A Unique Three-Step Cyclic Reaction Sequence of Heterotrimetallic Sulfide Clusters. Structures and Properties of $[\{Cp^*RhP(OEt)_3(\mu\text{-}WS_4)(CuCl)Cu\}_2(\mu\text{-}Cl)_2]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with a Branched Structure and $[\{Cp^*RhP(OEt)_3(\mu\text{-}WOS_3)(CuCl)Cu\}_2(\mu\text{-}Cl)_2]$ with a Linked Incomplete Cubane-Type Structure

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The chemistry of heterometallic sulfide clusters has been developed rapidly in recent years because of interest in their geometrical structures,[1] notably their relevance to the core structure of nitrogenase[2] and the reactivity of hydrodesulfurization (HDS) catalysts.[3] We have found a unique three-step cyclic reaction scheme starting with the linear heterotrimetallic sulfide cluster $[Cp^*RhP(OEt)_3(\mu\text{-}WS_4)CuCl]$ (**1**)[4] wherein significant structural changes occur upon stepwise addition of CuCl, H_2O, and H_2S as transformation agents (Scheme 1). From this reaction we have isolated a branched octanuclear cluster $[\{Cp^*RhP(OEt)_3(\mu\text{-}WS_4)(CuCl)Cu\}_2(\mu\text{-}Cl)_2]$ (**2**) and a linked incomplete cubane-type octanuclear cluster $[\{Cp^*RhP(OEt)_3(\mu\text{-}WOS_3)(CuCl)Cu\}_2(\mu\text{-}Cl)_2]$ (**3**). In the cyclic reaction the conversion of **2** into **3** is particularly interesting, where a ***bridging S*** atom in the $(\mu_2\text{-}S)_2W(\mu_3\text{-}S)_2$ group is changed to a terminal O atom in the $WO(\mu_3\text{-}S)_3$ group by ***the water saturated in dichloromethane***. Here, we describe the reactions, structures and properties of clusters **2** and **3**.

A reaction of trinuclear cluster **1** with an equimolar amount of CuCl in acetonitrile at room temperature gave immediately a precipitate of $[\{Cp^*RhP(OEt)_3(\mu\text{-}WS_4)(CuCl)Cu\}_2(\mu\text{-}Cl)_2]$ (**2**),[5] which was recrystallized from DMF/diethyl ether (DMF = *N,N*-dimethylformamide) to give red crystals. The molecular structure of **2** was determined by a single-crystal X-ray diffraction method.[6] Cluster **2** has an octanuclear framework with a crystallographic inversion center. Rh···W···Cu1 is almost linear (172.43(3)°) and Rh···W···Cu2 is an approximately right angle (90.73(3)°), and hence the eight metals are arranged in a branched configuration. The Rh and W atoms are octahedrally and tetrahedrally coordinated, respectively, similarly to those of **1**.[4] The Cu2 atom has a trigonal planar geometry, but the Cu1 atom has a slightly distorted tetrahedral one. The bond lengths of Cu1−Cl1 and Cu1−Cl1* are 2.332(3) and 2.387(3) Å, respectively. The two different coordination geometries around Cu atoms in a discrete molecule are also found in $[\{MS_4(CuCl)_3Cu\}_2(\mu\text{-}Cl)_2]^{4-}$ (M = W,[7] Mo[8]). The X-ray results described above indicate that cluster **1** performs a regiospecific CuCl addition at S1 (or S1*) and S2 atoms to form **2**, but not at other sets of S atoms. This regiospecific addition is attributed mainly to the steric demands of the Cp* and $P(OEt)_3$ ligands.

Analysis of **2** by fast atom bombardment mass spectrometry (FAB MS) produced no molecular ion under the conditions employed, but an isotopic distribution pattern (the most abundant peak: 914) of $C_{16}H_{30}Cl_2Cu_2O_3PRhS_4W$ corresponding to half of the molecular ion of **2** was observed. The observed molecular weight of **2** in dichloromethane is ca. 915, which is also half the value of the molecular weight in the solid state.[9] The infrared spectrum of a dichloromethane solution of **2** shows three ν_{W-S} bands at 478, 456, and 434 cm^{-1}; these values almost coincide with those in the solid state (in mineral oil, 478, 458, and 440 cm^{-1}), which suggests that the coordination geometry around $\mu\text{-}WS_4^{2-}$ of **2** is preserved in dichloromethane. In other words, CuCl groups of **2** do not release from $\mu\text{-}WS_4^{2-}$ in dichloromethane. Therefore, the cleavage in **2** occurs at the chloride bridges, and hence the cluster exists as a tetranuclear complex, $[Cp^*RhP(OEt)_3(\mu\text{-}WS_4)(CuCl)_2]$, in dichloromethane. Dimerization of two tetranuclear species takes place upon crystallization to form **2**. In contrast, dimerization of cluster **1** does not occur even in the solid state; Cluster **1** exists as a trinuclear rather than a hexanuclear cluster. The dimerization of **2** might be caused by the effects of crystal packing.[8] The Cu1−Cl1* distance, however, is almost same as that of Cu1−Cl1, indicating that Cu1 and Cl1* atoms have a bonding interaction to stabilize the octanuclear structure of **2** in the solid state.

