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Synthesis of Cubane-Type Mo_3NiS_4 Clusters and Their Catalytic Activity for the Cyclization of Alkynoic Acids to Enol Lactones

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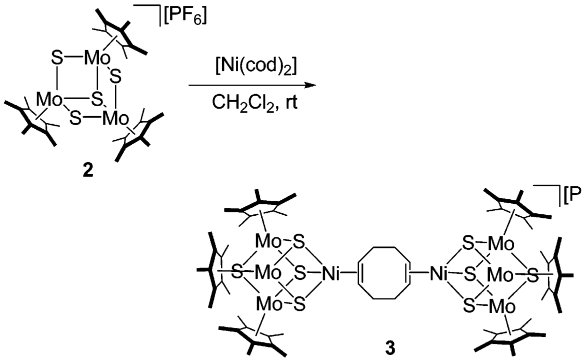
*Summary: Treatment of the cationic incomplete cubane-type sulfido complex [(Cp*Mo)$_3$(μ_2-S)$_3$(μ_3-S)][PF$_6$] (**2**; Cp* = η^5-C$_5$Me$_5$) with [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) afforded the heterobimetallic μ,η^2:η^2-cod double-cubane-type cluster [{(Cp*Mo)$_3$(μ_3-S)$_4$Ni}$_2$(μ,η^2:η^2-cod)][PF$_6$]$_2$ (**3**), which further reacted with dimethyl acetylenedicarboxylate (dmad) to produce [(Cp*Mo)$_3$(μ_3-S)$_4$Ni(η^2-dmad)][PF$_6$] (**4**). Cluster **3** or **4** showed high catalytic activity for the intramolecular cyclization of various alkynoic acids to give enol lactones in the presence of Et$_3$N.*

Transition-metal sulfido clusters with a cubane-type core have been attracting much attention with regard to metalloenzymes and industrial metal sulfido catalysts.[1,2] In the course of our extensive studies on multimetallic sulfur-bridged complexes ranging from dinuclear to hexanuclear cores,[2] we previously prepared cubane-type Mo$_3$M′S$_4$ clusters with M′ = Pd,[3] Pt[4] and demonstrated that the catalytic addition of alcohols and carboxylic acids to electron-deficient alkynes smoothly proceeds at the unique Pd center in the Mo$_3$PdS$_4$ cluster [{(tacn)Mo}$_3$PdCl(μ_3-S)$_4$][PF$_6$]$_3$ (**1**; tacn = 1,4,7-triazacyclononane), although conventional mononuclear Pd(II) complexes are not effective under similar conditions.[5] These provide rare examples of chemical transformations catalyzed by a synthetic cubane-type metal−sulfido cluster.[6] An attractive feature of this cluster is the presence of an electron-deficient tetrahedral Pd(II)-like site embedded in the Mo$_3$S$_4$ aggregate. Harris and co-workers claimed from theoretical calculations that the Mo$_3$ framework might be viewed as a tridentate π-acceptor to the Pd(0) atom.[7] Recently, we have synthesized a family of the heterobimetallic sulfido clusters with a cubane-type Mo$_3$M′S$_4$ core (M′ = Ni, Pd, Ru) by incorporating a metal fragment into the incomplete cubane-type cluster [(Cp*Mo)$_3$(μ_2-S)$_3$(μ_3-S)][PF$_6$] (**2**; Cp* = η^5-C$_5$Me$_5$).[8] By employing this method, we have now synthesized new cubane-type Mo$_3$NiS$_4$ clusters and found their novel catalytic activities for the cyclization of alkynoic acids to afford enol lactones.

When cluster **2** was treated with 1 equiv of [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) in CH$_2$Cl$_2$ at room temperature, the unprecedented cod-bridged double-cubane-type sulfido cluster [{(Cp*Mo)$_3$(μ_3-S)$_4$Ni}$_2$(μ,η^2:η^2-cod)][PF$_6$]$_2$ (**3**) was obtained in 75% yield as black crystals after recrystallization (eq 1).



