinds of iron carbonyls and isolated as yellowish brown crystals (Eq. (1)) [12].



(1)

The reaction of **A** with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ proceeds in refluxing THF. However, no reaction of **A** with $Fe(CO)_5$ was observed under the thermal conditions. In the reaction with $Fe(CO)_5$, addition of Me_3NO promoted the formation of **10**,

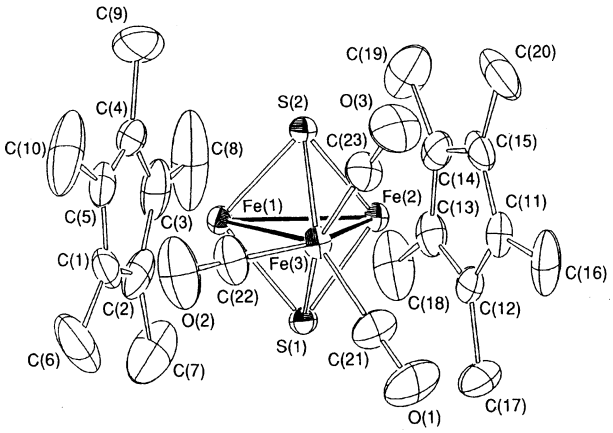
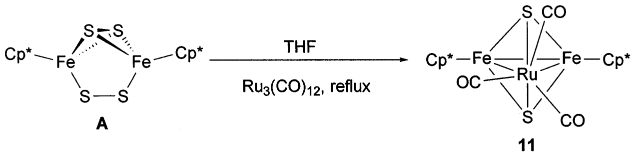


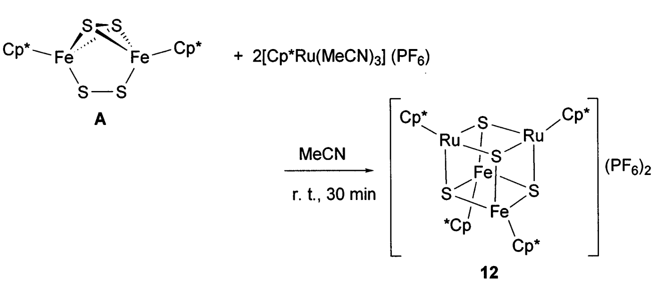
Fig. 1. ORTEP drawing of **10**.

where Me_3NO works as a decarbonylation reagent. Photolysis of a mixture of **A** and $Fe(CO)_5$ in THF also produced **10**. These results established that generation of the coordinatively unsaturated complex $Fe(CO)_4$ is crucial for the reaction of **A** with iron carbonyls to give **10**. An ORTEP drawing of **10** is shown in Fig. 1. The Fe_3S_2 core of **10** adopts a trigonal bipyramidal configuration: The three Fe atoms form a triangle which is capped by two μ_3-S ligands. Cluster **10** is the first example of *closo* cluster with Fe_3S_2 core. The iron and ruthenium mixed-metal trinuclear cluster $Cp^*_2(CO)_3Fe_2RuS_2$ (**11**) was formed in the reaction of **A** with $Ru_3(CO)_{12}$ in refluxing THF (Eq. (2)) [12].



(2)

Treatment of **A** with two equivalents $[Cp^*Ru(MeCN)_3](PF_6)$ in acetonitrile at room temperature resulted in the formation of the $Fe_2Ru_2S_4$ cubane-type cluster **12** (Eq. (3)) [12].



