Inorg. Chem. **2005**, *44*, 3768–3770

Inorganic Chemistry
Communication

Cleavage of Hydrazine N–N Bonds by $RuMo_3S_4$ Cubane-Type Clusters

Izuru Takei,[†] Keita Dohki,[†] Koji Kobayashi,[†] Toshiaki Suzuki,[‡] and Masanobu Hidai*,[†]

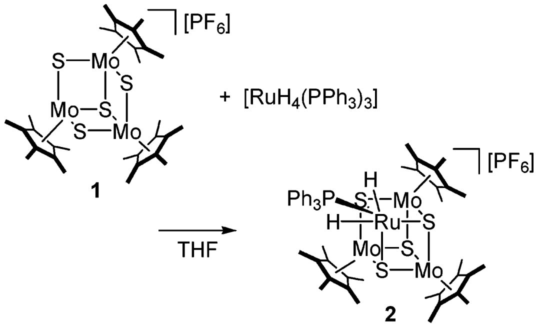
Department of Materials Science and Technology, Faculty of Industrial Science and Technology,
Tokyo University of Science, Noda, Chiba 278-8510, Japan, and RIKEN Institute,
Wako, Saitama 351-0198, Japan

Received January 14, 2005

The mixed-metal cubane-type clusters $[(Cp^*Mo)_3(\mu_3\text{-}S)_4RuH_2(PR_3)][PF_6]$ [$Cp^* = \eta^5\text{-}C_5Me_5$; R = Ph (**2**), Cy (**5**)] were effective for the N–N bond cleavage of hydrazine and phenylhydrazine via a disproportionation reaction. The ammonia cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Ru(NH_3)(PPh_3)][PF_6]$ (**3**) and/or the unprecedented double-cubane-type cluster with bridging nitrogenous ligands $[\{(Cp^*Mo)_3(\mu_3\text{-}S)_4Ru\}_2(\mu_2\text{-}NH_2)(\mu_2\text{-}NHNH_2)][PF_6]_2$ (**4**) were isolated from the reaction mixtures, and their structures were determined by X-ray diffraction studies.

The chemistry of cubane-type metal sulfido complexes has been receiving much attention in relation to the active sites of metalloenzymes such as ferredoxins and nitrogenases as well as hydrodesulfurization catalysts.[1] Coucouvanis et al. reported that $MoFe_3S_4$ and VFe_3S_4 clusters catalytically reduce hydrazine with certain proton and electron sources.[2] We have developed several rational synthetic routes to various cubane-type complexes with desired metal compositions, some of which show intriguing reactivities toward small molecules.[3] Clusters with a $PdMo_3S_4$ or $NiMo_3S_4$ core exhibit remarkable catalytic activity for some reactions of alkynes including intramolecular cyclization of alkynoic acids.[4] In these reactions, the substrates are activated via η^2-coordination to the unique Pd or Ni atom embedded in the Mo_3S_4 aggregate. Further, catalytic formation of *N*-methylaniline is observed when $MePhNNH_2$ is treated with certain proton and electron sources in the presence of $Mo_2M_2S_4$ (M = Rh, Ir) clusters.[5] During our continuous study of the catalysis of cubane-type clusters, we have now found that $RuMo_3S_4$ clusters are effective for the N−N bond cleavage of hydrazines, and cubane-type clusters containing nitrogenous ligands such as NH_3, NH_2, and $NHNH_2$ are obtained from the reaction mixtures.

Previously, we reported that the incomplete cubane-type cluster $[(Cp^*Mo)_3(\mu_2\text{-}S)_3(\mu_3\text{-}S)][PF_6]$ (**1**, $Cp^* = \eta^5\text{-}C_5Me_5$) serves as a versatile precursor for the synthesis of heterobimetallic MMo_3S_4 (M = Ru, Ni, and Pd) cubane-type clusters.[6] Thus, a heterobimetallic $RuMo_3S_4$ cluster bearing a phosphine and two hydrides on the ruthenium center, $[(Cp^*Mo)_3(\mu_3\text{-}S)_4RuH_2(PPh_3)][PF_6]$ (**2**), is readily available from the reaction of **1** and $[RuH_4(PPh_3)_3]$ (eq 1).



