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Syntheses of Mixed-Metal Sulfide Cubane-Type Clusters with the Novel $PdMo_3S_4$ Core and Reactivities of the Unique Tetrahedral Pd Site Surrounded by Sulfide Ligands toward Alkenes, CO, ^tBuNC, and Alkynes

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Abstract: An incomplete cubane-type cluster $[Mo_3S_4(H_2O)_9]Cl_4$ (**1**) reacted with Pd black in aqueous HCl to give a mixed-metal cubane-type cluster $[PdMo_3S_4(H_2O)_9Cl]Cl_3$ (**2**). Treatment of **2** with 3.3 equiv of 1,4,7-triazacyclononane (tacn) afforded a well-defined single cubane-type cluster $[PdMo_3S_4(tacn)_3Cl]Cl_3$ (**3**), while an anion metathesis of **2** by 4-toluenesulfonate (TsO) resulted in the formation of a double cubane-type cluster $[Pd_2Mo_6S_8(H_2O)_{18}](OTs)_8$ (**4**). Detailed structures of both **3** and **4** have been determined by X-ray crystallography. Crystal data for **3**$\cdot 4H_2O$: orthorhombic, space group $P2_12_12_1$, $a = 17.549(3)$ Å, $b = 20.032(4)$ Å, $c = 10.256(2)$ Å, $V = 3605$ Å^3, $Z = 4$, and R (R_w) = 0.051 (0.062) for 4014 reflections. For **4**$\cdot 24H_2O$: triclinic, space group $P1$, $a = 15.799(4)$ Å, $b = 18.079(6)$ Å, $c = 11.873(1)$ Å, $\alpha = 108.75(2)°$, $\beta = 108.73(1)°$, $\gamma = 70.87(3)°$, $V = 2944$ Å^3, $Z = 1$, R (R_w) = 0.028 (0.036) for 10 089 reflections. Cluster **3** was converted into a series of single cubane-type clusters $[PdMo_3S_4(tacn)_3(L)]^{4+}$ containing alkenes, CO, and ^tBuNC coordinated to the tetrahedral Pd site, by the initial anion exchange forming $[PdMo_3S_4(tacn)_3Cl]X_3$ (**8a**, X = ClO_4; **8b**, X = BF_4; **8c**, X = PF_6) followed by treatment with these molecules. The alkene cluster $[PdMo_3S_4(tacn)_3(cis\text{-}HOCH_2CH{=}CHCH_2OH)](ClO_4)_4$ (**5a′**) and the carbonyl cluster $[PdMo_3S_4(tacn)_3(CO)]Cl(ClO_4)_3$ (**6a**) have been fully characterized by X-ray analyses. Crystal data for **5a′**$\cdot 2H_2O$: monoclinic, space group $P2_1/m$, $a = 12.314(1)$ Å, $b = 12.732(2)$ Å, $c = 15.736(2)$ Å, $\beta = 94.01(1)°$, $V = 2461$ Å^3, $Z = 2$, R (R_w) = 0.068 (0.081) for 2743 reflections. For **6a**$\cdot 3H_2O$: orthorhombic, space group $Pbca$, $a = 15.485(13)$ Å, $b = 23.900(6)$ Å, $c = 23.326(7)$ Å, $V = 8633$ Å^3, $Z = 8$, and R (R_w) = 0.061 (0.069) for 7761 reflections. Interestingly, cluster **8c** catalyzes the reaction of a series of alkynic acid esters $R^2C{\equiv}CCOOR^1$ with alcohols R^3OH to give the trans addition products $(Z)\text{-}(R^3O)R^2C{=}CHCOOR^1$ (R^1 = Me, Et, ^tBu, Ph, R^2 = H, R^3 = Me; $R^1 = R^3$ = Me, R^2 = COOMe, Me; R^1 = Ph, R^2 = Et, R^3 = Me; R^1 = Me, R^2 = H, R^3 = Et, $PhCH_2$) with quite high selectivity under mild conditions with retention of the cluster core.

Introduction

A number of transition metal sulfide clusters with the cubane-type M_4S_4 core have been synthesized, and their structures and properties have been investigated extensively as the models of the active sites in biological catalysts. The most intensively studied clusters included in this class are those containing the Fe_4S_4 core, serving as excellent synthetic analogues for the redox site of iron–sulfur proteins.[2] The chemistry of cubane-type clusters has been extended not only to the homometallic clusters of a variety of metals such as Ru,[3] Co,[4] Rh,[5] Ir,[6] Ti,[7] V,[7] Mo,[8] etc., but also to the heterometallic clusters,[2a,9] the latter being of considerable interest in relation to, for example, the presence of polynuclear Mo/Fe/S and V/Fe/S cores in nitrogenase[10] and the promotion of hydrodesulfurization activity displayed by the addition of Co and Ni to the Mo- or W-based catalysts.[11] However, despite that the M_4S_4 cores are now ubiquitous in inorganic and organometallic compounds,[12] application of these clusters to the catalytic reactions has still been poorly exploited.[13]

Previously, we reported that the cubane-type Fe/S and M/Fe/S (M = Mo, W) clusters can facilitate the eletrochemical reduction of CO_2.[14] This finding has prompted us to study further the transformations of various substrate molecules on the mixed-metal sulfur clusters containing noble metals, since a variety of

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stoichiometric and catalytic reactions are known to be promoted by noble metal compounds.

Preparation of diruthenium complexes with thiolate and both thiolate and disulfide ligands[15] as well as the related M/Ru mixed-metal sulfur clusters (M = W, Mo,[15d] Pt, Pd[16]) has been carried out in this context, some of which have been demonstrated to display intriguing reactivities characteristic of their multimetallic sites.[15a–c,17] In addition to this chemistry involving ruthenium as the key component, we have found more recently that the reaction of Pd metal with the incomplete cubane-type cluster $[Mo_3S_4(H_2O)_9]^{4+}$ (**1**)[18] in aqueous HCl results in the formation of a mixed-metal cubane-type cluster $[PdMo_3S_4(H_2O)_9Cl]Cl_3$ (**2**). Full characterization of the novel $PdMo_3S_4$ clusters by X-ray crystallography has been carried out for a single cubane-type $[PdMo_3S_4(tacn)_3Cl]Cl_3$ (**3**) (tacn = 1,4,7-triazacyclononane) and a double cubane-type $[Pd_2Mo_6S_8(H_2O)_{18}](TsO)_8$ (**4**) (TsO = 4-$MeC_6H_4SO_3$), which are readily derived from **2** by treatment with tacn and by anion metathesis with TsO^-, respectively.[19] Although a significant number of heterometallic cubane-type MMo_3S_4 clusters have already been prepared from **1**,[20] clsuters **2**–**4** represent the first examples of this type containing noble metals for M. Furthermore, it has been demonstrated that the facile coordination of various substrate molecules such as alkenes, alkynes, CO, and ${}^tBuNC$ takes place at the unique Pd site in the clusters and in some cases unique catalytic reactions occur with the retention of the $PdMo_3S_4$ core. Here we wish to describe syntheses and reactivities of these new $PdMo_3S_4$ clusters.

Experimental Section

Preparation of Compounds. Preparation of the $PdMo_3S_4$ clusters was carried out under nitrogen, while purification of the products by column chromatography was conducted under air. Most of the $PdMo_3S_4$ clusters reported here are moderately stable under air except for the CO adduct **6**. However, the solutions of these clusters should be kept under an inert atmosphere for long period storage. Methanol was distilled from $Mg(OMe)_2$ before use. Compounds **1**[18e] and tacn[21] were prepared according to the literature methods, while Pd black, alkenes, alkynes, and ${}^tBuNC$ were commercially obtained and used without further purification.

Physical Methods. Absorption spectra were recorded on a Shimadzu UV-240 spectrophotometer, while IR spectra were obtained from a Shimadzu DR-8000 spectrometer. ${}^1H$ NMR spectra were recorded in D_2O on a JEOL GX-400 or EX-270 spectrometer; chemical shifts were referenced to HDO in D_2O at 4.7 ppm. Electrochemical measurements were made with Hokuto Denko instrumentation (HA-501 potentiostat and HB-105 function generator) using a glassy-carbon working electrode; potentials were measured vs a saturated calomel electrode (SCE) as reference. Quantitative analyses of organic compounds were performed by a Shimadzu GC-14A gas chromatograph equipped with a CBP-10 capillary column. Elemental analyses for C, H, N, S, and Cl were undertaken at the Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo, while the analysis data of Pd and Mo were obtained from Analytische Laboratorien, Gummersbach, Germany. For all new $PdMo_3S_4$ clusters, the presence of both Mo and Pd atoms has been confirmed by electron-probe microanalysis (EPMA) using a Kevex μX 7000 energy dispersive-type X-ray analyzer.

Preparation of $[PdMo_3S_4(H_2O)_9Cl]Cl_3$ (2). Into a solution of **1** (0.578 g, 1.02 mmol) in aqueous HCl (2.0 M, 200 mL) was added Pd black (1.06 g, 10.0 mmol), and the mixture was stirred for 2 days at room temperature. The resultant blue solution was separated from unreacted Pd black by filtration. After 50-fold dilution with H_2O, the products were loaded onto a Dowex 50W-X2 column (4 cm i.d. × 60 cm) and eluted with aqueous HCl (2.0 M). The first blue band was collected and dried in vacuo, giving **2** as a blue solid (0.75 g, 89%). UV–vis (H_2O, nm): λ_{max} 449, 580. Anal. Calcd for $H_{18}O_9Cl_4S_4Mo_3Pd{\cdot}HCl$: H, 2.21; Cl, 20.54; S, 14.86. Found: H, 1.71; Cl, 20.92; S, 13.60. The second minor green band contained unreacted **1**.