(3)

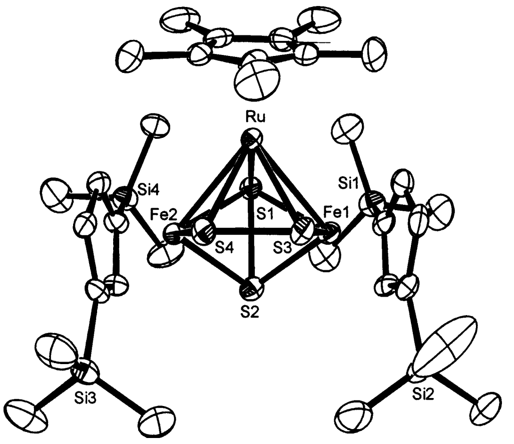
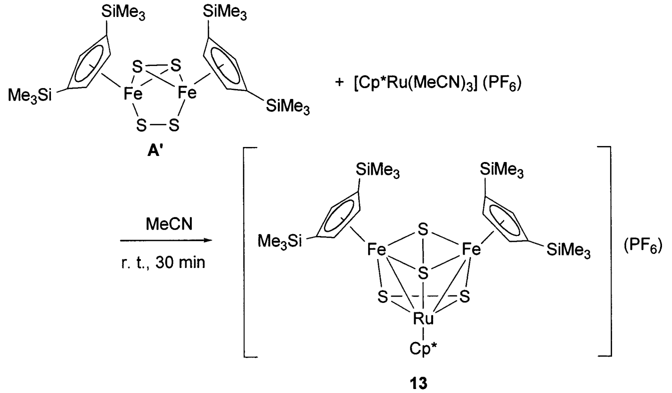


Fig. 2. ORTEP drawing of the cationic moiety in **13**.

The reaction of **A** with one equivalent [Cp*Ru(MeCN)$_3$](PF$_6$) was examined. It took place at room temperature to give **12** and several unidentified products. The isolation of the latter products was unsuccessful.

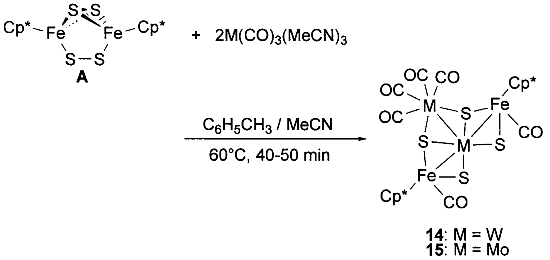
Treatment of Cp$_2^{S2}$Fe$_2$S$_4$ (**A′**) with one equivalent [Cp*Ru(MeCN)$_3$](PF$_6$) afforded a Fe$_2$RuS$_4$ cluster **13** (Eq. (4)), where Cp^{S2} (= 1,3-C$_5$H$_3$(SiMe$_3$)$_2$) is a much bulkier ligand than Cp*.



(4)

Even if two equivalents [Cp*Ru(MeCN)$_3$](PF$_6$) was added, no tetranuclear cluster [(Cp^{S2}Fe)$_2$(Cp*Ru)$_2$S$_4$](PF$_6$)$_2$ which corresponds to **12** was formed. This means that the use of the bulky Cp^{S2} ligand prevents the formation of the tetranuclear cluster such as **12**. The trinuclear cluster **13** is considered to be the intermediate to the tetranuclear cluster. The structure of **13** was determined by X-ray crystal structure analysis. The ORTEP drawing of the cationic moiety in **13** is shown in Fig. 2. The cluster contains an Fe$_2$Ru core with two μ_3-η^1:η^2:η^2 and μ_3-η^1:η^1:η^2 disulfido groups. The torsion angle of two disulfido groups is 84.1°. Cluster **13** can be considered as a Cp*Ru-capped Cp$_2^{S2}$Fe$_2$S$_4$ in which the Cp$_2^{S2}$Fe$_2$S$_4$ unit is coordinated in η^5-fashion to the ruthenium atom by the Fe1–S1–Fe2–S4–S3 five-membered ring.

Thermolysis of **A** and $W(CO)_3(MeCN)_3$ in 1:2 molar ratio at 60°C afforded a tetranuclear cluster **14** (Eq. (5)) [13].



