Syntheses and Structures of Mixed-Metal Sulfido Clusters Containing Incomplete Cubane-Type $M_2M'S_4$ and Cubane-Type $M_2M'_2S_4$ Cores ($M = Mo, W$; $M' = Rh, Ir$)

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The reactions of sulfido-bridged dimolybdenum and ditungsten complexes $[M_2S_2(\mu_2\text{-}S)_2(S_2CNEt_2)_2]$ (**1**; M = Mo, W) with an equimolar amount of $[M'Cl(PPh_3)_3]$ (M′ = Rh, Ir) gave a series of mixed-metal incomplete cubane-type sulfido clusters $[M'(PPh_3)_2(\mu_3\text{-}S)(\mu_2\text{-}S)_3\{M(S_2CNEt_2)\}_2(\mu_2\text{-}Cl)]$. On the other hand, mixed-metal cubane-type sulfido clusters $[\{M'(cod)\}_2\{MCl(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$ (M′ = Rh, Ir; cod = 1,5-cyclooctadiene) were obtained by the reactions of **1** with an equimolar amount of $[M'Cl(cod)]_2$. Detailed structures of $[Ir(PPh_3)_2(\mu_3\text{-}S)(\mu_2\text{-}S)_3\{W(S_2CNEt_2)\}_2(\mu_2\text{-}Cl)]\cdot 2CH_2Cl_2$ (**3b**·$2CH_2Cl_2$) and $[\{Rh(cod)\}_2\{MoCl(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]\cdot 0.5CH_2Cl_2$ (**4a**·$0.5CH_2Cl_2$) have been determined by X-ray crystallography. Compound **3b**·$2CH_2Cl_2$ crystallized in the monoclinic system, space group $P2_1/n$, with $a = 10.521(4)$ Å, $b = 32.325(5)$ Å, $c = 17.277(3)$ Å, $\beta = 96.34(2)°$, and $Z = 4$. Refinement by full-matrix least-squares techniques gave final residuals $R = 0.071$ and $R_w = 0.068$. Compound **4a**·$0.5CH_2Cl_2$ crystallized in the monoclinic system, space group $P2_1/c$, with $a = 32.900(3)$ Å, $b = 10.847(4)$ Å, $c = 26.312(4)$ Å, $\beta = 111.274(8)°$, and $Z = 8$. Refinement by full-matrix least-squares techniques gave final residuals $R = 0.047$ and $R_w = 0.048$.

Introduction

Intensive efforts have been devoted to the study of mixed-metal sulfido clusters[1] because of their possible relevance to the active sites in metalloenzymes including nitrogenases[2] as well as industrial hydrodesulfurization catalysts.[3] Stepwise construction of these sulfido clusters from smaller metal−sulfur aggregates is an attractive pathway since it provides the more reliable method by which to prepare clusters with the desired nuclearity and framework compared with the conventional self-assembly systems.[4] Among the numerous metal−sulfur polynuclear compounds, the dinuclear complexes containing M_2S_4 cores (M = V, Cr, Mo, W)[5−10] and the Mo_3S_4 incomplete cubane-type clusters[1g] have received much attention as the precursors for the synthesis of mixed-metal clusters. In these reactions, however, the heterometals involved in the derived clusters are generally selected from first-row transition metals because of their biological relevance.

In our continuing studies of the syntheses and reactivities of noble-metal sulfido clusters,[11] we have recently demonstrated that the sulfido-bridged dimolybdenum and ditungsten complexes $[M_2S_2(\mu_2\text{-}S)_2(S_2CNEt_2)_2]$ (**1a**, M = Mo; **1b**, M = W) react with $[M'(PPh_3)_4]$ (M′ = Pd, Pt) to give the mixed-metal

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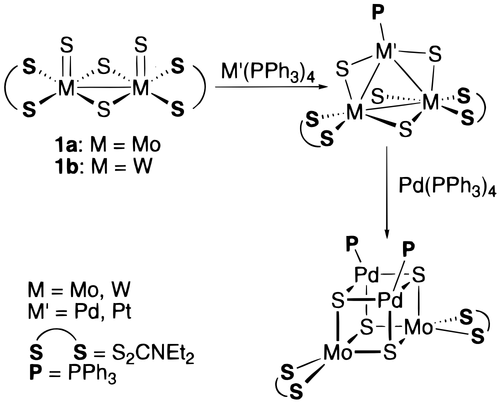
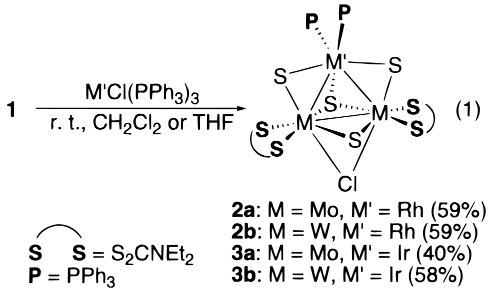
Scheme 1



sulfido clusters containing a unique triangular $M'(\mu_2\text{-}S)_2M_2(\mu_2\text{-}S)_2$ or a cubane-type $Pd_2Mo_2(\mu_3\text{-}S)_4$ core, $[M'(PPh_3)(\mu_2\text{-}S)_2\{M(S_2CNEt_2)\}_2(\mu_2\text{-}S)_2]$ and $[\{Pd(PPh_3)\}_2\{Mo(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$ (Scheme 1).[12] Interestingly, the reaction products depend strongly on the combination of the metals. Thus, from the reaction of **1** with 2 equiv of $[M'(PPh_3)_4]$, the cubane-type cluster is isolated for M = Mo and M′ = Pd, whereas only one Pt atom is incorporated to give exclusively the triangular cluster for M = W and M′ = Pt. This finding has stimulated us to extend these reactions to those with group 9 noble metals, which resulted in the formation of new incomplete cubane-type and cubane-type sulfido clusters containing rhodium and iridium. In this paper, we describe the details of the syntheses and structures of these new sulfido clusters.

