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A Heterotrimetallic Sulfide Cluster Having a Linear $Rh^{III}\cdots W^{VI}\cdots Cu^{I}$ Framework of an Octahedral - Tetrahedral - Trigonal Planar Sequence

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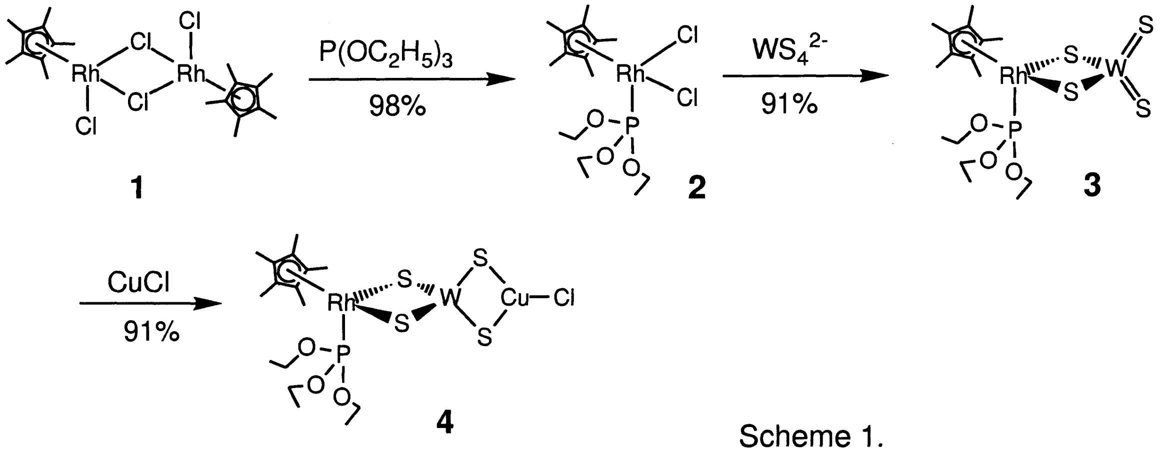
A heterotrimetallic sulfide cluster with an organometallic group, $[Cp^*Rh\{P(OEt)_3\}(\mu\text{-}S)_2W(\mu\text{-}S)_2CuCl]$ ($Cp^*=\eta^5\text{-}C_5Me_5$), was prepared stepwise by using mononuclear units of organorhodium(III), thiotungstate(VI), and chlorocopper(I). X-ray crystal structure analysis revealed that the cluster possesses a linear sequence of middle (Rh), early (W), and late (Cu) transition metal atoms with octahedral, tetrahedral, and trigonal planar coordination geometries, respectively.

Although heterotrimetallic sulfide clusters are expected to have more intriguing structures, reactions, and physicochemical properties owing to synergistic effects of three different metal atoms as compared with heterodimetallic systems, heterotrimetallic sulfide clusters, particularly, the organometallic clusters containing three different metals bridged linearly by sulfur atoms have not been well studied.1) The complex of $[\{(p\text{-cymene})RuCl(\mu\text{-}S)_2W(\mu\text{-}S)_2\}_2Pt]$, which has been synthesized by Rauchfuss's group, may have the linear type heterotrimetallic framework, but has not been characterized structurally.2) As the lack of studies in this field is mainly due to difficulties in synthesis of such sulfide clusters, we are trying to find a controlled synthetic method by introduction of an organometallic group into the cluster framework. Here we report our successful synthesis of a heterotrimetallic sulfide cluster and its structure involving a linear $Rh^{III}\cdots W^{VI}\cdots Cu^{I}$ sequence.

