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Synthesis of a New Family of Heterobimetallic Tetranuclear Sulfido Clusters with $Mo_2Ni_2S_x$ ($x = 4$ or 5) or $Mo_3M'S_4$ ($M' =$ Ru, Ni, Pd) Cores

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Summary: Treatment of $[\mathrm{Cp^*Mo(SBu^t)_3}]$ (***1***; $\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$) *with* $[\mathrm{Fc}][\mathrm{PF_6}]$ (*Fc = ferrocene*) *afforded the cationic sulfido-bridged dinuclear complex* $[(\mathrm{Cp^*MoS})(\mu_2\text{-}\mathrm{S})_2(\mathrm{Cp^*Mo})(\mathrm{S_2Bu^t})][\mathrm{PF_6}]$ (***2***) *and the cationic incomplete cubane-type complex* $[(\mathrm{Cp^*Mo})_3(\mu_2\text{-}\mathrm{S})_3(\mu_3\text{-}\mathrm{S})][\mathrm{PF_6}]$ (***3***) *in a ratio of ca. 1:4. The dinuclear complex* ***2*** *reacted with* $[\mathrm{NiCl_2(PPh_3)_2}]$ *and* $[\mathrm{Ni(cod)_2}]$ (*cod = 1,5-cyclooctadiene*) *to give the heterobimetallic cluster* $[(\mathrm{Cp^*Mo})_2\{\mathrm{Ni(PPh_3)}\}_2(\mu_2\text{-}\mathrm{S})_2(\mu_3\text{-}\mathrm{S})_3][\mathrm{PF_6}]$ (***4***) *with an unprecedented* $Mo_2Ni_2S_5$ *core and the edge-linked quadruple cubane-type cluster* $[(\mathrm{Cp^*Mo})_2\mathrm{Ni_2}(\mu_3\text{-}\mathrm{S})_2(\mu_4\text{-}\mathrm{S})_2]_4[\mathrm{PF_6}]_4$ (***5***) *with four* $Mo_2Ni_2S_4$ *cores, respectively. On the other hand, the incomplete cubane-type cluster* ***3*** *serves as a good precursor to the heterobimetallic cubane-type clusters* $[(\mathrm{Cp^*Mo})_3(\mu_3\text{-}\mathrm{S})_4\mathrm{M'L}][\mathrm{PF_6}]$ ($M' =$ *Ru, Ni, and Pd*).

The chemistry of multimetallic sulfido clusters has been receiving much attention in relevance to the active sites of metalloenzymes and industrial metal sulfide catalysts.[1] Most of homo- and heterometallic sulfido clusters have been prepared from simple metal compounds and various sulfur sources by the spontaneous self-assembly reactions. Recently, development of rational synthetic methods has realized the preparation of a wide range of multimetallic sulfido clusters with desired metal-sulfur frameworks.[2] Dinuclear sulfido- or hydrosulfido-bridged complexes with $\mathrm{M_2S_2}(\mu_2\text{-}\mathrm{S})_2$ or $\mathrm{M}(\mu_2\text{-}\mathrm{SH})_2\mathrm{M}$ units serve as versatile precursors for polynuclear sulfido clusters including cubane-type clusters.[3,4] Incorporation of heterometals (M′) into incomplete cubane-type clusters with $\mathrm{M_3}(\mu_2\text{-}\mathrm{S})_3(\mu_3\text{-}\mathrm{S})$ cores also provides a straightforward route to heterobimetallic cubane-type $\mathrm{M_3M'S_4}$ clusters.[5] We have previously applied this methodology to prepare cubane-type $\mathrm{Mo_3M'S_4}$ clusters containing noble metals (M′ = Pd, Pt)[6] and demonstrated that the catalytic addition of alcohols and carboxylic acids to electron-deficient alkynes proceeds smoothly at the unique Pd atom in $[\{(\mathrm{tacn})\mathrm{Mo}\}_3\mathrm{PdCl}(\mu_3\text{-}\mathrm{S})_4]^{3+}$ (tacn = 1,4,7-triazacyclononane), although conventional mononuclear Pd compounds are not effective under similar conditions.[7] Quite recently, Brorson and co-workers have prepared the incomplete cubane-type $(\mathrm{Cp'Mo})_3\mathrm{S_4}$ cluster ($\mathrm{Cp'} = \eta^5\text{-}\mathrm{C_5MeH_4}$), which incorporates transition metal complexes to form a new series of heterobimetallic cubane-type clusters.[8] These findings prompted us to prepare heterobimetallic tetranuclear sulfido clusters with more electron-donating Cp* ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$) ligands, which might be employed as unique catalysts for organic syntheses.