Preparation of $[PdMo_3S_4(tacn)_3Cl]Cl_3$ (3). A solution of **2** (1.00 g, 1.21 mmol) in degassed MeOH (150 mL) was refluxed over molecular sieves for 1 h. After cooling to ca. 40 °C, a solution of tacn (500 mg, 3.87 mmol) in MeOH (50 mL) was added dropwise, and the mixture was refluxed again for 1 h. After cooling, the resultant mixture was filtered, and the blue filtrate was dried in vacuo. The residue was redissolved in H_2O and loaded onto a Dowex 50W-X2 column. The major blue band followed the three minor blue bands upon elution with aqueous HCl (1.0 M). Evaporation of all volatile materials from this fourth band gave **3** in ca. 80% yield, recrystallization of which from aqueous HCl (2.0 M) afforded the blue single crystals of **3**$\cdot 4H_2O$ (524 mg, 41%). UV–vis (H_2O, nm): λ_{max} ($10^{-3}\,\epsilon_M$) 465 (0.73), 582 (1.0). The spectrum recorded in aqueous HCl (2.0 M) was essentially identical. IR (KBr, cm^{-1}): 3150 m, 1460 s, 1380 m, 1265 m, 1155 m, 1110 s, 1055 s, 975 s, 860 m, 830 m, and 800 m due to the tacn ligands. ${}^1H$ NMR: δ 3.1 (12H, m, NCH_2), 3.4 (12H, m, NCH_2), 3.7 (6H, m, NCH_2), 4.1 (6H, m, NCH_2). Anal. Calcd for $C_{18}H_{45}N_9Cl_4S_4Mo_3Pd{\cdot}4H_2O$: C, 19.23; H, 4.76; N, 11.21; S, 11.21; Cl, 12.61; Mo, 25.60; Pd, 9.46. Found: C, 18.81; H, 4.57; N, 11.14; S, 10.70; Cl, 13.28; Mo, 25.05; Pd, 9.19.

Preparation of $[Pd_2Mo_6S_8(H_2O)_{18}](TsO)_8$ (4). Cluster **2** in aqueous HCl was loaded on a Dowex 50W-X2 column and washed thoroughly with 0.5 M aqueous TsOH. A red-purple band separated by the subsequent elution with 4.0 M aqueous TsOH was collected and concentrated in vacuo. After removing the precipitated TsOH by filtration, the filtrate was kept at 3 °C for several weeks, giving dark blue crystals of **4**$\cdot 24H_2O$ together with colorless crystals of TsOH. Only the crystals of **4**$\cdot 24H_2O$ were collected manually and used for the spectroscopic measurement as well as the reactions with alkenes and alkynes. UV–vis (H_2O, nm): λ_{max} ($10^{-3}\,\epsilon_M$ per double cubane) 458 (1.5), 572 (2.1). Anal. Calcd for $C_{56}H_{92}O_{42}S_{16}Mo_6Pd_2{\cdot}24H_2O$: C, 21.21; H, 4.46; S, 16.18. Found: C, 22.10; H, 4.09; S, 16.16. The Mo:Pd ratio determined by inductively coupled plasma (ICP) atomic emission spectroscopy on a Nippon Jarrell-Ash ICAP-575 spectrometer was 3.09.

Generation of Alkene Clusters. Reactions of clusters **2**–**4** with alkenes were carried out in H_2O or MeOH at room temperature in the presence of excess alkenes. In a typical experiment, a mixture of 50 mg of **2** (0.60 mmol) in MeOH (5 mL) was stirred with 3–5 equiv of alkenes. In the reaction with ethylene, an ethylene gas was bubbled through the solution of **2** for a few minutes, and the mixture was then stirred under an ethylene atmosphere. Rapid color change from blue to red-purple was observed by treatment with ethylene, 1,5-cyclooctadiene (1,5-COD), $PhCH{=}CH_2$, etc., but not with *trans*-$PhCH{=}CHPh$, which was monitored by the absorption spectra of the reaction mixtures. Reactions of alkenes with **3** and **4** were conducted in essentially the same manner. Despite our intensive efforts, we could not isolate the expected alkene clusters in a pure form from any reactions attempted here.

Formation of $[PdMo_3S_4(tacn)_3(L)]^{4+}$ (5, L = Alkene) from 3/$AgBF_4$. In a typical experiment, ca. 50 mg of **3** was added to 5% aqueous $AgBF_4$ and stirred vigorously. After filtration, 3 equiv of an alkene was added to the filtrate, and the mixture was stirred at room temperature for 0.5 h. Upon standing for several days, a deposited red crystalline solid was collected. However, the solid was a mixture of **5** and Ag salts. Thus, complexes **5** could not be isolated in satisfactorily pure form and were characterized only spectroscopically as follows. **5b** (L = 4-MeC_6H_4-

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$CH{=}CH_2$). UV–vis (H_2O, nm): λ_{max} 482. ^1H NMR: δ 7.30 and 7.20 (d, 2H each, C_6H_4), 6.83 (dd, 1H, $CH{=}CH_2$), 4.95 and 4.05 (d, 1H each, $CH{=}CH_2$), 2.21 (s, 3H, Me), and those due to tacn. **5c** (L = *trans*-$PhCH{=}CHMe$). UV–vis (H_2O, nm): λ_{max} 480. ^1H NMR: δ 7.38 (m, 5H, Ph), 6.45 (d, 1H, $PhCH{=}CH$), 6.30 (m, 1H, $CH{=}CHMe$), 1.88 (d, 3H, Me), and those due to tacn. **5d** (L = 1,5-COD). UV–vis (H_2O, nm): λ_{max} 470. ^1H NMR: δ 6.3–6.6, 5.5–5.7 (brm, $CH{=}CH$), 1.9–2.7 (brm, CH_2), and those due to tacn.

Anion Exchange of 3 by Column Chromatography To Give [$PdMo_3S_4$(tacn)$_3$Cl]X_3 (8). A column packed with Dowex 2-8X was washed thoroughly with either aqueous $NaClO_4$, $AgBF_4$, or NH_4PF_6 solution and then with H_2O. Cluster **3** dissolved in H_2O was loaded onto the column and eluted with H_2O. The blue solution was collected and concentrated in vacuo at elevated temperatures, giving dark blue crystalline complexes [$PdMo_3S_4$(tacn)$_3$Cl]X_3 (**8a**, X = ClO_4; **8b**, X = BF_4; **8c**, X = PF_6) almost quantitatively, which were used for the subsequent reactions with a series of substrate molecules. **8b**. Anal. Calcd for $C_{18}H_{45}N_9ClF_{12}B_3S_4Mo_3Pd$: C, 17.93; H, 3.76; N, 10.45. Found: C, 18.01; H, 4.24; N, 10.67. **8c**. Anal. Calcd for $C_{18}H_{45}N_9ClF_{18}P_3S_4Mo_3Pd$: C, 15.66; H, 3.29; N, 9.13. Found: C, 15.97; H, 3.72; N, 9.42. (Anal. for **8a**: vide infra.) The EPMA data of **8b** and **8c** have confirmed the presence of one Cl atom per Pd atom.

Preparation of [$PdMo_3S_4$(tacn)$_3$(*cis*-$HOCH_2CH{=}CHCH_2OH$)]Cl(ClO_4)$_3$ (5a) from 8a. To a solution of **8a** (50 mg, 0.040 mmol) in H_2O (10 mL) was added excess *cis*-$HOCH_2CH{=}CHCH_2OH$ (0.05 mL), which resulted in a rapid color change from dark blue to dark red. After stirring for several hours, the product solution was concentrated in vacuo and stored at 3 °C. The dark red crystals of **5a** precipitated (43 mg, 80%). UV–vis (H_2O, nm): λ_{max} 481, 444 sh. ^1H NMR: δ 3.1 (12H, m, NCH_2), 3.3 (6H, m, NCH_2), 3.4 (6H, m, NCH_2), 3.5 (6H, m, NCH_2), 3.9 (6H, m, NCH_2), 3.7 (2H, br, CH_2OH), 4.1 (2H, br, CH_2OH), 5.2 (2H, pseudo t, $CH{=}CH$). Anal. Calcd for $C_{22}H_{53}N_9O_{14}Cl_4S_4Mo_3Pd$: C, 19.83; H, 4.02; N, 9.47. Found: C, 19.02; H, 4.13; N, 8.97. On the other hand, a single crystal collected for an X-ray analysis has been shown to contain the cluster formulated as [$PdMo_3S_4$(tacn)$_3$(*cis*-$HOCH_2CH{=}CHCH_2OH$)](ClO_4)$_4$ (**5a′**) with two solvating H_2O molecules per cluster unit. **CAUTION**: Compound **5a** should not be heated to high temperatures because it is explosive. Due to the explosion of **5a** encountered during the combustion analysis, elemental analyses of the clusters **5a′**, **6a** (vide infra), and **8a** containing the ClO_4 anion were not performed.

Preparation of [$PdMo_3S_4$(tacn)$_3$(CO)]Cl(PF_6)$_3$ (6c) from 8c. Carbon monoxide was bubbled through a solution of **8c** (50 mg, 0.036 mmol) in H_2O/MeOH (2:8) for several minutes. The initial dark blue solution smoothly changed in color to yellow-brown. The resultant solution was kept at 3 °C to deposit dark brown crystals of **6c** (19 mg, 37%). UV–vis (H_2O, nm): λ_{max} 465, 580. IR (KBr, cm^{-1}): 2085 s ($C{\equiv}O$), 845 brs (P–F), and those due to the tacn ligands. ^1H NMR: δ 3.9 (m, 6H, NCH_2), 3.5 (m, 12H, NCH_2), 3.3 (m, 6H, NCH_2), 3.1 (m, 12H, NCH_2). Anal. Calcd for $C_{19}H_{45}N_9OClF_{18}P_3S_4Mo_3Pd$: C, 16.20; H, 3.23; N, 8.95; S, 9.11. Found: C, 16.68; H, 3.44; N, 9.49; S, 8.79. Cluster [$PdMo_3S_4$(tacn)$_3$(CO)]Cl(ClO_4)$_3$ (**6a**) was prepared analogously from **8a**. IR (KBr, cm^{-1}): 2087 s ($C{\equiv}O$), 1100 s (Cl–O). The X-ray analysis by using a single crystal of **6a** disclosed its structure in detail as well as the presence of three H_2O molecules in the asymmetric unit.

