Stepwise Construction of Clusters Containing Ru_2PtWS_4 and $Ru_2Pt_2WS_4$ Cores by the Thermal Reaction of $[\{Cp^*Ru(CO)\}_2(WS_4)]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with $[PtMe_2(cod)]$ (cod = 1,5-cyclooctadiene)

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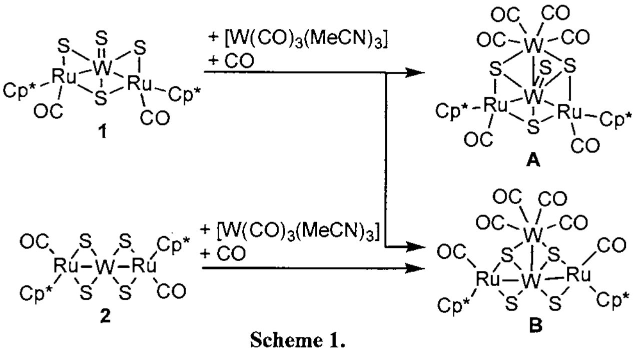
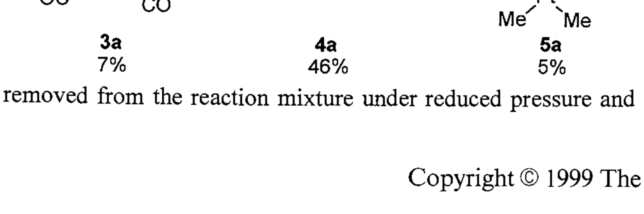
The stepwise construction of $[\{Cp^*Ru(CO)\}_2(WS_4)(PtMe_2)]$ and $[\{Cp^*Ru(CO)\}_2(WS_4)(PtMe_2)_2]$ clusters was achieved by the thermal reaction of $[\{Cp^*Ru(CO)\}_2\{W(\mu\text{-}S)_4\}]$ with $[PtMe_2(cod)]$.

The tetrathiometalates have been widely used as polydentate ligands for many transition-metals, which led to the formation of homo- and heteronuclear clusters.[1] Recently, we reported the formation of an isomeric pair of tetrathiotungstate clusters $[\{Cp^*Ru(CO)\}_2\{W(\mu_3\text{-}S)_3(=S)\}\{W(CO)_4\}]$ (**A**) and $[\{Cp^*Ru(CO)\}_2\{W(\mu_3\text{-}S)_2(\mu\text{-}S)_2\}\{W(CO)_4\}]$ (**B**) by the reaction of $[Cp^*_2Ru_2S_4]$ with $[W(CO)_3(MeCN)_3]$.[2] In the reaction, the isomeric pair of trinuclear clusters $[\{Cp^*Ru(CO)\}_2\{W(\mu_3\text{-}S)_3(=S)\}]$ (**1**) and $[\{Cp^*Ru(CO)\}_2\{W(\mu\text{-}S)_4\}]$ (**2**) are considered to be the intermediates to give the tetranuclear clusters **A** and **B**, because **A** and **B** could be derived by the reactions of **1** and **2** with $[W(CO)_3(MeCN)_3]$ and CO as shown in Scheme 1.[3] These results indicate that clusters **1** and **2** are useful precursors for the synthesis of the transition-metal sulfide clusters. This paper describes the stepwise construction of tetranuclear and pentanuclear clusters by the reaction of $[\{Cp^*Ru(CO)\}_2\{W(\mu\text{-}S)_4\}]$ (**2**) with $[PtMe_2(cod)]$ (cod = 1,5-cyclooctadiene).



Scheme 1.

A toluene solution (5 cm^3) of **2** (100 mg, 0.119 mmol), which was prepared by the reaction of $(NH_4)_2[WS_4]$ with $Cp^*Ru(CO)_2Cl$,[3] and *ca.* 1 equiv. $[PtMe_2(cod)]$ (43 mg, 0.130 mmol) was heated at 80 °C for 18 h (eq 1). Volatiles were



removed from the reaction mixture under reduced pressure and chromatographic work-up of the residue afforded two Ru_2PtWS_4 clusters **3a** and **4a** and a $Ru_2Pt_2WS_4$ cluster **5a** in 7%, 46%, and 5% isolated yield, respectively.[4]

