

Synthesis and Reactivities of Cubane-Type Sulfido Clusters Containing Noble Metals

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ABSTRACT

Cubane-type sulfido clusters containing noble metals are newcomers compared with the corresponding clusters of the first transition series metals and molybdenum, which have been extensively studied in relation to metalloenzymes and industrial hydrodesulfurization catalysts. This Account reviews the recent progress in studies on the synthesis and reactivities of these noble metal cubane-type clusters. One of the goals in this new area lies in development of the unique catalysis of the noble metals embedded in the robust and redox-active cubane-type cores. Rational synthetic approaches indispensable to the preparation of such effective cluster catalysts are discussed to a significant extent.

Introduction

The cubane-type sulfido clusters, characterized by a cubic core with four metal atoms occupying alternate corners of the cube along with four triply bridging sulfido ligands in the remaining corners, are ubiquitous and form an indispensable class in the chemistry of metal sulfido clusters. These clusters have drawn much attention, primarily owing to their relevance to metalloenzymes¹ and industrial metal sulfide catalysts.² Because noble metals

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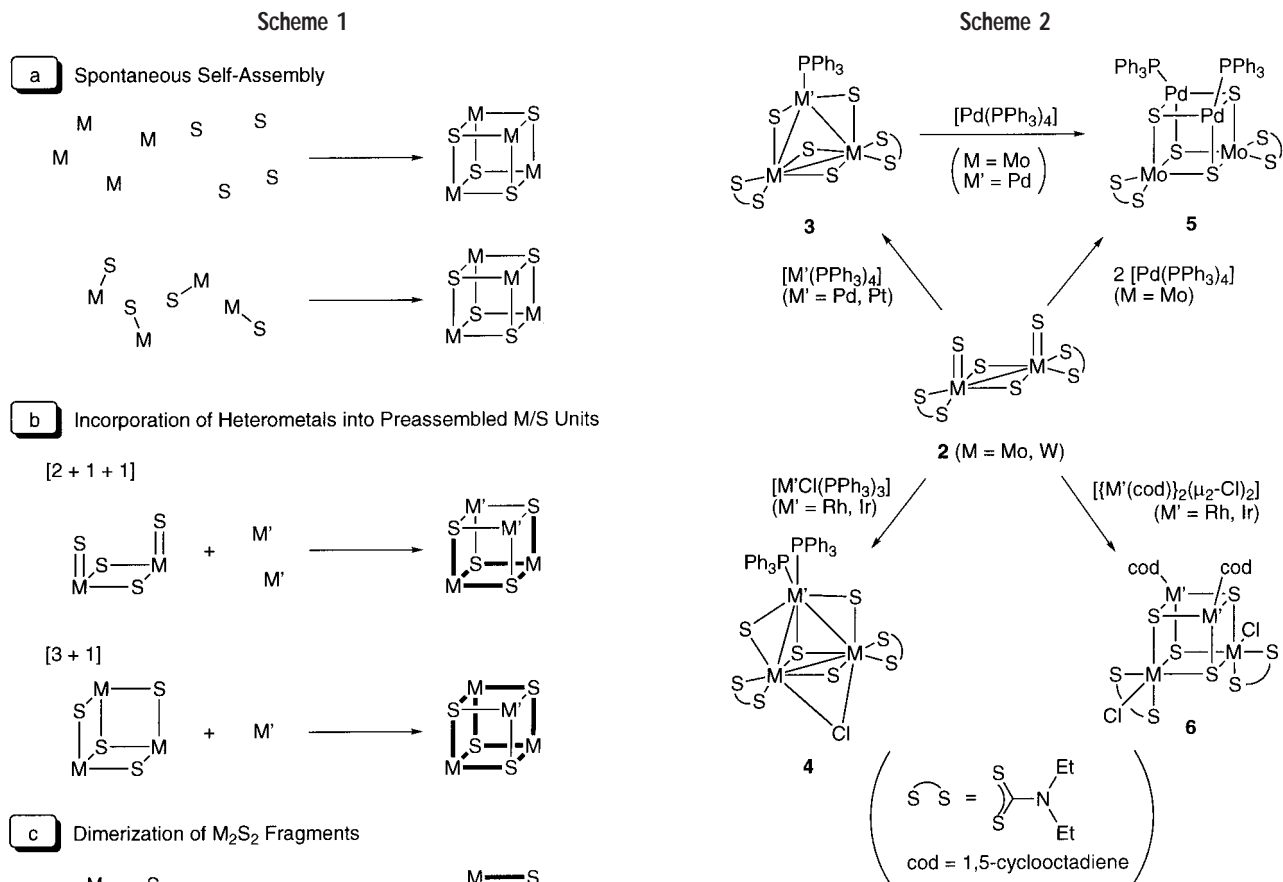
are not used in biological systems and are also believed to be poisoned by sulfur in their catalysis, the chemistry of sulfido clusters containing noble metals has long been unexplored compared with that of clusters containing the first transition series metals and molybdenum.³ However, taking into consideration that various organic reactions are catalyzed by mononuclear complexes of noble metals, it seems reasonable to expect unique reactivities of noble metal centers embedded in the robust and redox-active cubane-type cores. In this context, we embarked on our studies on the syntheses and reactivities of cubane-type sulfido clusters containing noble metals. This Account provides an overview of this area, with an emphasis on our recent work. Rational construction of the cubane-type core will first be described because it provides the synthetic methodology for the target metal–sulfur frameworks. The latter part of this paper is concerned with the reactivities of the noble metal centers in the cubane-type core. For simplicity, the metal–metal bonds in cubane-type sulfido clusters are not depicted in the structural formulas throughout this Account and will not be discussed in detail, although they have inherently attracted much interest.⁴ Readers can refer to comprehensive reviews covering the chemistry of metal sulfido clusters not restricted to the cubane-type ones.^{4–15}