Preparation of [$PdMo_3S_4$(tacn)$_3$(^tBuNC)]Cl(BF_4)$_3$ (7b). To a stirred solution of **8b** (275 mg, 0.228 mmol) in H_2O/EtOH (1:1) was added ^tBuNC (91 mg, 1.1 mmol) at room temperature. Rapid color change from dark blue to red-orange was observed. After stirring for 4 h, the mixture was cooled to 3 °C, giving **7b** as dark red needles (265 mg, 90%). UV–vis (H_2O, nm): λ_{max} 429, 501. IR (KBr, cm^{-1}): 2202 s ($C{\equiv}N$), 1110 brs (B–F), and those due to the tacn ligands. ^1H NMR: δ 1.3 (9H, s, ^tBu), 3.0 (12H, m, NCH_2), 3.2 (6H, m, NCH_2), 3.4 (12H, m, NCH_2), 3.8 (6H, m, NCH_2). Cluster [$PdMo_3S_4$(tacn)$_3$(^tBuNC)]Cl(ClO_4)$_3$ (**7a**) was obtained analogously from **8a**. IR (KBr, cm^{-1}): 2191 s ($C{\equiv}N$), 1100 s (Cl–O). Anal. Calcd for $C_{23}H_{45}N_{10}O_{12}Cl_4S_4Mo_3Pd$: C, 20.82; H, 4.10; N, 10.55. Found: C, 21.39; H, 5.25; N, 9.90.

Attempted Isolation of the Alkyne Cluster. Cluster **8b** in MeOH was treated with 3 equiv of $HC{\equiv}CCOOMe$ (**10**) at room temperature. After 1 h, the resultant red solution was evaporated to dryness in vacuo and the remaining red solid (**9a**) was washed thoroughly with ether. Reaction of **8c** with $MeOCOC{\equiv}CCOOMe$ was carried out analogously in MeOH/H_2O (1:1), giving a red solid (**9b**). **9a** (X = BF_4). IR (KBr, cm^{-1}): 2074 m ($C{\equiv}C$), 1715 m (C=O), 1100 brs (B–F). **9b** (X = PF_6). IR (KBr, cm^{-1}): 1734 s (C=O), 849 s (P–F). When redissolved in H_2O or MeOH, **9** readily loses the coordinated alkyne either by the reaction with these solvents or by simple dissociation to regenerate **8**, and characterization of **9** by ^1H NMR spectroscopy and isolation of pure **9** were unsuccessful. Spectral features of the solid product obtained from the reaction of **8b** with a large excess of **10** in MeOH at reflux are essentially the same as that of **9a** shown above, whereby the GLC analysis of the product solution showed that almost all the added alkyne was consumed during the reaction. Attempted purification of the red solid product resulted in the regeneration of **8b** (from UV–vis spectrum).

Catalytic Conversion of Alkynic Acid Esters into Alcohol Adducts in the Presence of 8c. The following procedure is representative. To a mixture of **8c** (12.1 mg, 8.77 μmol) in MeOH (2 mL) was added $HC{\equiv}CCOOMe$ (**10**; 254 mg, 3.02 mmol) under air. Rapid color change from blue to red-purple was observed. After stirring for 6 h at 40 °C, the resultant mixture was subjected to GLC analysis by using $^nBu_2O$ as an internal standard, which disclosed the 100% conversion of **10** as well as the formation of (*Z*)-$MeOCH{=}CHCOOMe$ (**11**) in 97% yield based on **10**. Formation of small amounts of (*E*)-$MeOCH{=}CHCOOMe$ (0.8% yield) and $(MeO)_2CHCH_2COOMe$ (0.6% yield) was also observed. The reaction mixture was diluted with ether/hexane (1:1; 50 mL) and filtered. Evaporation of the filtrate and subsequent Kugelrohr distillation of this residue (3–5 mmHg, 70 °C) gave pure **11** as colorless oil (289 mg, 82% yield). GC–MS *m/z*: 116 M^+. IR (neat, cm^{-1}): 1651 (C=C), 1718 (C=O). ^1H NMR ($CDCl_3$): δ 3.69, 3.88 (s, 3H each, OMe), 4.86 (d, *J* = 7.1 Hz, 1H, $=CHCOOMe$), 6.46 (d, *J* = 7.1 Hz, 1H, $=CHOMe$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 50.8, 62.4 (OMe), 95.8 ($=CHCOOMe$), 159.9 ($=CHOMe$), 165.5 (COOMe). Other catalytic reactions of the alkynic acid esters with MeOH were carried out similarly, and the products were purified either by Kugelrohr distillation or by column chromatography.

Modified reaction conditions were adopted for catalytic reactions of **10** with EtOH or $PhCH_2OH$. In these cases, **8c**, **10**, and either EtOH (15 mmol) or $PhCH_2OH$ (9 mmol) were dissolved in acetone (2 mL), and the mixture was refluxed for 20 h for the former or 8 h for the latter, respectively. Workup of the reaction mixture analogous to that described above gave pure (*Z*)-$EtOCH{=}CHCOOMe$ (83% yield after Kugelrohr distillation) or (*Z*)-$PhCH_2OCH{=}CHCOOMe$ (70% yield after column chromatography).

X-ray Data Collection and Reduction. Suitable crystals of **3**, **5a′**, and **6a** were mounted in glass capillaries and sealed under nitrogen. For **4**, a single crystal was sealed in a capillary together with a small amount of a saturated aqueous solution of **4** under air. Diffraction studies were performed at room temperature on four-circle automated diffractometers by using graphite-monochromatized Mo Kα radiation (λ = 0.7107 Å). Orientation matrices and unit cell parameters were determined by least-squares treatment of 19–25 machine-centered reflections having $25° < 2\theta < 35°$. The intensities of three check reflections were monitored every 100 or 150 reflections during data collection, which revealed no significant changes in intensities for all crystals. Details of crystal and data collection parameters are listed in Table 1. Intensity data were corrected for Lorentz and polarization effects, and absorption corrections were also applied.

Structures Solution and Refinement. Calculations were carried out at The Computer Center of The University of Tokyo for **3**, **5a′**, and **6a**, or at The Institute of Physical and Chemical Research, Wako, Saitama, Japan, for **4**, by using the UNIX-III program package.[22] The positions of the heavy atoms were determined by the direct methods program MULTAN78 for **3** and **4** or SHELXS86 for **5a′** and **6a**. All remaining non-hydrogen atoms were located with the use of successive cycles of difference Fourier maps and block-diagonal least-squares refinement. Atomic scattering factors were taken from a standard source.[23] For **3**, refinements obtained by inverting the coordinates of all atoms did not improve the *R* values. For **4**, structure solutions and refinements were performed by selecting the space group of both *P*1 and $P\bar{1}$, and only the choice of *P*1 led to the successful solution and refinement of the whole structure. This is consistent with the fact that the structure of the double cubane core in **4** determined by employing the space group of *P*1 is not centrosymmetric (vide infra).

Results and Discussion

Preparation of [$PdMo_3S_4$(tacn)$_3$Cl]Cl_3 (3) and [$Pd_2Mo_6S_8(H_2O)_{18}$](TsO)$_8$ (4). When cluster **1** dissolved in 2.0 M aqueous HCl was stirred vigorously at room temperature in the presence

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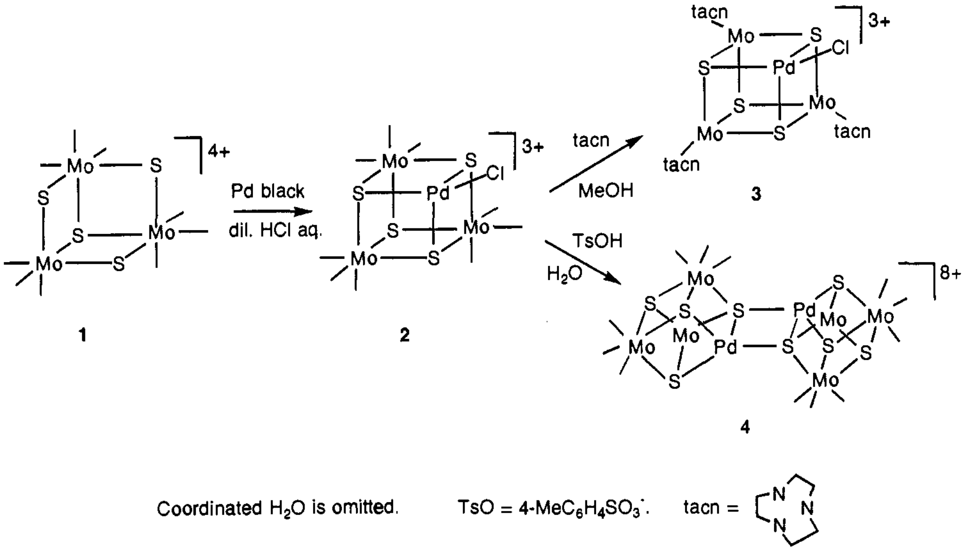
Table 1. Crystallographic Data for $PdMo_3S_4$ Clusters