(5)

Elemental analysis and mass spectral data indicate that **14** has the formula $Cp_2^*Fe_2W_2S_4(CO)_6$. The composition is the same as a cubane-type mixed-metal sulfur cluster $(Cp^*Fe)_2\{W(CO)_3\}_2(\mu_3\text{-}S)_4$. However, X-ray diffraction study disclosed that this is not the case. Cluster **14** was unequivocally determined to be $\{Cp^*Fe(CO)\}_2\{W(\mu_3\text{-}S)_2(\mu\text{-}S)_2\}\{W(CO)_4\}$ by X-ray crystal structure analysis (Fig. 3). The WS_4 unit is bound to one tungsten by two S atoms and two iron atoms by four S atoms, two of which bridge one iron and two tungsten atoms in a μ_3-fashion and the others are bound to one iron and one tungsten atoms in a μ_2-fashion. The W1 atom with four S ligands and W2 atom with two S and four CO ligands adopts a distorted tetrahedral and octahedral geometry, respectively. In the reaction of Eq. (5), six MeCN ligands were released, and two $W(CO)_3$ moieties were converted to WS_4 and $W(CO)_4$. Interestingly, redistribution of CO and S ligands took place between Fe and W atoms without the loss of any CO and S ligands, where the driving force for the formation of **14** may be due to the exceptionally high stability of the $[WS_4]^{2-}$.

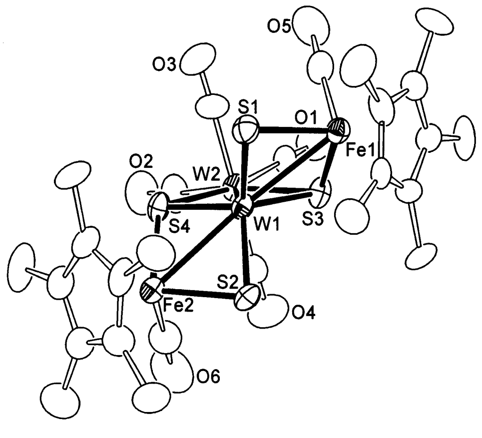
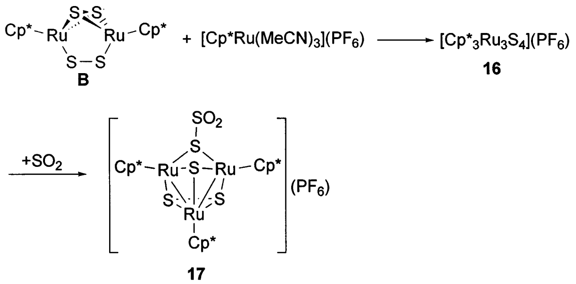


Fig. 3. ORTEP drawing of **14**.

The iron–molybdenum cluster **15** was also obtained by the reaction of **A** with $Mo(CO)_3(MeCN)_3$ in 1:2 molar ratio at 60°C (Eq. (5)) [13].

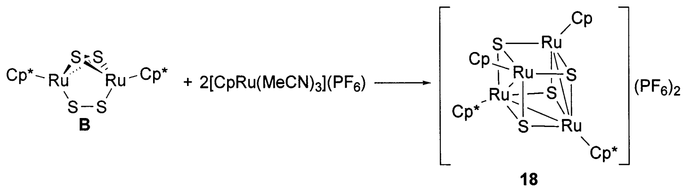
3. Cluster construction by the reactions of $Cp^*_2Ru_2S_4$ with transition-metals

Rauchfuss et al. showed a versatility of $Cp^*_2Ru_2S_4$ (**B**) as a precursor for synthesis of polynuclear transition-metal sulfur clusters. The reaction of $Cp^*_2Ru_2S_4$ with $[Cp^*Ru(MeCN)_3](PF_6)$ in refluxing acetonitrile afforded a trinuclear cluster $[Cp^*_3Ru_3S_4](PF_6)$ (**16**) (Eq. (6)) [14].



