Synthesis and Characterization of Hydride and Carbonyl $RuMo_3S_4$ Cubane Clusters

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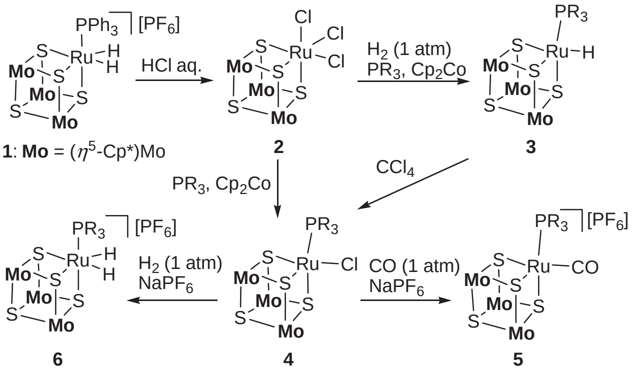
Treatment of $[(Cp^*Mo)_3(\mu_3\text{-}S)_4RuH_2(PPh_3)][PF_6]$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$) with aqueous HCl afforded the trichloride cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4RuCl_3]$ (**2**), which was reduced with Cp_2Co in the presence of PR_3 under H_2 to give the hydride cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4RuH(PR_3)]$ (R = Cy (**3a**), *i*-Pr (**3b**); Cy = *cyclo*-C_6H_{11}). Cluster **3** was further converted into the chloride cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4RuCl(PR_3)]$ (R = Cy (**4a**), *i*-Pr (**4b**)) by reaction with CCl_4. Reaction of cluster **4** with $NaPF_6$ under CO resulted in the formation of the carbonyl cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Ru(CO)(PR_3)][PF_6]$ (R = Cy (**5a**), *i*-Pr (**5b**)), while the reaction under H_2 gave the dihydride cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4RuH_2(PR_3)][PF_6]$ (R = Cy (**6a**), *i*-Pr (**6b**)).



Scheme 1.

The chemistry of M_4S_4 cubane clusters has been receiving much attention in relevance to the active sites of metalloproteins such as nitrogenase.[1] Up to date, a variety of cubane-type metal sulfide clusters have been synthesized which contain carbonyl, ammonia, nitrile, cyanide, alkene, and alkyne ligands including nitrogenase substrates and inhibitors.[2] However, cubane-type metal sulfide clusters containing hydride ligands are not known except for $[(Cp^*Mo)_3(\mu_3\text{-}S)_4RuH_2(PPh_3)][PF_6]$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$)[3a] and $[\{W(dmpe)\}_3\{Pd(CO)\}(\mu_3\text{-}S)_4H_3][PF_6]$ (dmpe = 1,2-bis(dimethylphosphino)ethane),[3b] the first example of which was prepared by our group. The pursuit of hydrides of this type as well as dinitrogen metal sulfide clusters is of particular interest because dihydrogen is evolved concurrent with biological nitrogen fixation by nitrogenase and dinitrogen reduction is inhibited by dihydrogen.[4] Our studies have long been focused on the rational synthesis of metal sulfide clusters containing especially noble metals and development of their unique catalytic activity for chemical transformations including dinitrogen reduction.[5] We wish here to report synthetic routes to several new $HRuMo_3S_4$ and $H_2RuMo_3S_4$ hydride cubane clusters derived from the direct reaction with dihydrogen as well as $(CO)RuMo_3S_4$ carbonyl cubane clusters with low $\nu(CO)$ values. It is to be noted that dinitrogen and CO are isoelectronic and CO strongly inhibits biological nitrogen fixation.

Previously, we reported that the first hydride cubane-type metal sulfide cluster **1** is readily available from the reaction of the trimolybdenum sulfide cluster $[(Cp^*Mo)_3(\mu_2\text{-}S)_3(\mu_3\text{-}S)][PF_6]$ with $[RuH_4(PPh_3)_3]$.[3a,6] Treatment of cluster **1** with an excess of aqueous HCl in THF at 60 °C for 3 h afforded the trichloride cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4RuCl_3]$ (**2**) in 70% yield (Scheme 1).[7] Evolution of H_2 gas (1.9 equiv. based on cluster **1**) in the reaction has been confirmed by GLC analysis. The X-ray analysis has shown that cluster **2** has a pseudo C_3 symmetry (Figure 1), which is consistent with the appearance of the Cp* resonance as one singlet (δ, 2.11 ($CDCl_3$)) in its ^1H NMR spectrum. The core structure with six metal–metal bonds is compatible with its total electron count of $60e^-$.

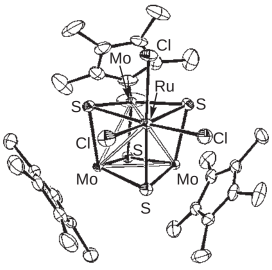


Figure 1. Molecular structure of **2**.

