Bull. Chem. Soc. Jpn., *73*, *931—938 (2000)* 931

Synthesis and Characterization of Mixed-Metal Sulfido Clusters with the Cubane-Type $PtMo_3S_4$ Core

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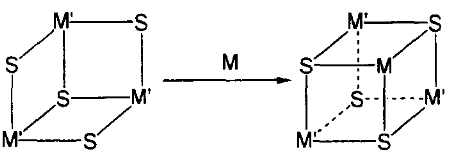
(Received November 19, 1999)

The reaction of the incomplete cubane-type cluster $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]Cl_4$ (**1**) and $[Pt(dba)_2]$ (dba = 1,5-diphenyl-1,4-pentadien-3-one) in MeOH gave a brown precipitate (**4**) that contains platinum and molybdenum in the atomic ratio of 1 : 3. Further treatment of **4** with 3 equiv of dppe (dppe = 1,2-bis(diphenylphosphino)ethane) gave the cubane-type cluster $[PtMo_3(\mu_3\text{-}S)_4Cl_4(dppe)_3]$ (**5**) in 37% yield, whose molecular structure was unambiguously characterized by X-ray diffraction study of $\mathbf{5}\cdot 2CH_2ClCH_2Cl\cdot 2H_2O$. A similar reaction of **4** with 4 equiv of dppe afforded the cationic cluster $[PtMo_3(\mu_3\text{-}S)_4Cl_3(dppe)_4]Cl$ (**6**) in 29% yield, which was characterized spectroscopically. The Pd–Mo and Ni–Mo analogues of the above Pt–Mo clusters, $[PdMo_3(\mu_3\text{-}S)_4Cl_3(dppe)_4]Cl\cdot CH_2Cl_2$ (**7**) and $[NiMo_3(\mu_3\text{-}S)_4Cl_4(dppe)_3]$ (**8**), were also synthesized by the reactions of the corresponding aqua clusters with dppe.

The cubane-type sulfido clusters have been attracting much attention, because they serve as excellent model systems for the active sites in metalloproteins[1—3] and industrial catalysts.[4—6] A large number of clusters of this class, especially those of the first row transition metals and/or group 6 metals, have been synthesized.[7—10] Among the synthetic methods for the cubane-type sulfido clusters, incorporation of a metal fragment (M) into a trinuclear incomplete cubane-type sulfido core ($M'_3(\mu_3\text{-}S)(\mu\text{-}S)_3$) provides a rational and straightforward route to heterobimetallic $MM'_3(\mu_3\text{-}S)_4$ clusters and related species (Scheme 1). Most typically, various mixed-metal clusters with the cubane-type $MMo_3(\mu_3\text{-}S)_4$ core or related cuboidal cores have been synthesized by the reaction of the incomplete cubane-type cluster $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]Cl_4$ (**1**) with metals or metal ions in the presence of a reducing agent.[9,11—18] The molecular and electronic structures of the $MMo_3(\mu_3\text{-}S)_4$ type clusters thus obtained as well as their reactivities have recently been actively investigated.[13,19—23]

We have long been interested in syntheses and reactivities of multinuclear group 8—10 noble metal complexes with sulfur ligands,[24—36] since they are expected to provide robust multimetallic reaction sites which can assist or catalyze unique transformations of organic substrates. In particular, mixed-metal cubane-type sulfido clusters containing noble metal elements are intriguing synthetic targets, and in fact several new series of cubane-type clusters have been prepared in this laboratory by utilizing dinuclear[25—29,35] or trinuclear[12,13] complexes with bridging hydrogensulfido or sulfido ligands.[36] In the course of this study, we previously synthesized the mixed-metal cubane-type cluster $[PdMo_3(\mu_3\text{-}S)_4Cl(H_2O)_9]Cl_3\cdot HCl$ (**2**) and its tacn derivatives $[PdMo_3(\mu_3\text{-}S)_4Cl(tacn)_3]X_3$ (**3a**, X = Cl; **3b**, X = ClO_4; **3c**, X = PF_6; tacn = 1,4,7-triazacyclononane) by the reaction of cluster **1** with palladium black. Clusters **2** and **3** represent the first examples of the $MMo_3(\mu_3\text{-}S)_4$ clusters containing a noble metal element as the heterometal M. Quite interestingly, clusters **2** and **3** can bind various small molecules such as CO, ^{t}BuNC, and alkenes,[12,13] and further, **3c** behaves as a highly effective catalyst for the addition reactions of alcohols or carboxylic acids to electron deficient alkynes[13,21] as well as for the lactonization of ω-alkynoic acids.[22] Noteworthy is that the selectivity and catalytic activity of **3c** in these reactions are far superior to those of conventional mononuclear palladium complexes, demonstrating potentiality of mixed-metal sulfido clusters as a novel type of homogenous catalysts for organic synthesis.

The remarkable reactivities of **3** prompted us to prepare the platinum analogues with a $PtMo_3(\mu_3\text{-}S)_4$ core. However, cluster **1** was unreactive toward metallic platinum, and the platinum analogue of **2** could not be obtained by the method adopted for the synthesis of **2**.[37] Now we have found that the reaction of cluster **1** with the low valent platinum complex $[Pt(dba)_2]$ (dba = 1,5-diphenyl-1,4-pentadiene-3-one) as a platinum source, followed by treatment with dppe (dppe = 1,2-bis(diphenylphosphino)ethane), gives cubane-type $PtMo_3(\mu_3\text{-}S)_4$ clusters containing three or four dppe ligands. Here we describe synthesis and characterization of these new Pt–Mo clusters. Preparation of their Ni–Mo and Pd–Mo analogues is also reported.



