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Structures, Bonding, and Reactivity of M−S−M′ (M and M′ = Rh, W, and Cu) Groups in Higher-Nuclearity Heterometallic Sulfide Clusters

Seiji Ogo,[1a] Takayoshi Suzuki,[1a,b] Yoshiki Ozawa,[1c] and Kiyoshi Isobe*,[1d]

Department of Structural Molecular Science, The Graduate University for Advanced Studies, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan, Department of Material Science, Himeji Institute of Technology, Harima Science Park City, Hyogo 678-12, Japan, and Department of Material Science, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

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This paper reports (i) a rational synthesis of heterometallic sulfide clusters with M−S−M′ (M and M′ = Rh, W, and Cu) groups, (ii) structures and bonding of the M−S−M′ groups determined by X-ray crystallographic analysis and IR spectroscopy, and (iii) reactivity of the M−S−M′ groups unique to higher-nuclearity heterometallic sulfide clusters toward H_2O and H_2S. A branched-type octanuclear sulfide cluster $[\{Cp^*RhP(OEt)_3(\mu\text{-}WS_4)(CuCl)Cu\}_2(\mu\text{-}Cl)_2]$ (**4**, Cp* = η^5-C_5Me_5) was stepwise prepared from the following sequence: $[Cp^*RhP(OEt)_3Cl_2]$ (**1**, mononuclear) → $[Cp^*RhP(OEt)_3WS_4]$ (**2**, dinuclear) → $[Cp^*RhP(OEt)_3(\mu\text{-}WS_4)CuCl]$ (**3**, linear-type trinuclear) → **4** by a systematic building-block method. A bridging sulfide ligand in the W−S−Cu group of **4** reacts with a water-saturated CH_2Cl_2 solution to convert the terminal O atom of $[\{Cp^*RhP(OEt)_3(\mu\text{-}WOS_3)(CuCl)Cu\}_2(\mu\text{-}Cl)_2]$ (**5**, linked incomplete cubane-type octanuclear) with a drastic structural change in the cluster framework. The transformation reaction of **4** to **5** includes the first example of the conversion of the bridging S atom in the M−S−M′ group into the terminal O atom without releasing the metal atoms, and this reaction is peculiar to the higher-nuclearity heterometallic sulfide cluster **4**. Clusters **4**, **5**, and **6** ($[Cp^*RhP(OEt)_3(\mu\text{-}WOS_3)CuCl]$, butterfly-type trinuclear) react with H_2S in CH_2Cl_2 giving **3** as a major product. The formation of **3** in these reactions are based on the reactivity of M−S−Cu groups in the sulfide clusters toward H_2S: the (μ_3-S)−Cu bonds are easily broken by H_2S, but not the (μ_2-S)−Cu ones. The crystal data for **1**, **2**, **3**, **4**, **5**, and **6** confirmed by X-ray analysis are as follows. **1**: $C_{16}H_{30}Cl_2O_3PRh$, orthorhombic, $P2_1cn$, $a = 8.988(3)$ Å, $b = 28.591(5)$ Å, $c = 8.276(3)$ Å, $Z = 4$. **2**: $C_{16}H_{30}O_3PRhS_4W$, monoclinic, $P2_1/n$, $a = 14.633(2)$ Å, $b = 15.191(2)$ Å, $c = 11.490(1)$ Å, $\beta = 104.97(1)°$, $Z = 4$. **3**: $C_{16}H_{30}ClCuO_3PRhS_4W$, monoclinic, $P2_1/m$, $a = 10.221(2)$ Å, $b = 11.943(2)$ Å, $c = 10.809(1)$ Å, $\beta = 94.40(1)°$, $Z = 2$. **4**: $C_{32}H_{60}Cl_4Cu_4O_6P_2Rh_2S_8W_2$, monoclinic, $P2_1/n$, $a = 10.170(3)$ Å, $b = 14.495(3)$ Å, $c = 19.411(3)$ Å, $\beta = 104.42(1)°$, $Z = 2$. **5**·2DMF: $C_{38}H_{74}Cl_4Cu_4N_2O_{10}P_2Rh_2S_6W_2$, monoclinic, $P2_1/c$, $a = 10.011(3)$ Å, $b = 17.115(3)$ Å, $c = 18.678(3)$ Å, $\beta = 95.10(2)°$, $Z = 2$. **6**: $C_{16}H_{30}ClCuO_4PRhS_3W$, orthorhombic, $P2_1nb$, $a = 14.515(2)$ Å, $b = 17.225(3)$ Å, $c = 10.261(3)$ Å, $Z = 4$.

Introduction

The reactivity of bridging sulfide ligands linking transition metal atoms toward water, hydrogen sulfide, and atmospheric oxygen have been extensively studied,[2] so as to elucidate the mode of action of these bridging sulfide ligands in the biological systems (e.g. Fe−S−Mo systems in the active site of nitrogenase enzymes[3] and Mo−S−Cu systems that are known as the Mo−Cu antagonism for ruminant animals[4]) and in the industrially catalytic processes (e.g. Rh−S−Mo systems in hydrodesulfurization (HDS) catalysts[5]). The great majority of these studies have been carried out with sulfide ligands linking homometal atoms (represented by M−S−M groups; M = Mo[2]) of dinuclear complexes, while few have utilized sulfide ligands linking heterometal atoms (M−S−M′ groups; M = Mo,[6] and W,[7] M′ = Fe,[6] Rh,[7] and Cu[7]) of heterometallic sulfide clusters, because it is difficult to construct systematically the M−S−M′ frameworks in such sulfide clusters.[8] The reason thiotungstate ($[WS_4]^{2-}$) is used for preparation of the heterometallic sulfide clusters in this study is that the WS_4 unit is much more useful to construct rigid higher-nuclearity cluster frameworks than the MoS_4 unit.[9]

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* To whom all correspondence should be addressed.

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(1) (a) The Graduate University for Advanced Studies, Institute for Molecular Science. (b) Present address: Department of Chemistry, Faculty of Science, Osaka University, Toyonaka 560, Japan. (c) Himeji Institute of Technology. (d) Osaka City University.

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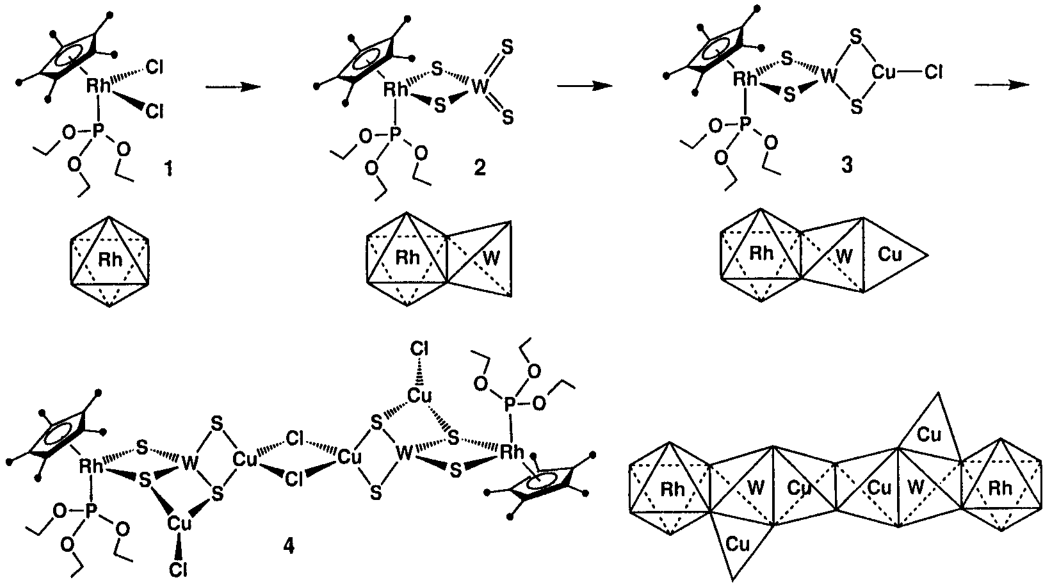
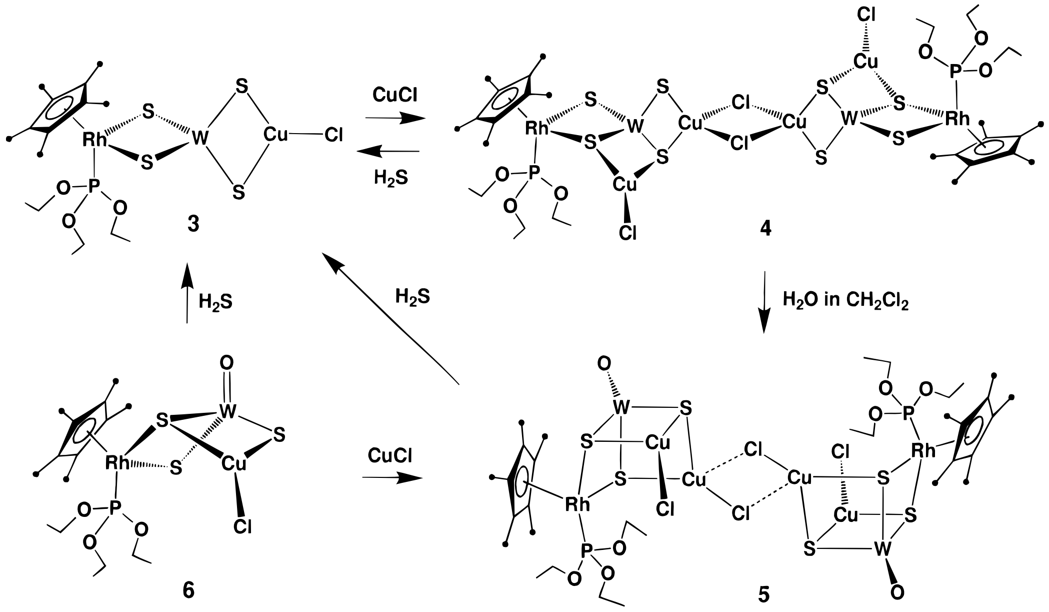
Scheme 1