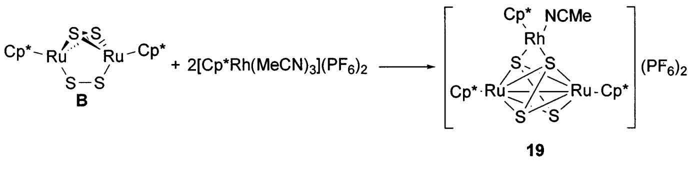
(6)

The structure of **16** is uncertain but can be inferred from its derivative. Treatment of **16** with SO_2 produced $[Cp^*_3Ru_3S_4{\cdot}SO_2](PF_6)$ (**17**) which was characterized crystallographically (Eq. (6)). Cluster **17** has an isosceles Ru_3 core with two Ru–Ru bonds. Three Ru metals are connected with μ_3-S, μ_3-η^1:η^1:η^2-S_2, and μ_2-S to which the SO_2 moiety is bound. The reaction of **B** with sterically less congested $[CpRu(MeCN)_3](PF_6)$ produced a cubane-type cluster $[Cp^*_2Cp_2Ru_4S_4](PF_6)_2$ (**18**) which was characterized crystallographically (Eq. (7)) [15].



(7)

Furthermore, Rauchfuss et al. succeeded in the isolation of a heteronuclear sulfido cluster by using **B**. The Ru dimer **B** reacted with $[Cp^*Rh(MeCN)_3](PF_6)_2$ in THF to afford a $RhRu_2S_4$ cluster **19** (Eq. (8)) [16].



(8)

Based on X-ray crystal structure analysis, the dication **19** consists of an unsymmetrical $RhRu_2S_4$ core with one Ru–Ru bond. Three transition-metals are connected with two μ_3-η^1:η^2:η^2 disulfido ligands.

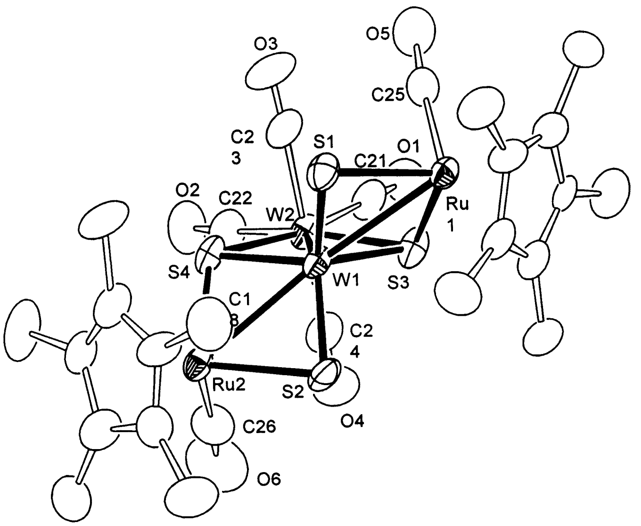
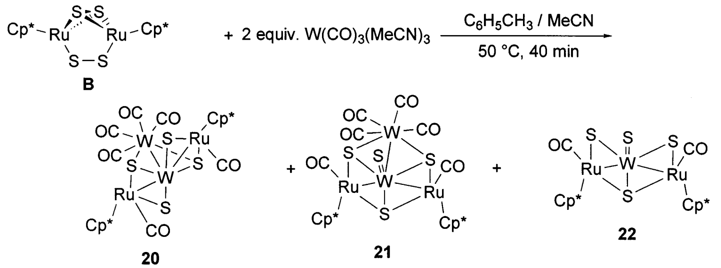


Fig. 4. ORTEP drawing of **20**.

We examined the reaction of **B** with an early-transition-metal complex. Thermal reaction of **B** with $W(CO)_3(MeCN)_3$ gave two kinds of $Ru_2W_2S_4$ clusters **20** and **21** and a Ru_2WS_4 cluster **22** (Eq. (9)) [17,18].