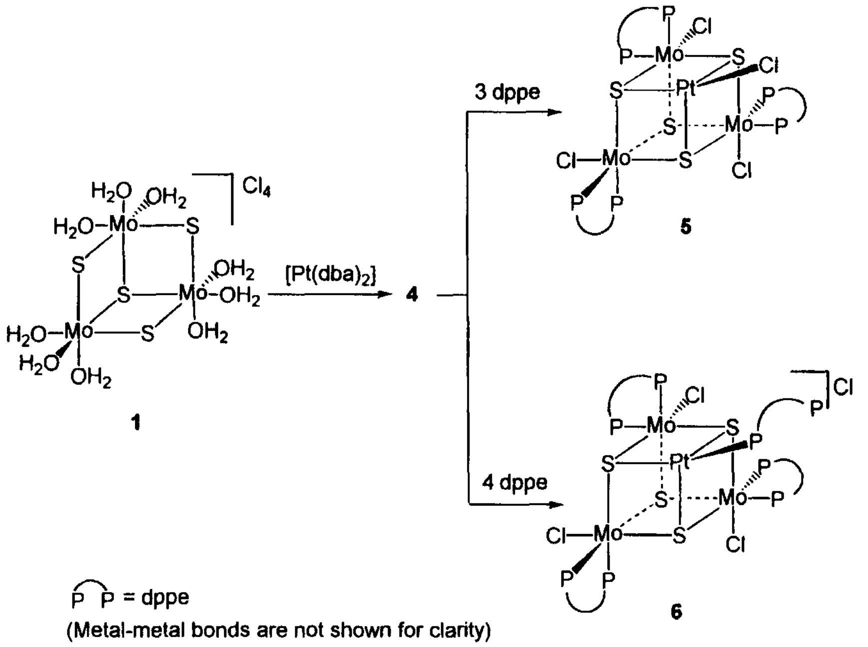
Scheme 1.

Results and Discussion

Preparation and Characterization of $[PtMo_3(\mu_3\text{-}S)_4Cl_4(dppe)_3]$ (5). As described in the introduction, cluster **1** usually reacts with a metal (M) to form the cubane-type cluster with a $MMo_3(\mu_3\text{-}S)_4$ core. Since cluster **1** was found to be inert to metallic platinum, we focussed our attention on reactions of **1** with low valent platinum complexes. An attempted reaction of **1** with $[Pt(PPh_3)_4]$ did not give any characterizable products. On the other hand, when **1** was allowed to react with 1 equiv of $[Pt(dba)_2]$ in MeOH for 3 d, a new compound **4** was obtained as a brown powder, concurrent with liberation of nearly 1 mol of dba ligand per **1**. The ^1H NMR spectrum of **4** in D_2O showed complicated signals at $\delta = 5.8$—7.6 that are attributable to the phenyl and vinyl groups of the coordinated dba. The $^{13}C\{^1H\}$ NMR also revealed the existence of phenyl, vinyl ($\delta = 128$—147) and carbonyl ($\delta = 199$) groups. However, the $\nu(C{=}O)$ of the dba ligand was obscured by overlapping with the broad absorption of the H_2O ligands at around 1620 cm^{-1} (KBr disk). Unfortunately, compound **4** failed to give crystals suitable for X-ray structural analysis. However, the electron-probe microanalysis (EPMA) of **4** indicated that it contains platinum and molybdenum atoms in the ratio of 1 : 3, and further reactions of **4** with dppe afforded the cubane-type $PtMo_3(\mu_3\text{-}S)_4$ clusters (vide infra). On the basis of these facts, we tentatively formulate compound **4** as $[PtMo_3S_4(H_2O)_9(dba)]Cl_4$, although satisfactory analytical data could not be obtained for this material.

The $PtMo_3(\mu_3\text{-}S)_4$ core was characterized as its dppe derivatives. When a MeOH solution of **4** was treated with 3 equiv of dppe in CH_2Cl_2, a reddish brown solution was formed. Purification of the crude product by silica gel column chromatography under a nitrogen atmosphere and recrystallization from CH_2Cl_2–hexane gave $[PtMo_3(\mu_3\text{-}S)_4Cl_4(dppe)_3]$ (**5**) as black purple crystals in 37% yield (Scheme 2). The UV-vis spectrum of **5** in CH_2Cl_2 showed peaks at 400 ($\varepsilon/M^{-1}\,cm^{-1} = 4.0\times10^3$), 530 ($1.4\times10^3$), 595 sh ($1.2\times10^3$), and 693 nm ($6.1\times10^2$) (1 M = 1 mol dm^{-3}).

The molecular structure of cluster **5** was established by X-ray diffraction study of a single crystal of $5\cdot2CH_2ClCH_2Cl\cdot2H_2O$ obtained by recrystallization of **5** from 1,2-dichloroethane–benzene–hexane. An ORTEP view of **5** is depicted in Fig. 1, and selected bond distances and angles are summarized in Table 1. Cluster **5** has a single cubane-type $PtMo_3(\mu_3\text{-}S)_4$ core which is further coordinated by four chloro ligands and three dppe ligands. The platinum atom is tetrahedrally bonded to three μ_3-S ligands and a chlorine atom, while each molybdenum atom has a distorted octahedral geometry with one chelating dppe, one chloro, and three μ_3-S ligands. The molecule has approximate C_3 symmetry around the Cl(1)–Pt(1)–S(4) axis. The Mo–Mo distances at 2.823(4), 2.813(3), and 2.816(4) Å as well as the Pt–Mo distances at 2.762(3), 2.741(3), and 2.762(3) Å are diagnostic of metal–metal bonds between these atoms. The core structure with six metal–metal bonds for **5** is consistent with its total electron count of 60 e^-. The Mo–Mo distances in **5** are close to those found in cluster **3a** (2.815(2)—2.825(2) Å)[13] in spite of their very different total charges and ancillary ligands. It should be noted that the Pd–Cl bond found in cluster **3a** (2.450(4) Å)[13] is considerably elongated, whereas the Pt–Cl bond distance in **5** at 2.388(8) Å is not unusual. Among the bond distances between the molybdenum atoms and the μ_3-S ligands capping the $PtMo_2$ faces, those at the *trans* positions to the Mo–P bonds are longer than the others by 0.01—0.04 Å. This may be attributed to the *trans* influence of the phosphine ligands being stronger than that of the chloro ligands.



Scheme 2.

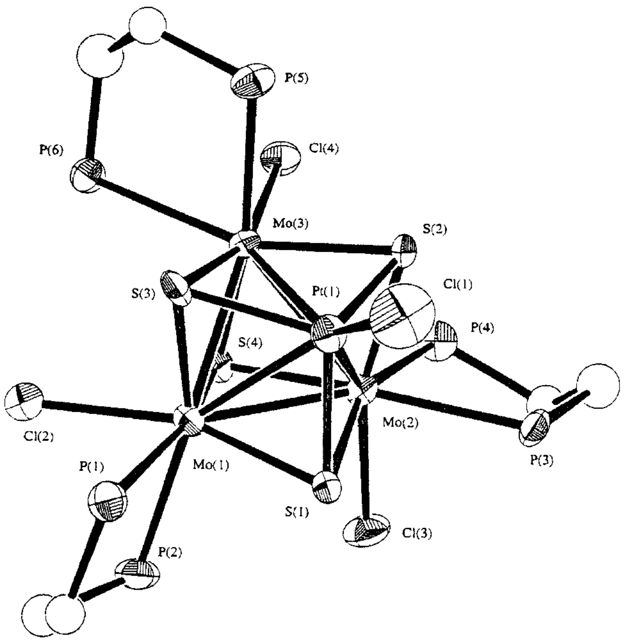


Fig. 1. An ORTEP drawing for $5\cdot2CH_2ClCH_2Cl\cdot2H_2O$. Solvent molecules, phenyl groups, and hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