Previously, Tatsumi and co-workers reported that C−S bond cleavage reactions of the *tert*-butylthiolate ligands take place in the mononuclear Mo(IV) complex $[\mathrm{Cp^*Mo(SBu^t)_3}]$ (**1**) under mild conditions.[9,10] For instance, treatment of complex **1** with $[\mathrm{Fc}][\mathrm{PF_6}]$ (Fc = ferrocene) or Na/Hg generates trinuclear incomplete cubane-type sulfido clusters $[(\mathrm{Cp^*Mo})_3(\mu_2\text{-}\mathrm{S})_3(\mu_3\text{-}\mathrm{S})][\mathrm{PF_6}]$ (**3**)[10a] or $[(\mathrm{Cp^*Mo})_3(\mu_2\text{-}\mathrm{S})_3(\mu_3\text{-}\mathrm{S})]$,[10b] respectively. We have now investigated the reaction of **1** with 1 equiv of $[\mathrm{Fc}][\mathrm{PF_6}]$ at room temperature and found that the

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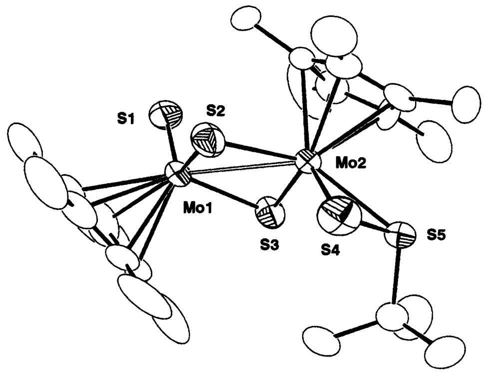


Figure 1. Structure of **2** showing 50% thermal ellipsoids. Hydrogen atoms and PF_6 anion are omitted for clarity.

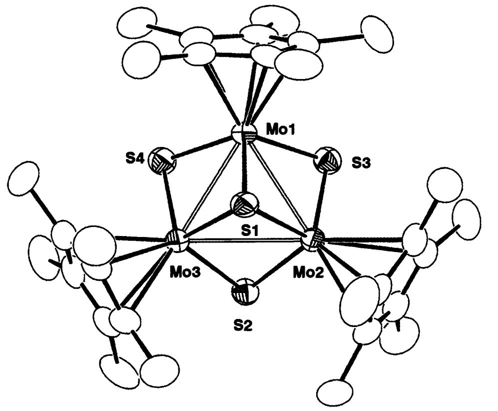
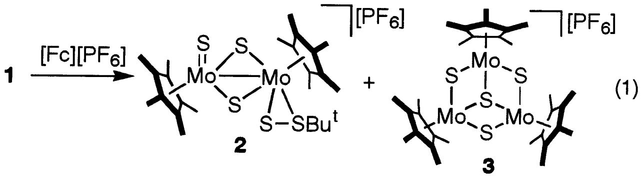


Figure 2. Structure of **3** showing 50% thermal ellipsoids. Hydrogen atoms and PF_6 anion are omitted for clarity.