(1)

The molecular structure of **3** has been confirmed by an X-ray diffraction study,[9] and an ORTEP drawing of the cationic part is given in Figure 1. The structure of the complex cation can be described as a centrosymmetric arrangement of two [(Cp*Mo)$_3$(μ_3-S)$_4$Ni]$^+$ moieties linked through a μ,η^2:η^2-cod ligand. As predicted

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(9) Crystallographic data for [{(Cp*Mo)$_3$(μ_3-S)$_4$Ni}$_2$(μ,η^2:η^2-cod)][PF$_6$]$_2$·2CH$_2$Cl$_2$ (**3**·2CH$_2$Cl$_2$): triclinic, $P\bar{1}$ (No. 2), a = 11.8482(6) Å, b = 12.1461(3) Å, c = 15.6670(6) Å, α = 75.997(7)°, β = 88.343(8)°, γ = 82.264(8)°, V = 2167.7(2) Å^3, Z = 2, D_{calcd} = 1.784 g cm^{-3}, μ = 16.78 cm^{-1}, R1 = 0.055 and wR2 = 0.145 for 9293 unique reflections (I > 3.00$\sigma(I)$), GOF = 1.054. All the structures were refined by least-squares methods against F^2.

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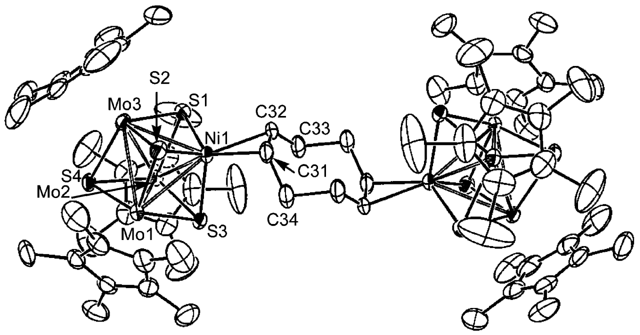
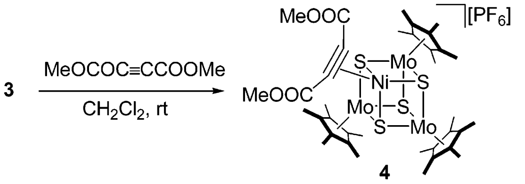


Figure 1. Structure of $[\{(Cp^*Mo)_3(\mu_3\text{-}S)_4Ni\}_2(\mu,\eta^2{:}\eta^2\text{-cod})][PF_6]_2\cdot 2CH_2Cl_2$ (**3**$\cdot 2CH_2Cl_2$) showing 40% thermal ellipsoids. Hydrogen atoms, solvating CH_2Cl_2, and PF_6 anions are omitted for clarity. Selected bond distances (Å): Ni(1)–Mo(1) = 2.7598(8), Ni(1)–Mo(2) = 2.7765(8), Ni(1)–Mo(3) = 2.7676(8), Ni(1)–S(1) = 2.2124(15), Ni(1)–S(2) = 2.2176(15), Ni(1)–S(3) = 2.2277(14), Ni(1)–C(31) = 2.145(5), Ni(1)–C(32) = 2.129(5), C(31)–C(32) = 1.361(9), Mo(1)–Mo(2) = 2.8370(6), Mo(2)–Mo(3) = 2.8340(6), Mo(3)–Mo(1) = 2.8552(6).

by the effective atomic number (EAN) rule, the 60-electron Mo_3NiS_4 cluster has three Mo–Ni bonds (2.7680(6) Å, average) and three Mo–Mo bonds (2.8420(6) Å, average), and the latter are slightly longer than those in cluster **2** (2.819(5) Å, average).[8] It should be noted that the two Mo_3NiS_4 cores are bridged by a labile μ-diene ligand through the Ni atoms.[10] Actually, the substitution of the cod ligand in cluster **3** by dimethyl acetylenedicarboxylate (dmad) took place smoothly to afford the single-cubane-type sulfido cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Ni(\eta^2\text{-dmad})][PF_6]$ (**4**) in 54% yield (eq 2).