Cluster **2** reacted slowly with ***the water saturated in dichloromethane*** (0.12 mol dm^{-3})[10] at room temperature, giving

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[5] Yield: 97% based on the Rh compound. 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. ^1H 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, $-CH_2-$).

[6] Crystal data for **2**: $C_{32}H_{60}Cl_4Cu_4O_6P_2Rh_2S_8W_2$, FW = 1828.81; monoclinic, space group $P2_1/n$ (No. 14), $a = 10.170(3)$ Å, $b = 14.495(3)$ Å $c = 19.411(3)$ Å, $\beta = 104.42(1)°$, $V = 2771.5(8)$ Å^3, $D_c = 2.192$ g cm^{-3}, $Z = 2$, μ(Mo Kα) = 67.5 cm^{-1}, and R (R_w) = 0.043 (0.043) for 5504 independent unique reflections ($|F_o| > 3\sigma(|F_o|)$). Crystal data for **3**·2DMF: $C_{38}H_{74}Cl_4Cu_4N_2O_{10}P_2Rh_2S_6W_2$, FW = 1942.86; monoclinic, space group $P2_1/c$ (No. 14), $a = 10.011(3)$ Å, $b = 17.115(3)$ Å, $c = 18.678(3)$ Å, $\beta = 95.10(2)°$, $V = 3188(1)$ Å^3, $D_c = 2.02$ g cm^{-3}, $Z = 2$, μ(Mo Kα) = 58.5 cm^{-1}, and R (R_w) = 0.047(0.051) for 5670 independent unique reflections ($|F_o| > 3\sigma(|F_o|)$).

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[9] The measurements of the molecular weights of **2** and **3** were performed by vapor pressure osmometry in dichloromethane at 35 °C.

[10] The use of the water saturated in dichloromethane is essential at present, because the several attempts to obtain **3** from **2** by using aqueous acetonitrile, two-phase conditions of water and halogenated solvents, and basic conditions in common solvents were not successful, but they gave $[Cp^*RhP(OEt)_3(\mu\text{-}WS_4)CuCl]$ (**1**), $[Cp^*RhP(OEt)_3(\mu\text{-}WOS_3)CuCl]$, and other unidentified products. The water content of dichloromethane was determined by the Karl Fischer method.

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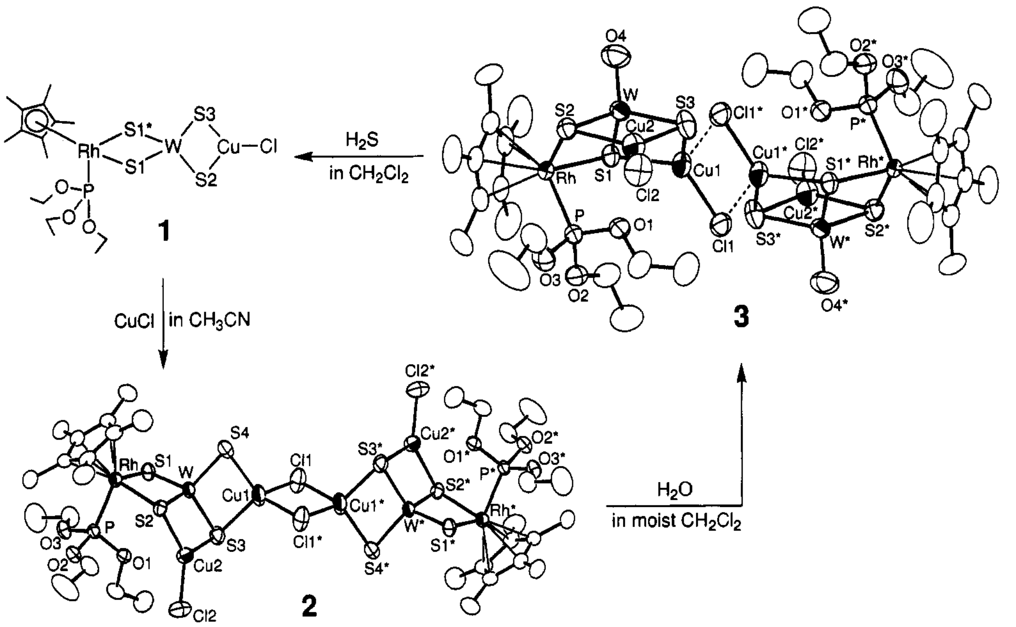
Scheme 1



$[\{Cp^*RhP(OEt)_3(\mu\text{-}WOS_3)(CuCl)Cu\}_2(\mu\text{-}Cl)_2]$ (3)[11] (eq 1).