Results and Discussion

Preparation of Incomplete Cubane-Type $M'Mo_2S_4$ and $M'W_2S_4$ Clusters 2 (M′ = Rh) and 3 (M′ = Ir). When the sulfido-bridged dimolybdenum and ditungsten complexes **1** were treated with an equimolar amount of $[RhCl(PPh_3)_3]$ in dichloromethane at room temperature, the incomplete cubane-type clusters $[Rh(PPh_3)_2(\mu_3\text{-}S)(\mu_2\text{-}S)_3\{M(S_2CNEt_2)\}_2(\mu_2\text{-}Cl)]$ (**2a**, M = Mo; **2b**, M = W) were obtained (eq 1). Because $[IrCl(PPh_3)_3]$ is readily oxidized in dichloromethane, the reactions of **1** with $[IrCl(PPh_3)_3]$ were carried out in THF, which resulted in the formation of Ir analogues of **2**, $[Ir(PPh_3)_2(\mu_3\text{-}S)(\mu_2\text{-}S)_3\{M(S_2CNEt_2)\}_2(\mu_2\text{-}Cl)]$ (**3a**, M = Mo; **3b**, M = W). In the IR spectra of **2** and **3**, the strong ν(M═S) bands characteristic of **1** are no longer observed. The ^1H NMR spectra of **2** and **3** exhibit the methyl resonances of two diethyldithiocarbamate ligands as two doublets of doublets. The inequivalence of the two methyl groups in the diethyldithiocarbamate ligand suggests that the C_{2v} symmetry found in the parent complexes **1** is absent in **2** and **3**. Furthermore, the $^{31}P\{^1H\}$ NMR spectra show two mutually coupled signals, and in the spectra of **2**, each of these signals is further split by the ^{103}Rh nuclei, indicating clearly that the two inequivalent PPh_3 ligands are bound to the Rh or Ir atom. These spectroscopic data are consistent with the incomplete cubane-type structure shown in eq 1.



(1)

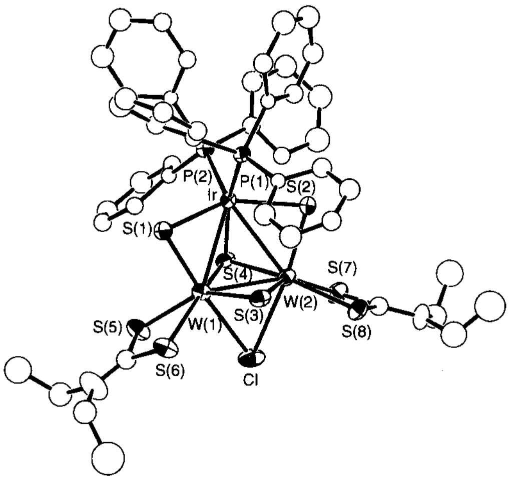


Figure 1. ORTEP drawing of **3b**·$2CH_2Cl_2$. Hydrogen atoms as well as solvating molecules are omitted for clarity.

Heterometallic incomplete cubane-type sulfido clusters are rare, although those derived from the dimolybdenum and ditungsten complexes with the $M_2S_2(\mu_2\text{-}S)_2$ cores (M = Mo, W) are not unprecedented. Thus, the reactions of $[Et_4N]_2[M_2S_2(\mu_2\text{-}S)_2(SCH_2CH_2S)_2]$ with group 11 metal−phosphine complexes, such as $[Cu\{S_2P(OEt)_2\}(PPh_3)_2]$ and $[Ag(NO_3)(PPh_3)_3]$, are known to afford $[Et_4N]_2[M'(PPh_3)(\mu_3\text{-}S)(\mu_2\text{-}S)_3\{M(S_2CH_2CH_2S)\}_2]$ (M′ = Cu,[6a,c] Ag[6b]) containing incomplete cubane-type $M_2M'(\mu_3\text{-}S)(\mu_2\text{-}S)_3$ cores. In contrast, the triangular clusters with *four* μ_2-S ligands $[M'(PPh_3)(\mu_2\text{-}S)_2\{M(S_2CNEt_2)\}_2(\mu_2\text{-}S)_2]$ (M′ = Pd, Pt) are obtained from the reaction of **1** with group 10 complexes $[M'(PPh_3)_4]$, as reported in the preceding paper,[12] indicating that the structure of the cluster framework depends strongly on the metal introduced.