Scheme 2



Recently, in our preliminary communications,[7] we reported a rationally stepwise synthesis of the heterometallic sulfide clusters with the M−S−M′ (M and M′ = Rh, W, and Cu) groups: [Cp*RhP(OEt)$_3$Cl$_2$] (**1**, mononuclear, Cp* = η^5-C$_5$Me$_5$)) → [Cp*RhP(OEt)$_3$WS$_4$] (**2**, dinuclear) → [Cp*RhP(OEt)$_3$(μ-WS$_4$)CuCl] (**3**, linear-type trinuclear) → [{Cp*RhP(OEt)$_3$(μ-WS$_4$)(CuCl)Cu}$_2$(μ-Cl)$_2$] (**4**, branched-type octanuclear) (Scheme 1) and a unique three-step cyclic reaction of **3**. In this paper, we will describe (i) the full account of the construction of the M−S−M′ framework in the higher-nuclearity heterometallic sulfide clusters, (ii) the structural and bonding study of the M−S−M′ groups of such sulfide clusters whose structures were unequivocally determined by X-ray analysis, and (iii) the scope of the reactivity elucidation of the M−S−M′ groups toward H_2O and H_2S by extending the sulfide compounds to **2**, **3**, **4**, **5**, and **6** ([Cp*RhP(OEt)$_3$(μ-WOS$_3$)CuCl], butterfly-type trinuclear) (Scheme 2).

Results and Discussion

Synthesis of Heterometallic Sulfide Clusters. The studies of organometallic tetrathiometalate complexes by Rauchfuss[5a,10] stimulated much interest in using the organometallic groups for synthesis of sulfide clusters. An organorhodium group, Cp*RhP(OEt)$_3$, in which the Rh atom has an octahedral coordination geometry with two vacant sites, appears to be a useful terminal building-block for the rational synthesis of several heterometallic sulfide clusters with the M−S−M′ groups.[7,8a] The reasons the organorhodium group is so important to construct such sulfide clusters are as follows: (i) The Cp*RhP(OEt)$_3$ group prevents the products from polymerizing and controls an expansion direction of the cluster frameworks by acting as the terminal building-block. (ii) The organorhodium group enables the clusters to be soluble in common organic solvents by hydrophobic Cp* and P(OEt)$_3$ groups.

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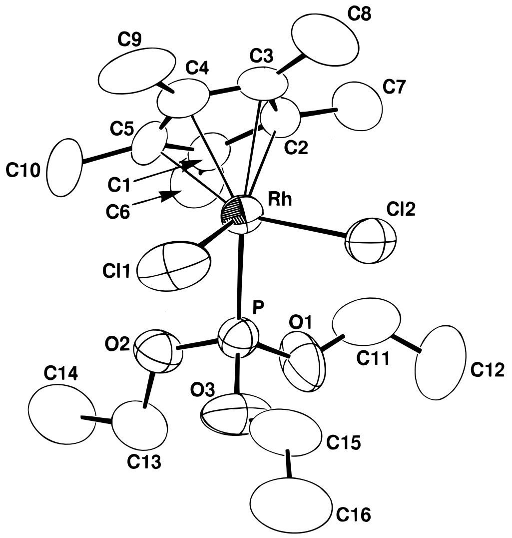

Figure 1. ORTEP drawing of [Cp*RhP(OEt)$_3$Cl$_2$] (**1**).

[WO$_n$S$_{4-n}$]$^{2-}$ ($n = 0$ or 1) and CuCl are employed as other building-blocks. [WO$_n$S$_{4-n}$]$^{2-}$ commonly function as polydentate ligands owing to the strong coordination ability of the S atoms.[11] CuCl readily binds to the S atoms of the tetrahedral [WO$_n$S$_{4-n}$]$^{2-}$ ligands with formation of a trigonal planar (μ-S)$_2$CuCl or a tetrahedral (μ-S)$_2$Cu(μ-Cl)$_2$ frame in which the μ-Cl atoms link the [WO$_n$S$_{4-n}$]$^{2-}$ units.[12] Thus, the clusters described in this paper are constructed from three types of building-blocks: tetrahedral [WO$_n$S$_{4-n}$]$^{2-}$ (W^{VI} belongs to early-[13] and 6th-), octahedral Cp*RhP(OEt)$_3$ (Rh^{III} to middle-[13] and 5th-), and trigonal planar or tetrahedral CuCl (Cu^{I} to late-transition[13] metal atoms and 4th-period in the periodic table).

We have obtained the starting material with the terminal building-block, [Cp*RhP(OEt)$_3$Cl$_2$] (**1**), from the reaction of [(Cp*RhCl)$_2$(μ-Cl)$_2$][14] with P(OEt)$_3$. The chloride ligands in complex **1** are readily replaced by S atoms of [WS$_4$]$^{2-}$ to give the neutral dinuclear complex [Cp*RhP(OEt)$_3$WS$_4$] (**2**), quantitatively. The dinuclear complex regiospecifically reacts with CuCl to afford the trinuclear cluster [Cp*RhP(OEt)$_3$(μ-WS$_4$)-CuCl] (**3**) because of the strong coordination ability of the terminal S atoms of the [WS$_4$]$^{2-}$ group (Scheme 1). The trinuclear cluster **3** performs regiospecific CuCl addition at S1 (or S1*) and S2 atoms to form the octanuclear cluster [{Cp*RhP(OEt)$_3$(μ-WS$_4$)(CuCl)Cu}$_2$(μ-Cl)$_2$] (**4**). This regiospecific addition is attributed to the steric demands of the Cp* and P(OEt)$_3$ ligands. Cluster **4**, however, did not react with further CuCl under several conditions, e.g., reflux in dichloromethane or acetonitrile for several hours. Clusters **5** and **6** were also prepared by the similar method by analogously regiospecific CuCl-additions to the [WOS$_3$]$^{2-}$ building-block.

Structure of [Cp*RhP(OEt)$_3$Cl$_2$] (1). The Rh atom has an octahedral coordination geometry (Figure 1) and bonding parameters similar to those of [Cp*RhPMe$_3$Cl$_2$][15] and [Cp*RhPPh$_3$Cl$_2$].[16] The distances between Rh atom and carbons of the Cp* ring of complex **1** in the solid state are not equivalent; the distances of Rh−C3 and Rh−C4 (2.22(1) and 2.21(1) Å, respectively) trans to the P(OEt)$_3$ ligand are longer than those of Rh−C1, Rh−C2, and Rh−C5 (2.16(1), 2.17(1), and 2.14(1) Å, respectively) trans to the Cl ligands. This result indicates that the P(OEt)$_3$ ligand has a greater trans influence than the Cl ligands. Thus, the bond distance of C3−C4 (1.39(2) Å) of the Cp* ring is shorter than those of C2−C3 and C4−C5 (1.43(1) and 1.45(2) Å, respectively).[17]

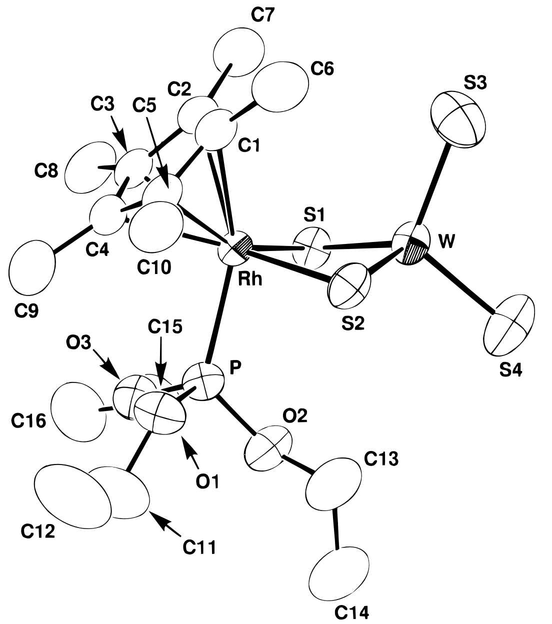

Figure 2. ORTEP drawing of [Cp*RhP(OEt)$_3$WS$_4$] (**2**).