Table 1. Selected Bond Distances and Angles in $5\cdot2CH_2ClCH_2Cl\cdot2H_2O$

	Bond distances (Å)		
Pt(1)–Mo(1)	2.762(3)	Pt(1)–Mo(2)	2.741(3)
Pt(1)–Mo(3)	2.762(3)	Mo(1)–Mo(2)	2.823(4)
Mo(1)–Mo(3)	2.813(3)	Mo(2)–Mo(3)	2.816(4)
Pt(1)–Cl(1)	2.388(8)	Pt(1)–S(1)	2.336(7)
Pt(1)–S(2)	2.324(7)	Pt(1)–S(3)	2.332(8)
Mo(1)–Cl(2)	2.482(8)	Mo(1)–S(1)	2.353(8)
Mo(1)–S(3)	2.363(8)	Mo(1)–S(4)	2.343(8)
Mo(1)–P(1)	2.623(8)	Mo(1)–P(2)	2.639(8)
Mo(2)–Cl(3)	2.496(7)	Mo(2)–S(1)	2.394(8)
Mo(2)–S(2)	2.355(7)	Mo(2)–S(4)	2.348(8)
Mo(2)–P(3)	2.612(8)	Mo(2)–P(4)	2.667(8)
Mo(3)–Cl(4)	2.475(7)	Mo(3)–S(2)	2.371(8)
Mo(3)–S(3)	2.351(8)	Mo(3)–S(4)	2.349(7)
Mo(3)–P(5)	2.622(8)	Mo(3)–P(6)	2.667(8)
	Bond angles (deg)		
Cl(1)–Pt(1)–S(1)	111.7(3)	Cl(1)–Pt(1)–S(2)	110.4(3)
Cl(1)–Pt(1)–S(3)	114.6(3)	S(1)–Pt(1)–S(2)	107.8(3)
S(1)–Pt(1)–S(3)	105.8(2)	S(2)–Pt(1)–S(3)	106.1(3)
S(1)–Mo(1)–S(3)	104.3(3)	S(1)–Mo(1)–S(4)	104.9(3)
S(3)–Mo(1)–S(4)	104.4(2)	S(1)–Mo(2)–S(2)	104.9(3)
S(1)–Mo(2)–S(4)	103.5(3)	S(2)–Mo(2)–S(4)	104.7(3)
S(2)–Mo(3)–S(3)	104.0(3)	S(2)–Mo(3)–S(4)	104.2(3)
S(3)–Mo(3)–S(4)	104.6(2)	Pt(1)–S(1)–Mo(1)	72.2(2)
Pt(1)–S(1)–Mo(2)	70.8(2)	Mo(1)–S(1)–Mo(2)	73.0(2)
Pt(1)–S(2)–Mo(2)	71.7(2)	Pt(1)–S(2)–Mo(3)	72.1(2)
Mo(2)–S(2)–Mo(3)	73.2(2)	Pt(1)–S(3)–Mo(1)	72.1(2)
Pt(1)–S(3)–Mo(3)	72.3(2)	Mo(1)–S(3)–Mo(3)	73.3(2)
Mo(1)–S(4)–Mo(2)	74.0(2)	Mo(1)–S(4)–Mo(3)	73.7(2)
Mo(2)–S(4)–Mo(3)	73.7(2)		

In the $^{31}P\{^1H\}$ NMR, cluster **5** showed two pseudo triplet signals at δ = 22.9 and 28.1 in harmony with the solid state structure possessing approximate C_3 symmetry. The splitting pattern can be interpreted as follows. Each phosphorus nucleus is coupled to its *gem* neighbor with the coupling constant $^2J_{P-Mo-P}$ of 5.5 Hz. In addition, it has a similar coupling constant $^3J_{P-Mo-Mo-P}$ with only one other phosphorus nucleus, making the signal an apparent triplet. We consider that the latter coupling corresponds to those between the P_A and $P_{B'}$, $P_{A'}$ and $P_{B''}$, and $P_{A''}$ and P_B nuclei (Chart 1), because each pair of the phosphorus nuclei of these combinations are located in nearly anti conformation with respect to the P–Mo–Mo–P bonds, where the average P–Mo–Mo–P dihedral angle is 157.2°. The average dihedral angle for the other P–Mo–Mo–P bonds is 84.0°. Similar coupling patterns were observed for some incomplete cubane-type clusters, such as $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(dmpe)_3]Cl$[38] (dmpe = 1,2-bis(dimethylphosphino)ethane) and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(dppe)_3]Cl$.[39]

In contrast to the above reaction, it has been reported that the trimolybdenum cluster $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(MeOH)_2(PEt_3)_3]$ with an incomplete cubane-type $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ core similar to **1** is converted into the pentanuclear cluster $[Mo_3Pt_2(\mu_3\text{-}S)_3(\mu\text{-}S)Cl_4(PEt_3)_4]$ by reaction with $[Pt(cod)_2]$ (cod = 1,5-cyclooctadiene) and PEt_3.[40] In this case, each platinum atom is attached to the respective $Mo_2(\mu\text{-}S)$ face of the starting cluster to form a planar Mo_3Pt_2 framework. On the other hand, we have previously reported that the reaction of the dimolybdenum and ditungsten complexes $[M_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ (M = Mo, W) with $[M'Cl(PPh_3)_3]$ (M′ = Rh, Ir) gives the trinuclear incomplete cubane-type clusters $[M'(PPh_3)_2(\mu_3\text{-}S)(\mu\text{-}S)_3\{M(S_2CNEt_2)\}_2(\mu_2\text{-}Cl)]$, while the reaction with $[M'Cl(cod)]_2$ (M′ = Rh, Ir) leads to the formation of the cubane-type clusters $[\{M'(cod)\}_2\{MCl(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$.[28,29] It is noteworthy that in these cluster syntheses, the ancillary ligands of the di- or trinuclear sulfido complexes as well as of the noble metal species seem to have profound effects on the structures of the clusters formed.