In the preceding paper, we have already demonstrated that treatment of the trinuclear cluster $[Pd(PPh_3)(\mu_2\text{-}S)_2\{Mo(S_2CNEt_2)\}_2(\mu_2\text{-}S)_2]$ with $[Pd(PPh_3)_4]$ readily affords the tetranuclear cubane-type cluster $[\{Pd(PPh_3)\}_2\{Mo(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$, which could also be obtained by the direct reaction of **1a** with 2 equiv of $[Pd(PPh_3)_4]$.[12] Taking this finding into account, we attempted the reaction of **1a** with 2 equiv of $[RhCl(PPh_3)_3]$. However, this resulted in the formation of **3a** along with uncharacterized product(s), and the expected tetranuclear cluster was not obtained. Nevertheless, incorporation of additional metal fragment(s) into **2** and **3** is still under investigation, because the reactions of these heterometallic incomplete cubane-type sulfido clusters with certain metal species may provide a rational synthetic route to the cubane-type sulfido clusters containing three kinds of metals.[13]

Structure of 3b. An X-ray analysis of **3b**·$2CH_2Cl_2$ has been carried out to elucidate the structures of **2** and **3**. The molecular structure of **3b** is shown in Figure 1, and selected bond distances and angles are collected in Table 1. In contrast to the related platinum cluster $[Pt(PPh_3)(\mu_2\text{-}S)_2\{W(S_2CNEt_2)\}_2(\mu_2\text{-}S)_2]$,[12] the IrW_2S_4 core in **3b** appears to be the incomplete cubane-type; the IrW_2 triangle in **3b** is capped by a μ_3-S ligand, and each of the edges in this triangle is further bridged by a μ_2-S ligand, although the two μ_2-S atoms bridging the Ir−W edge are almost

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Table 1. Selected Bond Distances and Angles in **3b**·$2CH_2Cl_2$

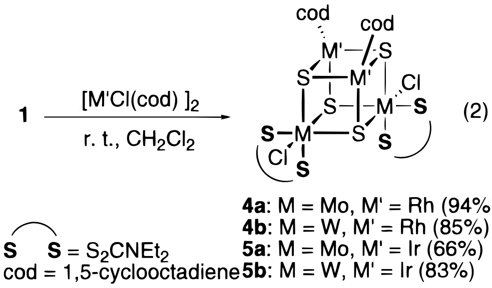
Bond Distances (Å)			
Ir(1)−W(1)	2.859(2)	Ir(1)−W(2)	2.878(2)
W(1)−W(2)	2.661(2)		
Ir(1)−P(1)	2.321(8)	Ir(1)−P(2)	2.324(8)
Ir(1)−S(1)	2.389(8)	Ir(1)−S(2)	2.400(8)
Ir(1)−S(4)	2.382(7)		
W(1)−S(1)	2.215(8)	W(2)−S(2)	2.203(8)
W(1)−S(3)	2.328(8)	W(2)−S(3)	2.341(8)
W(1)−S(4)	2.411(8)	W(2)−S(4)	2.428(8)
W(1)−Cl(1)	2.744(9)	W(2)−Cl(1)	2.677(8)
Bond Angles (deg)			
Ir(1)−W(1)−W(2)	62.74(5)	Ir(1)−W(2)−W(1)	61.99(5)
W(1)−Ir(1)−W(2)	55.27(5)		
P(1)−Ir(1)−S(4)	166.3(3)	P(2)−Ir(1)−S(4)	90.0(3)
P(2)−Ir(1)−S(1)	107.4(3)	P(2)−Ir(1)−S(2)	108.3(3)
S(1)−Ir(1)−S(2)	144.1(3)		
S(1)−W(1)−Cl(1)	167.8(3)	S(2)−W(2)−Cl(1)	165.7(3)
S(3)−W(1)−S(6)	147.3(3)	S(3)−W(2)−S(8)	149.0(3)
S(4)−W(1)−S(5)	156.5(3)	S(4)−W(2)−S(7)	158.6(3)

coplanar with the Ir and two W atoms, as are the μ_2-S atoms bound to the Pt−W edges in $[Pt(PPh_3)(\mu_2\text{-}S)_2\{W(S_2CNEt_2)\}_2(\mu_2\text{-}S)_2]$. In addition, a chloro ligand bridges the W−W edge. The W−Cl distances of 2.744(9) and 2.677(8) Å are much longer than those found in, e.g., $[W_2Cl_4(\mu_2\text{-}Cl)_2(PR_3)_4]$ (R = Me, Et), $[W_2Cl_3(\mu_2\text{-}Cl)_3(PEt_3)_3]$, and $[HPEt_3][W_2Cl_4(\mu_2\text{-}Cl)_3(PEt_3)_2]$ (2.37−2.55 Å),[14] suggesting the quite weak interaction of this Cl anion with the W centers in **3b**.

The W−W distance of 2.661(2) Å is slightly shorter than that in the parent **1b** (2.795(2) Å)[15] and is comparable with that in $[Pt(PPh_3)(\mu_2\text{-}S)_2\{W(S_2CNEt_2)\}_2(\mu_2\text{-}S)_2]$ (2.698(1) Å),[12] which contrasts with the essentially immutable W−W distance in the W_2S_4 core upon the formation of the $M_2M'S_4$ (M′ = Cu, Ag) incomplete cubane-type clusters.[6a,b] The distances between the Ir and W atoms (2.859(2) and 2.878(2) Å) are also similar to those in the other Ir−W single bonds (2.723(2)−2.893(1) Å).[16] Ignoring these metal−metal interactions, the W atoms in **3b** have a distorted octahedral configuration, while the geometry around the Ir atom is distorted trigonal bipyramidal with the S(4) and P(1) atoms at the apical positions.