(1)

Reaction of cluster **2** with 20 equiv (1 equiv = 1 mol per mole of cluster **2**) of anhydrous hydrazine in THF at room

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* To whom correspondence should be addressed. E-mail: hidai@rs.noda.tus.ac.jp.

[†] Tokyo University of Science.

[‡] RIKEN Institute.

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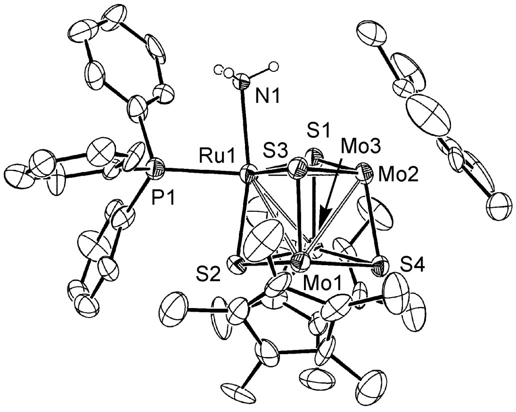

Figure 1. Structure of $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Ru(NH_3)(PPh_3)][PF_6]$ (**3**) showing 30% thermal ellipsoids. Hydrogen atoms and a PF_6 anion are omitted for clarity. Selected bond lengths (Å): Ru1−Mo$_{av}$, 2.869(2); Mo−Mo$_{av}$, 2.877(2); Ru1−N1, 2.30(2); Ru1−P1, 2.366(5).

temperature for 3 h gave ammonia (1.2 equiv) and N_2 (0.45 equiv).[7,8] Further, the ammonia cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4\text{-}Ru(NH_3)(PPh_3)][PF_6]$ (**3**) (0.50 equiv) was isolated as brown crystals by addition of hexanes to the filtered and concentrated THF solution. The ^1H NMR spectrum of **3** (THF-d_8) exhibits a signal at δ 2.45 (br s, 3H) due to the NH_3 ligand, and the IR spectrum of **3** shows weak absorptions at 3279, 3304, and 3371 cm^{-1} assignable to ν_{N-H}. The molecular structure of **3** was determined by an X-ray diffraction study, and an ORTEP drawing of the cationic part is given in Figure 1.[9] The Ru−N bond distance [2.30(2) Å] is compatible with conventional Ru−NH_3 bond distances. As predicted by the effective atomic number (EAN) rule, the 60-electron $RuMo_3S_4$ cluster has three Ru−Mo bonds [2.869(2) Å, average] and three Mo−Mo bonds [2.877(2) Å, average], which are slightly longer than those in cluster **2** [Ru−Mo, 2.861(1) Å; Mo−Mo, 2.848(1) Å, average]. The Ru−P bond distance [2.366(5) Å] is also longer than that in cluster **2** [2.328(1) Å]. On the other hand, the THF-insoluble precipitate separated from the reaction mixture was recrystallized from CH_2Cl_2−hexanes to afford the unprecedented double-cubane-type cluster $[\{(Cp^*Mo)_3(\mu_3\text{-}S)_4Ru\}_2(\mu_2\text{-}NH_2)(\mu_2\text{-}NHNH_2)]\text{-}[PF_6]_2$ (**4**) (0.041 equiv) as dark green crystals. The ^1H NMR spectrum of **4** (CD_2Cl_2) exhibits bands at δ 4.13 (m, 2H, NH_2) and 5.07 (m, 1H, NH), indicating the presence of a hydrazido(1−) ligand. A signal at δ 5.70 (br s, 2H) might be due to the NH_2 ligand. The IR spectrum of **4** shows characteristic ν_{N-H} bands at 3290 and 3380 cm^{-1}. X-ray analysis revealed that the two $RuMo_3S_4$ cubane-type cores are bridged by both a μ_2-NH_2 amido ligand and a μ_2-$NHNH_2$ hydrazido(1−) ligand (Figure 2).[10]