A heterotrimetallic sulfide cluster, $[Cp^*Rh\{P(OEt)_3\}(\mu\text{-}S)_2W(\mu\text{-}S)_2CuCl]$ (**4**), was prepared stepwise



Scheme 1.

from $[(Cp^*RhCl)_2(\mu\text{-}Cl)_2]$(3) (**1**) by the methods as illustrated in Scheme 1. To a suspension of **1** (10.6 g, 17.1 mmol) in toluene (250 cm^3) was added triethylphosphite (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 $[Cp^*Rh\{P(OEt)_3\}Cl_2]$ (**2**) were obtained and dried in vacuo (15.9 g, 98% yield). The monomeric structure of **2** was confirmed by X-ray analysis.(4)

A heterodimetallic sulfide cluster, $[Cp^*Rh\{P(OEt)_3\}(\mu\text{-}S)_2WS_2]$ (**3**), was prepared by addition of a methanol solution (50 cm^3) of **2** (2.00 g, 4.21 mmol) to a methanol solution (1.2×10^3 cm^3) of $(PPh_4)_2WS_4$(5) (4.17 g, 4.21 mmol) at room temperature. The mixture was stirred for 12 h to yield a red precipitate of **3**, 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 **3** were obtained by evaporating the filtrate to ca. 100 cm^3 below 30 °C. Total yield : 2.72 g (91%). The molecular structure of **3** determined by X-ray analysis(6) is shown in Fig. 1. The Rh···W distance, 2.9044(7) Å is similar to that of $[\{Cp^*RhCl(\mu\text{-}S)_2\}_2W]$ (2.908(2) Å).(7) The Rh-S-W angles are av. 77.21°. The W-S(terminal) bond distances (av. 2.152 Å), which are considerably shorter than the W-S(bridge) distances (av. 2.249 Å), correspond to a double bond character. The similar framework is found in the heterodimetallic *p*-cymene ruthenium complex of $[(p\text{-cymene})Ru(PPh_3)(\mu\text{-}S)_2WS_2]$ which has the Ru···W distance of 2.934(1) Å, the W-S(terminal) bond distances (av. 2.153 Å), and the W-S(bridge) distances (av. 2.237 Å).(2) The infrared spectrum of complex **3** exhibits two $\nu_{W\text{-}S}$ bands, one for W-S(bridge) (430 cm^{-1}) and the other for W-S(terminal) (492 cm^{-1}).

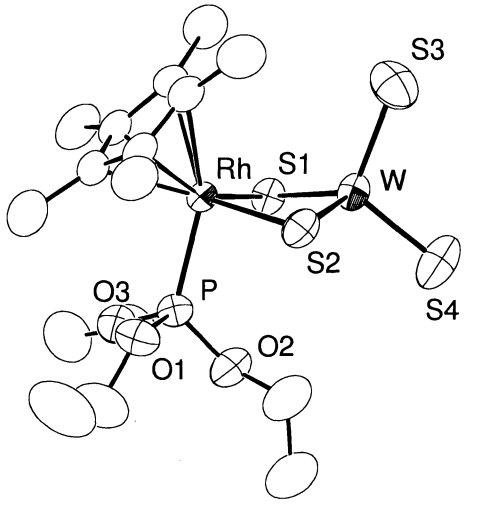


Fig. 1. ORTEP drawing of **3**. Selected bond distances (l / Å) and angles (ϕ / °) : Rh-P=2.253(2), Rh-S1=2.407(2), Rh-S2=2.397(2), W-S1=2.250(2), W-S2=2.248(2), W-S3=2.155(3), W-S4=2.148(3), S1-Rh-S2=95.52(7), Rh-S1-W=77.09(5), Rh-S2-W=77.33(6), S1-W-S2=104.53(7), S1-W-S3=111.01(10), S1-W-S4=110.37(9), S2-W-S3=111.22(9), S2-W-S4=109.69(10), S3-W-S4=109.91(13). The distance of Rh···W is 2.9044(7) Å.