Synthesis

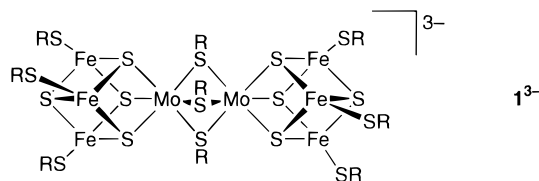
A variety of methods have been used to synthesize cubane-type sulfido clusters, as summarized in Scheme 1. They are categorized into two groups: one is the spontaneous self-assembly (Scheme 1a), and the other is a more rational approach, in which cubane-type clusters are constructed stepwise from smaller building blocks (Scheme 1b and c). The former method conveniently affords thermodynamically preferred products from appropriate sulfur sources and mononuclear or oligomeric metal species. However, this approach is somewhat ad hoc, and the products are essentially unpredictable. On the other hand, substantial knowledge has now been accumulated concerning the methodology for the rational synthesis of cubane-type sulfido clusters with desired metal compositions. Here we mainly outline the synthesis of noble metal clusters through these rational methods after touching on the self-assembly approach briefly.

Spontaneous Self-Assembly. Myriad cubane-type sulfido clusters have been synthesized through the self-assembly approach, especially for the first transition series metals and molybdenum. By contrast, cubane-type noble metal clusters prepared by this method are rather limited; examples are conversion of the hydrosulfido complex $[\text{Cp}'\text{Ru}(\text{SH})(\text{PPh}_3)_2]$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{Me}$) into the ruthenium cluster $[(\text{Cp}'\text{Ru})_4(\mu_3\text{-S})_4]$ upon heating,¹⁶ and the synthesis of the platinum cluster $\text{K}_4[\text{Pt}_4(\mu_3\text{-S})_4(\text{S}_3)_6]$ from K_2PtCl_4 and K_2S_4 .¹⁷ This is in marked contrast to the fact that trigonal bipyramidal $\text{M}_3(\mu_3\text{-S})_2$ clusters have been prepared for all of the noble metals by self-assembly.

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Tetrathiometalate anions such as $[MS_4]^{2-}$ ($M = Mo, W$) are the most versatile sources of heterometals for mixed-metal sulfido clusters.⁹ For example, treatment of MoS_4^{2-} with $FeCl_3$ and $NaSR$ gives a series of double-cubane clusters such as $[Mo_2Fe_6S_8(SR)_9]^{3-}$ (**1**³⁻), which contain $MoFe_3S_4$ cubane-type components.^{18,19} On the other hand,

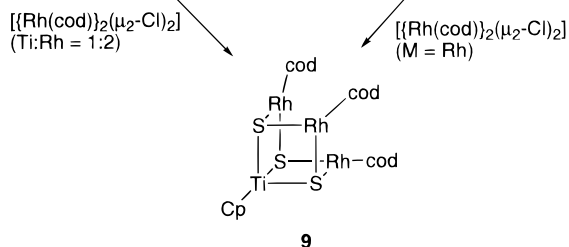
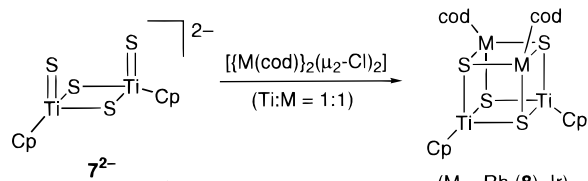


although reactions of noble metal complexes with tetrathio-metalate anions afford a number of di- and trinuclear mixed-metal sulfido complexes containing noble metals, cubane-type clusters have not yet been obtained from these reactions.