(9)

In the reaction of the iron dimer **A** with $M(CO)_3(MeCN)_3$ (M = Mo, W), only one $Fe_2M_2S_4$ cluster was obtained (Eq. (5)). Clusters **20** and **21** were characterized by single-crystal X-ray diffraction analysis. The ORTEP drawings of **20** and **21** are shown in Figs. 4 and 5, respectively. In cluster **20**, the WS_4 fragment is bound to one W by two S atoms and two Ru atoms by four S atoms, two of which bridge one Ru and two W atoms in a μ_3-fashion and the other two are bound to one Ru and one W atoms in a μ_2-fashion. The W2 atom with four CO and two S ligands adopts a distorted octahedral geometry. Unlike cluster **20**, there is a terminal S ligand in 21. The WS_4 fragment is bound to one W atom by two S atoms and two Ru atoms by three S atoms, two of which bridge one Ru and two W atoms in a μ_3-fashion and the other one is bound to two Ru and one W atoms in a μ_3-fashion. The crystal structure of **22** is shown in Fig. 6. The structure of **22** is similar to **21** except that **22** has no $W(CO)_4$ moiety. The $[WS_4]^{2-}$ fragment is bound to two Ru atoms by three S atoms, two of which bridge one W and one Ru atoms in a

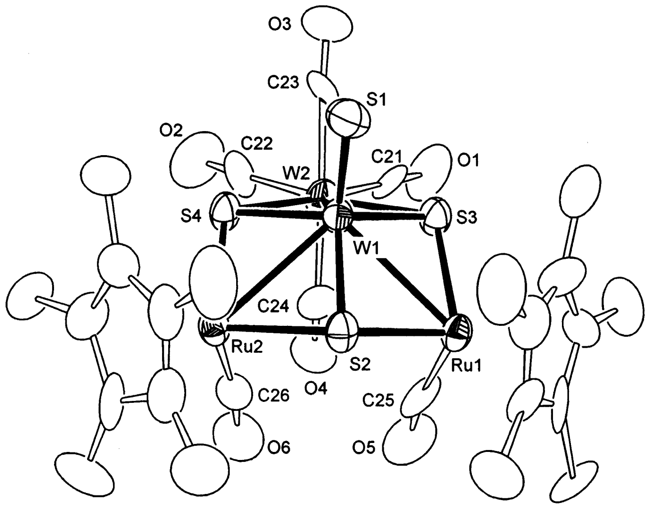
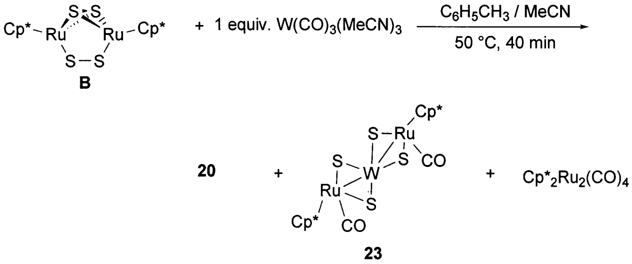


Fig. 5. ORTEP drawing of **21**.

μ_2-fashion, and the other one bridges one W and two Ru atoms in a μ_3-fashion. The residual S atom is bound to the W atom in a terminal mode. Cluster **22** has a pseudo-mirror plane composed of S1, S2, and W atoms.

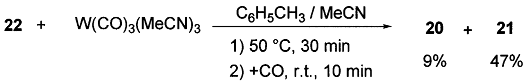
When the reaction of **B** with one equivalent $W(CO)_3(MeCN)_3$ was performed at 50°C, a Ru_2WS_4 trinuclear cluster **23** was obtained (Eq. (10)).