We tried to prepare the heterotrimetallic cluster by using the S atoms of the WS_4^{2-} group in **3** as ligating atoms. The cluster, $[Cp^*Rh\{P(OEt)_3\}(\mu\text{-}S)_2W(\mu\text{-}S)_2CuCl]$ (**4**), was obtained from a reaction of **3** (1.00 g, 1.40 mmol) and CuCl (0.140 g, 1.40 mmol) in acetonitrile (100 cm^3). After stirring 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 (1.04 g, 91% yield). Crystal structure of **4** was also determined by the X-ray method.(8) As depicted in Fig. 2, the cluster possesses a crystallographic plane of symmetry. The Cu atom is chelated by two terminal S atoms of **3** forming a trigonal planar coordination geometry. Hence, the three metal ions are arranged in a linear fashion (Rh···W···Cu=166.17(4)°) and all of S atoms in **4** have a μ_2-coordination mode. The S2-W-S3 angle (108.4(1)°) is larger than S1-W-S1' angle (105.31(7)°). The Cu-S bond distances (av. 2.234 Å) correspond well to those in $[\{CuCl(\mu\text{-}S)_2\}_2W]$ (av. 2.237 Å).(9) The W-S(-Cu) bonds in

4 (av. 2.196 Å) are considerably elongated from the W-S(terminal) bonds in **3**, suggesting that the bonds have a single bond character. The W-S(-Rh) bonds in **4** (2.226(2) Å) are slightly longer than the W-S(-Cu) bonds, suggesting that the rhodium atom has a stronger affinity for the sulfur atoms than does the copper atom. These W-S bonds in **4** are, however, shorter compared to the W-S(bridge) bonds in **3** (av. 2.249 Å). These differences in W-S bonds of **3** and **4** agree with shifts of ν_{W-S} bands in the infrared spectra. The cluster **4** shows two bands at 446 cm^{-1} and 466 cm^{-1}, which are upshifted and downshifted, respectively, from those of **3** as described above. Although the Rh···W distance in **3** (2.9044(7) Å), the Rh···W in **4** (2.8996(9) Å) and the W···Cu in **4** (2.631(1) Å) are relatively short, the X-ray photoelectron spectra10) of **2**, **3**, and **4** suggest that there is not so strong interaction between W and Rh or W and Cu as to change their oxidation states.