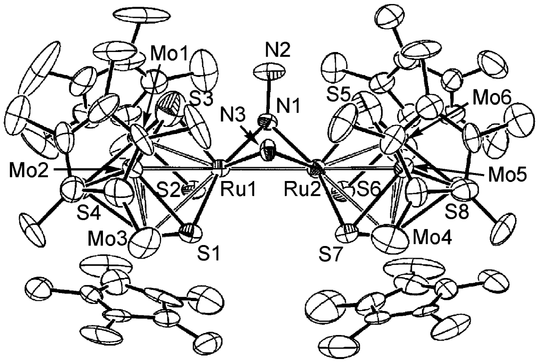

Figure 2. Structure of $[\{(Cp^*Mo)_3(\mu_3\text{-}S)_4Ru\}_2(\mu_2\text{-}NH_2)(\mu_2\text{-}NHNH_2)][PF_6]_2$ (**4**) showing 30% thermal ellipsoids. Hydrogen atoms and a PF_6 anion are omitted for clarity. Selected bond lengths (Å): Ru1−Ru2, 2.690(2); Ru1−Mo$_{av}$, 2.800(2); Ru2−Mo$_{av}$, 2.803(2); Mo−Mo$_{av}$, 2.825(2); Ru1−N1, 2.124(14); Ru2−N1, 2.085(13); Ru1−N3, 2.084(12); Ru2−N3, 2.082(13); N1−N2, 1.46(2).

The Ru−Ru distance is 2.690(2) Å, which is slightly shorter than that of the typical Ru−Ru single bond, probably because of the presence of bridging μ-amido and μ-hydrazido ligands. The Ru−Mo distances [2.801(2) Å, average] and the Mo−Mo distances [2.825(2) Å, average] in cluster **4** are consistent with M−M single bonds, which are slightly shorter than the corresponding Ru−Mo bonds in clusters **2** and **3**. The N−N bond length of 1.46(2) Å in the μ_2-$NHNH_2$ ligand indicates a single bond,[11] and the N−N axis is nearly perpendicular to the Ru−Ru vector. The Ru_2N_2 face is folded with a dihedral angle of 106.6(7)° around the Ru−Ru axis.

A balanced equation for the above transformation of hydrazine into ammonia and N_2 in the presence of cluster **2** is described by eq 2.

$$3NH_2NH_2 \rightarrow 4NH_3 + N_2 \tag{2}$$

The effects of the reaction conditions on the transformation of hydrazine with cluster **2** were investigated, and the typical results are summarized in Table 1. When the reaction was carried out in THF at 60 °C, the disproportionation reaction proceeded catalytically. However, during the reaction, a part of cluster **2** was transformed into the THF-insoluble double-cubane-type cluster **4**. The $RuMo_3S_4$ cluster with PCy_3 (Cy = *cyclo*-C_6H_{11}), $[(Cp^*Mo)_3(\mu_3\text{-}S)_4RuH_2(PCy_3)][PF_6]$ (**5**), was prepared by the reaction of cluster **1** with $[RuH_2(H_2)_2\text{-}(PCy_3)_2]$.[12] The catalytic activity of cluster **5** for the disproportionation reaction of hydrazine was higher than that of cluster **2**. In contrast to the reaction with cluster **2**, the double-cubane-type cluster **4** was obtained in moderate yield from the reaction with cluster **5**, but the corresponding ammonia cluster was not isolated. It should be noted that ammonia

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(7) The formation of ammonia was quantitatively analyzed by the indophenol method, and the amount of the unreacted hydrazine was determined by the *p*-dimethylaminobenzaldehyde method. See: (a) Weatherburn, M. W. *Anal. Chem.* **1967**, *39*, 971. (b) Watt, G. W.; Chrisp, J. D. *Anal. Chem.* **1952**, *24*, 2006. (c) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461.

(8) The evolution of H_2 (0.10 equiv) was also observed, which probably arises from the reductive elimination of the two hydrides in cluster **2**.[6]

(9) Crystallographic data for $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Ru(NH_3)(PPh_3)][PF_6]$ (**3**): monoclinic, $P2_1/c$ (No. 14), $a = 11.1350(7)$ Å, $b = 23.9955(15)$ Å, $c = 19.7074(13)$ Å, $\beta = 95.005(3)°$, $V = 5245.5(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.706$ g cm^{-3}; $\mu = 12.576$ cm^{-1}, R1 = 0.065 and wR2 = 0.165 for 3816 unique reflections [$I > 3.00\sigma(I)$], GOF = 1.078. All structures were refined by least-squares methods against F^2.