	$3 \cdot 4H_2O$	$4 \cdot 24H_2O$	$5a' \cdot 2H_2O$	$6a \cdot 3H_2O$
formula	$C_{18}H_{44}N_9O_4Cl_4S_4Mo_3Pd$	$C_{56}H_{140}O_{66}S_{16}Mo_6Pd_2$	$C_{22}H_{57}N_9O_{20}S_4Cl_4Mo_3Pd$	$C_{19}H_{51}N_9O_{16}S_4Cl_4Mo_3Pd$
formula wt	1114.9	3170.42	1430.7	1326.0
cryst system	orthorhombic	triclinic	monoclinic	orthorhombic
space group	$P2_12_12_1$ (No. 19)	$P1$ (No. 1)	$P2_1/m$ (No. 11)	$Pbca$ (No. 61)
Z	4	1	2	8
a, Å	17.549(3)	15.799(4)	12.314(1)	15.485(13)
b, Å	20.032(4)	18.079(6)	12.732(2)	23.900(6)
c, Å	10.256(2)	11.873(1)	15.736(2)	23.326(7)
α, (deg)	90.00	108.75(2)	90.00	90.00
β, (deg)	90.00	108.73(1)	94.01 (1)	90.00
γ, (deg)	90.00	70.87(3)	90.00	90.00
V, Å^3	3605	2944	2461	8633
d_{calc}, g cm^{-3}	2.05	1.79	1.90	2.04
μ, cm^{-1}	20.44	10.78	15.36	17.43
diffractometer	MAC MXC18	Enraf-Nonius CAD4	Rigaku AFC5R	Rigaku AFC5R
trans. factors	0.537–0.607	0.66–0.76	1.002–1.226	1.024–1.164
unique data	4014 [$\|F_o\| > 3\sigma(\|F_o\|)$]	10089 [$\|F_o\| > 5\sigma(\|F_o\|)$]	2743 [$\|F_o\| > 5\sigma(\|F_o\|)$]	7761 [$\|F_o\| > 5\sigma(\|F_o\|)$]
no. of variables	389	1316	362	506
R^a	0.051	0.028	0.068	0.061
R_w^b	0.062	0.036	0.081	0.069

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

Scheme 1



Coordinated H_2O is omitted. TsO = 4-$MeC_6H_4SO_3^-$. tacn =

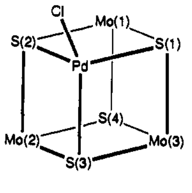
of excess Pd black under N_2, the color of the mixture gradually changed from green to blue. After 2 days, the product solution was subjected to column chromatography, which revealed that the reaction mixture contained essentially only one product in addition to a small amount of unreacted **1**. In more diluted HCl, this reaction is notably retarded. From a well-defined blue band, a novel mixed-metal cubane-type cluster tentatively formulated as $[PdMo_3S_4(H_2O)_9Cl]Cl_3$ (**2**) was obtained in ca. 90% yield by evaporating all volatile materials in vacuo (Scheme 1). However, despite the extensive trials to crystallize **2**, single crystals suitable for X-ray crystallography were not available, and full details of its structure could not be clarified.

Reactions of **2** with various N-, S-, and O-donor ligands were therefore attempted to derive the crystalline $PdMo_3S_4$ clusters. The reaction of **2** with 3.3 equiv of tacn in MeOH at reflux afforded a crystalline complex $[PdMo_3S_4(tacn)_3Cl]Cl_3$ (**3**) in moderate yield (Scheme 1). The ^{1}H NMR spectrum of **3** in D_2O exhibits sharp multiplets centered at 3.1, 3.4, 3.7, and 4.1 ppm in a 2:2:1:1 intensity ratio due to the methylene protons of the coordinated tacn ligands. Essentially diamagnetic nature of **3** in a solid state has also been confirmed by the Faraday method. Furthermore, the X-ray analysis has been carried out by using a blue single crystal of $3 \cdot 4H_2O$, which has unambiguously demonstrated the expectd cubane-type $PdMo_3S_4$ structure.

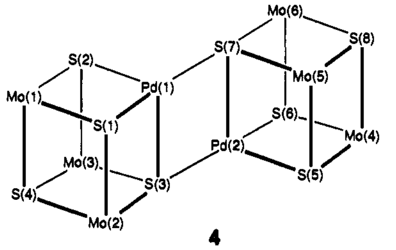
Anion metathesis was also carried out for **2**, and replacement of the Cl anion with the TsO anion resulted in the precipitation of $[Pd_2Mo_6S_8(H_2O)_{18}](TsO)_8$ (**4**) as dark blue crystals (Scheme 1), whose structure has been determined by X-ray crystallography. In contrast to the single cubane-type structure of **3**, cluster **4** has a double cubane-type core, in which two $PdMo_3S_4$ units are connected by the two Pd–S bonds, which might arise from the larger affinity of the sulfide to Pd than the TsO ligand. Absorption spectra of **3** and **4** are quite analogous to each other (λ_{max}: 465 and 582 nm for **3**; 458 and 572 nm for **4**), and the spectrum of **2** exhibits the similar feature (450 and 582 nm).

Capture of a heterometal into the trinuclear sulfide cluster appears to be a rational synthetic route toward the mixed-metal cubane-type clusters with a MM'_3S_4 core, which has already been demonstrated in two ways. One is the reaction of the incomplete cubane-type cluster **1** with metals or $NiCl_2/NaBH_4$ in acidic media to give either single cubane-type MMo_3S_4 clusters (M = Fe,[20a] Ni[20c,d]), double cubane-type $M_2Mo_6S_8$ clusters (M = Co,[20b] Cu[20e]), or a sandwich cubane-type MMo_6S_8 cluster (M = Hg[20b]). The other is the reaction of a linear triiron cluster $[Fe_3S_4(SEt)_4]^{3-}$ with $[Mo(CO)_3(MeCN)_3]$[24] or $[Ni(PPh_3)_4]$,[25] leading to the formation of the single cubane-type MFe_3S_4 clusters. Preparation of a VFe_3S_4 cluster[26] by treatment of the linear heterometallic trinuclear cluster $[VFe_2S_4Cl_4]^{3-}$ with $FeCl_2$ may also be included in the latter category. However, these reaction systems have not yet been extended to those containing noble metals, and clusters **2**–**4** reported here demomstrate the first examples of this type containing the unique noble metal site. Although some homometallic cubane clusters are known for the noble metals such as Ru,[3] Rh,[5] and Ir,[6] all these clusters consist of the metal sites capped by the cyclopentadienyl ligands. The Pd atom in the clusters obtained here can probably serve as the more potential site for chemical transformations than the noble metals firmly bound by cyclopentadienyl ligands.

X-ray Structures of 3 and 4. Single-crystal X-ray crystallography has unambiguously demonstrated the presence of the expected $PdMo_3S_4$ cores in **3** and **4**, ORTEP drawings of which have been given earlier.[19] It should be emphasized that the clusters have a tetrahedrally coordinated Pd site, which is not common for Pd(II) chemistry. The important bond distances and angles in these cluster cations are summarized in Table 2.



3



4

In a single cubane-type cluster **3**, one Pd and three Mo atoms form a tetrahedron with a small distortion, and the interatomic distances and angles within this tetrahedron fall in the ranges 2.790(2)–2.825(2) Å and 59.54(4)–60.71(4)°, respectively. The Mo–Mo distances in **3** are slightly elongated from those in **1** (2.735 Å (mean value))[27] as well as $[Mo_3S_4(tacn)_3]^{4+}$ (2.773 Å (mean value)),[28] and within **3** the Pd–Mo distances are a little shorter than the Mo–Mo distances. These structural features of the $PdMo_3S_4$ core correspond well to those in the related $FeMo_3S_4$[20a] and $NiMo_3S_4$[20c] clusters having the same MMo_3S_4 core charge of +4. Each face of this tetrahedron is capped by the μ_3-S ligand. Both the Pd–S bond lengths at 2.357(4)–2.378(4) Å and the Mo–S bond distances varying from 2.329(3) to 2.374(3) Å are unexceptional, although the former lengths are slightly longer than those in $[(PdCl)_2(\mu\text{-dppm})_2(\mu\text{-S})]$ (2.30 Å)[29] and $[\{(\eta^3\text{-}C_3H_5)Pd\}_2(\mu\text{-S})_4W]$ (2.34 Å).[30]

If the metal–metal interactions described above are ignored, the Pd atom has an essentially tetrahedral geometry surrounded by three μ_3-S ligands and one terminal Cl ligand, whereby the S–Pd–S angles (104–105°) are slightly acute relative to the Cl–Pd–S angles (108–120°). The Pd–Cl distance at 2.450(4) Å is fairly long if compared with the typical Pd(II)–Cl (terminal) bond lengths (2.25–2.43 Å).[31] Each Mo atom has a distorted octahedral structure with three μ_3-S ligands and a capped tridentate tacn ligand, in which the bond angles around Mo are as follows: S–Mo–S = 103–106°; S–Mo–N (cis) = 86–90°; N–Mo–N = 73–76°. These geometrical properties around the Mo atom correspond well to those in $[Mo_3S_4(tacn)_3]^{4+}$ cited above.[28]

In contrast to the single cubane-type structure in **3**, cluster **4** contains a double cubane-type cation in which two $PdMo_3S_4$ cores are linked by two Pd–S bonds. The Pd–Pd distance at 2.790(1) Å suggests the bonding interaction between the two Pd atoms. The structure of this double cubane-type core is not centrosymmetric, and the Pd_2S_2 plane is slightly folded with a dihedral angle of 168° along the Pd–Pd vector. This accounts for the successful solution and refinements of the structure for **4** only by selecting the space group $P1$ instead of $P\bar{1}$.