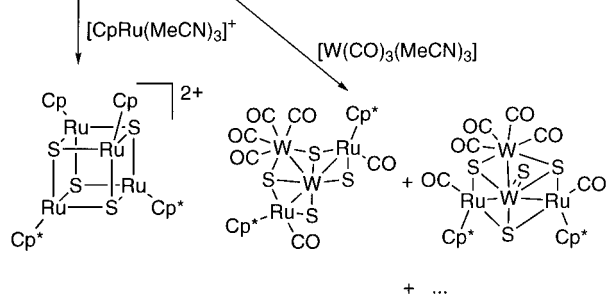
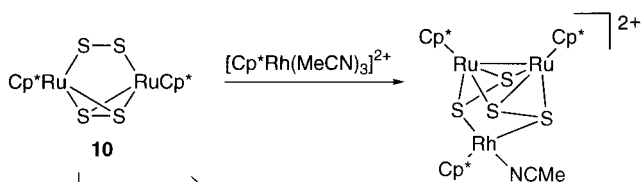
Incorporation of Heterometals into Preassembled Metal–Sulfur Aggregates with M_2S_4 and M_3S_4 Cores. To reach the cubane-type sulfido clusters with target metal compositions more reasonably, preassembled di- and trinuclear sulfido complexes are used as building blocks (Scheme 1b). These complexes behave as metalloligands toward heterometals by using the lone pair electrons of the sulfur atoms. From another point of view, these building block complexes may be regarded as possible intermediates in the self-assembly approach.

The sulfido-bridged dinuclear complexes with *syn*- $M_2S_2(\mu_2-S)_2$ cores, which are prevalent for group 6 metals, are useful precursors for the cubane-type sulfido clusters because capture of two metal atoms into the two missing corners completes the cubane-type core. Since the mixed-metal cubane-type sulfido clusters $\{[M(S_2CNEt_2)(MeCN)]_2\}$ ($\{Co(CO)_2\}_2(\mu_3-S)_4$) ($M = Mo, W$; $S_2CNEt_2 =$ diethyldithiocarbamate) were synthesized by the reactions of $[M_2S_2(\mu_2-S)_2(S_2CNEt_2)_2]$ (**2**) with $[Co_2(CO)_8]$,²⁰ several mixed-metal cubane-type sulfido clusters with $M_2M'S_4$ cores have been prepared from M_2S_4 clusters related to **2**.²¹ The metal atoms incorporated were, however, limited to the first transition series metals or coinage metals. Thus, we have examined the reactions of **2** with noble metal complexes in detail. Complexes **2** react with low-valent group 9 and 10 noble metal complexes to afford the trinuclear clusters **3** with a unique $M'(\mu_2-S)_2M_2(\mu_2-S)_2$ core, the incomplete cubane-type sulfido clusters **4**, and the cubane-type sulfido clusters **5** and **6** (Scheme 2).^{22,23} Notable is the strong dependence of the core structures of the products upon the combination of the metals and the ancillary ligands. When the titanium analogue $[(CpTiS)_2(\mu_2-S)_2]^{2-}$ (**7**²⁻; $Cp = \eta^5-C_5H_5$) is treated with noble metal complexes, the corresponding cubane-type sulfido clusters such as $[(CpTi)_2\{M(cod)\}_2(\mu_3-S)_4]$ ($M = Rh$ (**8**), Ir ; $cod = 1,5$ -cyclooctadiene) are obtained (Scheme 3).²⁴ Quite recently, Oro and co-workers have reported that **7**²⁻ reacts with 2 equiv of $[\{Rh(cod)\}_2(\mu_2-Cl)_2]$ to afford the sulfur-deficient incomplete cubane-type sulfido cluster $[(CpTi)\{Rh(cod)\}_3(\mu_3-S)_3]$ (**9**); they have proposed that **9** is formed via the cubane-

Scheme 3



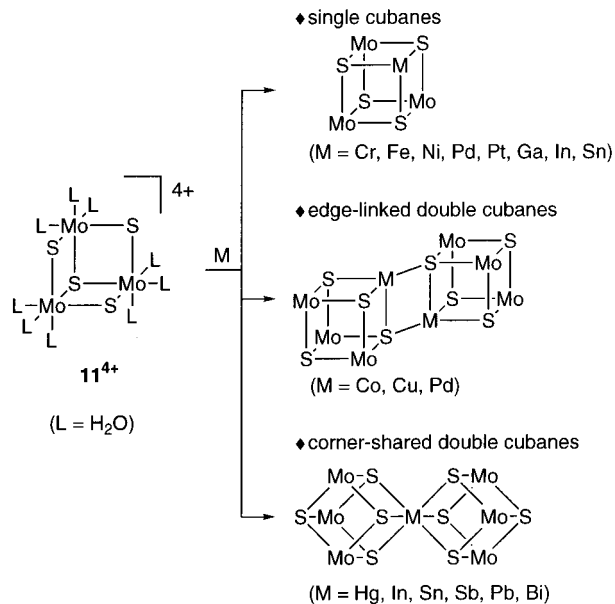
Scheme 4



type cluster **8**.²⁵ In agreement with their proposal, we have confirmed that the $\text{Ti}_2\text{Rh}_2\text{S}_4$ heterobimetallic cubane-type cluster **8** reacts with an equimolar amount of $[\{\text{Rh}(\text{cod})\}_2(\mu_2\text{-Cl})_2]$ to give the TiRh_3S_3 cluster **9**, although the fate of some of the Ti atoms in **8** is unclear at present.²⁶