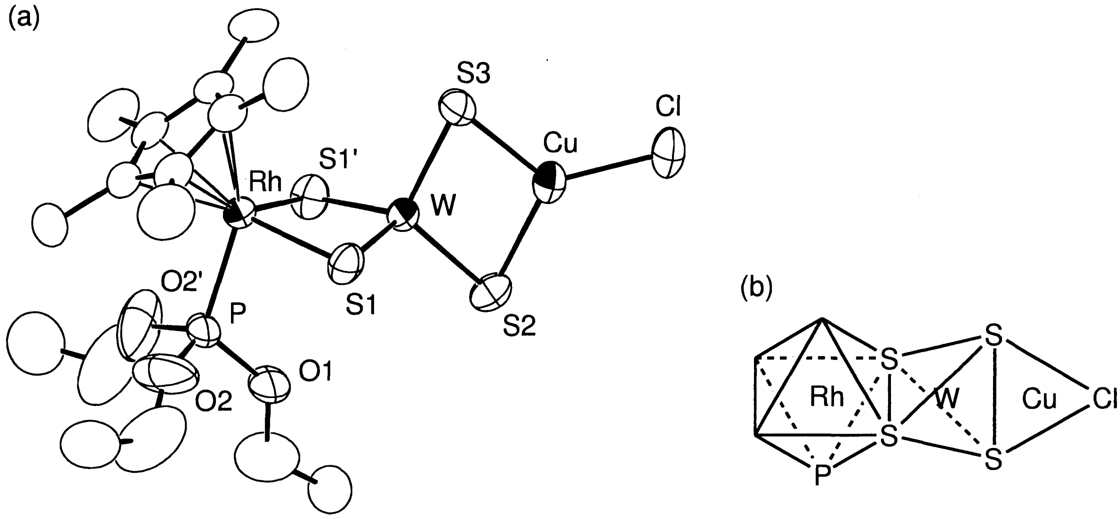


Fig. 2. (a) ORTEP drawing of **4** . Selected bond distances (*l* / Å) and angles (*ϕ* / °) : Rh-P=2.248(3), Rh-S1=2.396(2), W-S1=2.226(2), W-S2=2.205(3), W-S3=2.187(3), Cu-S2=2.231(3), Cu-S3=2.236(3), Cu-Cl=2.151(3), S1-Rh-S1'=95.24(7), Rh-S1-W=77.63(6), S1-W-S1'=105.31(7), S1-W-S2=111.18(6), S1-W-S3=110.37(7), S2-W-S3=108.4(1), W-S2-Cu=72.8(1), W-S3-Cu=72.99(9), S2-Cu-S3=105.8(1), S2-Cu-Cl=129.0(1), S3-Cu-Cl=125.2(1). The distances of Rh···W and W···Cu are 2.8996(9) and 2.631(1) Å, respectively. (b) Schematic drawing of the octahedral, tetrahedral and trigonal planar arrangements around the metal ions.

Although there are three presumed geometrical isomers for **4** based on the difference in the binding site of CuCl on the WS_4 core, the reaction between **3** and CuCl gave specifically **4** with the above structure in nearly quantitative yield. It is worthwhile to note that the linear-type framework of **4** is preserved in solution. Vapor pressure osmometry showed that the value of the molecular weight of **4** in dichloromethane is ca. 805, which corresponds to that of the undissociated molecule (calcd for **4** : 815.4). The infrared spectrum of **4** measured in dichloromethane showed two ν_{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 ^1H NMR spectrum of **4** in CD_2Cl_2 or CD_3CN did not show any temperature dependence. Thus, the specific formation of **4** is due to the strong coordination ability of the terminal S atoms in **3**. Further studies on formation of larger clusters in related systems are in progress.