The short W(1)−S(1) and W(2)−S(2) distances at 2.215(8) and 2.203(8) Å, respectively, indicate the significant π-donation of the lone pair electrons on these sulfur atoms to the W centers, as observed in $[Pt(PPh_3)(\mu_2\text{-}S)_2\{W(S_2CNEt_2)\}_2(\mu_2\text{-}S)_2]$ with the W−S distances of 2.187 Å (mean).[12] On the other hand, the Ir−S distances of 2.382(7)−2.400(8) Å in **3b** are close to those of the 18-electron Ir center in $[(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(\mu_2\text{-}S)_2Ir(\eta^5\text{-}C_5Me_5)]$ (2.340 Å (mean)) rather than those of the 16-electron Ir atom in the same complex (2.268 Å (mean)).[17]

Preparation of $M'_2Mo_2S_4$ and $M'_2W_2S_4$ Cubane-Type Clusters 4 (M′ = Rh) and 5 (M′ = Ir). Dinuclear precursors **1** also reacted with an equimolar amount of $[M'Cl(cod)]_2$ (M′ = Rh, Ir; cod = 1,5-cyclooctadiene) to afford the mixed-metal cubane-type clusters $[\{Rh(cod)\}_2\{MCl(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$ (**4a**, M = Mo; **4b**, M = W) and $[\{Ir(cod)\}_2\{MCl(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$ (**5a**, M = Mo; **5b**, M = W), as shown in eq 2. The IR spectra of **4** and **5** again show no bands assignable to ν(M=S). The ^1H NMR spectra indicate the presence of diethyldithiocarbamate and cyclooctadiene ligands in a ratio of 1:1. In each NMR spectrum, methyl and methylene protons of the diethyldithiocarbamate ligands are observed as two doublets of doublets and complicated multiplets, respectively, while the protons attached to the cyclooctadiene rings give several broad signals which are not well assignable.



(2)

Formation of $M_2M'_2S_4$ cubane-type clusters from dinuclear complexes with $M_2S_2(\mu_2\text{-}S)_2$ cores has been established as a practical synthetic method for mixed-metal cubane-type clusters. As to group 9 metals, for example, Stiefel and co-workers have demonstrated that the reaction of **1** with an equimolar amount of $[Co_2(CO)_8]$ affords $[\{Co(CO)\}_2\{M(S_2CNEt_2)(MeCN)\}_2(\mu_3\text{-}S)_4]$ (M = Mo, W) consisting of six metal−metal bonds.[5] Other closely related clusters $[\{Pd(PPh_3)\}_2\{Mo(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$[12] and $[\{Cu(PPh_3)\}_2\{M(SCH_2CH_2S)\}_2(\mu_3\text{-}S)_4]$ (M = Mo, W)[6d] prepared from **1a** or $[Et_4N]_2[M_2S_2(\mu_2\text{-}S)_2(SCH_2CH_2S)_2]$ are also known, which have a butterfly metal framework like **4** and **5** (vide infra) because only five metal−metal bonds are present.

In the reactions reported here, the products apparently depend upon the ancillary ligands of the noble-metal fragments incorporated. For example, even when **1a** was allowed to react with 0.5 equiv of $[RhCl(cod)]_2$, the expected trinuclear cluster was not formed and a mixture of **4a** and unreacted **1a** was obtained. This might relate to the difference in the electron density on the metal fragments; i.e., incorporation of the Rh and Ir atoms having the π-accepting cyclooctadiene ligands favors the formation of tetranuclear clusters **4** and **5**, while trinuclear clusters **2** and **3** are produced predominantly from incorporation of the more electron-rich Rh and Ir centers bound to the PPh_3 ligands. Similarly, in the reactions of **1a** with $[M'(PPh_3)_4]$ (M′ = Pd, Pt), the palladium tends to form the Pd_2Mo_2 tetranuclear cluster, although the more electron-rich platinum affords the triangular $PtMo_2$ cluster exclusively under the same conditions.[12]

Structure of 4a. To clarify the detailed structures of **4** and **5**, an X-ray analysis of **4a**·$0.5CH_2Cl_2$ has been performed. The unit cell contains two crystallographically independent molecules of **4a**, whose structures are essentially identical. An ORTEP drawing of one of these molecules is depicted in Figure 2, and selected bond distances and angles are collected in Table 2. Cluster **4a** has a $Rh_2Mo_2(\mu_3\text{-}S)_4$ cubane-type core with a pseudo-2-fold axis passing through the midpoints of the Rh−Rh vector and the Mo−Mo bond. The geometry around the Mo atoms is distorted octahedral if the metal−metal interactions are disregarded. Interestingly, the diethyldithiocarbamate ligand is bound to the Mo atom with its S_2CN plane being perpendicular to the $Mo(\mu\text{-}S)_2Mo$ plane in **4a**, while the corresponding S−S vector is essentially parallel to that of the $M(\mu\text{-}S)_2M$ moiety (M = Mo, W) in **1**−**3**. Besides the five sulfur atoms, the Mo atom is bound to the chloride. The Rh atom is surrounded by three μ_3-S ligands and the $\eta^2{:}\eta^2$-cod ligand. The Mo−Mo distances in **4a** (2.760(2) and 2.771(2) Å) are slightly shorter than that in **1a** (2.814(1)[18] and 2.817(2) Å[19]) and comparable