In **4**, the Pd atoms are tetrahedrally coordinated by three μ_3-S ligands and one μ_4-S ligand, while the Mo atoms have an octahedral geometry with three μ_3-S and three H_2O ligands. The Mo–Mo and Mo–S distances in the range 2.759(1)–2.789(1) and 2.332(2)–2.355(2) Å, respectively, are comparable to those in **3**. However, the significant difference in the core structure of **4** from that of **3** is observed in the bond lengths associated with the Pd atoms; the Pd–S distances around the Pd(1) atom, for example, vary significantly from 2.329(2) to 2.502(2) Å, increasing in the order Pd(1)–S(1) < Pd(1)–S(2) < Pd(1)–S(7) < Pd(1)–S(3). It is to be noted that the latter two are exceptionally long (typical Pd(II)–S bond: 2.23–2.40 Å),[31] and interestingly, the Pd(1)–S(3) bond comprising one edge of the cubane is much more lengthened than the Pd(1)–S(7) bridge. Accordingly, the Pd(1)–Mo(2) and Pd(1)–Mo(3) distances are substantially longer than the Pd(1)–Mo(1) distance. A similar relationship is observed between the Pd–S bonds around the Pd(2) atom. These structural features are in good agreement with those in $[Cu_2Mo_6S_8(H_2O)_{18}](TsO)_8\cdot 20H_2O$[20e] except that there exists a crystallographic inversion center in the middle of the Cu–Cu bond within this cluster.

For the $PdMo_3S_4$ clusters reported here, both single and double cubane-type clusters have been isolated and characterized in a well-defined manner. This situation has rarely been encountered for the other MMo_3S_4 clusters of this type. Thus, the corresponding Fe and Ni clusters isoalted from aqueous TsOH and HCl consist of a single cubane-type cation $[MMo_3S_4(H_2O)_{10}]^{4+}$, in which a H_2O molecule occupies the remaining site on the Fe and Ni atoms, while the Co cluster has a double cubane-type core $[Co_2Mo_6S_8(H_2O)_{18}]^{8+}$ analogous to **4** reported here. As for the $CuMo_3S_4$ cluster, it has been presumed that the interconversion between a single and a double cubane-type structure occurs upon replacement of the media with aqueous HCl and TsOH, respectively. However, only the double cubane-type structure cited above has been characterized by X-ray analysis. The structures of the related mixed-metal clusters containing the other noble metals instead of Pd are therefore of significant interest, and the efforts to synthesize these new clusters are now continuing.

Electrochemical Properteis of 3. A cyclic voltammogram of **3** in 0.1 M aqueous LiCl shows one quasi-reversible reduction wave at $E_{1/2}$ = –0.55 V and one irreversible oxidation wave at E_{pa} = 0.83 V. This presents a sharp contrast to the result obtained for **4** in aqueous TsOH solution; **4** revealed the complicated cyclic voltammogram consisting of several uncharacterizable waves, none of which exhibit reversible behavior. This feature observed for **4** is analogous to that reported for $[NiMo_3S_4(H_2O)_{10}]^{4+}$.[20d]

Coordination of Alkenes, CO, and ^{t}BuNC to the Pd Site in 3. Reactivities exhibited at the unique tetrahedral Pd site in the $PdMo_3S_4$ core are our principal interest, and the reactions of clusters **2**–**4** with various alkenes were examined. Treatment of **2** with excess alkenes such as ethylene, styrenes, and 1,5-COD in MeOH or H_2O resulted in a rapid color change from blue to red-purple, whereas the reaction with *trans*-PhCH=CHPh at room temperature did not show any change in its absorption spectrum. Coordination of ethylene and 1,5-COD to **2** at least in part was confirmed directly by recording the ^1H NMR spectra of the reaction mixtures. However, isolation of the pure alkene

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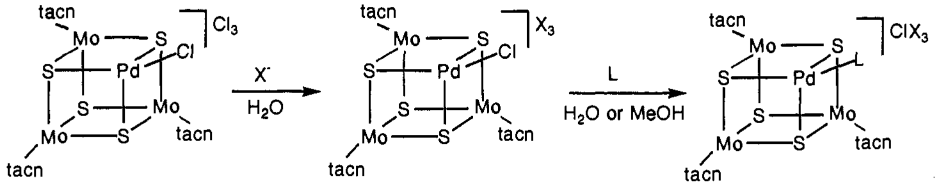
Table 2. Selected Bond Distances and Angles in **3** and **4**

3			
(a) Bond Distances (Å)			
Pd–S(1)	2.365(3)	Pd–S(2)	2.357(4)
Pd–S(3)	2.378(4)	Pd–Cl(1)	2.450(4)
Mo(1)–S(1)	2.329(3)	Mo(1)–S(2)	2.349(4)
Mo(1)–S(4)	2.364(3)	Mo(2)–S(2)	2.352(4)
Mo(2)–S(3)	2.349(4)	Mo(2)–S(4)	2.363(3)
Mo(3)–S(1)	2.333(3)	Mo(3)–S(3)	2.353(4)
Mo(3)–S(4)	2.374(3)		
Pd–Mo(1)	2.790(2)	Pd–Mo(2)	2.792(2)
Pd–Mo(3)	2.798(2)	Mo(1)–Mo(2)	2.815(2)
Mo(1)–Mo(3)	2.817(2)	Mo(2)–Mo(3)	2.825(2)
(b) Bond Angles (deg)			
S(1)–Pd–S(2)	104.3(1)	S(1)–Pd–S(3)	104.3(1)
S(1)–Pd–Cl(1)	108.8(1)	S(2)–Pd–S(3)	104.7(1)
S(2)–Pd–Cl(1)	119.9(1)	S(3)–Pd–Cl(1)	113.4(1)
S(1)–Mo(1)–S(2)	105.7(1)	S(1)–Mo(1)–S(4)	104.2(1)
S(2)–Mo(1)–S(4)	104.3(1)	S(2)–Mo(2)–S(3)	105.8(1)
S(2)–Mo(2)–S(4)	104.2(1)	S(3)–Mo(2)–S(4)	104.2(1)
S(1)–Mo(3)–S(3)	106.0(1)	S(1)–Mo(3)–S(4)	103.7(1)
S(3)–Mo(3)–S(4)	103.7(1)		
Pd–S(1)–Mo(1)	72.9(1)	Pd–S(1)–Mo(3)	73.1(1)
Mo(1)–S(1)–Mo(3)	74.4(1)	Pd–S(2)–Mo(1)	72.7(1)
Pd–S(2)–Mo(2)	72.7(1)	Mo(1)–S(2)–Mo(2)	73.6(1)
Pd–S(3)–Mo(2)	72.4(1)	Pd–S(3)–Mo(3)	72.5(1)
Mo(2)–S(3)–Mo(3)	73.9(1)	Mo(1)–S(4)–Mo(2)	73.1(1)
Mo(1)–S(4)–Mo(3)	73.0(1)	Mo(2)–S(4)–Mo(3)	73.2(1)
4			
(a) Bond Distances (Å)			
Pd(1)–S(1)	2.329(2)	Pd(1)–S(2)	2.363(3)
Pd(1)–S(3)	2.502(2)	Pd(1)–S(7)	2.414(2)
Pd(2)–S(3)	2.422(2)	Pd(2)–S(5)	2.323(3)
Pd(2)–S(6)	2.353(2)	Pd(2)–S(7)	2.457(2)
Mo(1)–S(1)	2.333(3)	Mo(1)–S(2)	2.350(2)
Mo(1)–S(4)	2.349(2)	Mo(2)–S(1)	2.332(2)
Mo(2)–S(3)	2.355(2)	Mo(2)–S(4)	2.345(3)
Mo(3)–S(2)	2.335(2)	Mo(3)–S(3)	2.334(3)
Mo(3)–S(4)	2.344(2)	Mo(4)–S(5)	2.340(2)
Mo(4)–S(6)	2.345(3)	Mo(4)–S(8)	2.348(2)
Mo(5)–S(5)	2.332(2)	Mo(5)–S(7)	2.344(3)
Mo(5)–S(8)	2.351(2)	Mo(6)–S(6)	2.336(2)
Mo(6)–S(7)	2.335(2)	Mo(6)–S(8)	2.339(3)
Pd(1)–Pd(2)	2.790(1)	Pd(1)–Mo(1)	2.746(1)
Pd(1)–Mo(2)	2.816(1)	Pd(1)–Mo(3)	2.820(1)
Pd(2)–Mo(4)	2.759(1)	Pd(2)–Mo(5)	2.814(1)
Pd(2)–Mo(6)	2.836(1)	Mo(1)–Mo(2)	2.767(1)
Mo(1)–Mo(3)	2.777(1)	Mo(2)–Mo(3)	2.789(1)
Mo(4)–Mo(5)	2.764(1)	Mo(4)–Mo(6)	2.759(1)
Mo(5)–Mo(6)	2.784(1)		
(b) Bond Angles (deg)			
S(1)–Pd(1)–S(2)	106.3(1)	S(1)–Pd(1)–S(3)	102.9(1)
S(1)–Pd(1)–S(7)	113.9(1)	S(2)–Pd(1)–S(3)	102.0(1)
S(2)–Pd(1)–S(7)	120.7(1)	S(3)–Pd(1)–S(7)	109.0(1)
S(3)–Pd(2)–S(5)	113.0(1)	S(3)–Pd(2)–S(6)	120.7(1)
S(3)–Pd(2)–S(7)	110.2(1)	S(5)–Pd(2)–S(6)	106.0(1)
S(5)–Pd(2)–S(7)	103.2(1)	S(6)–Pd(2)–S(7)	101.9(1)
S(1)–Mo(1)–S(2)	106.6(1)	S(1)–Mo(1)–S(4)	105.0(1)
S(2)–Mo(1)–S(4)	104.3(1)	S(1)–Mo(2)–S(3)	107.5(1)
S(1)–Mo(2)–S(4)	105.2(1)	S(3)–Mo(2)–S(4)	103.5(1)
S(2)–Mo(3)–S(3)	108.2(1)	S(2)–Mo(3)–S(4)	104.9(1)
S(3)–Mo(3)–S(4)	104.2(1)	S(5)–Mo(4)–S(6)	105.7(1)
S(5)–Mo(4)–S(8)	105.1(1)	S(6)–Mo(4)–S(8)	105.1(1)
S(5)–Mo(5)–S(7)	106.5(1)	S(5)–Mo(5)–S(8)	105.3(1)
S(7)–Mo(5)–S(8)	103.9(1)	S(6)–Mo(6)–S(7)	106.2(1)
S(6)–Mo(6)–S(8)	105.7(1)	S(7)–Mo(6)–S(8)	104.5(1)
Pd(1)–S(1)–Mo(1)	72.2(1)	Pd(1)–S(1)–Mo(2)	74.3(1)
Mo(1)–S(1)–Mo(2)	72.8(1)	Pd(1)–S(2)–Mo(1)	71.3(1)
Pd(1)–S(2)–Mo(3)	73.8(1)	Mo(1)–S(2)–Mo(3)	72.7(1)
Pd(1)–S(3)–Pd(2)	69.0(1)	Pd(1)–S(3)–Mo(2)	70.8(1)
Pd(1)–S(3)–Mo(3)	71.3(1)	Pd(2)–S(3)–Mo(2)	129.0(1)
Pd(2)–S(3)–Mo(3)	120.0(1)	Mo(2)–S(3)–Mo(3)	73.0(1)
Mo(1)–S(4)–Mo(2)	72.2(1)	Mo(1)–S(4)–Mo(3)	72.6(1)
Mo(2)–S(4)–Mo(3)	73.0(1)	Pd(2)–S(5)–Mo(4)	72.5(1)
Pd(2)–S(5)–Mo(5)	74.4(1)	Mo(4)–S(5)–Mo(5)	72.5(1)
Pd(2)–S(6)–Mo(4)	71.9(1)	Pd(2)–S(6)–Mo(6)	74.4(1)
Mo(4)–S(6)–Mo(6)	72.2(1)	Pd(1)–S(7)–Pd(2)	69.9(1)
Pd(1)–S(7)–Mo(5)	130.2(1)	Pd(1)–S(7)–Mo(6)	122.0(1)
Pd(2)–S(7)–Mo(5)	71.7(1)	Pd(2)–S(7)–Mo(6)	72.5(1)
Mo(5)–S(7)–Mo(6)	73.0(1)	Mo(4)–S(8)–Mo(5)	72.1(1)
Mo(4)–S(8)–Mo(6)	72.1(1)	Mo(5)–S(8)–Mo(6)	72.8(1)