Cluster **2** reacted with 5 equiv. of Cp_2Co and 1 equiv. of PR_3 (R = Cy, *i*-Pr; Cy = *cyclo*-C_6H_{11}) under H_2 atmosphere (1 atm) to give a new hydride cubane cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4RuH(PR_3)]$ (R = Cy (**3a**), *i*-Pr (**3b**)) in moderate yield,[7] which has a hydride and a phosphine on Ru atom as shown in Scheme 1. In the ^1H NMR spectrum (C_6D_6), the hydride proton was observed at δ −9.8 (**3a**) or −10.0 (**3b**) as a doublet with a $J_{P\text{–}H}$ value (**3a**, 26 Hz; **3b**, 27 Hz). This indicates the geometry around Ru atom with the hydride occupying the position cis to the PR_3 ligand. The molecular structure of **3** has been determined by X-ray diffraction study; an ORTEP drawing of **3a** is shown in Figure 2. The average Ru–Mo and Mo–Mo distances of 2.847(1) and 2.871(1) Å, respectively, are consistent with the presence of single bonds between metal atoms. There are no significant changes in the Mo–Mo bond lengths on going from cluster **2** to **3**, whereas the Ru–Mo bond distance is shortened by 0.02 Å.

When the monohydride cluster **3** was treated with 1 equiv. of CCl_4 in C_6H_6, substitution of a chloride ligand for the hydride ligand on Ru atom took place smoothly to give the monochloride cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4RuCl(PR_3)]$ (R = Cy (**4a**), *i*-Pr (**4b**))

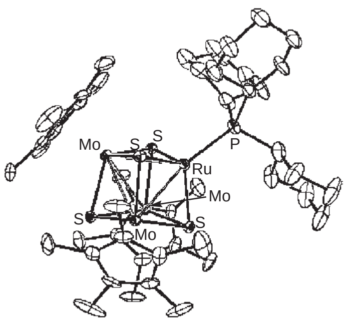


Figure 2. Molecular structure of **3a**.

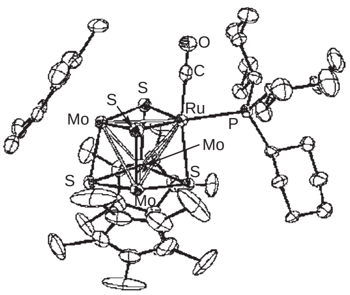


Figure 3. Molecular structure of **5a** (cationic part only).

in good yield (Scheme 1).[7] Quantitative formation of $CHCl_3$ was monitored by ^1H NMR analysis of the reaction mixture employing C_6D_6 as solvent. Cluster **4** was also obtained in moderate yield by treatment of cluster **2** with 2 equiv. of Cp_2Co and 1 equiv. of PR_3 under Ar atmosphere in THF.

The reactions of cluster **4** with CO (1 atm) at room temperature in the presence of $NaPF_6$ afforded the cationic carbonyl cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Ru(CO)(PR_3)][PF_6]$ (R = Cy (**5a**), *i*-Pr (**5b**)) in good yield (Scheme 1).[7] The molecular structure of the cationic part of **5a** is shown in Figure 3. The Ru–Mo distances (2.873(1)–3.007(1) Å) are slightly longer than those found in **2**, **3**, and **4** but still indicate the presence of metal–metal bonds. The Ru atom has a pseudotrigonal bipyramidal geometry, where the P–Ru–C angle (81.3(4)°) is almost equivalent to the P–Ru–Cl angle in **4a** (81.7(3)°).[7] The IR spectrum (KBr disk) of cluster **5** exhibits the CO stretching band at $1927\,cm^{-1}$ (**5a**) or $1915\,cm^{-1}$ (**5b**). These values are comparable to or slightly lower than that of a mononuclear thiolate/amine-coordinated Ru^{II} carbonyl complex $[Ru(CO)(PPr_3{}^i)(L)]$ (L = $S(o\text{-}C_6H_4)\text{-}NMeCH_2CH_2NMe(o\text{-}C_6H_4)S^{2-}$; $1930\,cm^{-1}$). It is to be noted that the dinitrogen complex $[Ru(N_2)(PPr_3{}^i)(L)]$ is available from the reaction of the nitrile complex $[Ru(MeCN)(PPr_3{}^i)(L)]$ with N_2 (1 atm).[8] This indicates that the Ru atom embedded in the Mo_3S_4 aggregate of cluster **4** provides an electron-rich site enough to bind dinitrogen. However, the formation of dinitrogen cubane clusters was not observed when cluster **4** was treated with $NaPF_6$ under dinitrogen. On the other hand, the reaction of cluster **4** with $NaPF_6$ under dihydrogen gave rise to the formation of the dihydride cubane cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4RuH_2(PR_3)][PF_6]$ (R = Cy (**6a**),[6a] *i*-Pr (**6b**)) in good yield (Scheme 1).[7] The ^1H NMR spectra (THF-d_8) of clusters **6a** and **6b** show a high-field doublet for the hydride ligands at δ -10.1 ($J_{P\text{-}H} = 23\,Hz$) and -10.9 ($J_{P\text{-}H} = 22\,Hz$), respectively, whose relaxation times (400 MHz, THF-d_8, 25 °C, $T_1 =$ 1050 ms for **6a** and 1110 ms for **6b**) are consistent with *classical* dihydride.[9]

In summary, we have developed synthetic routes to $HRuMo_3S_4$ and $H_2RuMo_3S_4$ hydride cubane clusters as well as $(CO)RuMo_3S_4$ carbonyl cubane clusters. Further investigations toward synthesis of dinitrogen metal sulfide clusters are now in progress.

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