Preparation and Characterization of $[PtMo_3(\mu_3\text{-}S)_4Cl_3(dppe)_4]Cl$ (6). When compound **4** was allowed to react with 4 equiv of dppe in MeOH, the cationic cluster $[PtMo_3(\mu_3\text{-}S)_4Cl_3(dppe)_4]Cl$ (**6**) was obtained in 29% yield after purification by silica gel column chromatography

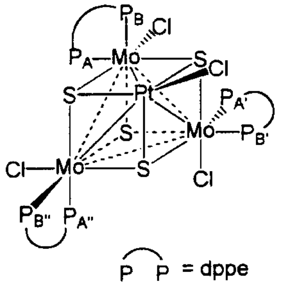


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Chart 1.

and recrystallization from CH_2Cl_2–hexane (Scheme 2). For the chromatographic purification, use of a highly polar eluent (MeOH–CH_2Cl_2 1 : 9) was necessary, which suggested the ionic nature of cluster **6**. In fact, the molar conductivity of **6** in CH_2Cl_2 (57.7 S cm^2 mol^{-1}) was comparable to that of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(dppe)_3]Cl$ (56.4 S cm^2 mol^{-1}), confirming that **6** is a 1 : 1 electrolyte. Cluster **6** showed two peaks in its UV-vis spectrum in CH_2Cl_2 at 455.5 (ε/M^{-1} cm^{-1} = 4.0×10^3) and 613.5 nm (6.9×10^2).

Cluster **6** was characterized spectroscopically. The $^{31}P\{^1H\}$ NMR spectrum of **6** revealed that it contains four types of chemically different phosphorus nuclei in the ratio of 3 : 3 : 1 : 1. The more intense signals at δ = 31.3 and 31.9 appeared as a pseudo quartet (J = 5.5 Hz) and a pseudo triplet (J = 5.5 Hz), respectively. These signals are assigned to the chelating dppe ligands on the molybdenum atoms. The signals with the lower intensity were observed at δ = 17.5 and −10.3 as a doublet of quartets (J = 42 and 6 Hz) and a doublet (J = 42 Hz), respectively, and the former signal is accompanied by satellite peaks with the $^1J_{Pt-P}$ coupling constant of 6133 Hz. It should be pointed out that this $^1J_{Pt-P}$ value is considerably larger than those observed for known sulfido clusters containing platinum such as $[Pt(PPh_3)(\mu\text{-}S)_2\{Mo(S_2CNEt_2)\}_2(\mu\text{-}S)_2]$ (J = 4381 Hz),[29] $[Pt_3\{Re(CO)_3\}(\mu_3\text{-}S)_2(\mu\text{-dppm})_3][PF_6]$ (J = 3850, 3038, 2987 Hz),[41] $[Mo_3Pt_2(\mu_3\text{-}S)_3(\mu\text{-}S)Cl_4(PEt_3)_4]$ (J = 4410, 3100 Hz),[40] and $[Pt_2(\mu\text{-}S)(dppe)(CS)(PPh_3)]$ (J = 3200, 3160, 2330 Hz).[42] The signal at δ = − 10.3 is clearly ascribed to an uncoordinated PPh_2 group, exhibiting that the platinum center is bonded to a monodentate dppe ligand. On the basis of this $^{31}P\{^1H\}$ NMR spectrum as well as the analytical data, cluster **6** is concluded to have a structure similar to that of **5** except that the chloro ligand on the platinum atom is replaced by the monodentate dppe ligand to make the cluster cationic. The pseudo quartet coupling pattern for the signal at δ = 31.3 described above is accounted for by the $^3J_{P-Pt-Mo-P}$ coupling constant between the P_C nucleus and the P_A, $P_{A'}$, or $P_{A''}$ nuclei (J = 6 Hz) being almost the same as the $^2J_{P-Mo-P}$ and $^3J_{P-Mo-Mo-P}$ values (J = 5.5 Hz) (Chart 2).

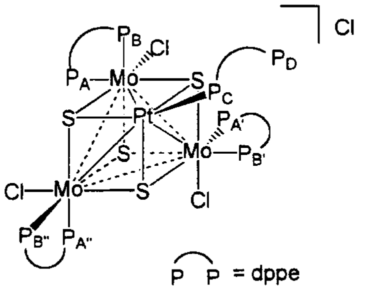

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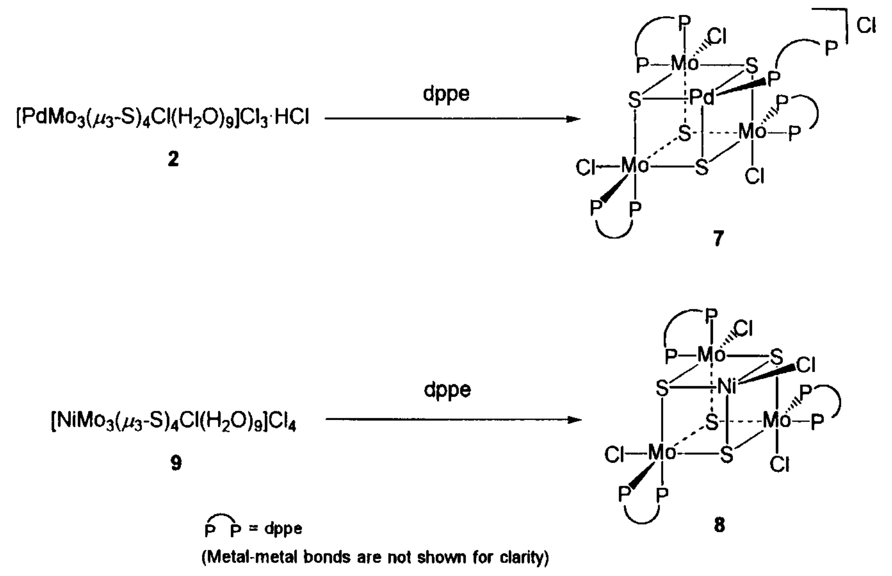
Chart 2.

Preparation and Characterization of $[PdMo_3(\mu_3\text{-}S)_4Cl_3(dppe)_4]Cl\cdot CH_2Cl_2$ (7) and $[NiMo_3(\mu_3\text{-}S)_4Cl_4(dppe)_3]$ (8). In order to prepare the palladium and nickel analogues of clusters **5** and **6** for comparison, reactions of the $PdMo_3$ cluster **2** and the $NiMo_3$ cluster $[NiMo_3(\mu_3\text{-}S)_4Cl(H_2O)_9]Cl_3$[43] (**9**) with dppe were also investigated (Scheme 3). When cluster **2** was treated with 4.5 equiv of dppe in MeOH, the cationic cluster $[PdMo_3(\mu_3\text{-}S)_4Cl_3(dppe)_4]Cl\cdot CH_2Cl_2$ (**7**) was obtained in 50% yield after purification by column chromatography on silica gel and recrystallization from CH_2Cl_2–benzene–hexane. The cationic nature of **7** was confirmed by its molar conductivity of 48.7 S cm^2 mol^{-1} in CH_2Cl_2.