cationic sulfido-bridged dinuclear complex $[(Cp^*MoS)(\mu_2\text{-}S)_2(Cp^*Mo)(S_2Bu^t)][PF_6]$ (**2**; 20%) is formed in addition to the cationic incomplete cubane-type cluster $[(Cp^*Mo)_3(\mu_2\text{-}S)_3(\mu_3\text{-}S)][PF_6]$ (**3**; 74%) (eq 1).[11] The molecular structures of **2** and **3** were unambiguously determined by X-ray diffraction studies, and ORTEP drawings of the cationic parts are given in Figures 1 and 2. The ^{1}H NMR spectrum ($CDCl_3$) of **2** showed two signals at δ 2.34 and 2.36 due to the Cp* ligands as well as one singlet at δ 1.34 assignable to the Bu^t group. The Mo–Mo bond distance is 2.893(2) Å, which is indicative of the presence of a Mo–Mo single bond. The Mo(1)–S(1) distance (2.145(3) Å) is shorter than the pure terminal Mo=S double bond length (2.24–2.25 Å) observed in $[\{syn\text{-}Me_8[16]aneS_4\}Mo(S)_2]$[12a] and $[Mo(S)_2(PMe_3)_4]$.[12b] This indicates triple-bond character of the Mo(1)–S(1) bond. Cluster **3** has a triangular Mo_3 core, where the three Mo–Mo contacts of 2.819(5) Å (average) are slightly shorter than those in the corresponding *neutral* trimolybdenum sulfido cluster $[(Cp^*Mo)_3(\mu_2\text{-}S)_3(\mu_3\text{-}S)]$ (average 2.861(6) Å).[10b] The ^{1}H NMR spectrum ($CDCl_3$) of **3** exhibits one Cp* singlet at δ 2.02 compatible with the solid-state structure.



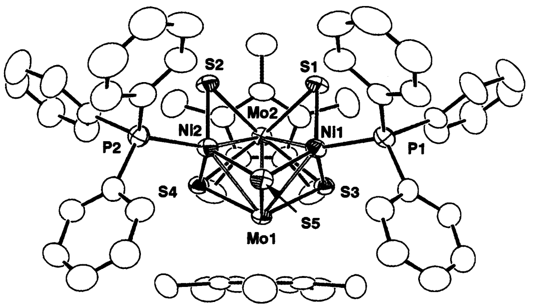
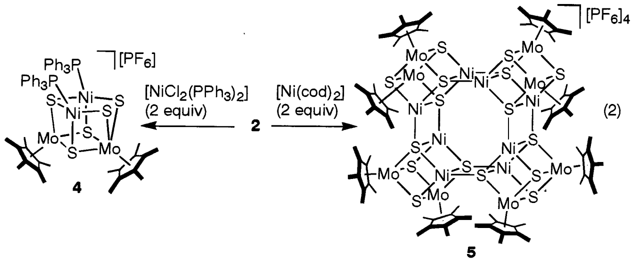


Figure 3. Structure of $\mathbf{4}\cdot CH_2Cl_2$ showing 50% thermal ellipsoids. Hydrogen atoms, solvating CH_2Cl_2, and PF_6 anion are omitted for clarity.

Interestingly, the cationic dinuclear complex **2** reacted with 2 equiv of a Ni(II) complex $[NiCl_2(PPh_3)_2]$ to afford the heterobimetallic tetranuclear cluster $[(Cp^*Mo)_2\{Ni(PPh_3)\}_2(\mu_2\text{-}S)_2(\mu_3\text{-}S)_3][PF_6]$ (**4**) with an unprecedented $Mo_2Ni_2S_5$ core as paramagnetic black crystals in 20% yield (eq 2; left). As shown in Figure 3, the X-ray analysis revealed that cluster **4** has a Mo_2Ni_2 butterfly core with the two Mo atoms on the hinge axis and the two Ni atoms at the wing tips (hinge angle = 80.2°).[13] Three μ_3-sulfido ligands cap the two Mo_2Ni and one $MoNi_2$ triangles, while the two Mo(2)–Ni edges are bridged by two μ_2-sulfido ligands. The distances of the Mo–Mo (2.9364(10) Å), Mo(1)–Ni (2.6702(13) and 2.6684(13) Å) and Mo(2)–Ni bonds (2.8254(13) and 2.8303(13) Å) indicate the presence of the metal–metal single bonds, whereas the Ni–Ni contact of 2.9905(16) Å is slightly longer than the common Ni–Ni single-bond distances.[13] This suggests that the interaction between the two nickel atoms is weak, as expected from the 61-valence-shell electrons (VSE) count for cluster **4**.