Structure of [Cp*RhP(OEt)$_3$WS$_4$] (2). The molecular structure of the dinuclear sulfide complex **2** determined by X-ray analysis is shown in Figure 2. Rh and W atoms have an octahedral and tetrahedral coordination geometries, respectively. The Rh···W distance, 2.9044(7) Å, is similar to that of the trinuclear sulfide cluster [{Cp*RhCl(μ-S)$_2$}$_2$W] (2.908(2) Å).[10c] The W−S(bridge) bond distances (average 2.249 Å) are considerably longer than the W−S(terminal) ones in **2** (average 2.152 Å) and in [NH$_4$]$_2$[WS$_4$] (average 2.165 Å)[18] with some double bond character.[11,19] A similar framework is found in the dinuclear complex of [(p-cymene)Ru(PPh$_3$)(μ-S)$_2$WS$_2$][5a] in which the W−S(bridge) and the W−S(terminal) bond distances average 2.237 and 2.153 Å, respectively. The infrared spectrum of complex **2**, therefore, exhibits two $\nu_{\mathrm{W-S}}$ bands, one for W−S(bridge) (430 cm^{-1}) and the other for W−S(terminal) (492 cm^{-1}). The Rh−W−S3 angle (111°) of **2** is smaller than the Rh−W−S4 angle (139°) owing to a steric effect of the triethylphosphite group.

Structure of [Cp*RhP(OEt)$_3$(μ-WS$_4$)CuCl] (3). Although there are geometrically several possible isomers for cluster **3** based on the difference in the binding site of CuCl on the WS$_4$ core, the CuCl addition takes place specifically at the terminal S3 and S4 atoms of **2**, but not at S1 (or S2) and S3 (or S4), giving a sole isomer of **3**.

As depicted in Figure 3, the trinuclear sulfide cluster **3** possesses a crystallographic plane of symmetry, and the three

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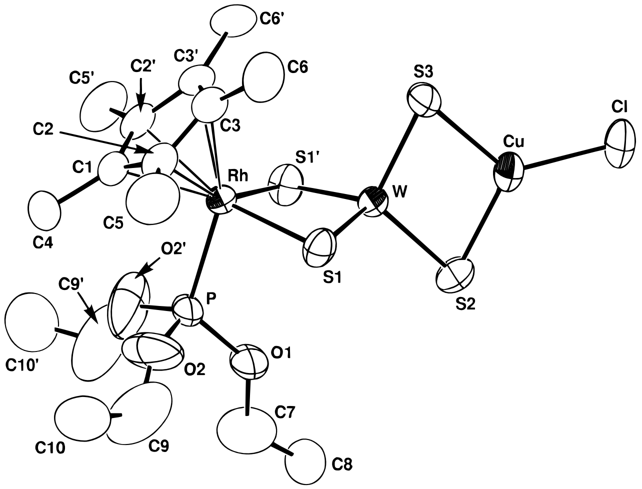

Figure 3. ORTEP drawing of [Cp*RhP(OEt)$_3$(μ-WS$_4$)CuCl] (**3**).

Table 1. Values of Formula Weights, Molecular Weights in Dichloromethane by Vapor Pressure Osmometry, and $\nu_{\mathrm{W-S}}$ (cm^{-1}) in Mineral Oil, Dichloromethane, and Acetonitrile for **3**−**6**

	compound			
	3	**4**	**5**	**6**
fw	815.4	1828.8	1796.7	799.3
mol wt in dichloromethane	805 ± 39	915 ± 30	903 ± 28	810 ± 18
$\nu_{\mathrm{W-S}}$ in mineral oil	466, 446	478, 456, 434	440	460, 444
$\nu_{\mathrm{W-S}}$ in dichloromethane	471, 448	478, 458, 440	442	466, 445
$\nu_{\mathrm{W-S}}$ in acetonitrile	470, 450	470, 450	465, 444	465, 446

metal ions are arranged in an approximately linear fashion (Rh−W−Cu = 166.17(4)°). The S1−W−S1′ bite angle (105.31(7)°) for the octahedral Rh atom is smaller than the S2−W−S3 bite angle (108.4(1)°) for the trigonal planar Cu atom. All of the M−S−M′ groups in **3** have μ_2-S coordination modes. The W−S2(−Cu) and W−S3(−Cu) bond distances in **3** are considerably elongated from the W−S(terminal) ones (average 2.152 Å) in **2**. The IR spectrum of **3** shows two bands at 466 cm^{-1} (W−S2(−Cu) and W−S3(−Cu)) and 446 cm^{-1} (W−S1(−Rh)) which are downshifted and upshifted, respectively, from those of **2** (Table 1). The Cu−S bond distances (average 2.234 Å) of cluster **3** correspond well to those in [{CuCl(μ-S)$_2$}$_2$W] (average 2.237 Å).[20]

The linear-type framework of **3** is preserved in dichloromethane or acetonitrile. Vapor pressure osmometry showed that the value of the molecular weight of **3** in dichloromethane is ca. 805, which corresponds to that of the undissociated molecule (formula weight of **3**: 815.4) (Table 1). The infrared spectrum of **3** measured in dichloromethane showed two $\nu_{\mathrm{w-s}}$ bands at 471 and 448 cm^{-1} and in acetonitrile at 470 and 450 cm^{-1}; these values agree well to those obtained in the solid state (in mineral oil, 466 and 446 cm^{-1}). Furthermore, the ^{1}H NMR spectrum of **3** in CD$_2$Cl$_2$ or CD$_3$CN did not show any temperature dependence.

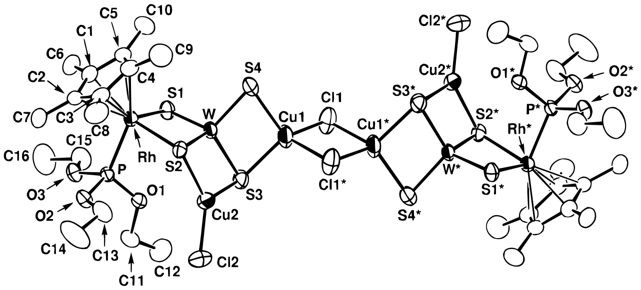

Figure 4. ORTEP drawing of [{Cp*RhP(OEt)$_3$(μ-WS$_4$)(CuCl)Cu}$_2$(μ-Cl)$_2$] (**4**).

Structure of [{Cp*RhP(OEt)$_3$(μ-WS$_4$)(CuCl)Cu}$_2$(μ-Cl)$_2$] (4). Cluster **4** has a branched-type octanuclear framework (Rh−W−Cu1 and Rh−W−Cu2 are 172.43(3) and 90.73(3)°, respectively) with a crystallographic inversion center (Figure 4). The distance Cu1−Cl1* (2.387(3) Å) is almost same as Cu1−Cl1 (2.332(3) Å) in the bridging system, indicating that Cu1 and Cl1* atoms have a bonding interaction to stabilize the octanuclear structure of **4** in the solid state. Cluster **4** has four kinds of bridging S atoms: two of them (S1 and S4) have a μ_2-coordination mode, and other two (S2 and S3) have a μ_3 one. The M−S (M = Rh$^{\mathrm{III}}$, W$^{\mathrm{VI}}$, and Cu$^{\mathrm{I}}$) bond distances are shown in Figure 5. The Rh−S bond distances are not different between Rh−(μ_2-S) and Rh−(μ_3-S) bonding modes, indicating a negligible contribution of the Rh−S π-conjugation by using the lone pairs of the S atoms.

Bernholc and Stiefel reported that the HOMO of the [MoS$_4$]$^{2-}$ ion is mainly composed of the S 3p orbitals, the LUMO contains a great portion of the Mo orbitals, and the interaction of the [MoS$_4$]$^{2-}$ ion with acceptor orbitals would primarily involve the S atoms.[21] In our case, the Cp*RhP(OEt)$_3$ fragment has no π-symmetry acceptor orbitals to interact with S 3p orbitals of the [WS$_4$]$^{2-}$ ion, and therefore σ-symmetry orbitals, but not π-symmetry ones, would be mainly used for the interaction of the [WS$_4$]$^{2-}$ ion with the Cp*RhP(OEt)$_3$ fragment.[22]

In contrast, the W−(μ_3-S) bond distances (W−S2(−Rh, −Cu2) and W−S3(−Cu1, −Cu2) are 2.267(2) and 2.236(2) Å, respectively) are significantly longer than the W−(μ_2-S) ones (W−S1(−Rh) and W−S4(−Cu1) are 2.223(2) and 2.173(2) Å, respectively), suggesting that the W−S bond would be weakened by coordination of the S center to Cu atoms due to a π-conjugation of the W−S−Cu groups like that of the allyl cation.[10b,23] The Cu1 atom has a slightly distorted tetrahedral coordination geometry,[24] but the Cu2 atom has a trigonal planar one.[25] Cu−S bond distances in the tetrahedral coordination are longer than these in the trigonal planar coordination. When Cu has a trigonal one, vacant Cu 4p orbitals may be used to form a strong π-conjugation of the W−S−Cu groups.[23]

The observed molecular weight of **4** in dichloromethane is ca. 915, which is half the value of the molecular weight in the solid state (formula weight of **4**: 1828.8) (Table 1). The IR spectrum of **4** in dichloromethane shows three $\nu_{\mathrm{w-s}}$ bands at 478, 458, and 440 cm^{-1} which agree well with the bands at 478, 456, and 434 cm^{-1} in the solid state (in mineral oil). The spectrum of **4** in acetonitrile gives two $\nu_{\mathrm{w-s}}$ bands at 470 and 450 cm^{-1} and corresponds to that of **3** in acetonitrile (Table 1). Thus, the coordination geometry around [μ-WS$_4$]$^{2-}$ of **4** is preserved in dichloromethane, but Cu2Cl2 groups release from [μ-WS$_4$]$^{2-}$ in acetonitrile. Judging from the consequences of both vapor pressure osmometry and infrared spectrometry of **4**, in dichloromethane cluster **4** exists as a tetranuclear complex, [Cp*RhP(OEt)$_3$(μ-WS$_4$)(CuCl)$_2$] cleaved at the crystallographic

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(24) Cu1−S4 = 2.291 Å, Cu1−S3 = 2.299 Å, Cu1−Cl1 = 2.332 Å, and Cu1−Cl1* = 2.387 Å. The distances between Cu1 and a centroid of the S3Cl1Cl1* plane (represented by Cu1−(S3Cl1Cl1*)) is 0.835 Å. Cu1−(S4Cl1Cl1*) = 0.787 Å, Cu1−(S3S4Cl1*) = 0.704 Å, and Cu1−(S3S4Cl1) = 0.735 Å.