(2)

The X-ray analysis of cluster **4** unequivocally shows the coordination of the alkyne to the tetrahedral Ni site in a side-on fashion (Figure 2).[11] The C–C (alkyne) bond distance (1.19(2) Å) is shorter than those in Ni(0) complexes (ca. 1.28 Å) with a η^2-dmad ligand such as $[Ni(PPh_3)_2(\eta^2\text{-dmad})]$ and $[Ni(dippe)(\eta^2\text{-dmad})]$ (dippe = bis(diisopropylphosphino)ethane),[12] while the Ni–C(alkyne) bond distances (1.96(1) and 2.00(1) Å) are much longer than those (1.85–1.89 Å) in the Ni(0) complexes. These findings imply that the dmad ligand in cluster **4** is weakly bound to the Ni site via mainly σ-donation of the π-electrons. This is compatible with the electron-deficient character of the Ni atom in cluster **4**, which is probably caused by the π-acceptor character of the Mo_3 framework toward the Ni(0) atom, as suggested in the case of the Mo_3PdS_4 cluster **1** (vide supra).

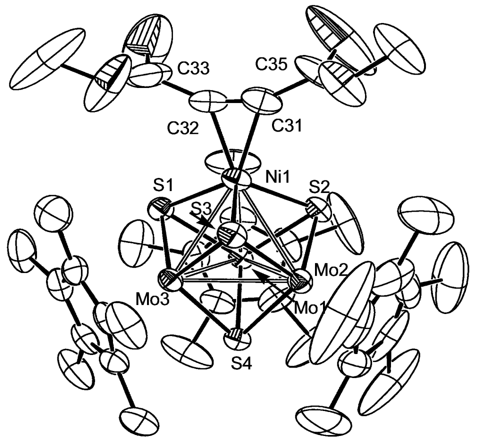
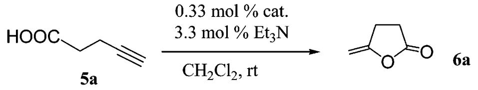


Figure 2. Structure of $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Ni(\eta^2\text{-dmad})][PF_6]$ (**4**$\cdot$0.5THF) showing 30% thermal ellipsoids. Hydrogen atoms, solvating THF, and PF_6 anion are omitted for clarity. Selected bond distances (Å): Ni(1)–Mo(1) = 2.787(1), Ni(1)–Mo(2) = 2.818(1), Ni(1)–Mo(3) = 2.809(1), Ni(1)–S(1) = 2.223(2), Ni(1)–S(2) = 2.229(3), Ni(1)–S(3) = 2.301(2), Ni(1)–C(31) = 2.00(1), Ni(1)–C(32) = 1.96(1), C(31)–C(32) = 1.19(2), Mo(1)–Mo(2) = 2.8441(9), Mo(2)–Mo(3) = 2.821(1), Mo(3)–Mo(1) = 2.8527(9).

Table 1. Catalytic Intramolecular Cyclization of 4-Pentynoic Acid (5a)[a]



run	catalyst	time (h)	conversn (%)[d]	yield (%)[d]
1	$[\{(Cp^*Mo)_3(\mu_3\text{-}S)_4Ni\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-cod})][PF_6]_2$ (**3**)	1	96	96
2	$[(Cp^*Mo)_3(\mu_2\text{-}S)_3(\mu_3\text{-}S)][PF_6]$ (**2**) + $[Ni(cod)_2]$	2	97	97
3	$[(Cp^*Mo)_3(\mu_3\text{-}S)_4Ni(\eta^2\text{-dmad})][PF_6)$ (**4**)	3	95	95
4	$[Ni(cod)_2]$	5	<1	<1
5	$[(Cp^*Mo)_3(\mu_2\text{-}S)_3(\mu_3\text{-}S)][PF_6]$ (**2**)	5	<1	<1
6	$[NiCl_2]$	5	<1	<1
7	$[NiCl_2(CH_3CN)_2]$	5	<1	<1
8	$[NiCl_2(PPh_3)_2]$	5	<1	<1
9	$[\{(Cp^*Mo)_3(\mu_3\text{-}S)_4Ni(PPh_3)][PF_6]$	12	10	10
10[b]	$[PdCl_2(PhCN)_2]$	5	63	63
11[b,c]	$[\{(tacn)Mo\}_3PdCl(\mu_3\text{-}S)_4][PF_6]_3$ (**1**)	0.1	>99	>99

[a] All of the reactions of 4-pentynoic acid (1.50 mmol) with catalyst (0.0050 mmol as Ni atom) were carried out in the presence of Et_3N (0.050 mmol) in CH_2Cl_2 (3.0 mL) at room temperature. [b] With catalyst (0.010 mmol as Pd atom). [c] In CH_3CN (3.0 mL) at room temperature.[5b] [d] Determined by GLC.