The M_2S_4 dinuclear precursors do not necessarily have the $\text{syn-M}_2\text{S}_2(\mu_2\text{-S})_2$ core. For example, the disulfido-bridged diruthenium complex $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^1\text{-S}_2)(\mu_2\text{-}\eta^2\text{-}\eta^2\text{-S}_2)]$ (**10**; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) serves as a useful building block for a series of sulfido clusters with higher nuclearity, including the cubane-type clusters (Scheme 4).^{27–29} Disulfido-bridged complexes of V, Cr, Mo, W, and Fe with M_2S_4 composition can also be potential building blocks for the synthesis of the clusters with $\text{M}_2\text{M}'_2\text{S}_4$ cores.⁶ Use of these M_2S_4 precursors other than the $\text{syn-M}_2\text{S}_2(\mu_2\text{-S})_2$ type, however, often results in the formation of sulfido clusters different from the cubane-type ones.

In pioneering investigations on the capture of heterometals into preassembled M_3S_4 aggregates, Shibahara et al.^{7,8,30} demonstrated that the incomplete cubane-type cluster $[\{\text{Mo}(\text{H}_2\text{O})_3\}_3(\mu_3\text{-S})(\mu_2\text{-S})_3]^{4+}$ (**11⁴⁺**) reacts with a variety of metals to afford a series of mixed-metal sulfido clusters containing $\text{M}'\text{Mo}_3\text{S}_4$ cubane-type cores (Scheme 5). As in the M_2S_4 systems, however, the elements incor-

Scheme 5^a

^a Charges and terminal ligands in the cubane-type clusters are omitted.

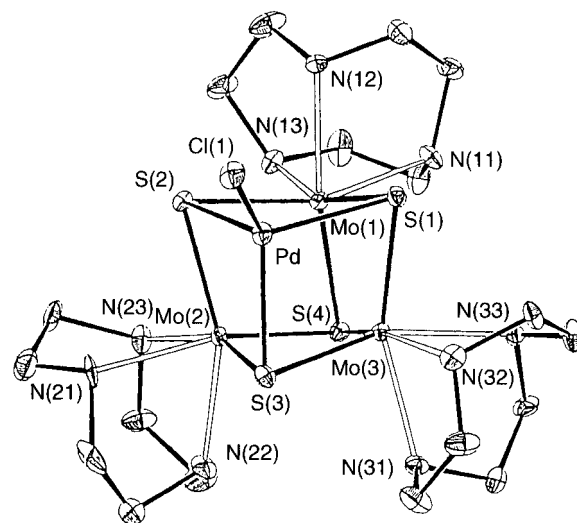
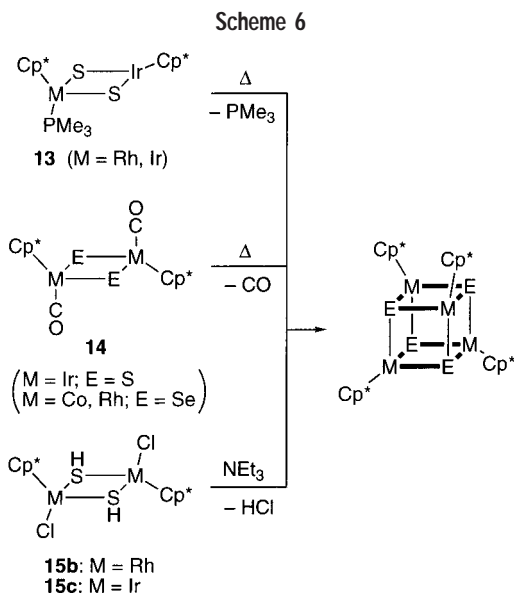


FIGURE 1. Crystal structure of the cationic part of $[(\text{PdCl})\{\text{Mo}(\text{tacn})\}_3(\mu_3\text{-S})_4]\text{Cl}_3\cdot 4\text{H}_2\text{O}$ (**12³⁺** $\cdot 3\text{Cl}_3\cdot 4\text{H}_2\text{O}$). Hydrogen atoms are omitted for clarity.