(25) The two different geometries around Cu atoms in a discrete molecule are also found in [{MS$_4$(CuCl)$_3$Cu}$_2$(μ-Cl)$_2$]$^{4-}$ (M = W, Mo; see ref 12).

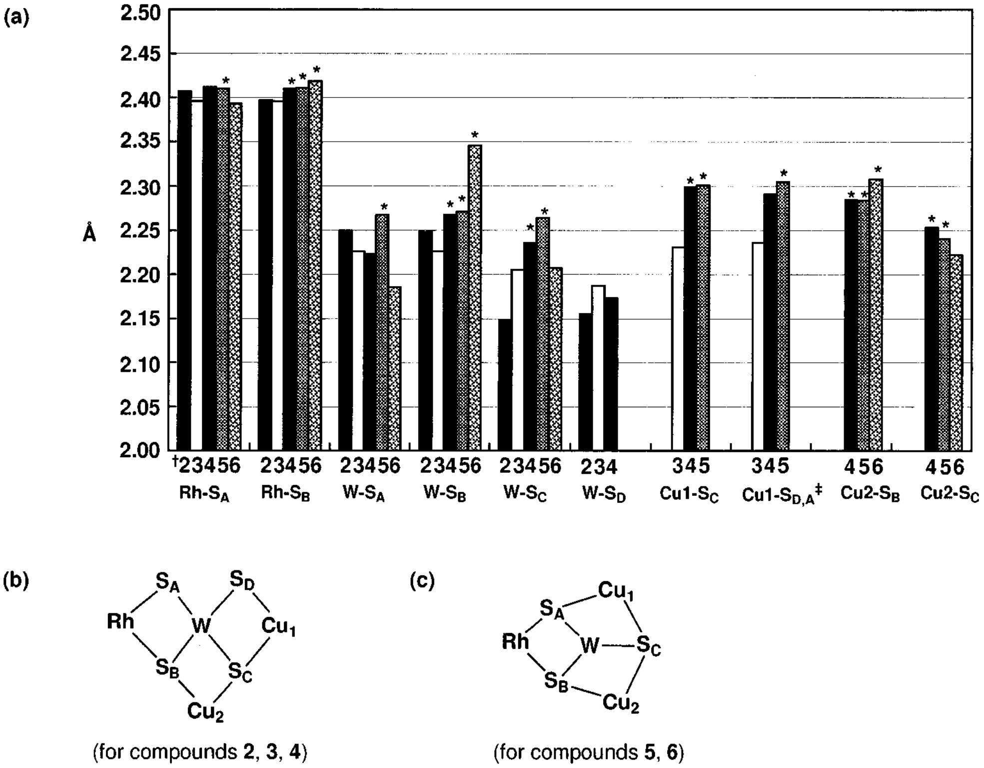

Figure 5. (a) M−S bond distances (Å) of compounds **2**−**6**. *M−(μ_3-S). † The numbering of the compounds. ‡ Cu1−S_D (for **3** and **4**) and Cu1−S_A (for **5**). (b) S_A = S1 (for **2** and **4**), S1* (for **3**); S_B = S1 (for **3**), S2 (for **2** and **4**); S_C = S2 (for **3**), S3 (for **4**), S4 (for **2**); S_D = S3 (for **2** and **3**), S4 (for **4**). (c) S_A = S1 (for **5**), S2 (for **6**); S_B = S1 (for **6**), S2 (for **5**); S_C = S_3 (for **5** and **6**).

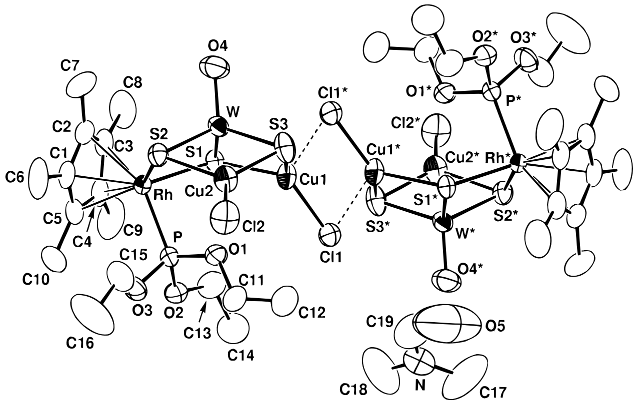

Figure 6. ORTEP drawing of [{Cp*RhP(OEt)$_3$(μ-WOS$_3$)(CuCl)Cu}$_2$(μ-Cl)$_2$]·2DMF (**5**·2DMF).

inversion center. In acetonitrile further dissociation takes place to form **3** and CuCl.

Structure of [{Cp*RhP(OEt)$_3$(μ-WOS$_3$)(CuCl)Cu}$_2$(μ-Cl)$_2$] (5). As depicted in Figure 6 cluster **5** has a linked incomplete cubane-type octanuclear framework in which two incomplete cuboidal subunits, M$_4$(μ_3-S)$_3$ (M = Rh, W, and Cu), are linked by two Cu−(μ_2-Cl)···Cu bridges. Although both Cu1 and Cu2 have a trigonal planar coordination geometry, Cu1 has a weak interaction with the neighboring Cl* atom to reflect a weak dimerization in cluster **5** (the distances of Cu1−Cl1 and Cu1−Cl1* are 2.232(3) and 2.531(3) Å, respectively).[26]

The W atom has a distorted tetrahedral coordination geometry with one W−O bond (1.699(7) Å)[27] and three W−(μ_3-S) bonds (all are approximately the same as one another: average 2.267 Å) reflecting one strong ν_{W-S} band at 440 cm^{-1} in the IR spectrum of **5** in mineral oil (Table 1).

Cluster **5** exists as a tetranuclear complex, [Cp*RhP(OEt)$_3$(μ-WOS$_3$)(CuCl)$_2$], in dichloromethane, but in acetonitrile converts to [Cp*RhP(OEt)$_3$(μ-WOS$_3$)CuCl] (**6**) and CuCl. The IR spectrum of **5** in dichloromethane shows one strong ν_{W-S} band at 442 cm^{-1}, which almost coincides with that in the solid state (440 cm^{-1}). The spectrum of **5** in acetonitrile displays two bands at 465 and 444 cm^{-1}. These values correspond to those (466 and 445 cm^{-1} in acetonitrile) for **6**. The observed molecular weight of **5** in dichloromethane is ca. 903, corresponding to half of the molecular weight of **5** in the solid state (formula weight of **5**: 1796.7) (Table 1).

Structure of [Cp*RhP(OEt)$_3$(μ-WOS$_3$)CuCl] (6). As shown in Figure 7 the trinuclear cluster **6** has a butterfly-type framework,[23a,28] in which the three metal atoms are arranged in a right-angled fashion (Rh−W−Cu = 91.87°) and the S1 atom has a μ_3-coordination mode. The W−O bond distance (1.72(1) Å) is in the normal double bond distance range.[12c]

The butterfly-type framework of **6** is preserved in dichloromethane and acetonitrile. The IR spectrum of cluster **6** measured in dichloromethane shows two ν_{W-S} bands at 466 and 445 cm^{-1} and in acetonitrile at 465 and 446 cm^{-1}; these values agree well with those obtained in the solid state (in mineral oil) at 460 and 444 cm^{-1} (Table 1). Vapor pressure osmometry shows that the value of the molecular weight of **6** in dichloromethane is ca. 810, indicating the undissociation (formula weight of **6**: 799.3) (Table 1).

Dimerization Ability. In dichloromethane clusters **4** and **5** exist as the tetranuclear clusters [Cp*RhP(OEt)$_3$(μ-WS$_4$)(CuCl)$_2$] and [Cp*RhP(OEt)$_3$(μ-WOS$_3$)(CuCl)$_2$], respectively, which dimerize to octanuclear in the solid state. In contrast, clusters **3** and **6** exist as the trinuclear forms both in dichloromethane

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(26) The distance between Cu1 and a centroid of the S1S3Cl1 plane (represented by Cu1−(S1S3Cl1)) is 0.323(1) Å. Cu2−(S2S3Cl2) is 0.092(2) Å.