Scheme 2



3

8a: X = ClO$_4$,
8b: X = BF$_4$,
8c: X = PF$_6$

5: L = olefin,
6: L = CO,
7: L = ^{t}BuNC

clusters failed due to the poor stability of these products. Upon removal of excess alkenes, these red products were easily converted back to the blue parent cluster **2**. Analogous instability was observed for the products derived from the reactions of **3** with various alkenes. As for the double cubane-type cluster **4**, although a smooth color change from blue to red-purple took place similarly upon mixing with alkenes, we could not get any evidence indicating the coordination of alkenes to **4** from ^{1}H NMR criteria.

Alternatively, we have found that the substantially stable alkene clusters can be obtained if the reactions with alkenes were carried out in the absence of excess Cl ions. Thus, the initial treatment of **3** with $AgBF_4$ followed by the reactions with styrenes and 1,5-COD in H_2O resulted in the rapid formation of $[PdMo_3S_4(tacn)_3(L)]^{4+}$ (**5b**, L = 4-$MeC_6H_4CH{=}CH_2$; **5c**: L = *trans*-$PhCH{=}CHMe$; **5d**, L = 1,5-COD), which were obtained as red solids and showed the ^{1}H NMR spectra diagnostic of this formulation. However, single crystals suitable for X-ray crystallography were not available for these clusters.

Since the dissociation of the coordinated alkene appears to be retarded by the removal of excess Cl anion, metatheses of the Cl anion in **3** by ClO_4^-, BF_4^-, and PF_6^- were carried out by using anion exchange column chromatography. Elemental analyses of the isolated latter two indicated the formation of $[PdMo_3S_4(tacn)_3Cl]X_3$ (**8**).[32] Although one Cl atom bound to Pd is still intact in **8**, these procedures prior to the reactions with alkene as well as CO and ^{t}BuNC facilitated the subsequent isolations of the product clusters to much extent (Scheme 2).

Thus, the reaction of **8a** (X = ClO_4) with the water-soluble alkene *cis*-$HOCH_2CH{=}CHCH_2OH$ readily afforded the adduct $[PdMo_3S_4(tacn)_3($*cis*-$HOCH_2CH{=}CHCH_2OH)]Cl(ClO_4)_3$ (**5a**) in high yield. On the other hand, a single crystal of $[PdMo_3S_4(tacn)_3($*cis*-$HOCH_2CH{=}CHCH_2OH)](ClO_4)_4$ (**5a′**·$2H_2O$) was obtained from the concentrated reaction mixture, in which the remaining Cl was further replaced by ClO_4. The X-ray structure analysis by using this crystal has clarified the η^2-coordination of this alkene to the Pd site in the cubane-type core.

Analogously, the reactions of **8a** or **8c** with CO proceeded smoothly and gave brown solutions almost spontaneously. In contrast to the reaction of **3** with CO, for which replacement of a CO atmosphere by N_2 or evacuation of atmospheric CO from the reaction mixture rapidly regenerates the original blue color of **3**, the product solutions obtained from **8** are moderately stable and can be handled under N_2 or air for some period. The CO clusters $[PdMo_3S_4(tacn)_3(CO)]ClX_3$ (**6a**, X = ClO_4; **6c**, X = PF_6) were isolated as crystals, and the X-ray crystal structure determination was successful for **6a**·$3H_2O$, demonstrating the presence of a terminal CO ligand coordinated to the Pd atom. Clusters **6a** and **6c** show the characteristic $\nu(C{\equiv}O)$ bands at 2085 and 2087 cm^{-1}, respectively. These values are significantly lower than those of terminal CO ligands in Pd(II) complexes, which commonly appear over 2100 cm^{-1} as in $(^nBu_4N)[Pd(CO)Cl_3]$ (2150 cm^{-1}),[33] *trans*-$[PdCl(CO)(PEt_3)_2](BF_4)$ (2130 cm^{-1}),[34] and $[CpPd(CO)(PPh_3)](ClO_4)$ (2113 cm^{-1}),[35] but still higher than the $\nu(C{\equiv}O)$ value in a Pd(0) complex $[Pd(CO)(PPh_3)_3]$ (1955 cm^{-1}).[36] This feature can be accounted for by the significant π-donating ability of the Pd site surrounded by three sulfide ligands, which results in the relatively firm Pd–C bond. It might be noted that the Pd(II) carbonyl complexes are generally unstable due to the high lability of the CO ligand and have rarely been isolated and fully characterized by the X-ray diffraction study.

The isocyanide adducts $[PdMo_3S_4(tacn)_3(^tBuNC)]ClX_3$ (**7a**, X = ClO_4; **7b**, X = BF_4) were also isolated from the reactions of **8a** or **8b** with ^{t}BuNC as dark red crystals. Although we could not disclose the detailed structure owing to the poor nature of these crystals, their IR spectra suggest the presence of the terminal ^{t}BuNC ligand; the $\nu(C{\equiv}N)$ values at 2191 and 2202 cm^{-1} for **8a** and **8b**, respectively, are somewhat higher than that of free ^{t}BuNC (2136 cm^{-1}), which is the common feature of the other Pd(II) isocyanide complexes having the linear Pd–C–N–R linkage.[37]

Syntheses of the cubane clusters, such as $[Fe_4S_4(LS_3)(L)]^{n-}$ (LS_3 = tridentate thiolate; L = CN^-, 3^{t}BuNC),[38] $[MoFe_3S_4(SR)_3(L')(L)]^{n-}$ (L′ = catecholates; L = CN^-, N_3^-, NH_3, N_2H_4, RCN, etc.),[39] $[\{MoFe_3S_4Cl_2(Cl_4cat)\}_2(\mu\text{-}S)(\mu\text{-}L)]^{n-}$ (L = CN^-, N_2H_4),[40] and $[\{MoFe_3S_4Cl_3(Cl_4cat)\}_2(\mu\text{-}N_2H_4)]$,[41] have been reported previously, in which a variety of ligands are bound to the unique metal site. More recently, the similar CO adduct $[NiMo_3S_4(H_2O)_9(CO)](OTs)_4$ was isolated and characterized by X-ray analysis.[42] However, coordination of alkenes to the cubane clusters has not yet been demonstrated, and it should be emphasized that **5a** is the first example of the cubane cluster containing the η^2-bound ligand.

X-ray Structures of 5a′ and 6a. The ORTEP drawing of the cation in **6a** is depicted in Figure 1, whereas that of **5a′** has been reported already.[19] Selected interatomic distances and bond angles within these cations are listed in Table 3. As expected, **5a′** and **6a** contain the single cubane-type core derived from the replacement of the Cl ligand on the tetrahedral Pd atom in **3** by a η^2-butenediol ligand and the terminal CO ligand, respectively. With respect to the $PdMo_3$ tetrahedron, significant elongation of the Pd–Mo distances occurs concurrent with the replacement of the Cl ligand with these π-acceptor ligands, while the Mo–Mo distances shorten slightly. Thus, the Pd–Mo distances at 2.847(2)–2.855(2) Å in **6a** with a strongly π-acidic CO ligand are much longer than those in **3** (2.790(2)–2.798(2) Å) and even than those in the alkene cluster **5a′** (2.815(3) and 2.830(2) Å). Analogous changes in the metal-metal distances are observed within the $NiMo_3S_4$ core; the mean Ni–Mo and Mo–Mo distances

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(32) Although **7a** could be analyzed without any trouble, the *explosive* nature was observed for **5a** during combustion analysis. Other clusters containing the ClO_4 anion, **6a** and **8a**, were therefore not analyzed.