porated were restricted to the first transition series metals and main group elements. We have applied this synthetic methodology to noble metals and succeeded in isolating the mixed-metal cubane-type sulfido clusters with Pd-Mo_3 ^{31,32} and PtMo_3 ³³ cores for the first time. Thus, **11⁴⁺** reacts with Pd black to afford the aqua cluster $[(\text{PdCl})\{\text{Mo}(\text{H}_2\text{O})_3\}_3(\mu_3\text{-S})_4]^{3+}$, which is further converted to $[(\text{PdCl})\{\text{Mo}(\text{tacn})\}_3(\mu_3\text{-S})_4]^{3+}$ (**12³⁺**; $\text{tacn} = 1,4,7\text{-triazacyclononane}$) by ligand substitution; the cubane-type core of **12³⁺** has been confirmed by X-ray analysis (Figure 1). Interestingly, the PdMo_3S_4 cluster **12³⁺** exhibits unique reactivities at the noble metal center (vide infra). The synthetic utility of **11⁴⁺** for mixed-metal cubane-type sulfido clusters has also been demonstrated by Sykes and co-workers.³⁴

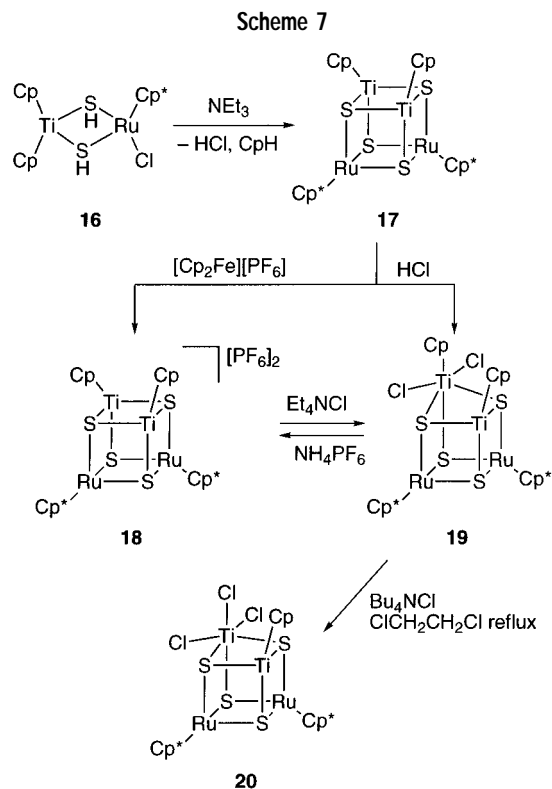
The other M_3S_4 precursor is the linear triiron complex $[\text{Fe}_3(\mu_2\text{-S})_4(\text{SR})_4]^{3-}$.⁹ Although Mo, W, Fe, Co, and



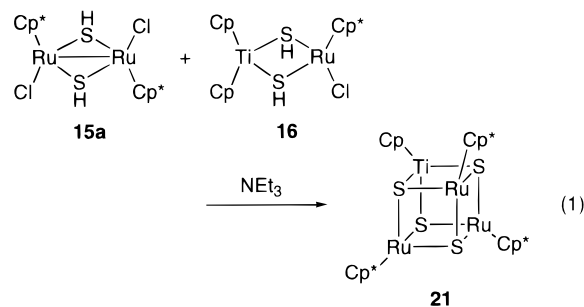
Ni complexes react with this precursor to form the cubane-type clusters, noble metals have not been incorporated.

Dimerization of M_2S_2 Fragments. Another rational and promising approach to the cubane-type sulfido clusters is the dimerization of $\text{M}(\mu_2\text{-S})_2\text{M}'$ fragments (Scheme 1c). For example, the sulfido-bridged dinuclear complexes $[\text{Cp}^*\text{M}(\text{PMe}_3)(\mu_2\text{-S})_2\text{IrCp}^*]$ (**13**; M = Rh, Ir) are converted into the cubane-type sulfido clusters $[(\text{Cp}^*\text{M})_2(\text{Cp}^*\text{Ir})_2(\mu_3\text{-S})_4]$ with a loss of PMe_3 upon heating (Scheme 6).³⁵ Kinetic studies have demonstrated that the doubly unsaturated sulfido-bridged intermediate $[\text{Cp}^*\text{M}(\mu_2\text{-S})_2\text{IrCp}^*]$ dimerizes to give the cubane-type sulfido clusters. Similar intermediates may also be involved in the thermal transformation of the dicarbonyl complexes $[(\text{Cp}^*\text{M}(\text{CO})_2(\mu_2\text{-E})_2)]$ (**14**; M = Co, Rh, Ir; E = S, Se) into the cubane-type clusters $[(\text{Cp}^*\text{M})_4(\mu_3\text{-E})_4]$.^{36,37}