(27) The W−O bond distance is in the normal double bond distance range (see ref 12c).

(28) Zhu, N.; Du, S.; Chen, P.; Wu, X.; Lu, J. *J. Coord. Chem.* **1992**, *26*, 35.

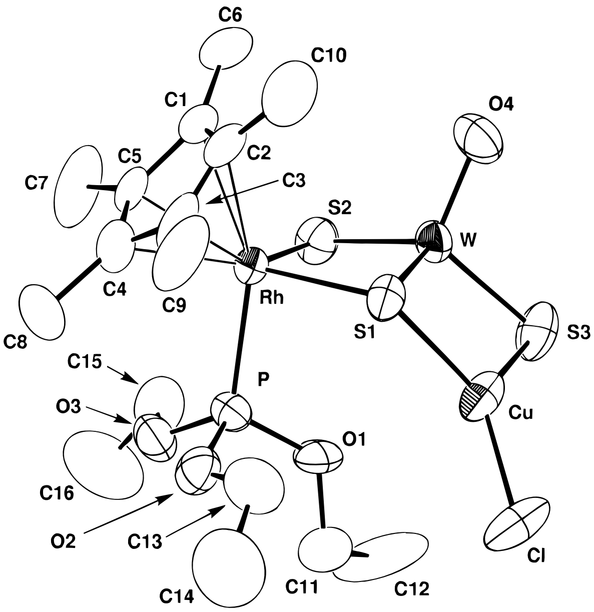

Figure 7. ORTEP drawing of $[Cp^*RhP(OEt)_3(\mu\text{-}WOS_3)CuCl]$ (**6**).

and in the solid state. These differences in the dimerization ability may depend on the amount of the positive charges on the Cu atoms. The binding energy of Cu $2p_{3/2}$ for X-ray photoelectron spectra of the dimeric **4**, $[Cp^*RhP(OEt)_3(\mu\text{-}WS_4)(CuCl)_2]_2$, displays Cu atoms having a slightly higher positive charge (932.6(1) eV) than that of cluster **3** (932.3(1) eV, Table 2) even though the Cu atoms in the dimeric **4** bind to the bridging negative Cl ligands to construct the $(\mu\text{-}S)_2Cu(\mu\text{-}Cl)_2$ frame. Thus, it is reasonable to suppose that the monomeric **4** with the $(\mu\text{-}S)_2CuCl$ frame has much higher positive charged Cu atoms to bind the Cl ligands in the other monomeric form, to afford the dimeric **4**.

The X-ray crystallographic analysis indicates that the further association of cluster **4** does not take place at the Cu2Cl2 (or Cu2*Cl2*) group owing to the increasing steric hindrance of the $P(OEt)_3$ groups on the dimerization. Similarly, in cluster **5** the steric hindrance of the $P(OEt)_3$ groups prevents the Cu1 and Cu2 atoms from having a tetrahedral coordination geometry, reflecting the weak interaction between Cu1Cl1 and Cu1*Cl1* groups in cluster **5**.

Reactivity toward Water. The branched-type sulfide cluster **4** reacts with a water-saturated dichloromethane solution at room temperature for 60 days to give incomplete cubane-type sulfide cluster **5** in a 51% yield (eq 1, Scheme 2). This transformation

$$[\{Cp^*RhP(OEt)_3(\mu\text{-}WS_4)(CuCl)Cu\}_2(\mu\text{-}Cl)_2] + 2H_2O \rightarrow [\{Cp^*RhP(OEt)_3(\mu\text{-}WOS_3)(CuCl)Cu\}_2(\mu\text{-}Cl)_2] + 4H^+ + 2S^{2-} \quad (1)$$

reaction of **4** to **5** is peculiar to the higher-nuclearity (tetranuclear in CH_2Cl_2) heterometallic sulfide cluster **4**, but not to the dinuclear sulfide complex **2** and the trinuclear sulfide cluster **3** under similar conditions. The reaction includes the first example of the conversion of the bridging sulfide ligand in the W−S−Cu groups into the terminal oxide ligand without releasing the Cu atoms.[6] As the reaction proceeds, the amount of H_2O in the reaction system decreases, which was confirmed by ^1H NMR, but H_2S was not detected by ^1H NMR or by an H_2S gas detector tube.

The use of the water-saturated dichloromethane solution is essential. If the content of water in the reaction system is increased, the decomposition reaction of cluster **4** takes place, vide infra. The several attempts to obtain **5** from **4** by using two-phase conditions (water and dichloromethane), aqueous acetonitrile solution, and basic conditions in common solvents were not successful. Under two-phase conditions (water: dichloromethane = 1:1) the reaction of **4** with vigorous stirring at room temperature rapidly gave ^1H NMR signals due to **3** (ca. 50% for 48 h, calculated by ^1H NMR based on the signal intensity of Cp*), **6** (ca. 28%), **1** (ca. 9%), and uncharacterized products.

A tentative mechanism of the transformation reaction (**4** → **5**) is shown in Scheme 3.[29] The water molecules in the water-saturated dichloromethane solution interact with the W and S4 atoms of **4** to give an intermediary species that has W−O−H and Cu−S4−H groups, and then it is transformed to **5**. X-ray results of **4** and **5** indicate that the S4 atom is replaced with the O atom, specifically. The reasons the H_2O molecule specifically interacts with the S4 atom of the four S atoms in the $[\mu\text{-}WS_4]^{2-}$ group in cluster **4** are as follows. (i) The steric hindrance due to the presence of the bulky Cp* and $P(OEt)_3$ ligands prevents the interaction of water at S1 and S3 atoms. (ii) The μ_2-S4 atom has much enough electrons to easily interact with the H_2O molecule compared with the μ_3-S3 atom; i.e., the lone pairs of electrons on bridging sulfide ligands might be influencing the reactivity observed.

It was confirmed that the W atoms of cluster **4** have higher positive charge than those of **2** and **3** by the measurements of binding energies of W $4f_{7/2}$ for the X-ray photoelectron spectra of **2** (33.5(1) eV), **3** (33.3(1) eV), and **4** (33.8(1) eV, Table 2). Hence the W atoms of cluster **4** can readily attract the OH^- group of water molecules. The differences in the reactivity of the W−S(−Cu) groups of **2**, **3**, and **4** toward water seem to be dependent on the charge densities of W atoms.

Reactivity toward Hydrogen Sulfide. Cluster **5** reacts with H_2S in dichloromethane at room temperature giving **3** and Cu_2S[30] immediately (Scheme 2). This reaction is based on a unique reactivity of the W−S−Cu groups in the cluster toward excess H_2S, that is, the Cu-(μ_3-S) bonds are easily broken by H_2S, but not the Cu-(μ_2-S) one.

$$\tfrac{1}{2}[\{Cp^*RhP(OEt)_3(\mu\text{-}WOS_3)(CuCl)Cu\}_2(\mu\text{-}Cl)_2] + \tfrac{3}{2}H_2S \rightarrow [Cp^*RhP(OEt)_3(\mu\text{-}WS_4)CuCl] + \tfrac{1}{2}Cu_2S + H^+ + Cl^- + H_2O \quad (2)$$

Although we performed the reaction of **4** or **6** with H_2S gas—each reaction also gave **3** and Cu_2S as major products—to elucidate the mechanism of the reaction represented by eq 2, we did not find clearly reaction intermediates and which sulfurization of the W=O or the CuCl groups in **5** is faster. Probably, the CuCl sulfurization to give **6** as an intermediate is much faster than the W=O one to give **4** as shown in a possible mechanism (Scheme 4).

Experimental Section

Materials and Methods. Compounds **1**, **2**, **3**, **5**, and **6** are stable to air, and cluster **4** is slightly moisture-sensitive. All preparative procedures were routinely carried out under an argon atmosphere. Acetone was dried with anhydrous $CaSO_4$ and then distilled. Acetonitrile, dichloromethane, *N*,*N*-dimethylformamide (DMF), and toluene were distilled from calcium hydride. Diethyl ether was distilled from lithium aluminum hydride. Methanol was distilled from magnesium turnings and iodine. The organorhodium complex $[(Cp^*RhCl)_2(\mu\text{-}Cl)_2]$ was prepared by the method described in the literature.[14] The

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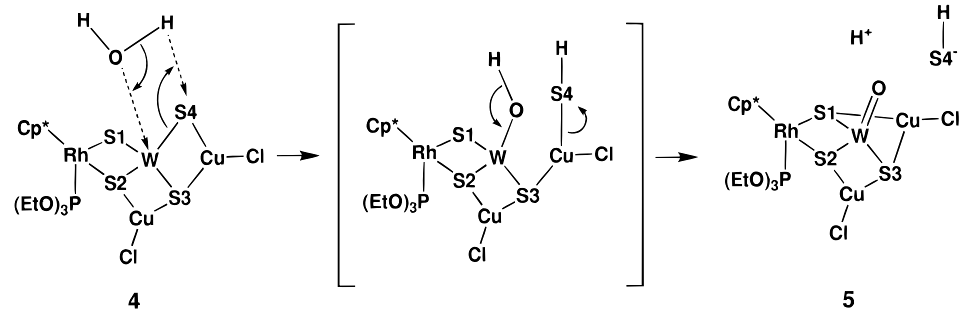
(29) This is referred to the mechanism of the conversion of $[MoS_4]^{2-}$ to $[MoOS_3]^{2-}$ by Harmer and Sykes (see ref 9).