References

1) P. Zanello, *Coord. Chem. Rev.*, **87**, 1 (1988).
2) K. E. Howard, J. R. Lockemeyer, M. A. Massa, T. B. Rauchfuss, S. R. Wilson, and X. Yang, *Inorg. Chem.*, **29**, 4385 (1990).
3) C. White, A. Yates, and P. M. Maitlis, *Inorg. Synth.*, **29**, 228 (1992).
4) Anal. Found: C, 40.31; H, 6.08%. Calcd for $C_{16}H_{30}Cl_2O_3PRh$: C, 40.44; H, 6.36%. ^{1}H NMR ($CDCl_3$, 23 °C, TMS) : δ 1.30 (t, $^3J_{H,H}$=7.0 Hz, 9H, -CH_2CH_3), 1.66 (d, $^4J_{P,H}$=5.2 Hz, 15H, -CH_3(Cp*)), 4.25 (dq, $^3J_{P,H}$=7.0 Hz, $^3J_{H,H}$=7.0 Hz, 6H, -CH_2-). A red crystal suitable for X-ray analysis was obtained from acetone/diethyl ether. Crystallographic data for **2** : $C_{16}H_{30}Cl_2O_3PRh$, *MW* 475.2, orthorhombic, space group $P2_1cn$ (No. 33), a=8.988(3) , b=28.591(5), c=8.276(3) Å, V=2127(1) Å^3, Z=4, D_c=1.484 g cm^{-3} and μ (MoKα)=11.4 cm^{-1}, R=0.049 and R_w=0.053 for 1952 independent unique reflections ($|F_o| > 3\sigma(|F_o|)$). The details of the structure will be reported elsewhere in a full paper.
5) $(Ph_4P)_2WS_4$ was prepared by a method similar to that for $(PPh_4)_2MoS_4$; see A. I. Hadjikyriacou and D. Coucouvanis, *Inorg. Synth.*, **27**, 39 (1990).
6) Anal. Found: C, 26.89; H, 4.04%. Calcd for $C_{16}H_{30}O_3PRhS_4W$: C, 26.83; H, 4.22%. ^{1}H NMR : ($CDCl_3$, 23 °C, TMS) δ 1.27 (t, $^3J_{H,H}$=7.0 Hz, 9H, -CH_2CH_3), 2.02 (d, $^4J_{P,H}$=5.2 Hz, 15H, -CH_3(Cp*)), 4.04 (dq, $^3J_{P,H}$=7.0 Hz, $^3J_{H,H}$=7.0 Hz, 6H, -CH_2-). A red crystal obtained from acetonitrile/diethyl ether was used for X-ray analysis. Crystallographic data for **3** : $C_{16}H_{30}O_3PRhS_4W$, *MW* 716.4, monoclinic, space group $P2_1/n$ (No. 14), a=14.633(2), b=15.191(2), c=11.490(1) Å, β=104.97(1)°, V=2467.3(5) Å^3, Z=4, D_c=1.929 g cm^{-3} and μ (MoKα)=58.223 cm^{-1}, R=0.040 and R_w=0.053 for 4407 independent unique reflections ($|F_o| > 3\sigma(|F_o|)$).
7) K. E. Howard, T. B. Rauchfuss, and, S. R. Wilson, *Inorg. Chem.*, **27**, 3561 (1988). At the present stage of our study we do not know the exact factors to produce the trinuclear complex [{Cp*RhCl(μ-S)$_2$}$_2$W] from [(Cp*$RhCl_2$)(μ-Cl)$_2$] (**1**) and, in our case, the dinuclear complex [Cp*Rh{P(OEt)$_3$}(μ-S)$_2$$WS_2$] (**3**) from [Cp*Rh{P(OEt)$_3$}Cl_2] (**2**). An electroneutrality principle, however, probably plays a role to produce the neutral clusters in these complexations.
8) Anal. Found: C, 23.36; H, 3.48%. Calcd for $C_{16}H_{30}ClCuO_3PRhS_4W$: C, 23.57; H, 3.71%. ^{1}H NMR : (CD_2Cl_2, 23 °C, TMS) δ 1.33 (t, $^3J_{H,H}$=7.0 Hz, 9H, -CH_2CH_3), 2.05 (d, $^4J_{P,H}$=5.2 Hz, 15H, -CH_3(Cp*)), 4.05 (dq, $^3J_{P,H}$=7.0 Hz, $^3J_{H,H}$=7.0 Hz, 6H, -CH_2-). A red crystal for X-ray analysis was obtained from dimethylformamide/diethyl ether. Crystallographic data for **4** : $C_{16}H_{30}ClCuO_3PRhS_4W$, *MW* 815.4, monoclinic, space group $P2_1/m$ (No. 11), a=10.221(2), b=11.943(2), c=10.809(1) Å, β=94.40(1)°, V=1315.6(3) Å^3, Z=2, D_c=2.058 g cm^{-3} and μ (MoKα)=62.8 cm^{-1}, R=0.045 and R_w=0.052 for 3168 independent unique reflections ($|F_o| > 3\sigma(|F_o|)$).
9) F. Sécheresse, M. Salis, C. Potvin, and J. M. Manoli, *Inorg. Chim. Acta*, **114**, L19 (1986).
10) The binding energies from X-ray photoelectron spectra for **2** : Rh $3d_{5/2}$=308.8 eV; for **3** : Rh $3d_{5/2}$=309.4 eV, W $4f_{7/2}$=33.5 eV; for **4** : Rh $3d_{5/2}$=309.1 eV, W $4f_{7/2}$=33.3 eV, Cu $2p_{3/2}$=932.3 eV. These values are corrected by assuming C 1S binding energy in the compounds as 284.6 eV.

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