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Table 2. Selected Bond Distances and Angles in **4a**·$0.5CH_2Cl_2$

molecule 1		molecule 2	
	Bond Distances (Å)		
Rh(1)−Mo(1)	2.882(2)	Rh(3)−Mo(3)	2.873(1)
Rh(1)−Mo(2)	2.884(1)	Rh(3)−Mo(4)	2.868(2)
Rh(2)−Mo(1)	2.868(2)	Rh(4)−Mo(3)	2.864(2)
Rh(2)−Mo(2)	2.885(2)	Rh(4)−Mo(4)	2.887(2)
Mo(1)−Mo(2)	2.760(2)	Mo(3)−Mo(4)	2.771(2)
Rh(1)−S(1)	2.346(4)	Rh(3)−S(9)	2.345(4)
Rh(1)−S(3)	2.348(4)	Rh(3)−S(11)	2.352(4)
Rh(1)−S(4)	2.436(3)	Rh(3)−S(12)	2.445(4)
Rh(2)−S(2)	2.337(4)	Rh(4)−S(10)	2.339(4)
Rh(2)−S(3)	2.422(3)	Rh(4)−S(11)	2.433(5)
Rh(2)−S(4)	2.354(5)	Rh(4)−S(12)	2.351(3)
Rh(1)−C	2.14(1)−2.30(2)	Rh(3)−C	2.17(2)−2.30(2)
Rh(2)−C	2.16(1)−2.28(2)	Rh(4)−C	2.13(2)−2.32(2)
Mo(1)−S(1)	2.314(4)	Mo(3)−S(9)	2.319(4)
Mo(1)−S(2)	2.323(3)	Mo(3)−S(10)	2.328(5)
Mo(1)−S(3)	2.294(4)	Mo(3)−S(11)	2.305(4)
Mo(2)−S(1)	2.330(3)	Mo(4)−S(9)	2.330(4)
Mo(2)−S(2)	2.307(4)	Mo(4)−S(10)	2.314(4)
Mo(2)−S(4)	2.297(4)	Mo(4)−S(12)	2.294(4)
Mo(1)−Cl(1)	2.500(4)	Mo(3)−Cl(3)	2.482(4)
Mo(2)−Cl(2)	2.499(5)	Mo(4)−Cl(4)	2.498(4)
	Bond Angles (deg)		
Mo(1)−Rh(1)−Mo(2)	57.18(4)	Mo(3)−Rh(3)−Mo(4)	57.73(4)
Mo(1)−Rh(2)−Mo(2)	57.33(4)	Mo(3)−Rh(4)−Mo(4)	57.61(4)
Rh(1)−Mo(1)−Rh(2)	75.04(5)	Rh(3)−Mo(3)−Rh(4)	76.03(4)
Rh(1)−Mo(1)−Mo(2)	61.45(4)	Rh(3)−Mo(3)−Mo(4)	61.05(4)
Rh(2)−Mo(1)−Mo(2)	61.65(5)	Rh(4)−Mo(3)−Mo(4)	61.62(5)
Rh(1)−Mo(2)−Rh(2)	74.73(4)	Rh(3)−Mo(4)−Rh(4)	75.74(5)
Rh(1)−Mo(2)−Mo(1)	61.37(4)	Rh(3)−Mo(4)−Mo(3)	61.22(4)
Rh(2)−Mo(2)−Mo(1)	61.01(5)	Rh(4)−Mo(4)−Mo(3)	60.77(5)
Cl(1)−Mo(1)−S(1)	160.2(1)	Cl(3)−Mo(3)−S(9)	160.9(1)
Cl(1)−Mo(1)−S(2)	87.0(1)	Cl(3)−Mo(3)−S(10)	88.9(2)
Cl(2)−Mo(2)−S(1)	88.0(1)	Cl(4)−Mo(4)−S(9)	88.9(1)
Cl(2)−Mo(2)−S(2)	160.3(1)	Cl(4)−Mo(4)−S(10)	161.6(2)
S(1)−Mo(1)−S(5)	83.4(1)	S(9)−Mo(3)−S(13)	83.6(1)
S(2)−Mo(1)−S(5)	158.3(2)	S(10)−Mo(3)−S(13)	157.0(1)
S(1)−Mo(1)−S(6)	81.8(1)	S(9)−Mo(3)−S(14)	82.4(1)
S(3)−Mo(1)−S(6)	159.4(1)	S(11)−Mo(3)−S(14)	160.3(2)
S(2)−Mo(2)−S(7)	81.4(1)	S(10)−Mo(4)−S(15)	83.2(1)
S(1)−Mo(2)−S(7)	156.6(2)	S(9)−Mo(4)−S(15)	156.1(2)
S(2)−Mo(2)−S(8)	81.8(2)	S(10)−Mo(4)−S(16)	84.7(1)
S(4)−Mo(2)−S(8)	161.6(1)	S(12)−Mo(4)−S(16)	160.0(2)

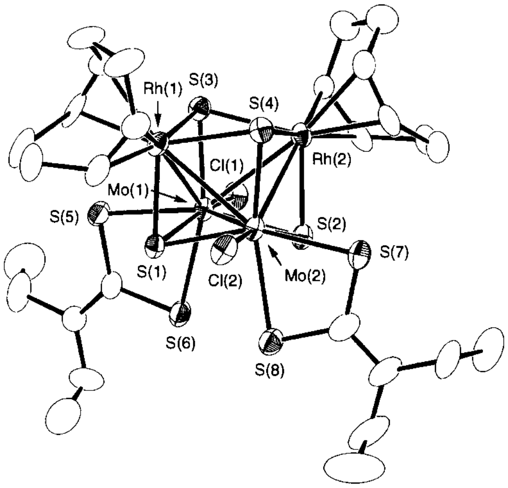

Figure 2. ORTEP drawing of one of the two independent molecules of **4a**·$0.5CH_2Cl_2$ (molecule 1). Hydrogen atoms as well as solvating molecules are omitted for clarity.