(10)

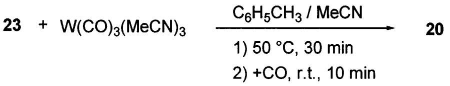
The structure of the C_5Me_4Et analog $\{(C_5Me_4Et)Ru(CO)\}_2\{W(\mu\text{-}S)_4\}$ (**24**) was determined by the X-ray crystal structure analysis. An ORTEP drawing of **24** is shown in Fig. 7. The $[WS_4]^{2-}$ fragment adopts a slightly distorted tetrahedral geometry, and each of four S atoms is bound to one ruthenium and one tungsten atoms in a μ_2-fashion. Thus, cluster **20** can be regarded as the cluster **23** capped with a $W(CO)_4$ in which the tetrathiotungstate moiety of **23** is coordinated in η^3-fashion to the tungsten atom by two sulfur and one tungsten atoms.

Trinuclear clusters **22** and **23** may be the intermediates to give tetranuclear clusters **20** and **21**. To clarify this, the reactions of **22** and **23** with $W(CO)_3(MeCN)_3$ and CO were carried out. Upon heating a solution of the trinuclear cluster **22** and $W(CO)_3(MeCN)_3$, followed by bubbling CO, **21** with a small amount of **20** was obtained (Eq. (11)).



$$\mathbf{22} + \mathrm{W(CO)_3(MeCN)_3} \xrightarrow[\substack{\text{1) 50 °C, 30 min} \\ \text{2) +CO, r.t., 10 min}}]{C_6H_5CH_3 / MeCN} \underset{9\%}{\mathbf{20}} + \underset{47\%}{\mathbf{21}} \qquad (11)$$

On the other hand, thermolysis of **23** and W(CO)$_3$(MeCN)$_3$, followed by bubbling CO, led to the exclusive formation of **20** (Eq. (12)).



$$\mathbf{23} + \mathrm{W(CO)_3(MeCN)_3} \xrightarrow[\substack{\text{1) 50 °C, 30 min} \\ \text{2) +CO, r.t., 10 min}}]{C_6H_5CH_3 / MeCN} \mathbf{20} \qquad (12)$$

Under the same conditions as those in Eq. (9) (50°C, 40 min), no isomerization reactions between **20** and **21** and between **22** and **23** were observed. The cross-reaction of a 1:1 molar mixture of **B** and its C$_5$Me$_4$Et derivative (C$_5$Me$_4$Et)$_2$Ru$_2$S$_4$ with [W(CO)$_3$(MeCN)$_3$] gave **20**, {(C$_5$Me$_4$Et)Ru(CO)}$_2${W(μ_3-S)(μ_2-S)}{W(CO)$_4$} (**20′**), **21**, and {(C$_5$Me$_4$Et)Ru(CO)}$_2${W(μ_3-S)$_3$(=S)}{W(CO)$_4$} (**21′**). No crossover

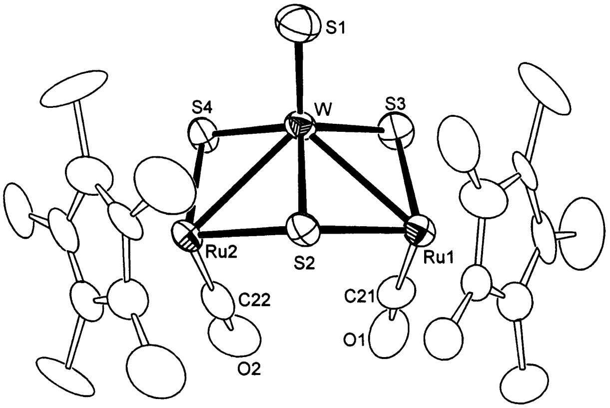


Fig. 6. ORTEP drawing of **22**.