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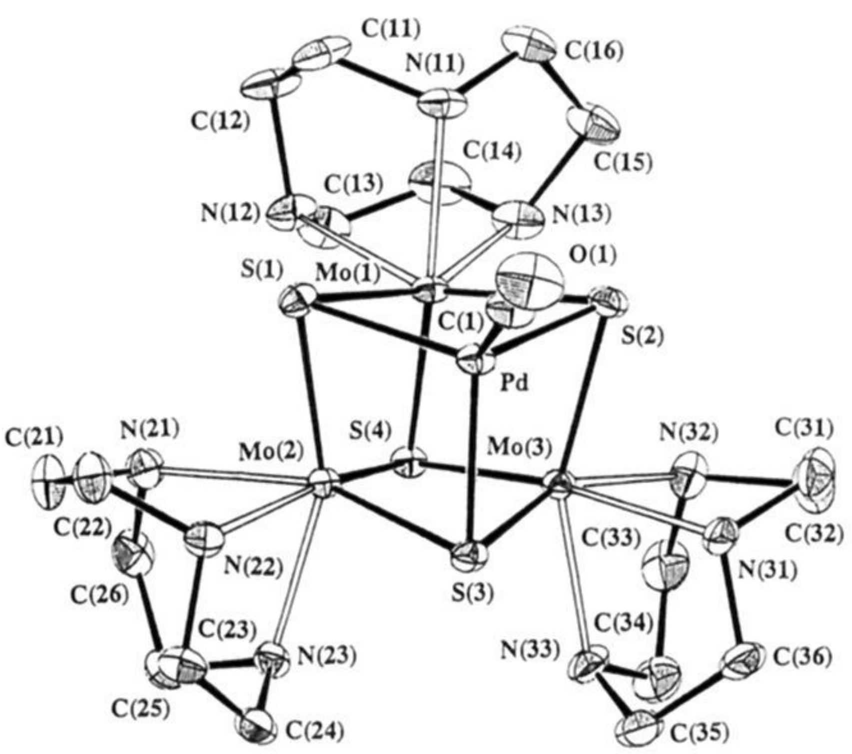
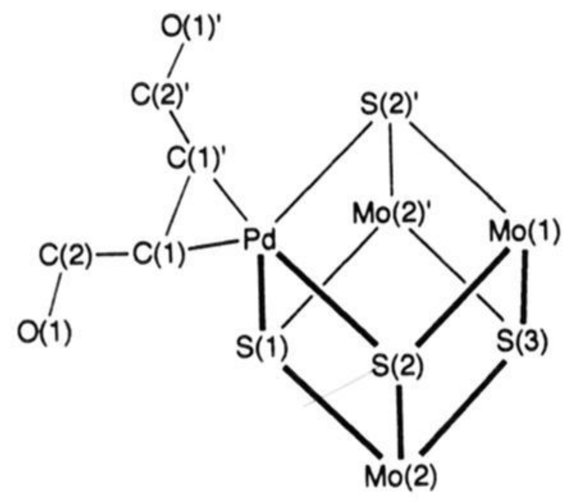


Figure 1. ORTEP drawing and atom-numbering scheme for the cation in **6a**·3H_2O.

in $[NiMo_3S_4(H_2O)_{10}]^{4+}$ at 2.64 and 2.76 Å[20c] turn to 2.68 and 2.74 Å, respectively, in $[NiMo_3S_4(H_2O)_9(CO)]^{4+}$[42] upon coordination of the CO molecule. Both the Pd–S and Mo–S distances in **5a′** and **6a** are not exceptional.



5a′

Cluster **5a′** has a crystallographically imposed mirror plane containing the Pd, Mo(1), S(1), S(3), and N(11) atoms, which bisects the C(1)–C(1)′ double bond in the butenediol ligand bound to the Pd atom. Appearance of the olefinic protons in the butenediol ligand as the single resonance in the ^1H NMR spectrum is consistent with the presence of this mirror plane. The C(1)–C(1)′ distance at 1.38(3) Å is slightly elongated from the typical C–C double bond (1.35 Å) and comparable to those in the other Pd(II) alkene complexes such as $[(L)PdCl_2]$ (L = 1,4- or 1,5-COD; 1.37–1.39 Å),[43] [(cyclooctatetraene)$PdCl_2$] (1.38(1), 1.39(1) Å),[44] and [(norbornadiene)$PdCl_2$] (1.37(1) Å).[45]

In **6a**, the CO ligand coordinates to the Pd atom with essentially linear Pd–C–O linkage (178(1)°). The short Pd–C bond length at 1.95(1) Å[31] suggests the substantial π-back-donation from the Pd center to the CO ligand, as expected from the low ν(C≡O) frequency in the IR spectrum. The C–O distance at 1.10(1) Å is not unusual for the CO ligands coordinated to transition metals and is in good agreement with that in $[NiMo_3S_4(H_2O)_9(CO)]^{4+}$ (1.10(2) Å),[20c] despite that the C–O distance in the range of bond order between 2 and 3 is not sensitive to the bond order,[46] and the C–O bond length observed in **6a** does not provide a criterion to estimate the π-donating ability of the Pd site.

Table 3. Selected Bond Distances and Angles in **5a′** and **6a**

	5a′		
	(a) Bond Distances (Å)		
Pd–S(1)	2.365(6)	Pd–S(2)	2.365(5)
Pd–C(1)	2.26(2)	Mo(1)–S(2)	2.335(5)
Mo(1)–S(3)	2.357(6)	Mo(2)–S(1)	2.323(5)
Mo(2)–S(2)	2.342(4)	Mo(2)–S(3)	2.356(5)
O(1)–C(2)	1.43(2)	C(1)–C(1)′	1.38(3)
C(1)–C(2)	1.50(3)		
Pd–Mo(1)	2.815(3)	Pd–Mo(2)	2.830(2)
Mo(1)–Mo(2)	2.805(2)	Mo(2)–Mo(2)′	2.787(2)
	(b) Bond Angles (deg)		
S(1)–Pd–S(2)	102.9(1)	S(1)–Pd–C(1)	108.2(5)
S(2)–Pd–S(2)′	103.6(2)	S(2)–Pd–C(1)	102.1(5)
S(2)–Pd–C(1)′	133.6(5)	S(2)–Mo(1)–S(2)′	105.5(2)
S(2)–Mo(1)–S(3)	104.2(1)	S(1)–Mo(2)–S(2)	104.9(2)
S(1)–Mo(2)–S(3)	104.7(1)	S(2)–Mo(2)–S(3)	104.1(2)
Pd–S(1)–Mo(2)	74.3(2)	Mo(2)–S(1)–Mo(2)′	73.7(2)
Pd–S(2)–Mo(1)	73.6(1)	Pd–S(2)–Mo(2)	73.9(1)
Mo(1)–S(2)–Mo(2)	73.7(1)	Mo(1)–S(3)–Mo(2)	73.1(2)
Mo(2)–S(3)–Mo(2)′	72.6(2)		
Pd–C(1)–C(2)	111.2(11)	Pd–C(1)–C(1)′	72.2(9)
C(2)–C(1)–C(1)′	124(2)	C(1)–C(2)–O(1)	110.4(15)
	6a		
	(a) Bond Distances (Å)		
Pd–S(1)	2.363(3)	Pd–S(2)	2.356(3)
Pd–S(3)	2.369(2)	Pd–C(1)	1.95(1)
Mo(1)–S(1)	2.329(3)	Mo(1)–S(2)	2.323(3)
Mo(1)–S(4)	2.358(2)	Mo(2)–S(1)	2.331(3)
Mo(2)–S(3)	2.328(3)	Mo(2)–S(4)	2.354(3)
Mo(3)–S(2)	2.330(3)	Mo(3)–S(3)	2.323(3)
Mo(3)–S(4)	2.362(3)	O(1)–C(1)	1.10(1)
Pd–Mo(1)	2.847(2)	Pd–Mo(2)	2.855(2)
Pd–Mo(3)	2.849(1)	Mo(1)–Mo(2)	2.802(1)
Mo(1)–Mo(3)	2.800(1)	Mo(2)–Mo(3)	2.799(1)
	(b) Bond Angles (deg)		
S(1)–Pd–S(2)	102.3(1)	S(1)–Pd–S(3)	102.2(1)
S(1)–Pd–C(1)	116.4(4)	S(2)–Pd–S(3)	102.3(1)
S(2)–Pd–C(1)	115.3(4)	S(3)–Pd–C(1)	116.2(3)
S(1)–Mo(1)–S(2)	104.4(1)	S(1)–Mo(1)–S(4)	104.2(1)
S(2)–Mo(1)–S(4)	104.6(1)	S(1)–Mo(2)–S(3)	104.5(1)
S(1)–Mo(2)–S(4)	104.3(1)	S(3)–Mo(2)–S(4)	104.4(1)
S(2)–Mo(3)–S(3)	104.5(1)	S(2)–Mo(3)–S(4)	104.2(1)
S(3)–Mo(3)–S(4)	104.3(1)		
Pd–S(1)–Mo(1)	74.7(1)	Pd–S(1)–Mo(2)	74.9(1)
Mo(1)–S(1)–Mo(2)	73.9(1)	Pd–S(2)–Mo(1)	75.0(1)
Pd–S(2)–Mo(3)	74.9(1)	Mo(1)–S(2)–Mo(3)	74.0(1)
Pd–S(3)–Mo(2)	74.9(1)	Pd–S(3)–Mo(3)	74.7(1)
Mo(2)–S(3)–Mo(3)	74.0(1)	Mo(1)–S(4)–Mo(2)	73.0(1)
Mo(1)–S(4)–Mo(3)	72.8(1)	Mo(2)–S(4)–Mo(3)	72.8(1)
Pd–C(1)–O(1)	178(1)		

Addition of Alcohols to Alkynic Acid Esters Catalyzed by $PdMo_3S_4$ Clusters. Reactivities of **2–4** as well as **8** with alkynes were also investigated under similar conditions. Rapid color change occurred in the reactions of these clusters with HC≡CCOOMe (**10**) and MeOCOC≡CCOOMe. The IR data of the products **9** obtained from **8** may imply the coordination of these alkynes to the Pd site (see the Experimental Section). However, any attempts to isolate and characterize the alkyne clusters in a well-defined manner were yet unsuccessful, since the products **9** readily regenerated **8** upon recrystallization.