The $^{31}P\{^1H\}$ NMR spectrum of **7** exhibited four distinct signals with the intensity ratio of 3 : 3 : 1 : 1. The splitting pattern of these signals is closely related to that of **6** and can be interpreted by considering the P–Mo–P, P–Mo–Mo–P, and P–Mo–Pd–P couplings as described for **5** and **6**. Thus, the more intense signals at δ = 27.4 and 27.9 appeared as a pseudo quartet and a pseudo triplet, respectively, with the



Scheme 3.

coupling constant of 6 Hz, and are assignable to the signals of the three chelating dppe ligands on the molybdenum atoms. The other two signals, a doublet of quartets at δ = 25.5 (J = 37, 6 Hz) and a doublet at δ = -14.0 (J = 37 Hz), are considered to be due to the monodentate dppe ligand coordinated to the palladium atom. The electronic spectrum of **7** in CH_2Cl_2 showed peaks at 464 ($\varepsilon/M^{-1}\,cm^{-1} = 2.4\times10^3$), 538.5 sh ($1.0\times10^3$), and 661.5 nm ($3.0\times10^2$).

Several attempts to prepare the palladium analogue of **5** failed. In the reaction of cluster **2** with 3 equiv of dppe in MeOH, cluster **7** was the only product characterized by the $^{31}P\{^1H\}$ NMR analysis of the crude reaction mixture.

In contrast, when cluster **9** was allowed to react with 3 equiv of dppe in $MeOH-CH_2Cl_2$, the dppe derivative $[NiMo_3(\mu_3\text{-}S)_4Cl_4(dppe)_3]$ (**8**) was obtained as dark brown needles in 43% yield after recrystallization from CH_2Cl_2–hexane. Interestingly, cluster **8** was also obtained in 42% yield as the only isolable product by the reaction of the aqua cluster **9** with 4 equiv of dppe, and the cationic $NiMo_3$ cluster analogous to **6** and **7** was not obtained. Therefore the ligand substitution product of $[MMo_3(\mu_3\text{-}S)_4Cl(H_2O)_9]Cl_3$ (M = Pd, Ni) cluster depends on the heterometal M, but at present the reason for this phenomenon is not clear.

The electronic spectrum of **8** in CH_2Cl_2 exhibited peaks at 533.5 ($\varepsilon/M^{-1}\,cm^{-1} = 5.7\times10^2$), 712.5 ($4.2\times10^2$), and 849 nm ($3.9\times10^2$). The $^{31}P\{^1H\}$ NMR spectrum of **8**, displaying two pseudo triplets (J = 6 Hz) at δ = 25.3 and 25.7, is very similar to that of cluster **5**, revealing that the structures of **5** and **8** are closely related to each other. Analytical data were also in full agreement with the formulation.

Electrochemical Properties of 5—8. Electrochemical properties of the newly prepared cubane-type clusters **5**—**8** were investigated by cyclic voltammetry. Each cyclic voltammogram of the $PtMo_3$ cluster **5** and the $NiMo_3$ cluster **8** in 0.1 M $^nBu_4NBF_4/CH_2Cl_2$ showed one reversible oxidation wave at $E_{1/2}$ = 0.67 and 0.66 V, respectively. It should be pointed out that the effect of the heterometal atom (platinum or nickel) on the redox potential of the cluster is very small. Shibahara et al. also reported that the cathodic peak potentials for the reduction of $[FeMo_3(\mu_3\text{-}S)_4(H_2O)_{10}][CH_3C_6H_4SO_3]_4$ (E_p = -0.91, -1.47, -1.81 V) and $[NiMo_3(\mu_3\text{-}S)_4(H_2O)_{10}][CH_3C_6H_4SO_3]_4$ (E_p = -0.91, -1.48, -1.72 V) are close to each other, although the reduction processes for these compounds are essentially irreversible.[20] These observations differ very sharply from the recently reported electrochemical properties of the heterobimetallic $MFe_3(\mu_3\text{-}S)_4$ cubane-type clusters[44] and the $MIr_4(\mu_3\text{-}S)_4$ bow-tie clusters,[34] where the redox potentials are affected significantly and systematically by the nature of the heterometal M.

On the other hand, the cationic $PtMo_3$ cluster **6** showed one irreversible oxidation wave at E_p = 1.41 V, which is assigned to the oxidation of the uncoordinated PPh_2 group by comparison with the redox potential of free dppe (1.21 V, irreversible). The cationic $PdMo_3$ cluster **7** also exhibited a similar irreversible oxidation wave at E_p = 1.39 V, and in addition, a reversible reduction wave at $E_{1/2}$ = -0.83 V, although the reason why the reduction process was observed only with cluster **7** is not clear.

Reactivities of 5, 6, and 8. As already mentioned, we have previously demonstrated that the $PdMo_3$ cubane-type cluster **3c** acts as an excellent catalyst for some addition reactions of alkynes.[13,21,22] We at first attempted to use the $PtMo_3$ cubane-type clusters **5** and **6** as the catalysts for similar reactions of alkynes. However, both **5** and **6** were found ineffective for the addition of MeOH to methyl propiolate under the same conditions as the reaction with **3c**.

We also investigated reactions of **5** and **8** with CO or monophosphines such as PMe_3 and PMe_2Ph, but no formation of either carbonyl or monophosphine derivatives was confirmed by the IR or $^{31}P\{^1H\}$ NMR analyses of the crude reaction mixtures. Unexpectedly, treatment of **5** with dppe did not give rise to generation of cluster **6**. This finding suggests that **5** and **6** are independently derived from **4**, and **5** is not the intermediate for the conversion of **4** to **6**, although the detailed reaction courses for the formation of **5** and **6** have not been established. All these results indicate that the chloro ligand on the platinum atom in **5** or on the nickel atom in **8** is inert toward ligand substitution, and make a sharp contrast to the fact that the chloro ligand on the palladium or nickel atom in aqua clusters **2**, **3**,[13] and **9**[19] readily undergoes ligand exchange reactions with CO, ^{t}BuNC, alkenes and/or alkynes. The difference in the reactivities may reflect, at least in part, the structural feature that cluster **3a** has a rather long Pd–Cl bond while the Pt–Cl bond distance in **5** is normal. The large $^1J_{Pt-P}$ value observed for **6** (vide supra) is also in accord with the tendency of the platinum center in **6** to have strong interactions with the terminal ligand. It is of great interest that the coordination of dppe and chloro ligands on the molybdenum centers strongly affects the reactivities of the platinum and nickel centers in **5**, **6**, and **8** through the cluster metal–metal bonds.