The reaction of **2** with *ca.* 2 equiv. $[PtMe_2(cod)]$ was also examined (eq 2). The thermal reaction of **2** (163 mg, 0.194 mmol) with $[PtMe_2(cod)]$ (151 mg, 0.453 mmol) at 80 °C for 18 h led to the formation of **3a**, **4a**, and **5a** in 5%, 34%, and 52% isolated yield, respectively. In the reaction, pentanuclear cluster **5a** was obtained as a major product. The C_5Me_4Et derivatives **3b**, **4b**, and **5b** were also obtained by the reaction of $[\{(C_5Me_4Et)Ru(CO)\}_2\{W(\mu\text{-}S)_4\}]$ with $[PtMe_2(cod)]$.

$$\mathbf{2} + 2\text{equiv. } PtMe_2(cod) \xrightarrow[80^\circ C,\ 18\ h]{\text{toluene}} \underset{5\%}{\mathbf{3a}} + \underset{34\%}{\mathbf{4a}} + \underset{52\%}{\mathbf{5a}} \qquad (2)$$

The reaction of isolated **4a** with 1.3 equiv. $[PtMe_2(cod)]$ in C_6D_6 was carried out at 80 °C for 11 h. The ^1H NMR spectrum revealed that the resulting solution contains **4a** (26%) and **5a** (60%) and a half of $[PtMe_2(cod)]$ remained intact. Thus, **4** is considered to be the intermediate for the formation of **5**.

Single crystals of **4b** suitable for X-ray structure analysis were obtained by recrystallization from dichloromethane-hexane. ORTEP drawing of **4b** is depicted in Figure 1.[5] Cluster **4b** consists of two $(C_5Me_4Et)Ru(CO)$ fragments and one $PtMe_2$ fragment which are connected by a tetrathiotungstate ligand. The structure of **4b** is similar to that of $[\{Cp^*Ru(CO)\}_2\{W(\mu_3\text{-}S)_2(\mu\text{-}S)_2\}\{W(CO)_4\}]$ (**B**), but the latter has a $W(CO)_4$ fragment instead of a $PtMe_2$ fragment. Two of four S atoms in $[WS_4]^{2-}$ (S1, S2)

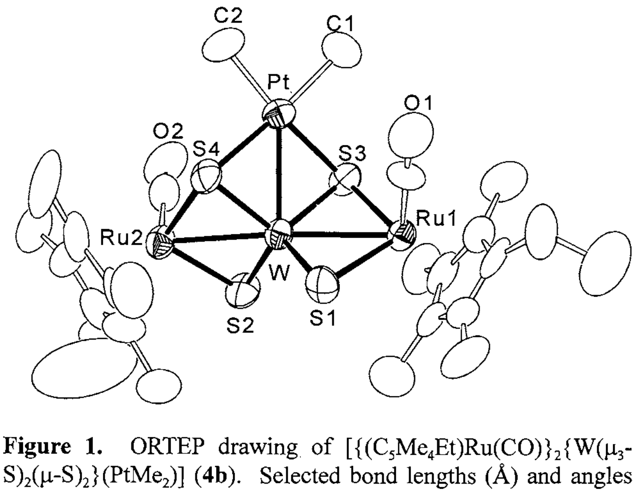


Figure 1. ORTEP drawing of $[\{(C_5Me_4Et)Ru(CO)\}_2\{W(\mu_3\text{-}S)_2(\mu\text{-}S)_2\}(PtMe_2)]$ (**4b**). Selected bond lengths (Å) and angles (°); W-Pt 2.777(2), W-Ru1 2.860(2), W-Ru2 2.870(2), W-S1 2.210(6), W-S2 2.199(6), W-S3 2.252(6), W-S4 2.245(6), Pt-S3 2.352(6), Pt-S4 2.364(7), Ru1-S1 2.404(6), Ru1-S3 2.370(6), Ru2-S2 2.391(7), Ru2-S4 2.386(7), S3-Pt-S4 102.2(2), S3-Pt-C2 166.4(8), S4-Pt-C1 164.1(8), C1-Pt-C2 84(1).