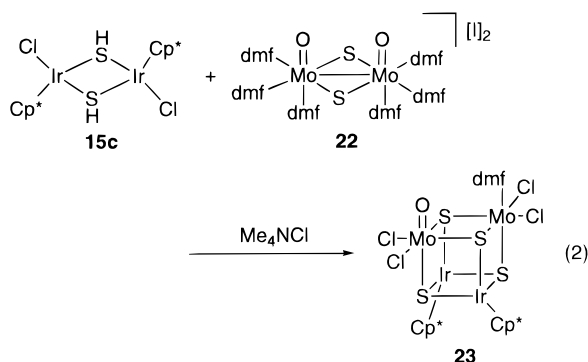
In contrast to the thermal loss of donor ligands described above, α -elimination of hydrogen chloride or alkanes from hydrosulfido-bridged dinuclear complexes proceeds under ambient conditions to generate sulfido-bridged species with coordinative unsaturation. Thus, when the hydrosulfido-bridged dinuclear complexes $[(\text{Cp}^*\text{MCl})_2(\mu_2\text{-SH})_2]$ (M = Ru (**15a**), Rh (**15b**), Ir (**15c**)) are treated with triethylamine at room temperature or below, a series of cubane-type sulfido clusters $[(\text{Cp}^*\text{M})_4(\mu_3\text{-S})_4]$ (M = Ru, Rh, Ir) are obtained (Scheme 6).^{38–41} In these reactions, initial formation of the coordinatively unsaturated dinuclear intermediates $[(\text{Cp}^*\text{M})_2(\mu_2\text{-S})_2]$ with bridging sulfido ligands has been deduced by monitoring the reaction with the ^1H NMR spectroscopy for iridium complexes.^{39,40} For ruthenium, this intermediate can be trapped with alkynes, giving the dithiolene-bridged diruthenium complexes $[\text{Cp}^*\text{Ru}(\mu_2\text{-}\eta^2\text{-}\eta^4\text{-S}_2\text{C}_2\text{RR}')\text{RuCp}^*]$.⁴¹ For main group elements, thermal α -elimination of isobutane from $[(\text{Bu}'_2\text{Ga})_2(\mu_2\text{-SH})_2]$ is known, which results in the formation of the cubane-type gallium sulfido cluster $[(\text{Bu}'\text{Ga})_4(\mu_3\text{-S})_4]$.⁴² This type of reaction is not limited to homometallic complexes: the heterobimetallic hydrosul-



ido-bridged complex $[\text{Cp}_2\text{Ti}(\mu_2\text{-SH})_2\text{RuClCp}^*]$ (**16**) is converted into the mixed-metal cubane-type sulfido cluster $[(\text{CpTi})_2(\text{Cp}^*\text{Ru})_2(\mu_3\text{-S})_4]$ (**17**) upon treatment with triethylamine (Scheme 7).^{43,44} It is to be noted that not only HCl but also cyclopentadiene are eliminated from the hydrosulfido-bridged dinuclear complex in this reaction. Furthermore, we have recently extended these self-condensation reactions to the crossed condensation of two different hydrosulfido-bridged dinuclear complexes. Thus, treatment of the mixture of the hydrosulfido-bridged dinuclear complexes **15a** and **16** with triethylamine predominantly affords the crossed condensation product $[(\text{CpTi})(\text{Cp}^*\text{Ru})_3(\mu_3\text{-S})_4]$ (**21**), as shown in eq 1.⁴⁵ Another type of conden-



sation of two different sulfur-bridged dinuclear fragments is the dehydration condensation of the hydrosulfido-bridged diiridium complex **15c** and the sulfido-bridged dimolybdenum oxo complex $[(\text{MoO}(\text{dmf})_3)_2(\mu_2\text{-S})_2][\text{I}]_2$ (**22**; dmf = dimethylformamide) in the presence of Me_4NCl , which results in the formation of the mixed-metal cubane-type sulfido cluster $[(\text{Cp}^*\text{Ir})_2(\text{MoCl}_2\text{O})\{\text{MoCl}_2(\text{dmf})\}(\mu_3\text{-S})_4]$ (**23**; eq 2).⁴⁶



Structures and Reactivities of $\text{Ti}_2\text{Ru}_2\text{S}_4$ Cubane-Type Clusters

The $\text{Ti}_2\text{Ru}_2\text{S}_4$ cluster **17** described above is unique in having a heterobimetallic cubane-type sulfido core containing not only noble metal atoms but also electron-deficient group 4 metal atoms. On the basis of the effective atomic number rule, the presence of six metal–metal bonds is expected for the $60e^-$ cluster **17**; however, this early–late heterobimetallic cluster has only four $\text{Ru}\rightarrow\text{Ti}$ dative bonds.^{43,44} This is because the $\text{Ru}\text{--}\text{Ru}$ antibonding orbital lies below the $\text{Ti}\text{--}\text{Ti}$ bonding orbital owing to the high-lying titanium d orbitals.