(30) The reaction gives a black precipitate of Cu_2S immediately.

Scheme 3



Scheme 4

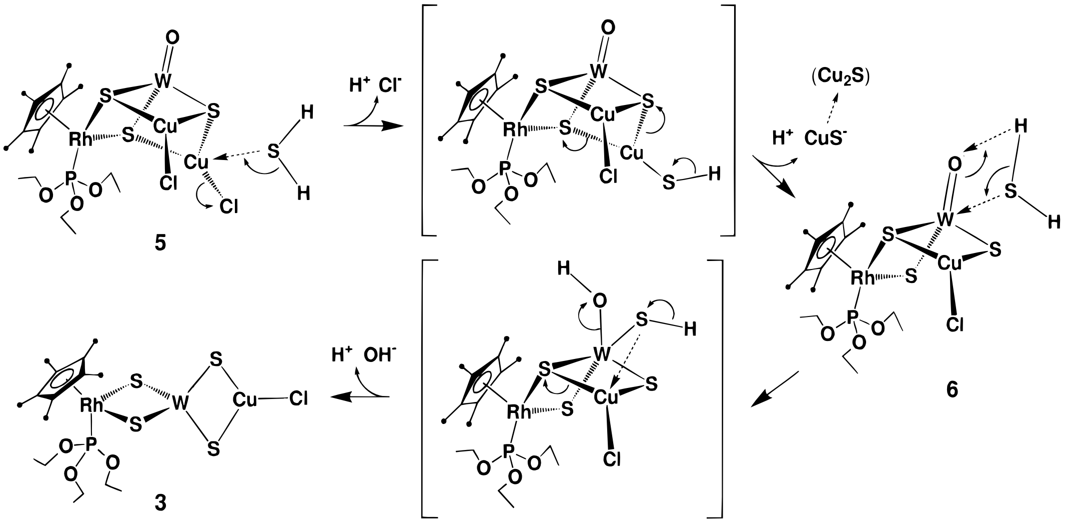


Table 2. Binding Energies (eV) for X-ray Photoelectron Spectra[a]

compound	Rh ($3d_{5/2}$)	W ($4f_{7/2}$)	Cu ($2p_{3/2}$)
[Cp*RhP(OEt)$_3$Cl$_2$] (**1**)	308.8 ± 1		
[Cp*RhP(OEt)$_3$WS$_4$] (**2**)	309.4 ± 1	33.5 ± 1	
[Cp*RhP(OEt)$_3$(μ-WS$_4$)-CuCl] (**3**)	309.1 ± 1	33.3 ± 1	932.3 ± 1
[{Cp*RhP(OEt)$_3$(μ-WS$_4$)-(CuCl)Cu}$_2$(μ-Cl)$_2$] (**4**)	309.7 ± 1	33.8 ± 1	932.6 ± 1

[a] These values are corrected by assuming C 1s binding energy in the compounds as 284.6 eV.

thiometalates [Ph$_4$P]$_2$[WS$_4$] and [NH$_4$]$_2$[WOS$_3$] were prepared by a method similar to that for [PPh$_4$]$_2$[MoS$_4$][31] and by the method described in the literature,[32] respectively. [NH$_4$]$_2$[WS$_4$] and AgPF$_6$ were purchased from Aldrich Chemicals. Triethyl phosphite and copper(I) chloride were purchased from Wako Pure Chemical Industries, Ltd. Hydrogen sulfide gas (99.99%) was purchased from Nippon Sanso Corporation and was used without further purification. Hydrogen sulfide gas detector tube (the lower limit is 0.1 ppm) was purchased from Gastec Corporation.

^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL 270 and 400 MHz spectrometers (JNM-EX 270 and 400) and reported in ppm vs TMS. IR spectra of solid compounds in mineral oil (Merck Paraffin flüssig) were measured on a Hitachi 270-30 IR spectrophotometer in the range 4000−400 cm^{-1}, and those in dichloromethane or acetonitrile were measured by using a KBr cell for liquid on a Perkin-Elmer 1600 series FTIR spectrophotometer in the range 800−400 cm^{-1}. The values of molecular weights of compounds were obtained from the measurement of vapor pressure of the samples by using a Knauer vapor pressure osmometer and calibrated with benzil in dichloromethane. X-ray photoelectron spectra were measured on a VG Scientific ESCALAB MK II electron spectrometer by use of MgKα radiation, and the binding energies were corrected by assuming the C 1s binding energy of the carbon atoms of the ligand in specimens as 284.6 eV.[33]

[Cp*RhP(OEt)$_3$Cl$_2$] (1). To a suspension of [(Cp*RhCl)$_2$(μ-Cl)$_2$] (10.6 g, 17.1 mmol) in toluene (250 cm^3) was added triethyl phosphite (6.08 g, 36.6 mmol) at room temperature, and the mixture was stirred for 2 h giving a deep red solution. On evaporation of the solvent, red crystals of **1** were obtained and dried in vacuo (yield: 98%). Anal. Calcd for C$_{16}$H$_{30}$Cl$_2$O$_3$PRh: C, 40.44; H, 6.36. Found: C, 40.31; H, 6.08. ^{1}H NMR (CDCl$_3$, 23 °C): δ 1.30 (t, $^3J_{H,H}$ = 7.0 Hz, 9H, −CH$_2$C*H*$_3$), 1.66 (d, $^4J_{P,H}$ = 5.2 Hz, 15H, −C*H*$_3$(Cp*)), 4.25 (dq, $^3J_{P,H}$ = 7.0 Hz, $^3J_{H,H}$ = 7.0 Hz, 6H, −C*H*$_2$−).

[Cp*RhP(OEt)$_3$WS$_4$] (2). A methanol solution (50 cm^3) of **1** (2.00 g, 4.21 mmol) was added to a methanol solution (1.2 × 10^3 cm^3) of [PPh$_4$]$_2$[WS$_4$] (4.17 g, 4.21 mmol) at room temperature. The mixture was stirred for 12 h to yield a red precipitate of **2**, which was collected by filtration, washed with methanol (3 × 50 cm^3) and diethyl ether (3 × 20 cm^3), and dried in vacuo. Further crystals of **2** were obtained by evaporating the filtrate to ca. 100 cm^3 below 30 °C (yield: 91%). Anal. Calcd for C$_{16}$H$_{30}$O$_3$PRhS$_4$W: C, 26.83; H, 4.22. Found: C, 26.89; H, 4.04. ^{1}H NMR (CDCl$_3$, 23 °C): δ 1.27 (t, $^3J_{H,H}$ = 7.0 Hz, 9H, −CH$_2$C*H*$_3$), 2.02 (d, $^4J_{P,H}$ = 5.2 Hz, 15H, −C*H*$_3$(Cp*)), 4.04 (dq, $^3J_{P,H}$ = 7.0 Hz, $^3J_{H,H}$ = 7.0 Hz, 6H, −C*H*$_2$−).

[Cp*RhP(OEt)$_3$(μ-WS$_4$)CuCl] (3). Cluster **3** was obtained from a reaction of **2** (1.00 g, 1.40 mmol) and CuCl (0.140 g, 1.40 mmol) in acetonitrile (100 cm^3). After being stirred for 12 h at room temperature, the mixture was concentrated to 30 cm^3 giving red crystals, which were collected by filtration, washed with a small amount of diethyl ether, and dried in vacuo (yield: 91%). Anal. Calcd for C$_{16}$H$_{30}$ClCuO$_3$PRhS$_4$W: C, 23.57; H, 3.71. Found: C, 23.36; H, 3.48. ^{1}H NMR (CD$_2$Cl$_2$, 23 °C): δ 1.33 (t, $^3J_{H,H}$ = 7.0 Hz, 9H, −CH$_2$C*H*$_3$), 2.05 (d, $^4J_{P,H}$ = 5.2 Hz, 15H, −C*H*$_3$(Cp*)), 4.05 (dq, $^3J_{P,H}$ = 7.0 Hz, $^3J_{H,H}$ = 7.0 Hz, 6H, −C*H*$_2$−).

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(31) Hadjikyriacou, A. I. and Coucouvanis, D. *Inorg. Synth.* **1990**, *27*, 39.
(32) McDonald, J. W.; Friesen, G. D.; Rosenhein, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, *72*, 205.
(33) Mullenberg, G. E., Ed. *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, **1979**.