Cluster **3** showed high catalytic activity for the intramolecular cyclization of various alkynoic acids to afford enol lactones in the presence of Et_3N (Table 1). Treatment of 4-pentynoic acid (**5a**; 1.50 mmol) in CH_2Cl_2 in the presence of **3** (0.0025 mmol) and Et_3N (0.050 mmol) at room temperature for 1 h afforded the corresponding enol lactone **6a** in almost quantitative yield (96% GLC). It should be noted that the reaction proceeds smoothly by using a catalyst formed in situ by mixing cluster **2** and $[Ni(cod)_2]$ in CH_2Cl_2. Cluster **4** can also promote the intramolecular cyclization with almost the same catalytic activity as cluster **3**. However, the reaction did not proceed by employing cluster **2** or $[Ni(cod)_2]$ alone. It is worth noting that conventional

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(10) Double-cubane-type clusters with two $[(Cp'Mo)_3(\mu_3\text{-}S)_4Ni]^+$ (Cp′ = $\eta^5\text{-}C_5MeH_4$) fragments bridged by bis(monodentate) sulfur or nitrogen σ-donor ligands, 1,4-dithiane or 4,4′-bipyridine, have been reported: Herbst, K.; Monari, M.; Brorson, M. *Inorg. Chem.* **2002**, *41*, 1336.

(11) Crystallographic data for $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Ni(\eta^2\text{-dmad})][PF_6]\cdot$0.5THF (**4**$\cdot$0.5THF): monoclinic, $P2_1/c$ (No. 14), a = 16.495(5) Å, b = 13.686(4) Å, c = 20.822(6) Å, β = 96.308(4)°, V = 4672.1(24) Å^3, Z = 4, D_{calcd} = 1.711 g cm^{-3}, μ = 14.57 cm^{-1}, R1 = 0.064 and wR2 = 0.172 for 6031 unique reflections ($I > 3.00\sigma(I)$), GOF = 1.08.

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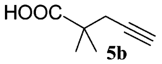
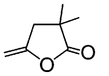
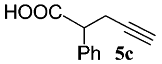
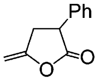
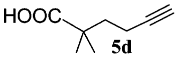
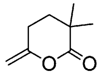
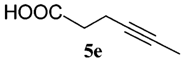
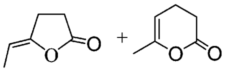
Table 2. Catalytic Intramolecular Cyclization of Various Alkynoic Acids (5b−e)[a]

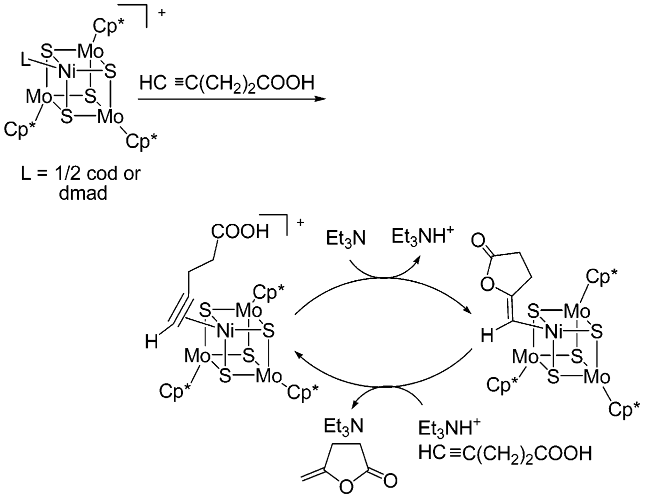
run	alkynoic acid	time (h)	conv. (%)[b]	yield (%)[b]	product
1	 **5b**	0.5	98	98	 **6b**
2	 **5c**	1	>99[c]	>99[c]	 **6c**
3	 **5d**	2.5	>99	>99	 **6d**
4	 **5e**	8	>99	>99	 **6e** 73 : 27[c] **6e′**