bridge one W atom and one Ru atom in a μ_2-fashion. The others (S3, S4) bridge three metals W, Ru, and Pt in a μ_3-fashion. The Pt metal center with two methyl and two sulfide ligands adopts a square planar geometry. The metal-metal bond lengths (W-Pt 2.777(2), W-Ru1 2.860(2), W-Ru2 2.870(2) Å) lie in the normal range expected for each metal-metal single bond length.[6] The elemental analysis and mass spectral data established that **3a** and **4a** has the same formula $\{Cp^*Ru(CO)\}_2(WS_4)(PtMe_2)$. Spectroscopic features of **3a** are quite similar to those of **4a**. The ^{1}H NMR spectra of **3a** and **4a** show two kinds of singlet, which are assignable to chemically equivalent two Cp* ligands and two methyl groups connected to a Pt center. The IR spectrum of each cluster exhibits a CO stretching absorption band in the terminal CO region. The structure of **3a** is tentatively assigned to $[\{Cp^*Ru(CO)\}_2\{W(\mu_3\text{-}S)_3({=}S)\}(PtMe_2)]$ which corresponds to **A**.

Structure of **5a** was determined as shown in Figure 2.[7]

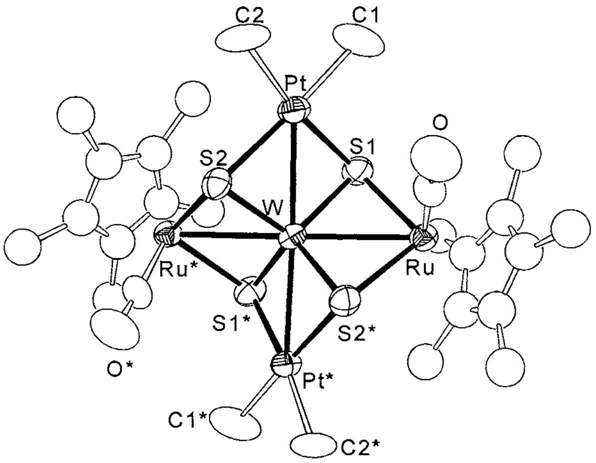
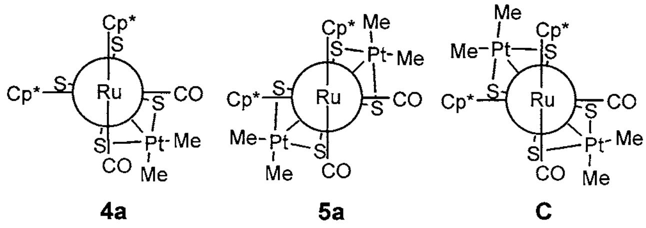


Figure 2. ORTEP drawing of $[\{Cp^*Ru(CO)\}_2\{W(\mu_3\text{-}S)_4\}(PtMe_2)_2]$ (**5a**). Selected bond lengths (Å) and angles (°); W-Pt 2.7835(7), W-Ru 2.872(2), W-S1 2.241(5), W-S2 2.246(5), Pt-S1 2.350(5), Pt-S2 2.375(5), Ru-S1 2.400(5), Ru-S2* 2.412(5), S1-Pt-S2 101.3(2), S1-Pt-C2 170.9(7), S2-Pt-C1 171.5(7), C1-Pt-C2 85(1).

Cluster **5a** possesses C_2 axis on the W atom and contains two Cp*Ru(CO) fragments and two $PtMe_2$ fragments which are connected by a tetrathiotungstate ligand. Each of four S atoms bridges three metals W, Ru, and Pt. The Pt(II) metal center with two methyl and two S ligands adopts a square planar geometry. The distances of W-Pt (2.7835(7) Å) and W-Ru (2.872(2) Å) bonds are almost the same as those of **4b**.

Newman projections of **4a** and **5a** along the Ru-W-Ru axis are depicted in Figure 3. In cluster **4a**, the $PtMe_2$ fragment occupies the position between the CO ligand on the front Ru atom and that on the rear Ru atom to minimize the steric interaction between $PtMe_2$, CO, and Cp* groups. The same position is used by $W(CO)_4$ fragment in cluster **B**. It should be noted that the position occupied by the $PtMe_2$ fragment in **4a** is not used by any $PtMe_2$ fragment in **5a**. If this is the case, **5a** must adopt the structure shown as conformer **C** in Figure 3: The second $PtMe_2$ fragment occupies the position between two bulky Cp* ligands. To avoid this severe steric crowding, in the real structure of **5a**, each $PtMe_2$ fragment occupies the position between CO and Cp* ligands.