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

As the reaction proceeds the amount of H_2O in the reaction system decreases. H_2S was not detected by ^1H NMR[12] or by an H_2S gas detector tube.[13] Recrystallization from DMF/diethyl ether gave purple crystals of **3**·2DMF. The molecular structure of **3** was determined by X-ray analysis[6] as shown in Scheme 1. In **3** all metal ions and sulfur atoms form a linked incomplete cubane-type octanuclear framework. The W atom has a distorted tetrahedral coordination geometry with one terminal O and three μ_3-S atoms. The Cu1 and Cu2 have a trigonal planar geometry with two S and one Cl atoms, but Cu1 has a weak interaction with the neighboring Cl* atom; the Cu1–Cl1* distance is 2.531(3) Å (Cu1–Cl1 (2.232(3) Å), however, is in the normal bond distance range). Cluster **3** in dichloromethane exists in a tetranuclear species, $[Cp^*RhP(OEt)_3(\mu\text{-}WOS_3)(CuCl)_2]$, similarly to **2**. The observed molecular weight of **3** in dichloromethane is ca. 903, which corresponds to half of the molecular weight in the solid state.[9] The infrared spectrum of **3** measured in dichloromethane shows one strong ν_{W-S} band at 442 cm^{-1}; this agrees well with that obtained in the solid state (in mineral oil, 440 cm^{-1}).

The characteristic points for the change of **2** into **3** are as follows: first, one ***bridging S*** atom of the $W(\mu_2\text{-}S)_2(\mu_3\text{-}S)_2$ group in **2** is replaced by the oxygen atom from water molecule under mild conditions to give specifically the monosubstituted $W(O)(\mu_3\text{-}S)_3$ group with the terminal O atom in **3**. To our knowledge, this is the first example of the conversion of the bridging S atom into the terminal O atom by water. Second, the transformation results in a significant alteration in the cluster framework, that is, from the branched structure in **2** to the linked incomplete cubane-type structure in **3**. Another interesting point is that the binding abilities of CuCl (Cu1Cl1 for **2** and **3**) group in **1**, **2**, and **3** are ordered in strength as follows. **2** > **3** ≫ **1**.

Cluster **3** was also prepared stepwise from $[Cp^*RhP(OEt)_3Cl_2]$ and $(NH_4)_2[WOS_3]$[14] as follows (eqs 2 and 3).[15]

$$[Cp^*RhP(OEt)_3Cl_2] + (NH_4)_2[WOS_3] \rightarrow [Cp^*RhP(OEt)_3(\mu\text{-}WOS_3)] + 2NH_4Cl \quad (2)$$

$$2\,[Cp^*RhP(OEt)_3(\mu\text{-}WOS_3)] + 4CuCl \rightarrow [\{Cp^*RhP(OEt)_3(\mu\text{-}WOS_3)(CuCl)Cu\}_2(\mu\text{-}Cl)_2] \quad (3)$$

The reaction of **3** with H_2S in dichloromethane proceeded to form cluster **1** at room temperature in 15 min (eq 4).[16]

$$^1/_2[\{Cp^*RhP(OEt)_3(\mu\text{-}WOS_3)(CuCl)Cu\}_2(\mu\text{-}Cl)_2] + {}^3/_2\,H_2S \rightarrow [Cp^*RhP(OEt)_3(\mu\text{-}WS_4)CuCl] + {}^1/_2Cu_2S + H^+ + Cl^- + H_2O \quad (4)$$

This reaction indicates that one of the two CuCl moieties in **3** and the CuCl moiety in **1** are inert toward excess H_2S. Thus the trinuclear cluster of **1** is recycled through the branched cluster of **2** and the linked incomplete cubane-type cluster of **3** by the three-step reaction with CuCl, H_2O, and H_2S agents. Further studies on the reactivities of **1**, **2**, and **3** are in progress.

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Supplementary Material Available: Text giving the 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, together with the ORTEP drawings for **2** and **3**·2DMF (17 pages). Ordering information is given on any current masthead page.

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(11) Yield: 51% for 60 days. $[\{Cp^*RhP(OEt)_3(\mu\text{-}WOS_3)(CuCl)Cu\}_2(\mu\text{-}Cl)_2]\cdot 2CH_3CN$ recrystallized from acetonitrile was used for 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. ^1H 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, $-CH_2-$).

(12) Very small peaks due to $[Cp^*RhP(OEt)_3Cl_2]$[4] and uncharacterized products were observed around the ethyl of $P(OEt)_3$ and the methyl of Cp* regions in the ^1H NMR spectrum.

(13) The detective limit is 0.1 ppm for H_2S gas.

(14) McDonald, J. W.; Friesen, G. D.; Rosenhein, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, *72*, 205.

(15) Yield: 84% based on $[Cp^*RhP(OEt)_3Cl_2]$.

(16) Yield: 91% based on the Rh compound. In this reaction H_2S converts μ-WOS_3 to μ-WS_4 in dichloromethane. The kinetic study of an analogous conversion of $MoO_xS_{4-x}{}^{2-}$ by H_2S in an aqueous solution was reported in detail by Harmer and Sykes: Harmer, M. A.; Sykes, A. G. *Inorg. Chem.* **1980**, *19*, 2881.