Noteworthy is that treatment of **2** with 2 equiv of a Ni(0) compound $[Ni(cod)_2]$ (1,5-cyclooctadiene) gives the edge-linked quadruple cubane-type cluster $[(Cp^*Mo)_2Ni_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)_2]_4[PF_6]_4$ (**5**) with four $Mo_2Ni_2S_4$ cores in 19% yield (eq 2, right). The molecular structure of **5** was determined by combination of FAB^+ mass spectroscopy and X-ray crystallography (Figure 4). The Mo_2Ni_2 cores have distorted tetrahedral structures, whose faces are each capped by μ_3- or μ_4-sulfido ligands, in which the

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(11) Concomitant formation of $(^t\text{BuS})_2$ was confirmed by ^{1}H NMR and GC–MS analysis of the reaction mixture.

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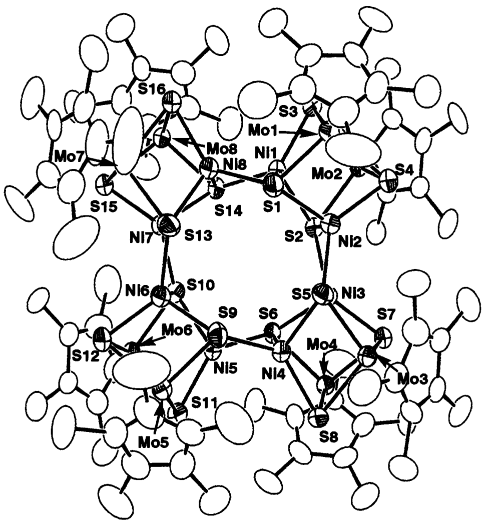
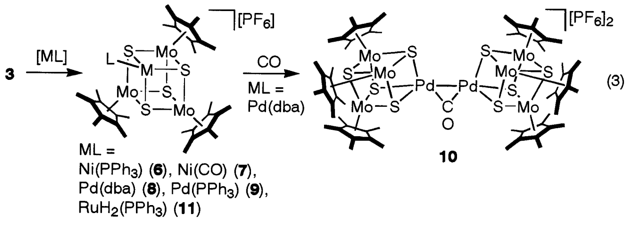


Figure 4. Structure for one enantiomer of $\mathbf{5}\cdot CH_2Cl_2$ showing 50% thermal ellipsoids. Hydrogen atoms, solvating CH_2Cl_2, and PF_6 anions are omitted for clarity.

distances of the Mo−Mo (average, 2.847(2) Å), Ni−Ni (average, 2.595(2) Å), and four Mo−Ni bonds (2.675(2)−2.724(2) Å) suggest the presence of the metal−metal single bonds. The four $Mo_2Ni_2S_4$ cubane-type cores in cluster **5** are each linked by the two Ni−S bonds (average, 2.228(4) Å) and one Ni−Ni bond (average, 2.547(3) Å), which is similar to edge-linked double cubane-type clusters such as $[\{(H_2O)_3Mo\}_3M'S_4]_2^{8+}$ (M′ = Co, Pd, and Cu).[6a,14] It is to be mentioned that polycubane-type clusters containing three or more metal sulfido cubane cores are quite rare. The triple cubane-type cluster $[(Cp^*Mo)_2Fe_2S_4]_3(\mu\text{-}S_4)_3$ was prepared by aggregation of three $Mo_2Fe_2S_4$ cubane units with $S_4(2-)$ ligands,[15] while the quadruple cubane-type sulfido cluster $[Fe_4S_4(PR_3)_2]_4$ was synthesized from four $Fe_4S_4(PR_3)_4$ ($R = {}^iPr, {}^tBu$) cubane-type clusters by dissociation of the phosphine ligands.[16]