Table 3. Crystal Data for Clusters **1**−**6**

	compound					
	1	**2**	**3**	**4**	**5**·(DMF)$_2$	**6**
chem formula	$C_{16}H_{30}Cl_2O_3PRh$	$C_{16}H_{30}O_3PRhS_4W$	$C_{16}H_{30}ClCuO_3PRhS_4W$	$C_{32}H_{60}Cl_4Cu_4O_6P_2Rh_2S_8W_2$	$C_{38}H_{74}Cl_4Cu_4N_2O_{10}P_2Rh_2S_6W_2$	$C_{16}H_{30}ClCuO_4PRhS_3W$
fw	475.20	716.41	815.40	1828.81	1942.86	799.34
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1cn$ (No. 33)	$P2_1/n$ (No. 14)	$P2_1/m$ (No. 11)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1nb$ (No. 33)
a/Å	8.988(3)	14.633(2)	10.221(2)	10.170(3)	10.011(3)	14.515(2)
b/Å	28.591(5)	15.191(2)	11.943(2)	14.495(3)	17.115(3)	17.225(3)
c/Å	8.276(3)	11.490(1)	10.809(1)	19.411(3)	18.678(3)	10.261(3)
β/deg	90	104.97(1)	94.40(1)	104.42(1)	95.10(2)	90
V/Å^3	2127(1)	2467.3(5)	1315.6(3)	2771.5(8)	3188(1)	2565.4(7)
Z	4	4	2	2	2	4
radiation (Mo Kα) Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
temp/°C	23	23	23	23	23	23
D_x/g cm^{-3}	1.484	1.929	2.058	2.192	2.024	2.069
D_m/g cm^{-3}	*e*	1.863^f	2.015	2.239^f	1.943^f	2.032
μ(Mo Kα)/cm^{-1}	11.4	58.2	62.8	67.5	58.5	63.6
no. of indep reflcns used for calculation^a	1952	4407	3168	5504	5670	3325
R^b	0.049	0.040	0.045	0.043	0.047	0.054
$R_w{}^c$	0.053	0.053	0.052	0.043	0.051	0.061
S^d	1.305	1.160	1.925	1.418	1.607	2.389

[a] $2\theta \le 60$, $|F_o| > 3\sigma(|F_o|)$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$. [d] $S = (\Sigma w(|F_o| - |F_c|)^2)^{1/2}/(n_{data} - n_{par})$. [e] It can not be determined because the crystal of **1** is highly soluble in common solvents used for the measurements. [f] Crystals **2**, **4**, and **5** were slightly soluble in the mixture of the liquids.

[{Cp*RhP(OEt)$_3$(μ-WS$_4$)(CuCl)Cu}$_2$(μ-Cl)$_2$] (4). A reaction of cluster **3** (0.20 g, 0.25 mmol) with CuCl (0.025 g, 0.25 mmol) in acetonitrile (20 cm^3) at room temperature gave immediately a precipitate of **4**, which was recrystallized from DMF/diethyl ether to give red crystals (yield: 97%). Anal. Calcd for $C_{32}H_{60}Cl_4Cu_4O_6P_2Rh_2S_8W_2$: C, 21.02; H, 3.31. Found: C, 20.76; H, 3.10. ^{1}H NMR (CD_2Cl_2, 23 °C): δ 1.34 (t, $^3J_{H,H} = 7.0$ Hz, 18H, $-CH_2CH_3$), 2.09 (d, $^4J_{P,H} = 5.2$ Hz, 30H, $-CH_3$(Cp*)), 4.02 (dq, $^3J_{P,H} = 7.0$ Hz, $^3J_{H,H} = 7.0$ Hz, 12H, $-CH_2-$).

[{Cp*RhP(OEt)$_3$(μ-WOS$_3$)(CuCl)Cu}$_2$(μ-Cl)$_2$] (5). Cluster **4** (1.00 g, 0.55 mmol) slowly reacted with the water-saturated dichloromethane solution (0.12 mol dm^{-3})[34] at room temperature giving **5**. After 60 days the solvent was removed to give a mixture of **4** and **5**. The desired cluster **5** is soluble in chloroform but **4** is not. Thus, the difference in the solubility for chloroform enables to separate cluster **5** from the mixture. Cluster **5** was recrystallized from acetonitrile (yield: 51%). Cluster **5** was also prepared from a reaction of cluster **6** with an equimolar amount of CuCl in acetonitrile at room temperature (yield: 95%). [{Cp*RhP(OEt)$_3$(μ-WOS$_3$)(CuCl)Cu}$_2$(μ-Cl)$_2$]·2CH$_3$CN was subjected to elemental analysis and NMR measurements. Anal. Calcd for $C_{36}H_{66}Cl_4Cu_4N_2O_8P_2Rh_2S_6W_2$: C, 23.02; H, 3.54, N, 1.49. Found: C, 22.65; H, 3.40, N, 1.61. ^{1}H NMR (CD_2Cl_2, 23 °C): δ 1.36 (t, $^3J_{H,H} = 7.0$ Hz, 18H, $-CH_2CH_3$), 2.05 (d, $^4J_{P,H} = 5.2$ Hz, 30H, $-CH_3$(Cp*)), 3.98 (dq, $^3J_{P,H} = 5.8$ Hz, $^3J_{H,H} = 7.0$ Hz, 12H, $-CH_2-$).

[Cp*RhP(OEt)$_3$(μ-WOS$_3$)CuCl] (6). A mixture of **1** (0.68 g, 1.43 mmol) and [NH$_4$]$_2$[WOS$_3$] (0.47 g, 1.43 mmol) in water (25 cm^3) was stirred at room temperature for 12 h to give an orange precipitate. The precipitate was collected by filtration, washed with water (3 × 5 cm^3), and dissolved in acetone (50 cm^3). The solution was dried over Na_2SO_4, and then the solvent was removed to give a red solid which was treated with CuCl (0.14 g, 1.43 mmol) in acetonitrile (50 cm^3). After being stirred for 6 h at room temperature, the mixture was concentrated to 10 cm^3 under reduced pressure giving red crystals of **6**, which were collected by filtration, washed with a small amount of diethyl ether, and dried in vacuo (yield: 80%). Anal. Calcd for $C_{16}H_{30}ClCuO_4PRhS_3W$: C, 24.04; H, 3.78. Found: C, 24.19; H, 4.01. ^{1}H NMR (CD_2Cl_2, 23 °C, TMS): δ 1.29 (t, $^3J_{H,H} = 7.0$ Hz, 9H, $-CH_2CH_3$), 1.98 (d, $^4J_{P,H} = 5.5$ Hz, 15H, $-CH_3$(Cp*)), 3.98 (dq, $^3J_{P,H} = 7.0$ Hz, $^3J_{H,H} = 7.0$ Hz, 6H, $-CH_2-$).

Table 4. Selected Interatomic Distances (l/Å) and Angles (ϕ/deg) for [Cp*RhP(OEt)$_3$Cl$_2$] (**1**)

Rh−Cl1	2.381(3)	Rh−C5	2.14(1)
Rh−Cl2	2.411(4)	P−O1	1.55(1)
Rh−P	2.268(3)	P−O2	1.570(9)
Rh−C1	2.16(1)	P−O3	1.59(1)
Rh−C2	2.17(1)	O1−C11	1.35(2)
Rh−C3	2.22(1)	O2−C13	1.44(2)
Rh−C4	2.21(1)	O3−C15	1.38(3)
Cl1−Rh−Cl2	92.8(2)	Cl2−Rh−P	90.7(1)
Cl1−Rh−P	88.2(1)		

Crystal Structure Determination of 1−**6.** Single crystals used for X-ray analysis were obtained from mixed solvents: acetone/diethyl ether for compound **1**, acetonitrile/diethyl ether for **2**, and DMF/diethyl ether for **3**−**6**. Crystal data and final R values are listed in Table 3. The X-ray intensities were measured at 23 °C using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) on Rigaku AFC-5 (for **1**), AFC-5R (for **3**−**6**), or Enraf-Nonius CAD4 (for **2**) automated four-circle diffractometer. The ω scan technique was employed at a scan rate of 4.0° min^{-1} (for **1**), and the $\omega - 2\theta$ scan technique was employed at scan rates of 1.6−5.0° min^{-1} (for **2**), 6.0° min^{-1} (for **3** and **5**), and 4.0° min^{-1} (for **4** and **6**) in θ. The lattice constants were determined by 25 setting angles in the range $20° < 2\theta < 30°$. The intensities were corrected for Lorentz−polarization factors and absorption corrections were made by the numerical Gauss integration method[35] (for **1**, **3**, and **6**) or by the empirical Ψ scan method[36] (for **2**, **4**, and **5**). The densities of **2**−**6** were measured by using a Kyoto Electronics Manufacturing Co., Ltd. Density/Specific Gravity Meter, Model DA-110, with 1,1,2,2-tetrabromoethane and carbon tetrachloride at 25.2 °C. Crystals **2**, **4**, and **5** were slightly soluble in the mixture of the liquids. The density of **1** cannot be determined because the crystal is highly soluble in common solvents used for the measurements.

All calculations were carried out using Xtal3.2 software[37] on a Fujitsu S-4/IX workstation (for **1**, **3**, **4**, **5**, and **6**) or using the UNICS III computational program[38] on a HITAC M680H computer (for **2**). All non-hydrogen and all hydrogen atoms were refined anisotropically and isotropically (except for **2** in which all hydrogen atoms were refined positionally with fixed isotopic temperature factors), respectively, using

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(34) The water content of dichloromethane was determined by the Karl Fischer method.

(35) Busing, W. R.; Levy, H. A. *Acta Crystallogr.*, **1957**, *10*, 180.