Experimental

General Consideration. All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled by common methods. Complexes $[Pt(dba)_2]$,[45] $[Pt(PPh_3)_4]$,[46] $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]Cl_4$ (**1**),[47] $[PdMo_3(\mu_3\text{-}S)_4Cl(H_2O)_9]Cl_3$ (**2**),[13] and $[NiMo_3(\mu_3\text{-}S)_4Cl(H_2O)_9]Cl_3$ (**9**)[43] were prepared according to the literature procedures. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were measured on a JEOL LA-400 (^1H, 400 MHz; ^{13}C, 100 MHz) spectrometer and on a JEOL EX-270 (^{31}P, 108 MHz) spectrometer. Elemental analyses were performed with a Perkin–Elmer 2400II CHN analyzer (for C and H) or at the Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo (for S and Cl). GLC analyses were performed using a Shimadzu GC-14A gas chromatograph equipped with a HiCap-CBP10-M25-025 capillary column and an FID detector. GC-MS spectra were taken on a Shimadzu GCMS-QP5000 spectrometer. Electroconductivities were measured at 22 °C in CH_2Cl_2 solution under a nitrogen atmosphere with a Toa CM-20A digital conductivity meter. Electron probe microanalyses were performed on a Kevex μX7000 dispersive-type X-ray analyzer. Electrochemical measurements were made with Hokuto Denko instrumentation (HA-501 potentiostat and HB-105 function generator) using a glassy carbon electrode;

potentials were measured in CH_2Cl_2–0.1 M $^n Bu_4NBF_4$ vs. a saturated calomel electrode as the reference. UV-vis spectra were measured using a Shimadzu UV-2400PC spectrophotometer.

Reaction of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]Cl_4$ with $[Pt(dba)_2]$ (Preparation of 4). To a green solution of **1** (500 mg, 690 μmol) in MeOH was added $[Pt(dba)_2]$ (460 mg, 690 μmol), and the mixture was stirred for 3 d at room temperature. The color of the solution gradually changed to brown during the reaction. Then, the mixture was evaporated to dryness, and the residue was extracted with MeOH. The MeOH solution was dried up, and the resultant brown solid was washed with several portions of CH_2Cl_2 and dried in vacuo to give **4** (510 mg, 440 μmol, 85% yield) as a brown powder. Anal. Found: C, 17.70; H, 2.32; Cl, 15.56; S, 12.64%. Calcd for $C_{17}H_{32}Cl_4Mo_3O_{10}PtS_4$: C, 17.76; H, 2.81; Cl, 12.34; S, 11.16%. The combined CH_2Cl_2 washings were evaporated and extracted with ether. The ethereal solution was filtered through Celite and dried up to give yellow crystals of dba (154 mg, 657 μmol, 95% per complex **1**).

Preparation of $[PtMo_3(\mu_3\text{-}S)_4Cl_4(dppe)_3]$ (5). To a solution of **4** (205 mg, 174 μmol) in MeOH (50 ml) was added dppe (230 mg, 577 μmol) in CH_2Cl_2 (5 ml), and the mixture was stirred for 8 h at room temperature. The resultant reddish brown solution was evaporated, and the residue was dissolved in acetone and charged on a silica gel column. The first purple band eluted by acetone–hexane (1 : 2) was collected and recrystallized from CH_2Cl_2–hexane to give black purple crystals of **5** (125 mg, 64 μmol, 37% yield). ^1H NMR (CD_2Cl_2) δ = 1.93—2.10 (m, 3H, CH_2), 2.40—2.49 (m, 3H, CH_2), 3.00—3.18 (m, 6H, CH_2), 6.81—8.00 (m, 60H, aryl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ = 22.9 (pseudo t, J_{P-P} = 5.5 Hz), 28.1 (pseudo t, J_{P-P} = 5.5 Hz). Anal. Found: C, 48.45; H, 3.99; Cl, 7.24; S, 6.30%. Calcd for $C_{78}H_{72}Cl_4Mo_3P_6PtS_4$: C, 48.09; H, 3.73; Cl, 7.28; S, 6.58%. Crystals of $\mathbf{5}\cdot 2CH_2ClCH_2Cl\cdot 2H_2O$ suitable for X-ray diffraction study were obtained as black needles by slow diffusion of hexane into a concentrated solution of **5** in 1,2-dichloroethane–benzene.

Preparation of $[PtMo_3(\mu_3\text{-}S)_4Cl_3(dppe)_4]Cl$ (6). A solution of compound **4** (202 mg, 176 μmol) and dppe (280 mg, 703 μmol) in MeOH (30 ml) was stirred for 3 d at room temperature. The reaction mixture was dried up, and the residue was washed by ether (3×10 ml). The resulting solid was dissolved in CH_2Cl_2 and loaded on a silica gel column, and the first brown band eluted by CH_2Cl_2–MeOH (9 : 1) was collected and recrystallized from CH_2Cl_2–hexane to give **6** as brown needles (119 mg, 51 μmol, 29% yield). ^1H NMR (CD_2Cl_2) δ = 1.55—1.98 (m, 12H, CH_2), 2.64—2.95 (m, 2H, CH_2), 3.00—3.23 (m, 2H, CH_2), 6.10—7.98 (m, 80H, aryl). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = -10.3 (d, J_{P-P} = 42 Hz), 17.5 (dq, J_{P-P} = 42,6 Hz, J_{Pt-P} = 6133 Hz), 31.3 (pseudo q, J_{P-P} = 5.5 Hz), 31.9 (pseudo t, J_{P-P} = 5.5 Hz). Anal. Found: C, 52.98; H, 4.44%. Calcd for $C_{104}H_{96}Cl_4Mo_3P_8PtS_4$: C, 53.23; H, 4.12%. Electroconductivity (0.464 mM in CH_2Cl_2): 57.7 S cm^2 mol^{-1}.