[a] All of the reactions of alkynoic acid (1.50 mmol) with **3** (0.0025 mmol) were carried out in the presence of Et_3N (0.050 mmol) in CH_2Cl_2 (3.0 mL) at room temperature. [b] Determined by GLC. [c] Determined by ^1H NMR.

mononuclear Ni(II) complexes such as [$NiCl_2$], [$NiCl_2(CH_3CN)_2$], and [$NiCl_2(PPh_3)_2$] did not work at all for this reaction. On the other hand, the cubane-type cluster [$(Cp^*Mo)_3(\mu_3\text{-}S)_4Ni(PPh_3)$][$PF_6$] prepared previously[8] exhibited low catalytic activity, which is probably due to some difficulty in the substitution of substrate **5a** for the PPh_3 ligand. Interestingly, the catalytic activity of cluster **3** is remarkably higher than that of [$PdCl_2(PhCN)_2$],[13] although the Mo_3PdS_4 cluster **1** is superior to the Mo_3NiS_4 cluster **3** for this cyclization reaction.[5b]

The results of the catalytic cyclization of various alkynoic acids by employing **3** as catalyst are summarized in Table 2. Employment of 4-pentynoic acids such as **5b** and **5c** gave the corresponding γ-lactones, while the reaction of 5-hexynoic acid (**5d**) produced the δ-lactone. When 4-hexynoic acid (**5e**) was employed, a mixture of γ- and δ-lactones (**6e**:**6e′** = 73:27) was obtained, the ratio being slightly different from that (**6e**:**6e′** = 86:14) of the reaction with the Mo_3PdS_4 cluster **1**.[5b]

Scheme 1



The UV/vis spectrum of a CH_2Cl_2 solution of cluster **3** showed two bands at λ_{max} 557 nm ($\epsilon = 2600\ M^{-1}\ cm^{-1}$) and 677 nm ($\epsilon$ = 1750), while that of cluster **4** also exhibited similar bands at 563 nm (sh; ϵ = 860) and 703 nm (ϵ = 980). When cluster **3** or **4** was employed as the catalyst for the cyclization of alkynoic acids, analogous bands at λ_{max} 570 and 708 nm were observed in the UV/vis spectrum of the reaction solution during the reaction. These observations support that the Mo_3NiS_4 cubane-type core is retained throughout the catalysis. A plausible catalytic cycle for the cyclization of **5a** is shown in Scheme 1. The initial coordination of the alkyne occurs at the Ni site of the cubane-type core, and the subsequent intramolecular nucleophilic attack of the carboxylate anion on the C≡C bond leads to the formation of a vinylnickel intermediate. The Ni−C bond of the vinylnickel species is finally cleaved by protonolysis to give the enol lactone product. This mechanism is essentially the same as that proposed for the intramolecular lactonization of alkynoic acids catalyzed by the Mo_3PdS_4 cluster **1**.[5b]

In summary, we have prepared new cubane-type Mo_3NiS_4 clusters and demonstrated their novel catalytic activities for the cyclization of alkynoic acids to afford enol lactones. To the best of our knowledge, there are few known catalytic reactions where alkenes or alkynes coordinated to nickel undergo nucleophilic attack from the outer coordination sphere.[14]

Acknowledgment. This work was supported by the JSPS FS2001 “Research for the Future Program”.

Supporting Information Available: Text giving full experimental details and tables of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **3**·$2CH_2Cl_2$ and **4**·0.5THF. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP: The footnotes in Table 2 were improperly designated in the version posted on October 14, 2003. The correct version was posted on October 15, 2003.

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(14) Recently, catalytic hydroamination by nickel complexes has been reported. (a) For alkynes (intramolecular): Müller, T. E.; Pleier, A.-K. *J. Chem. Soc., Dalton Trans.* **1999**, 583. (b) For activated olefins: Fadini, L.; Togni, A. *Chem. Commun.* **2003**, 30.