(36) A set of Ψ scans was employed.

(37) Hall, S. R.; Flack, H. D.; Stewart, J. M. Xtal3.2, Program for X-ray crystal structure analysis. Universities of Western Australia, Geneva, & Maryland, 1992.

(38) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyusho Hokoku* **1979**, *55*, 69.

Table 5. Selected Interatomic Distances (l/Å) and Angles (ϕ/deg) for [Cp*RhP(OEt)$_3$WS$_4$] (**2**)

Rh−W	2.9044(7)	W−S4	2.148 (3)
W−S1	2.250 (2)	Rh−S1	2.407 (2)
W−S2	2.248 (2)	Rh−S2	2.397 (2)
W−S3	2.155 (3)	Rh−P	2.253 (2)
W−S1−Rh	77.09 (5)	S1−W−S4	110.37 (9)
W−S2−Rh	77.33 (6)	S2−W−S3	111.22 (9)
S1−Rh−S2	95.52 (7)	S2−W−S4	109.69 (10)
S1−W−S2	104.53 (7)	S3−W−S4	109.91 (13)
S1−W−S3	111.01 (10)		

Table 6. Selected Interatomic Distances (l/Å) and Angles (ϕ/deg) for [Cp*RhP(OEt)$_3$(μ-WS$_4$)CuCl] (**3**)

Rh−W	2.8996(9)	Rh−P	2.248(3)
W−Cu	2.631(1)	Rh−S1	2.396(2)
W−S1	2.226(2)	Cu−Cl	2.151(3)
W−S2	2.205(3)	Cu−S2	2.231(3)
W−S3	2.187(3)	Cu−S3	2.236(3)
Rh−W−Cu	166.17(4)	W−Cu−Cl	177.8(1)
Cu−W−S1	127.34(5)	W−Cu−S2	53.17(8)
Cu−W−S2	54.08(8)	W−Cu−S3	52.66(7)
Cu−W−S3	54.35(8)	Cl−Cu−S2	129.0(1)
S1−W−S2	111.18(6)	Cl−Cu−S3	125.2(1)
S1−W−S3	110.37(7)	S2−Cu−S3	105.8(1)
S1−W−S1′	105.31(7)	W−S1−Rh	77.63(6)
S2−W−S3	108.4(1)	W−S2−Cu	72.8(1)
S1−Rh−S1	95.24(7)	W−S3−Cu	72.99(9)

Table 7. Selected Interatomic Distances (l/Å) and Angles (ϕ/deg) for [{Cp*RhP(OEt)$_3$(μ-WS$_4$)(CuCl)Cu}$_2$(μ-Cl)$_2$] (**4**)

Rh−W	2.9187(8)	W−S3	2.236(2)
W−Cu1	2.686(1)	W−S4	2.173(2)
W−Cu2	2.638(1)	Cu1−Cl1	2.332(3)
Cu1−Cu1*	3.146(2)	Cu1−Cl1*	2.387(3)
Rh−P	2.261(1)	Cu1−S3	2.299(2)
Rh−S1	2.412(2)	Cu1−S4	2.291(3)
Rh−S2	2.410(2)	Cu2−Cl2	2.151(2)
W−S1	2.223(2)	Cu2−S2	2.284(2)
W−S2	2.267(2)	Cu2−S3	2.253(2)
S1−W−S2	106.70(7)	Cl2−Cu2−S3	125.18(9)
S1−W−S3	109.05(7)	S2−Cu2−S3	107.77(7)
S1−W−S4	112.69(8)	W−S1−Rh	77.93(6)
S2−W−S3	108.96(7)	W−S2−Rh	77.15(6)
S2−W−S4	109.65(7)	W−S2−Cu2	70.85(6)
S3−W−S4	109.69(8)	Rh−S2−Cu2	114.95(8)
S1−Rh−S2	96.67(7)	W−S3−Cu1	72.63(6)
Cl1−Cu1−S3	113.42(9)	W−S3−Cu2	71.98(7)
Cl1−Cu1−S4	113.95(9)	Cu1−S3−Cu2	112.38(9)
S3−Cu1−S4	103.49(8)	W−S4−Cu1	73.95(6)
Cl2−Cu2−S2	127.05(9)		

Table 8. Selected Interatomic Distances (l/Å) and Angles (ϕ/deg) for [{Cp*RhP(OEt)$_3$(μ-WOS$_3$)(CuCl)Cu}$_2$(μ-Cl)$_2$]·2DMF (**5**·2DMF)

Rh−W	2.9241(9)	W−S3	2.264(3)
W−Cu2	2.656(1)	W−O4	1.699(7)
W−Cu1	2.676(1)	Cu1−Cl1	2.232(3)
Cu1−Cu1*	3.227(2)	Cu1−Cl1*	2.531(3)
Rh−P	2.270(2)	Cu1−S1	2.305(3)
Rh−S1	2.410(2)	Cu1−S3	2.301(3)
Rh−S2	2.411(2)	Cu2−Cl2	2.152(3)
W−S1	2.267(2)	Cu2−S2	2.283(3)
W−S2	2.271(2)	Cu2−S3	2.240(3)
S1−W−S2	106.40(8)	S2−Cu2−Cl2	120.7(1)
S1−W−S3	109.2(1)	S3−Cu2−Cl2	130.5(1)
S1−W−O4	111.8(2)	W−S1−Rh	77.33(7)
S2−W−S3	107.92(9)	W−S1−Cu1	71.64(7)
S2−W−O4	110.4(3)	Rh−S1−Cu1	123.48(9)
S3−W−O4	110.9(3)	W−S2−Rh	77.25(7)
S1−Rh−S2	97.81(8)	W−S2−Cu2	71.35(8)
S1−Cu1−S3	106.6(1)	Rh−S2−Cu2	115.8(1)
S1−Cu1−Cl1	120.0(1)	W−S3−Cu1	71.76(8)
S3−Cu1−Cl1	127.3(1)	W−S3−Cu2	72.27(9)
S2−Cu2−S3	108.3(1)	Cu1−S3−Cu2	110.6(1)

Table 9. Selected Interatomic Distances (l/Å) and Angles (ϕ/deg) for [Cp*RhP(OEt)$_3$(μ-WOS$_3$)CuCl] (**6**)

Rh−W	2.910(1)	Rh−S1	2.419(4)
W−Cu	2.672(2)	Rh−S2	2.393(4)
W−S1	2.346(4)	Rh−P	2.264(4)
W−S2	2.185(4)	Cu−Cl	2.166(6)
W−S3	2.207(4)	Cu−S1	2.308(4)
W−O4	1.72(1)	Cu−S3	2.222(6)
S1−W−S2	105.9(1)	Cl−Cu−S3	127.9(2)
S1−W−S3	107.0(2)	S1−Cu−S3	107.8(2)
S1−W−O4	107.5(5)	W−S1−Rh	75.3(1)
S2−W−S3	112.5(2)	W−S1−Cu	70.1(1)
S2−W−O4	114.2(5)	Rh−S1−Cu	116.2(2)
S3−W−O4	109.4(4)	W−S2−Rh	78.8(1)
S1−Rh−S2	97.5(1)	W−S3−Cu	74.2(2)
Cl−Cu−S1	124.1(2)		

complex neutral atom scattering factors.[39] The structures were solved by the usual heavy-atom method. The space groups of **2**, **4**, and **5** were uniquely determined as $P2_1/n$, $P2_1/n$, and $P2_1/c$, respectively, by the Laue symmetry check and systematic absences, but for the others both centrosymmetric and non-centrosymmetric space groups were possible, i.e., *Pmcn* and $P2_1cn$ for **1**, $P2_1/m$ and $P2_1$ for **3**, and *Pmnb* and $P2_1nb$ for **6**. The structure of **3** was solved reasonably, assuming the centrosymmetric space group, $P2_1/m$. For **1** and **6**, the Patterson functions could be analyzed based on the noncentrosymmetric space groups ($P2_1cn$ for **1** and $P2_1nb$ for **6**), but not on the centrosymmetric ones (*Pmcn* and *Pmnb*, respectively). The structure models of noncentrosymmetric space groups could not be transferred into those of the centrosymmetric ones. When the inverted structural model of **1** was assumed, the R factor did not alter significantly; therefore, the polar direction of the a axis could not be assigned. For **6**, however, the polar direction of the a axis could be determined by Hamilton's R factor test.[40] The reporting structure model converged to $R = 0.054$ and the inverted structure model to $R' = 0.071$ for 3325 reflections and 372 parameters. The ratio of $R'/R = 1.31$ is much larger than the Hamilton criteria.[41]

Selected interatomic distances and angles for compounds **1**−**6** are listed in Tables 4−9, respectively. The atomic parameters of compounds **1**−**6** are given in Supporting Information.

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Supporting Information Available: Conditions of measurements and descriptions of X-ray analysis including tables of experimental and refinement conditions, atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations for compounds **1**, **2**, **3**, **4**, **5**, and **6** and a figure showing CpRhP fragment orbitals (43 pages). Ordering information is given on any current masthead page.

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(41) $\boldsymbol{R}_{1,2953,0.005} < \boldsymbol{R}_{1,120,0.005} = 1.034$.