tothat in the related cobalt−molybdenum cluster $[\{Co(CO)\}_2\{Mo(S_2CNEt_2)(MeCN)\}_2(\mu_3\text{-}S)_4]$ (2.788(1) Å).[5] These as well as the Rh−Mo distances ranging from 2.864(2) to 2.887(2) Å in **4a** are all consistent with the metal−metal bond order of unity. However, there is no bonding interaction between the two Rh atoms (Rh−Rh separation: 3.502(2) and 3.533(2) Å). Thus, **4a** has a Rh_2Mo_2 butterfly framework with five metal−metal bonds, which is expected for 62-electron clusters. The Mo−S distance for the terminal sulfido ligand in **1a** (2.09[18] and 2.10 Å[19]) is elongated to 2.30 Å (mean) for the Mo−μ_3-S distances in **4a** as observed previously in $[\{Co(CO)\}_2\{Mo(S_2CNEt_2)(MeCN)\}_2(\mu_3\text{-}S)_4]$ (2.316(1) Å),[5] and these Mo−μ_3-S bond lengths are slightly shorter than those in cubane-type Mo_4S_4 clusters (2.334−2.76 Å).[1g]

In summary, we have demonstrated that incorporation of noble metals such as rhodium and iridium into **1** provides a rational route to prepare a series of tri- or tetranuclear mixed-metal sulfido clusters containing noble metals. It is noteworthy that the structure of the mixed-metal sulfido cluster strongly depends upon the nature of the ancillary ligands attached to the noble metals. Further studies are now under way to investigate the reactivities at the noble metal sites embedded in these sulfido clusters and to synthesize trimetallic cubane-type clusters from the triangular clusters reported here.

Experimental Section

General Methods. All reactions were carried out under a dry nitrogen atmosphere by using standard Schlenk techniques. Solvents

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were dried by the usual methods and distilled before use. Complexes **1a**,[20] **1b**,[21] [RhCl(PPh$_3$)$_3$],[22] [IrCl(PPh$_3$)$_3$],[23] [RhCl(cod)]$_2$,[24] and [IrCl(cod)]$_2$[25] were prepared according to the literature. IR spectra were obtained from a Shimadzu FTIR-8000M spectrometer, while ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a JEOL EX-270, LA-400, or LA-500 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHN analyzer.

Preparation of [Rh(PPh$_3$)$_2$(μ_3-S)(μ_2-S)$_3${Mo(S$_2$CNEt$_2$)}$_2$(μ_2-Cl)] (2a). A mixture of **1a** (123 mg, 0.200 mmol) and [RhCl(PPh$_3$)$_3$] (185 mg, 0.200 mmol) in dichloromethane (30 mL) was stirred at room temperature for 17 h. Addition of hexane (40 mL) to the concentrated filtrate (ca. 15 mL) afforded **2a** as black crystals. Yield: 152 mg (59%). ^{1}H NMR (CDCl$_3$): δ 1.36, 1.40 (dd, 6H each, NCH$_2$*CH$_3$*), 3.87−4.09 (m, 8H, N*CH$_2$*CH$_3$), 6.85−7.24 (m, 30H, PPh$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 35.3 (dd, 1P, $J_{\mathrm{P-P}} = 51$ Hz, $J_{\mathrm{Rh-P}} = 119$ Hz, PPh$_3$), 48.4 (dd, 1P, $J_{\mathrm{P-P}} = 51$ Hz, $J_{\mathrm{Rh-P}} = 184$ Hz, PPh$_3$). Anal. Calcd for $C_{46}H_{50}N_2P_2S_8ClMo_2Rh$: C, 43.18; H, 3.94; N, 2.19. Found: C, 42.73; H, 4.01; N, 2.21.

Preparation of [Rh(PPh$_3$)$_2$(μ_3-S)(μ_2-S)$_3${W(S$_2$CNEt$_2$)}$_2$(μ_2-Cl)] (2b). Cluster **2b** was obtained as black crystals from **1b** (159 mg, 0.200 mmol) and [RhCl(PPh$_3$)$_3$] (185 mg, 0.200 mmol) by using a procedure similar to that used for **2a**. Yield: 171 mg (59%). ^{1}H NMR (CDCl$_3$): δ 1.37, 1.41 (dd, 6H each, NCH$_2$*CH$_3$*), 3.80−3.97 (m, 8H, N*CH$_2$*CH$_3$), 6.85−7.36 (m, 30H, PPh$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 38.1 (dd, 1P, $J_{\mathrm{P-P}} = 57$ Hz, $J_{\mathrm{Rh-P}} = 177$ Hz, PPh$_3$), 61.7 (dd, 1P, $J_{\mathrm{P-P}} = 57$ Hz, $J_{\mathrm{Rh-P}} = 238$ Hz, PPh$_3$). Anal. Calcd for $C_{46}H_{50}N_2P_2S_8ClW_2Rh$: C, 37.96; H, 3.46; N, 1.92. Found: C, 37.09; H, 3.26; N, 1.81.