(10) Crystallographic data for $[\{(Cp^*Mo)_3(\mu_3\text{-}S)_4Ru\}_2(\mu_2\text{-}NH_2)(\mu_2\text{-}NHNH_2)]\text{-}[PF_6]_2$ (**4**): orthorhombic, *Pban* (No. 50), $a = 29.4581(9)$ Å, $b = 29.3083(11)$ Å, $c = 19.9652(7)$ Å, $V = 17237(1)$ Å^3, $Z = 12$, $D_{calcd} = 2.459$ g cm^{-3}; $\mu = 21.997$ cm^{-1}, R1 = 0.067 and wR2 = 0.189 for 6257 unique reflections [$I > 3.00\sigma(I)$], GOF = 1.115.

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(12) See Supporting Information.

Table 1. Catalytic Disproportionation of Hydrazine[a]

cluster	temp (°C)	time (h)	conv of NH_2NH_2[b,c]	yield of products (equiv)[d]			
				NH_3[c]	N_2[e]	**3**	**4**
2	rt[f]	3	1.7	1.2	0.45	0.50	0.041
2	rt[f]	18	3.4	3.1	0.88	0.56	0.070
2	60	18	5.9	6.6	1.6	0.38	0.15
2	60	48	11.5	12.1	3.0	0.39	0.14
5	rt[f]	18	3.6	4.0	1.2	−	0.19
5	60	18	15.2	20.0	4.7	−	0.23
3	60	18	6.0	6.9	2.0	0.54	0.12
6	60	18	<0.5	<0.1	<0.1	0	0

[a] Reaction conditions: cluster, 0.050 mmol; NH_2NH_2, 1.00 mmol; THF, 20 mL; under Ar. [b] Moles of NH_2NH_2 consumed per mole of cluster. [c] See ref 7. [d] 1 equiv = 1 mol per mole of cluster. [e] Determined by GLC. [f] Room temperature.

cluster **3** was effective for the disproportionation reaction, whereas the CO cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Ru(CO)(PPh_3)][PF_6]$ (**6**)[13] exhibited no catalytic activity, presumably because of the difficulty of substituting hydrazine for the CO ligand.

Treatment of cluster **2** with 20 equiv of phenylhydrazine in THF at 60 °C for 18 h produced aniline (2.3 equiv), N_2 (1.6 equiv), benzene (2.1 equiv), and ammonia (1.2 equiv), and ammonia cluster **3** (0.35 equiv) was isolated from the reaction mixture. A similar transformation of phenylhydrazine proceeded when cluster **5** was employed. A balanced equation for the transformation of phenylhydrazine may be shown in eq 3.

$$2PhNHNH_2 \rightarrow PhNH_2 + N_2 + PhH + NH_3 \qquad (3)$$

Cleavage of hydrazine N−N bonds in relation to biological nitrogen fixation has previously been reported for mononuclear and dinuclear complexes with sulfur ligands as well as cubane-type metal sulfido clusters (vide supra). Mononuclear molybdenum thiolate complexes[14] and a dinuclear ruthenium complex with bridging thiolate ligands[15] promote the catalytic disproportionation reaction of hydrazine to form ammonia and N_2. Furthermore, a sulfido-bridged dinuclear molybdenum complex is also effective for the catalytic reduction of hydrazine,[16] and a sulfido-bridged diiron(II) compound cleaves the N−N bond of phenylhydrazine.[17] The catalytic activities of clusters **2**, **3**, and **5** for hydrazine disproportionation were lower than those of the mononuclear molybdenum and dinuclear ruthenium thiolate complexes described above.

In summary, we have demonstrated the N−N bond cleavage of hydrazines by using $RuMo_3S_4$ cubane-type clusters and succeeded in the isolation of the ammonia cluster **3** and the double-cubane-type cluster with bridging NH_2 and $NHNH_2$ ligands **4**. Further investigations are now in progress to elucidate the reaction mechanisms for the disproportionation of hydrazines catalyzed by $RuMo_3S_4$ clusters.

Acknowledgment. This work was supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan, including the "Open Research Center" Project.

Supporting Information Available: Experimental details and crystallographic data for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The $RuMo_3S_4$ carbonyl cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Ru(CO)(PPh_3)][PF_6]$ (**6**) was prepared from the reaction of **2** with CO gas in THF (see Supporting Information).

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