Interestingly, the GLC study of the reaction mixtures obtained by treatment of **8** or **2** and these alkynes in MeOH has shown that the alkynes added are smoothly consumed under mild conditions. In contrast, alkynes such as 4-MeC_6H_4C≡CH and

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Scheme 3

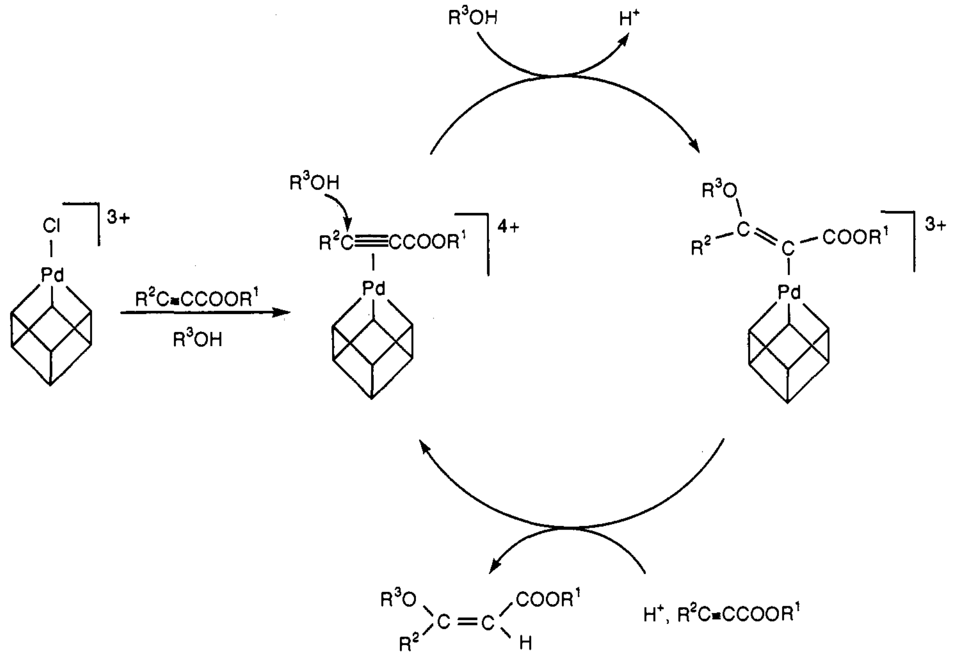

Table 4. Conversion of Alkynic Acid Esters $R^2C\equiv CCOOR^1$ into (*Z*)-$(MeO)R^2C{=}CHCOOR^1$ Catalyzed by the $PdMo_3$ Cluster **8c**[a]

R^1	R^2	temp (°C)	reaction time (h)	conversion (%)	yield (%)[b]
Me	H	40	6	100	82 (97)
Me	H	40	24	98	89 (95)[c]
Et	H	40	6	100	93 (97)
^{t}Bu	H	40	6	100	93
Ph	H	40	6	97	94
Me	COOMe	50	24	100	76
Me	Me	30	30	95	82
Et	Ph	40	21	93	89

[a] Reaction conditions: alkynic acid ester, 3.0 mmol; **8c**, 8.8 μmol (molar ratio **10**/**8c** = 340); MeOH, 2 mL. [b] Isolated yield. The GLC yields are in parentheses. The (*E*)-isomer and $(MeO)_2CR^2CH_2COOR^1$ are produced in 0–3% yields. [c] **10**, 14.7 mmol (molar ratio **10**/**8c** = 1680).

$PhC\equiv CH$ remained unreacted under similar conditions. Quantitative analysis of the reaction stoichiometry was undertaken for the system including **10** and **8c** (molar ratio of **10**/**8c**: 344), which disclosed that **10** was selectively converted into (*Z*)-$MeOCH{=}CHCOOMe$ (**11**) in 97% yield after the reaction for 6 h at 40 °C (conversion of **10**: 100%). Concomitant formation of small amounts of (*E*)-$MeOCH{=}CHCOOMe$ (0.8% yield) and $(MeO)_2CHCH_2COOMe$ (0.6% yield) was observed. The UV–vis spectra of the reaction mixture were invariable throughout this reaction period, and the spectrum recorded after addition of aqueous HCl to the final reaction mixture was in good agreement with that of **3**, which strongly suggests that this reaction is catalyzed by **8c** with retention of the cubane-type core structure. As consistent with this feature, the reaction using a larger amount of **10** (molar ratio of **10**/**8c**: 1680) proceeded with comparable catalytic efficiency and selectivity of the product; the conversion of **10** and the yield of **11** after 24 h reached 98 and 95%, respectively.

A series of propiolic acid esters, $HC\equiv CCOOR^1$ (R^1 = Et, ^{t}Bu, Ph), also reacted with MeOH in the presence of **8c** to give the corresponding trans addition products (*Z*)-$MeOCH{=}CHCOOR^1$ in high yields. These results are summarized in Table 4. High selectivity to the trans addition products is noteworthy; both the cis addition product (*E*)-$MeOCH{=}CHCOOR^1$ and the sole detectable byproduct $(MeO)_2CHCH_2COOR^1$ were produced in only negligible amounts, if any (<3% yield). Reactions of alkynic acid esters $R^2C\equiv CCOOR^1$ (R^1 = Me, R^2 = COOMe, Me; R^1 = Et, R^2 = Ph) were considerably slower, and a longer reaction time was required to complete the reactions (Table 4). However, increase of the reaction temperature resulted in a lower selectivity of the trans addition products because of the increase in the amount of the byproducts shown above. Reactions of EtOH or $PhCH_2OH$ with **10** were performed by adding acetone as a solvent because of the low solubility of **8c** in these alcohols. The trans addition products (*Z*)-$R^3OCH{=}CHCOOMe$ (R^3 = Et, $PhCH_2$) were selectively obtained, as in the reactions with MeOH.

Conversion of the alkynic acid esters into the MeOH adducts presumably proceeds at the unique Pd site in the $PdMo_3S_4$ core, which is supported by the fact that the reaction of **10** with MeOH does not take place in the presence of the Mo_3 cluster **1**. It is to be noted that the corresponding $PdMo_3$ aqua cluster **2** also catalyzes the formation of **11** from **10**, although the reaction is much slower than that using **8c** (20% conversion and 15% yield after 6 h at 40 °C). Catalytic activities of several Pd compounds for the present reaction have therefore been investigated for comparison. The alkyne **10** reacted with MeOH at 40 °C in the presence of $[PdCl_2(PhCN)_2]$, and the conversion of **10** after 6 h reached 49%. However, the yield of **11** was only 18%, and the major products were nonvolatile substances with high molecularity. Other Pd compounds such as $Na_2[PdCl_4]$, $Pd(OAc)_2$, $Pd(dba)_2$, and $[PdCl_2(PPh_3)_2]$ afforded **11** in lower yields than $[PdCl_2(PhCN)_2]$.

Reactions of Pd complexes with alkynes have already been studied in detail, most of which result in the formation of the alkyne complexes and the oligomerization of alkynes.[47] Formation of alkenyl ethers from the addition reactions of alcohols across the $C\equiv C$ bonds in alkynes is known to be catalyzed by certain inorganic and organic bases as well as by Cu(I) salts. However, the alkenyl ethers are mainly the cis addition product or a mixture of cis and trans addition products.[48] The addition of alcohols to alkynes catalyzed by Pd complexes has not yet been reported, except for the intramolecular cyclization of hydroxyl alkynes forming oxaheterocycles promoted in the presence of Pd(II)

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catalysts,[49] although alkoxypalladation reactions of coordinated alkynes to give (*E*)-(2-alkoxyvinyl)palladium complexes are known.

High selectivity of the trans addition of alcohols observed here is noteworthy. The reaction reported here presumably involves the initial coordination of the alkynic acid ester to the Pd site in the cluster and the successive nucleophilic attack of the alcohol at the electron-deficient carbon atom from the outer coordination sphere (Scheme 3). In a final step, protonolysis of the Pd–C bond may afford the trans addition product. Since the tetrahedral Pd site in **2** comprises three firmly bound sulfide ligands and can provide only a single vacant site, oligomerization of the alkyne may become unfavorable. Finally, it is to be noted that the reaction described here provides one of the rare examples in which catalytic reactions proceed with retention of the cluster structure of the catalysts.

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Supplementary Material Available: Crystallographic data for **6a**, including details of crystal data, intensity collection and structure refinement parameters, positional parameters and anisotropic temperature factors of non-hydrogen atoms, and interatomic distances and angles, and a figure showing all non-hydrogen atoms and the atom-numbering scheme for **6a** (9 pages); listings of structure factors (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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