4a **5a** **C**

Figure 3. Newman projections of **4a**, **5a**, and conformer **C**.

The tetrathiotungstate $[WS_4]^{2-}$ ligand has been used for building up transition-metal sulfide clusters. However, the tetrathiometalates with organometallic fragments are still limited.[8] To our knowledge, cluster **5** is the first example in which four organometallic fragments are connected by a tetrathiotungstate ligand.

References and notes

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4 Data for **3a**: ^{1}H NMR (300 MHz, C_6D_6) δ 2.24 (s, 6H, $^2J_{Pt\text{-}H}$ = 88 Hz, $PtMe_2$), 1.61 (s, 30H, Cp*). IR (KBr) 1984 cm^{-1} (ν_{CO}). FAB MS (Xe, *m*-nitrobenzyl alcohol matrix) *m/z* 1052 (M^+ - Me). Anal. Found: C, 26.93; H 3.54%. Calcd for $C_{24}H_{36}O_2PtRu_2S_4W$: C, 27.05; H, 3.40%. For **4a**: ^{1}H NMR (300 MHz, C_6D_6) δ 2.49 (s, 6H, $^2J_{Pt\text{-}H}$ = 88 Hz, $PtMe_2$), 1.61 (s, 30H, Cp*). IR (KBr) 1959 cm^{-1} (ν_{CO}). FAB MS (Xe, *m*-nitrobenzyl alcohol matrix) *m/z* 1052 (M^+ - Me). Anal. Found: C, 27.17; H 3.29%. Calcd for $C_{24}H_{36}O_2PtRu_2S_4W$: C, 27.05; H, 3.40%. For **5a**: ^{1}H NMR (300 MHz, C_6D_6) δ 2.43 (s, 6H, $^2J_{Pt\text{-}H}$ = 85 Hz, $PtMe_2$), 2.28 (s, 6H, $^2J_{Pt\text{-}H}$ = 89 Hz, $PtMe_2$), 1.53 (s, 30H, Cp*). IR (KBr) 1963 cm^{-1} (ν_{CO}). FAB MS (Xe, *m*-nitrobenzyl alcohol matrix) *m/z* 1176 (M^+ - 2Me - 2CO). Anal. Found: C, 23.75; H 3.38%. Calcd for $C_{26}H_{42}O_2Pt_2Ru_2S_4W$: C, 24.19; H, 3.28%.

5 Crystallographic data for **4b**: $C_{26}H_{40}O_2PtRu_2S_4W$, M = 1093.93, *orthorhombic*, space group *Pbca* (variant No.61), a = 16.458(10) Å, b = 26.13(1) Å, c = 15.661(4) Å, V = 6736(4) Å^3, Z = 8, D_c = 2.16 gcm^{-3}, μ(Mo-Kα) = 86.81 cm^{-1}. The structure was solved by Patterson methods and refined by full-matrix least-squares methods using teXsan. Hydrogen atoms were not located. All non-hydrogen atoms were refined anisotropically. 7731 unique reflections were collected by ω scan in the range $3° < 2\theta < 55°$ and 3480 data with $I > 2\sigma(I)$ were used in calculations. The final reliability factors converged R = 0.059 and R_w = 0.082.

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7 Crystallographic data for **5a**: $C_{26}H_{42}O_2Pt_2Ru_2S_4W$, M = 1291.02, *monoclinic*, space group *C2/c* (variant No.15), a = 15.069(9) Å, b = 15.529(7) Å, c = 16.542(7) Å, β = 95.69(4)°, V = 3851(3) Å^3, Z = 4, D_c = 2.23 gcm^{-3}, μ(Mo-Kα) = 111.90 cm^{-1}. The structure was solved by direct methods and refined by full matrix least-squares methods using teXsan. The carbon atoms of disordered Cp* ligand were treated as two rigid groups. Hydrogen atoms were not located. All non-hydrogen atoms were refined anisotropically without disordered Cp* ligand, which was refined isotropically. 5622 unique reflections were collected by ω-2θ scan in the range $3° < 2\theta < 60°$ and 3038 data with $I > 3\sigma(I)$ were used in calculations. The final reliability factors converged R = 0.059 and R_w = 0.099.

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