Preparation of $[PdMo_3(\mu_3\text{-}S)_4Cl_3(dppe)_4]Cl\cdot CH_2Cl_2$ (7). A solution of cluster **2** (106 mg, 123 μmol) and dppe (219 mg, 550 μmol) in MeOH (10 ml) was stirred for 1 d at room temperature. The reaction mixture was then dried up and chromatographed on silica gel. The first brown band eluted by CH_2Cl_2–MeOH (9 : 1) was collected and evaporated to give a brown powder. Recrystallization of the powder from CH_2Cl_2–benzene–hexane afforded cluster **7** as brown needles (138 mg, 61 μmol, 50% yield). ^1H NMR ($CDCl_3$) δ = 1.52—1.77 (m, 6H, CH_2), 1.77—2.05 (m, 6H, CH_2), 2.71—3.00 (m, 2H, CH_2), 3.02—3.21 (m, 2H, CH_2), 5.29 (s, 2H, CH_2Cl_2), 6.05—8.02 (m, 80H, aryl). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = -14.0 (d, J_{P-P} = 37 Hz), 25.5 (dq, J_{P-P} = 37, 6 Hz), 27.4 (pseudo q, J_{P-P} = 6 Hz), 27.9 (pseudo t, J_{P-P} = 5 Hz). Anal. Found: C, 53.61; H, 4.31%. Calcd for $C_{105}H_{98}Cl_6Mo_3P_8PdS_4$: C, 53.83; H, 4.22%. Electroconductivity (0.465 mM in CH_2Cl_2): 48.7 S cm^2 mol^{-1}.

Preparation of $[NiMo_3(\mu_3\text{-}S)_4Cl_4(dppe)_3]$ (8). A suspension of cluster **9** (50 mg, 63 μmol) and dppe (73 mg, 180 μmol) in MeOH (2 ml)–acetone (2 ml) was stirred for 1 h. Then CH_2Cl_2 (5 ml) was added to the suspension, and the mixture was further stirred for 30 min and was dried up in vacuo. The residue was dissolved in a small amount of CH_2Cl_2, and the solution was diluted by MeOH to give a brown precipitate, which was collected and recrystallized from CH_2Cl_2–hexane to give cluster **8** as dark brown needles (49 mg, 27 μmol, 43% yield). ^1H NMR (CD_2Cl_2) δ = 1.78—1.98 (m, 3H, CH_2), 2.24—2.40 (m, 3H, CH_2), 2.92—3.14 (m, 6H, CH_2), 6.70—6.74 (m, 6H, aryl), 6.83—6.88 (m, 12H, aryl), 6.96—6.99 (m, 3H, aryl), 7.18—7.43 (m, 27H, aryl), 7.59—7.69 (m, 6H, aryl), 7.97—8.01 (m, 6H, aryl); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 25.3 (pseudo t, J_{P-P} = 6 Hz), 25.7 (pseudo t, J_{P-P} = 6 Hz). Anal. Found: C, 51.44; H, 3.99%. Calcd for $C_{78}H_{72}Cl_4Mo_3NiP_6S_4$: C, 51.71; H, 4.01%. A similar reaction of **9** (51 mg, 64 μmol) with 4 equiv of dppe (100 mg, 250 μmol) also afforded cluster **8** (49 mg, 27 μmol, 42% yield).

X-Ray Diffraction Study for $\mathbf{5}\cdot 2CH_2ClCH_2Cl\cdot 2H_2O$. A single crystal of $\mathbf{5}\cdot 2CH_2ClCH_2Cl\cdot 2H_2O$ suitable for X-ray diffraction study was sealed in a glass capillary under an argon atmosphere and used for data collection. Diffraction data were collected on a Rigaku AFC7R four-circle automated diffractometer with graphite-monochromatized Mo $K\alpha$ radiation (λ = 0.71069 Å) at 21 °C using the ω–2θ scan technique. The orientation matrices and unit cell parameters were determined by least-squares refinement of 25 machine-centered reflections with $37.6° < 2\theta < 40.0°$. Intensity data were corrected for Lorentz and polarization effects and for absorption (empirical, ψ scans). No significant decay was observed for respective three standard reflections monitored every 150 reflections during the data collection. Details of the X-ray diffraction study are summarized in Table 2.

Table 2. X-Ray Crystallographic Data for $\mathbf{5}\cdot 2CH_2ClCH_2Cl\cdot 2H_2O$

Formula	$C_{82}H_{84}Cl_8Mo_3O_2P_6PtS_4$
Fw	2182.18
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	14.614(6)
b/Å	15.101(4)
c/Å	21.359(7)
α/deg	91.78(3)
β/deg	100.58(3)
γ/deg	100.01(4)
V/Å^3	4553(2)
Z	2
T/°C	21
λ (Mo $K\alpha$)/Å	0.71069
D_{calcd}/g cm^{-3}	1.592
2θ range	$5.0 < 2\theta < 50.0°$
Scan mode	ω–2θ
Scan width/deg	$1.78 + 0.30 \tan\theta$
No. of unique data	16676
No. of observations	5903 ($I > 3\sigma(I)$)
$R^{a)}$	0.082
$R_w^{b)}$	0.070

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, where $w = 1/\sigma^2(F_o)$.

The structure solution and refinements were carried out by using the teXsan program package.[48] The positions of the non-hydrogen atoms were determined by Patterson methods (DIRDIF PATTY[49]) and subsequent Fourier syntheses. All non-hydrogen atoms were refined by full-matrix least-squares techniques. The carbon and oxygen atoms were refined isotropically, while the other non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms except for those of water molecules in the crystal were placed at the calculated positions (d(C–H) 0.95 Å) and were included in the final stage of refinements with fixed isotropic parameters.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 140101. Lists of the structure factors, positional and thermal parameters for all atoms, and bond lengths and angles for the non-hydrogen atoms have been deposited as Document No. 73030 at the Office of the Editor of Bull. Chem. Soc. Jpn.

This work was supported by a Grant-in-Aid for Specially Promoted Research No. 09102004 from the Ministry of Education, Science, Sports and Culture.

References

1 J. Kim and D. C. Rees, *Science*, **257**, 1677 (1992).

2 R. R. Eady and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, **1994**, 2739.

3 D. C. Rees, M. K. Chan, and J. Kim, *Adv. Inorg. Chem.*, **40**, 89 (1994).

4 A. N. Startsev, *Catal. Rev. -Sci. Eng.*, **37**, 353 (1995).

5 C. Bianchini and A. Meli, *J. Chem. Soc., Dalton Trans.*, **1996**, 801.

6 M. D. Curtis and S. H. Druker, *J. Am. Chem. Soc.*, **119**, 1027 (1997).

7 S. Harris, *Polyhedron*, **8**, 2843 (1989).

8 R. H. Holm, *Adv. Inorg. Chem.*, **38**, 1 (1992).

9 T. Shibahara, *Coord. Chem. Rev.*, **123**, 73 (1993).

10 H. Ogino, S. Inomata, and H. Tobita, *Chem. Rev.*, **98**, 2093 (1998).

11 T. Shibahara, H. Akashi, and H. Kuroya, *J. Am. Chem. Soc.*, **108**, 1342 (1986).

12 T. Murata, H. Gao, Y. Mizobe, F. Nakano, S. Motomura, T. Tanase, S. Yano, and M. Hidai, *J. Am. Chem. Soc.*, **114**, 8287 (1992).