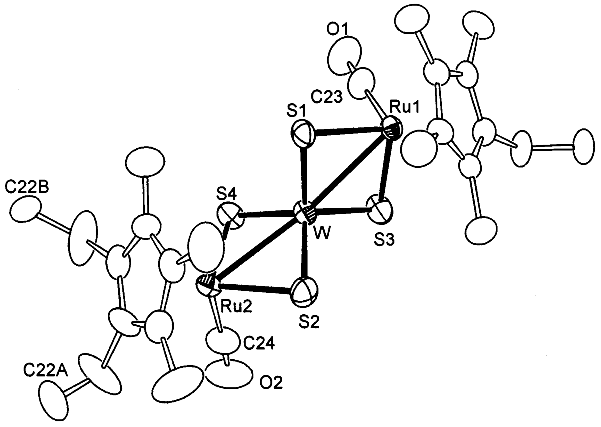
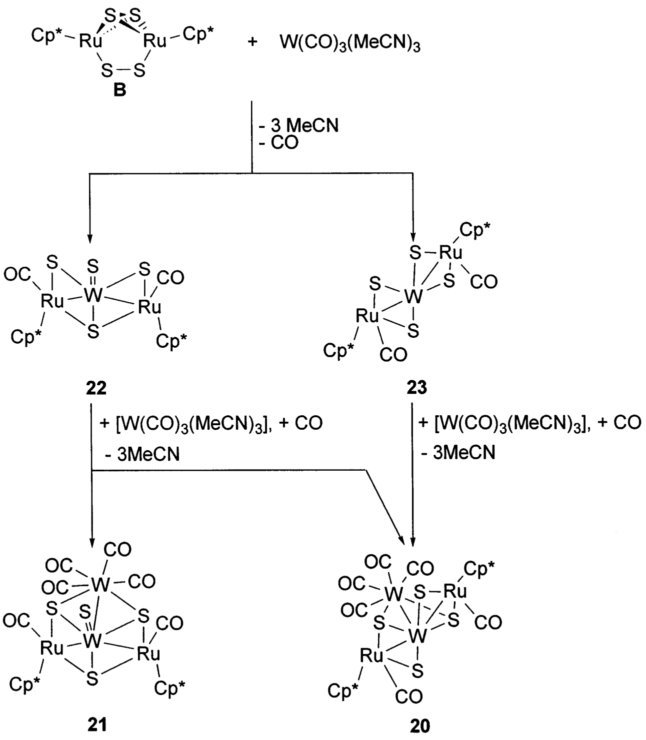


Fig. 7. ORTEP drawing of **24**.



Scheme 3. A plausible reaction pathway for the formation of **20** and **21**.

product such as {Cp*Ru(CO)}{(C_5Me_4Et)Ru(CO)}{W(μ_3-S)(μ_2-S)}{W$(CO)_4$} or {Cp*Ru(CO)}{(C_5Me_4Et)Ru(CO)}{W$(\mu_3\text{-S})_3$(= S)}{W$(CO)_4$} was detected. This indicates that the reaction of $Cp^*_2Ru_2S_4$ (**B**) with $W(CO)_3(MeCN)_3$ takes place intramolecularly. A plausible reaction pathway for the formation of **20** and **21** is illustrated in Scheme 3. The reaction of **B** with $W(CO)_3(MeCN)_3$ gives two kinds of trinuclear clusters **22** and **23** intramolecularly via liberation of one CO and three MeCN ligands. During the reaction, reorganization of CO and S ligands took place between one W and two Ru atoms, where the driving force may be the high stability of the tetrathiotungstate $[WS_4]^{2-}$. Upon subsequent reactions of **22** and **23** with $W(CO)_3(MeCN)_3$ and CO, cluster **22** is converted to **21** with a small amount of **20**, whereas **23** is converted to **20**, exclusively.

4. Conclusion

This review has described the cluster construction methodology by the reactions of the reactive transition-metal sulfur complexes of the type $Cp'M_2S_4$ with various transition-metals. The iron or ruthenium dimers were shown to be excellent starting materials for synthesizing not only homo- but also heteronuclear clusters.

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