Preparation of [Ir(PPh$_3$)$_2$(μ_3-S)(μ_2-S)$_3${Mo(S$_2$CNEt$_2$)}$_2$(μ_2-Cl)] (3a). A mixture of **1a** (123 mg, 0.200 mmol) and [IrCl(PPh$_3$)$_3$] (203 mg, 0.200 mmol) in THF (20 mL) was stirred at room temperature. The initial brown suspension turned to a reddish brown solution after several hours of stirring, and the stirring was continued for a further 2 days. The solvent was removed in vacuo, and the residual dark brown solid was extracted with 18 mL of dichloromethane. Addition of hexane (28 mL) to the filtrate afforded black crystals. Yield: 109 mg (40%). ^{1}H NMR (CDCl$_3$): δ 1.36, 1.43 (dd, 6H each, NCH$_2$*CH$_3$*), 3.89−4.13 (m, 8H, N*CH$_2$*CH$_3$), 6.28−6.81(m, 30H, PPh$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 1.7 (d, 1P, $J_{\mathrm{P-P}} = 20$ Hz, PPh$_3$), 24.5 (d, 1P, $J_{\mathrm{P-P}} = 20$ Hz, PPh$_3$). Anal. Calcd for $C_{46}H_{50}N_2P_2S_8ClMo_2Ir$: C, 40.36; H, 3.68; N, 2.05. Found: C, 37.50; H, 3.65; N, 1.94. To obtain the analytically pure compounds for **3a** and **3b** (vide infra), further purifications have been attempted extensively but have turned out to be unsuccessful.

Preparation of [Ir(PPh$_3$)$_2$(μ_3-S)(μ_2-S)$_3${W(S$_2$CNEt$_2$)}$_2$(μ_2-Cl)] (3b). Cluster **3b** was obtained as black crystals from **1b** (159 mg, 0.200 mmol) and [IrCl(PPh$_3$)$_3$] (203 mg, 0.200 mmol) by using a procedure similar to that used for **3a**. Yield: 180 mg (58%). ^{1}H NMR (CDCl$_3$): δ 1.37, 1.41 (dd, 6H each, NCH$_2$*CH$_3$*), 3.87−4.13 (m, 8H, N*CH$_2$*CH$_3$), 6.81−7.36 (m, 30H, PPh$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 0.8 (d, 1P, $J_{\mathrm{P-P}} = 22$ Hz, PPh$_3$), 36.1 (d, 1P, $J_{\mathrm{P-P}} = 22$ Hz, PPh$_3$). Anal. Calcd for $C_{46}H_{50}N_2P_2S_8ClW_2Ir$: C, 35.77; H, 3.26; N, 1.81.[26] Found: C, 33.18; H, 3.27; N, 1.87.

Preparation of [{Rh(cod)}$_2${MoCl(S$_2$CNEt$_2$)}$_2$(μ_3-S)$_4$]·0.5CH$_2$Cl$_2$ (4a·0.5CH$_2$Cl$_2$). A mixture of **1a** (61.7 mg, 0.100 mmol) and [RhCl(cod)]$_2$ (49.4 mg, 0.100 mmol) in dichloromethane (20 mL) was stirred at room temperature for 30 h. Addition of diethyl ether to the concentrated filtrate (ca. 4 mL) afforded black crystals. Yield: 108 mg (94%). ^{1}H NMR (C$_6$D$_6$): δ 0.87, 0.90 (dd, 6H each, NCH$_2$*CH$_3$*), 3.07−3.41 (m, 8H, N*CH$_2$*CH$_3$). Anal. Calcd for $C_{26.5}H_{45}N_2S_8Cl_3Mo_2Rh_2$: C, 27.62; H, 3.94; N, 2.43. Found: C, 27.96; H, 4.04; N, 2.51. Amounts of the solvent molecules in the crystals were determined by specific gravity measurement as well as elemental analysis.

Table 3. X-ray Crystallographic Data for **3b**·2CH$_2$Cl$_2$ and **4a**·0.5CH$_2$Cl$_2$

	3b·2CH$_2$Cl$_2$	**4a**·0.5CH$_2$Cl$_2$
empirical formula	$C_{48}H_{54}N_2Cl_5P_2S_8W_2Ir$	$C_{26.50}H_{45}N_2S_8Cl_3Mo_2Rh_2$
fw	1714.58	1152.19
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	10.521(4)	32.900(3)
b, Å	32.325(5)	10.847(4)
c, Å	17.277(3)	26.312(4)
β, deg	96.34(2)	111.274(8)
V, Å^3	5839(2)	8749(3)
Z	4	8
λ, Å	0.710 69	0.710 69
ρ_{calcd}, g cm^{-3}	1.950	1.749
μ(Mo Kα), cm^{-1}	68.18	18.84
transmission factors	0.4195−0.9051	0.6536−1.0000
temp, K	296	296
R_{int}	0.146	0.015
R^a	0.071	0.047
$R_w{}^b$	0.068	0.048

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

Preparation of [{Rh(cod)}$_2${WCl(S$_2$CNEt$_2$)}$_2$(μ_3-S)$_4$] (4b). Cluster **4b** was obtained as a brown solid from **1b** (79.3 mg, 0.100 mmol) and [RhCl(cod)]$_2$ (49.4 mg, 0.100 mmol) by using a procedure similar to that used for **4a**. Yield: 109 mg (85%). ^{1}H NMR (C$_6$D$_6$): δ 0.86, 0.90 (dd, 6H each, NCH$_2$*CH$_3$*), 3.03−3.27 (m, 8H, N*CH$_2$*CH$_3$). Anal. Calcd for $C_{26}H_{44}N_2S_8Cl_2W_2Rh_2$: C, 24.29; H, 3.45; N, 2.18. Found: C, 24.09; H, 3.47; N, 2.15.