When the electron-deficient cluster **17** is oxidized with $[\text{Cp}_2\text{Fe}][\text{PF}_6]$, the cationic $58e^-$ cluster $[(\text{CpTi})_2(\text{Cp}^*\text{Ru})_2(\mu_3\text{-S})_4][\text{PF}_6]_2$ (**18**) is obtained (Scheme 7).⁴⁴ It is of interest that oxidation of **17** with HCl gas affords the neutral $62e^-$ cluster $[(\text{CpTiCl}_2)(\text{CpTi})(\text{Cp}^*\text{Ru})_2(\mu_3\text{-S})_4]$ (**19**), in which the Ti atom with two chloro ligands extends far from the cubane-type core. The cationic cluster **18** has latent vacancy on the Ti atom: treatment of **18** with an excess of Et_4NCl gives the dichloro cluster **19**, whereas **19** reacts with 2 equiv of NH_4PF_6 to afford **18**. Furthermore, one of the Cp ligands in **19** is substituted by a chloride anion to give the trichloro cluster $[(\text{TiCl}_3)(\text{CpTi})(\text{Cp}^*\text{Ru})_2(\mu_3\text{-S})_4]$ (**20**) under more drastic conditions; the molecular structure of **20** is depicted in Figure 2. These unusual reactivities of the titanium center in the $\text{Ti}_2\text{Ru}_2\text{S}_4$ clusters **17**–**19** may be ascribed to the steric and electronic flexibility of the early–late heterobimetallic cubane-type sulfido core.

Reactivities of PdMo_3S_4 Cubane-Type Clusters

Having acquired cubane-type sulfido clusters containing noble metals as described above, we next investigated the reactivities of the noble metal centers in these clusters. In agreement with our initial expectation, the PdMo_3S_4 cubane-type cluster $\mathbf{12}^{3+}$ exhibits unique reactivities at the Pd atom.

Coordination of Substrates. Various substrates (L), including alkenes, CO, and isocyanides, bind to the Pd atom in $\mathbf{12}^{3+}$ to give the corresponding adducts $[(\text{PdL})\{\text{Mo}(\text{tacn})\}_3(\mu_3\text{-S})_4]^{4+}$.^{31,32} The electron-poor nature of the tetrahedral palladium center is deduced from the relatively high CO stretching frequency of $[\{\text{Pd}(\text{CO})\}\{\text{Mo}(\text{tacn})\}_3(\mu_3\text{-S})_4][\text{Cl}][\text{PF}_6]_3$ (2085 cm^{-1}). The assignment of the formal oxidation state of the Pd atom is in controversy. Harris and co-workers have assigned a zero oxidation state to

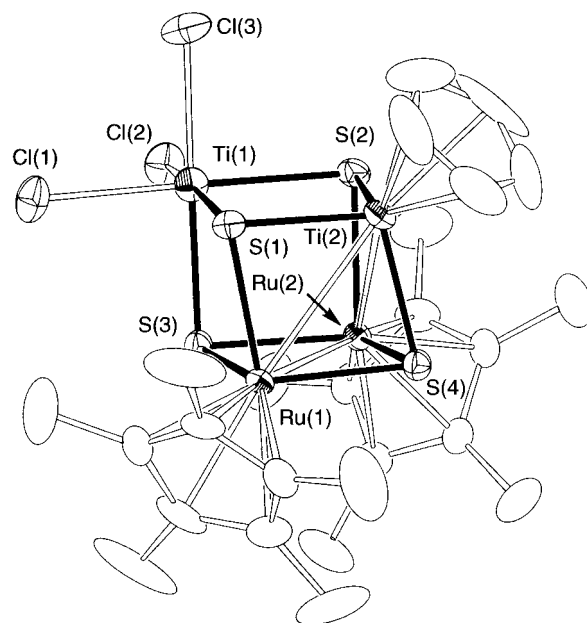
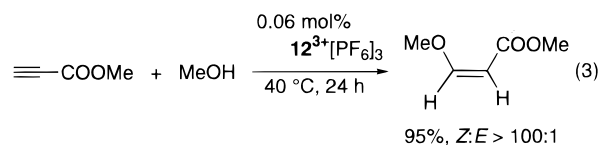