Incorporation of metal species (M′) into the incomplete cubane-type cluster **3** has also been investigated to obtain new cubane-type $Mo_3M'S_4$ clusters.[17] When cluster **3** was allowed to react with 1 equiv of $[Ni(cod)_2]$ in the presence of PPh_3 or under CO atmosphere, the cationic heterobimetallic cubane-type clusters $[(Cp^*Mo)_3(\mu_3\text{-}S)_4NiL][PF_6]$ (L = PPh_3 (**6**), CO (**7**)) are obtained in moderate yields (eq 3). The structures of **6** and **7** have been confirmed by X-ray crystallography.[18] The ^1H NMR spectra of **6** and **7** ($CDCl_3$) show one Cp* singlet (δ 1.88; **6**, δ 1.98; **7**). This indicates the equivalence of three Cp* ligands on Mo, which is consistent with the pseudo C_{3v} symmetry observed in the solid state. The IR spectrum of **7** shows a ν(CO) band at 2020 cm^{-1}, which is slightly lower than that (2031 cm^{-1}) of the Cp′ analogue $[(Cp'Mo)_3(\mu_3\text{-}S)_4Ni(CO)][pts]$ (pts = *p*-toluenesulfonate).[8c] This is due to the stronger electron-donating ability of Cp* ligand compared with Cp′ ligand.



Furthermore, treatment of cluster **3** with 1 equiv of $[Pd(dba)_2]$ (dba = dibenzylideneacetone) in CH_2Cl_2 gives rise to the formation of the Mo_3PdS_4 cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd(dba)][PF_6]$ (**8**) in moderate yield. The substitution of the dba ligand on the Pd atom by PPh_3 took place smoothly to give $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd(PPh_3)][PF_6]$ (**9**). Interestingly, when a solution of cluster **8** was stirred under a CO atmosphere, the carbonyl-bridged double cubane-type cluster $[\{(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd\}_2(\mu\text{-}CO)][PF_6]_2$ (**10**) was obtained as dark brown crystals (eq 3). The structure of **10** has been determined by NMR and FAB$^+$ mass spectroscopy as well as preliminary X-ray crystallography. The infrared spectrum of **10** shows a ν(CO) band at 1864 cm^{-1}, characteristic of the bridging carbonyl group.

The reaction of **3** with 1 equiv of a Ru(IV) complex $[RuH_4(PPh_3)_3]$ under an atmosphere of dihydrogen resulted in the formation of the heterobimetallic cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4RuH_2(PPh_3)][PF_6]$ (**11**) in 71% yield. The molecular structure of **11** was determined by X-ray crystallography.[18] The ^1H NMR spectrum (THF-d_8) of **11** shows a doublet at δ −9.70 (J_{HP} = 23 Hz) with 2H intensity assignable to two hydrides on the Ru atom split by one phosphorus nucleus ($^{31}P\{^1H\}$ NMR: δ 41.6 (s)). Cluster **11** provides the first cubane-type sulfido cluster containing hydrido ligands. When Ar gas was bubbled into a solution of **11** in THF-d_8 for 1 h at ambient temperature, a new signal was observed at δ 24.5 (s) in place of δ 41.6 (s) in the $^{31}P\{^1H\}$ NMR spectrum, while the above doublet signal due to the hydrides almost disappeared in the ^1H NMR spectrum. Replacement of the Ar atmosphere with 1 atm of H_2 regenerated the hydrido cluster **11**. This indicates that the unique Ru atom in cluster **11** reversibly binds H_2 under mild conditions.

In summary, our studies showed that both the dinuclear compound $[(Cp^*Mo)_2S_5]^+$ and the incomplete cubane-type cluster $[(Cp^*Mo)_3S_4]^+$ readily available from $[Cp^*Mo(SBu^t)_3]$ are promising building blocks for synthesis of a new series of mixed-metal clusters. Further investigation is now in progress to elucidate the reaction mechanism of eqs 1 and 2 and to explore novel catalytic activities of the heterobimetallic tetranuclear clusters obtained here.

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Supporting Information Available: Text giving experimental details. Tables of crystallographic data for **2**−**9** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) It is to be noted that employment of the neutral incomplete cubane-type cluster $[(Cp^*Mo)_3(\mu_2\text{-}S)_3(\mu_3\text{-}S)]$ in place of the cationic cluster **3** did not give any characterizable heterobimetallic cubane-type sulfido clusters in the reactions described here under similar conditions.

(18) See Supporting Information.