13 T. Murata, Y. Mizobe, H. Gao, Y. Ishii, T. Wakabayashi, F. Nakano, T. Tanase, S. Yano, M. Hidai, I. Echizen, H. Nanikawa, and S. Motomura, *J. Am. Chem. Soc.*, **116**, 3389 (1994).

14 D. M. Saysell and A. G. Sykes, *J. Cluster Sci.*, **6**, 449 (1995).

15 M. Brorson, C. J. H. Jacobsen, H. K. M. Helgesen, and I. Schmidt, *Inorg. Chem.*, **35**, 4808 (1996).

16 D. M. Saysell, Z. X. Huang, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, **1996**, 2623.

17 T. Shibahara, S. Kobayashi, N. Tsuji, G. Sakane, and M. Fukuhara, *Inorg. Chem.*, **36**, 1702 (1997).

18 G. Sakane, K. Hashimoto, M. Takahashi, M. Takeda, and T. Shibahara, *Inorg. Chem.*, **37**, 4231 (1998).

19 T. Shibahara, S. Mochida, and G. Sakane, *Chem. Lett.*, **1993**, 89.

20 T. Shibahara, G. Sakane, Y. Naruse, K. Taya, H. Akashi, A. Ichimura, and H. Adachi, *Bull. Chem. Soc. Jpn.*, **68**, 2769 (1995).

21 T. Wakabayashi, Y. Ishii, T. Murata, Y. Mizobe, and M. Hidai, *Tetrahedron Lett.*, **36**, 5585 (1995).

22 T. Wakabayashi, Y. Ishii, K. Ishikawa, and M. Hidai, *Angew. Chem., Int. Ed. Engl.*, **35**, 2123 (1996).

23 C. S. Bahn, A. Tan, and S. Harris, *Inorg. Chem.*, **37**, 2770 (1998).

24 M. Hidai and Y. Mizobe, in "Transition Metal Sulfur Chemistry: Biological and Industrial Significance," ed by E. I. Stiefel and K. Matsumoto, ACS Symposium Series 653, American Chemical Society, Washington, DC (1996), p. 310.

25 T. Kochi, Y. Nomura, Z. Tang, Y. Ishii, Y. Mizobe, and M. Hidai, *J. Chem. Soc., Dalton Trans.*, **1999**, 2575.

26 S. Kabashima, S. Kuwata, and M. Hidai, *J. Am. Chem. Soc.*, **121**, 7837 (1999).

27 T. Amemiya, S. Kuwata, and M. Hidai, *Chem. Commun.*, **1999**, 711.

28 T. Ikada, S. Kuwata, Y. Mizobe, and M. Hidai, *Inorg. Chem.*, **38**, 64 (1999).

29 T. Ikada, S. Kuwata, Y. Mizobe, and M. Hidai, *Inorg. Chem.*, **37**, 5793 (1998).

30 S. Kuwata, M. Andou, K. Hashizume, Y. Mizobe, and M. Hidai, *Organometallics*, **17**, 3429 (1998).

31 D. Masui, Y. Ishii, and M. Hidai, *Chem. Lett.*, **1998**, 717.

32 J. P. Qü, D. Masui, Y. Ishii, and M. Hidai, *Chem. Lett.*, **1998**, 1003.

33 Z. Tang, Y. Nomura, Y. Ishii, Y. Mizobe, and M. Hidai, *Inorg. Chim. Acta*, **267**, 73 (1998).

34 Z. Tang, Y. Nomura, S. Kuwata, Y. Ishii, Y. Mizobe, and M. Hidai, *Inorg. Chem.*, **37**, 4909 (1998).

35 S. Kuwata and M. Hidai, *Chem. Lett.*, **1998**, 885.

36 M. Hidai, S. Kuwata, and Y. Mizobe, *Acc. Chem. Res.*, **33**, 46 (2000).

37 Saysell and Sykes mentioned that the edge-shared cubane-type $[PtMo_3(\mu_3\text{-}S)_4]_2$ cluster is formed by the reaction of **1** with Pt^{2+} in the presence of BH_4^-, but the details of the structure are not clear.[14]

38 F. A. Cotton, P. A. Kibala, M. Matusz, C. S. McCaleb, and R. B. W. Sandor, *Inorg. Chem.*, **28**, 2623 (1989).

39 V. P. Fedin, M. N. Sokolov, Y. V. Mironov, B. A. Kolesov, S. V. Tkachev, and V. Y. Fedorov, *Inorg. Chim. Acta*, **167**, 39 (1990).

40 T. Saito, T. Tsuboi, Y. Kajitani, T. Yamagata, and H. Imoto, *Inorg. Chem.*, **30**, 3575 (1991).

41 L. Hao, J. Xiao, J. J. Vittal, and R. J. Puddephatt, *Organometallics*, **16**, 2165 (1997).

42 H. Werner, M. Ebner, and H. Otto, *J. Organomet. Chem.*, **350**, 257 (1988).

43 It is reported that the $NiMo_3(\mu_3\text{-}S)_4$ aqua cluster predominantly exists as $[NiMo_3(\mu_3\text{-}S)_4Cl(H_2O)_9]^{3+}$ in aqueous HCl. T. Shibahara, M. Yamasaki, H. Akashi, and T. Katayama, *Inorg. Chem.*, **30**, 2693 (1991).

44 J. Zhou, J. W. Raebiger, C. A. Crawford, and R. H. Holm, *J. Am. Chem. Soc.*, **119**, 6242 (1997).

45 K. Moseley and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, **1974**, 169.

46 R. Ugo, F. Cariati, and G. L. Monica, *Inorg. Synth.*, **11**, 105 (1968).

47 T. Shibahara, M. Yamasaki, G. Sakane, K. Minami, T. Yabuki, and A. Ichimura, *Inorg. Chem.*, **31**, 640 (1992).

48 "teXsan: Crystal Structure Analysis Package," Molecular Structure Corp., The Woodlands, TX (1985 and 1992).

49 PATTY: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, and C.

Smykalla, "The DIRDIF Program System," Technical Report of the Crystallography Laboratory, University of Nijmegen, Nijmegen, The Netherlands (1992).