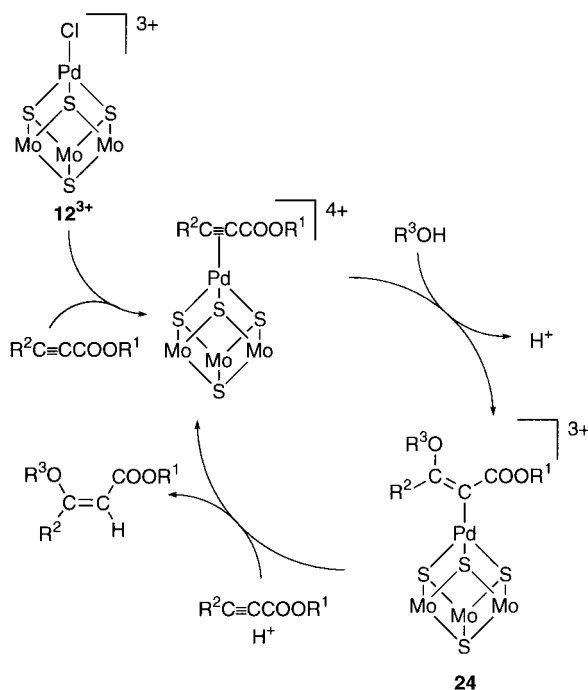
FIGURE 2. Crystal structure of $[(\text{TiCl}_3)(\text{CpTi})(\text{Cp}^*\text{Ru})_2(\mu_3\text{-S})_4]\cdot\text{CH}_2\text{Cl}_2$ (**20**· CH_2Cl_2). The solvating molecule and hydrogen atoms are omitted for clarity.

this Pd atom according to the Fenske–Hall molecular orbital calculations.⁴⁷ Their calculations have clearly demonstrated that the metal electrons are delocalized throughout the metal tetrahedron; however, this simply means that the complete two-electron oxidation of heterometals as in the tin–molybdenum cluster $[(\text{SnCl}_3)\{\text{Mo}(\text{NCS})_3\}_3(\mu_3\text{-S})_4]^{6-}$ does not occur in the PdMo_3S_4 cluster $\mathbf{12}^{3+}$. Indeed, as pointed out by Harris, there may be polarized charge distribution in these delocalized orbitals, through which the d electrons in the Pd atom are provided to the Mo_3 fragment to some extent and the Pd atom is partially oxidized. It is to be noted that whatever formal oxidation state one prefers, the observed properties of the Pd atom in $\mathbf{12}^{3+}$ are apparently Pd(II)-like, although the tetrahedral geometry of Pd(II) is not common.⁴⁸

Catalysis. We have found that the PdMo_3S_4 cluster $\mathbf{12}^{3+}$ – $[\text{PF}_6]_3$ can promote the stereoselective addition of methanol to methyl propiolate with high efficiency, which is not achieved by conventional mononuclear Pd complexes (eq 3).³² The proposed mechanism for the reaction of alkyne



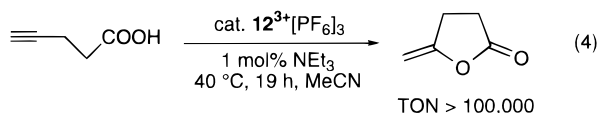
acid esters with alcohols is shown in Scheme 8. Initial coordination of the alkyne and the following nucleophilic attack of the alcohol on the coordinated alkyne from the outer coordination sphere give the vinylpalladium intermediate **24**. The facile nucleophilic attack toward the coordinated alkyne indicates the electron-poor nature of the Pd atom in $\mathbf{12}^{3+}$. Upon subsequent protonolysis, the trans addition product is formed with retention of the stereochemistry around the double bond. The Pd atom

Scheme 8^a

^a Coordinated tacn ligands on the Mo atoms are omitted for clarity.

firmly embedded in the Mo₃S₄ aggregate seems to provide a unique reaction site to realize the high stereoselectivity and to suppress oligomerization of alkynes. The UV–vis spectrum of the reaction mixture indicates that the PdMo₃S₄ cubane-type core is retained during the catalytic reactions.

Cluster **12**³⁺[PF₆]₃ also catalyzes the stereoselective addition of carboxylic acids to alkynes with electron-withdrawing groups.⁴⁹ When alkynoic acids are used as substrates, intramolecular cyclization takes place, and the corresponding enol lactones are obtained in high yields; the turnover number reaches 100 000 in the cyclization of 4-pentynoic acid (eq 4).⁵⁰ The catalytic activity of **12**³⁺-



[PF₆]₃ in the intramolecular cyclization is remarkably higher than those of mononuclear palladium complexes such as [PdCl₂(PhCN)₂]. These reactions provide additional examples of a still limited number of well-defined cluster compounds that effectively catalyze organic reactions with retention of their cluster cores.⁵¹

Concluding Remarks

The chemistry of cubane-type sulfido clusters has been extended from the first transition series metals to noble metals. The building block approach has led to development of useful and rational pathways to the cubane-type clusters containing noble metals, some of which exhibit unique reactivities and catalysis. Further studies will be directed toward the establishment of general synthetic

methods for clusters of this type containing any kind of transition metals. Investigations are now in progress to explore novel catalysis of noble metals as well as early transition metals embedded in the cubane-type metal sulfur cores. Such reactivities will be elicited from creation of vacant coordination sites (or latent vacancy) around the metal(s) in the cubane-type clusters.

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