Preparation of [{Ir(cod)}$_2${MoCl(S$_2$CNEt$_2$)}$_2$(μ_3-S)$_4$] (5a). Cluster **5a** was obtained as brown solid from **1a** (61.7 mg, 0.100 mmol) and [IrCl(cod)]$_2$ (67.2 mg, 0.100 mmol) by using a procedure similar to that used for **4a**. Yield: 84.4 mg (66%). ^{1}H NMR (C$_6$D$_6$): δ 0.88, 0.89 (dd, 6H each, NCH$_2$*CH$_3$*), 3.21−3.40 (m, 8H, N*CH$_2$*CH$_3$). Anal. Calcd for $C_{26}H_{44}N_2S_8Cl_2Mo_2Ir_2$: C, 24.24; H, 3.44; N, 2.17. Found: C, 24.08; H, 3.56; N, 2.07.

Preparation of [{Ir(cod)}$_2${WCl(S$_2$CNEt$_2$)}$_2$(μ_3-S)$_4$] (5b). Cluster **5b** was obtained as brown solid from **1b** (79.3 mg, 0.100 mmol) and [IrCl(cod)]$_2$ (67.2 mg, 0.100 mmol) by using a procedure similar to that used for **4a**. ^{1}H NMR (C$_6$D$_6$): δ 0.86, 0.88 (dd, 6H each, NCH$_2$*CH$_3$*), 2.96−3.26 (m, 8H, N*CH$_2$*CH$_3$). Yield: 122 mg (83%). Anal. Calcd for $C_{26}H_{44}N_2S_8Cl_2W_2Ir_2$: C, 21.33; H, 3.03; N, 1.91. Found: C, 21.53; H, 3.17; N, 2.06.

X-ray Diffraction Studies. For the X-ray difraction studies, a single crystal of **3b**·2CH$_2$Cl$_2$ was sealed in a glass capillary under N$_2$ together with a saturated solution of **3b** in CH$_2$Cl$_2$/hexane, whereas a single crystal of **4a**·0.5CH$_2$Cl$_2$ was thoroughly dried and sealed in a glass capillary under N$_2$. Both were transferred to a Rigaku AFC7R diffractometer equipped with a graphite-monochromatized Mo Kα source. Orientation matrixes and unit cell parameters were determined by least-squares treatment of 18 (**3b**·2CH$_2$Cl$_2$) or 25 (**4a**·0.5CH$_2$Cl$_2$) reflections with $20° < 2\theta < 40°$. The intensities of three check reflections were monitored every 150 reflections during data collection, which revealed no significant decay for both crystals. Intensity data were corrected for Lorentz and polarization effects and for absorption (ψ scans). Details of crystal and data collection parameters are summarized in Table 3. Structure solution and refinements were carried out by using the teXsan program package.[27] The positions of heavy atoms were determined by Patterson methods and subsequent Fourier syntheses (DIRDIF PATTY[28]). Non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques (based on *F*),

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(21) Cohen, S. A.; Stiefel, E. I. *Inorg. Chem.* **1985**, *24*, 4657.

(22) Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1967**, *10*, 67.

(23) Bennett, M. A.; Latten, J. L. *Inorg. Synth.* **1989**, *26*, 200.

(24) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.

(25) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.

(26) As confirmed by the X-ray analysis, the crystals of **3b** obtained from CH$_2$Cl$_2$/hexane contain two solvating CH$_2$Cl$_2$ molecules. However, once dried in vacuo, these black crystals turned to a brown powder, whose ^{1}H NMR spectrum showed the absence of the solvating CH$_2$Cl$_2$ molecules. Elemental analysis has been done by the use of the thoroughly dried **3b**, and therefore, the calculated values are based on the formula without solvating CH$_2$Cl$_2$.

(27) *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985 and 1992.

(28) PATTY: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF Program System*; Technical Report of the Crystallography Laboratory: University of Nijmegen, The Netherlands, 1992.

whereby the C atoms in **3b**·2CH_2Cl_2 were refined isotropically. One of the methyl carbon atoms in diethyldithiocarbamate ligands in **4a**·0.5CH_2Cl_2 was disordered and placed at two positions with the occupancies of 60% for C(34A) and 40% for C(34B). The C atoms in the solvating CH_2Cl_2 molecules in **4a**·0.5CH_2Cl_2 were also found at two disordered positions. These C atoms as well as the Cl atoms attached to them were refined as rigid groups with occupancies of 50%, respectively. Hydrogen atoms, except for those attached to C(33) in **4a**·0.5CH_2Cl_2 and those in the solvating CH_2Cl_2 molecules in **4a**·0.5CH_2Cl_2, were placed at the calculated positions and were included in the final stages of the refinements with fixed parameters. The atomic scattering factors were taken from ref 29, and anomalous dispersion effects were included; the values of $\Delta f'$ and $\Delta f''$ were taken from ref 30.

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Supporting Information Available: X-ray crystallographic files in CIF format are available for **3b**·2CH_2Cl_2 and **4a**·0.5CH_2Cl_2 on the Internet only. Access information is given on any current masthead page.

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