Intramolecular Cyclization of Aminoalkynes Catalyzed by $PdMo_3S_4$ Cubane Clusters

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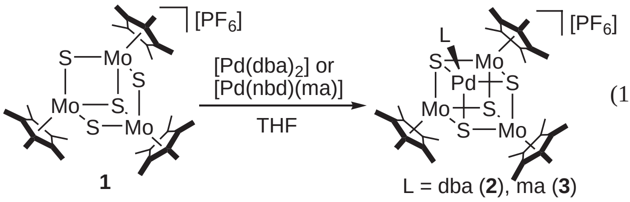
$PdMo_3S_4$ cubane clusters $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd(L)][PF_6]$ ($Cp^* = \eta^5\text{-}C_5Me_5$; L = dba (**2**), ma (**3**); dba = dibenzylideneacetone, ma = maleic anhydride) showed high catalytic activity for the intramolecular hydroamination of aminoalkynes to afford the corresponding cyclic imines in good yields under mild conditions. A molecular structure of **3** has been determined by X-ray diffraction study.

Although the chemistry of transition-metal sulfide clusters with the M_4S_4 cubane core has been receiving much attention in relevance to the active sites of metalloproteins such as ferredoxins and nitrogenases as well as industrial hydrodesulfurization catalysts,[1] catalytic activities of such cubane clusters are still left undeveloped.[2] In the course of our extensive studies on multimetallic sulfur-bridged complexes, we have developed several rational synthetic routes to various cubane clusters with a desired metal composition, some of which show intriguing reactivities toward small molecules.[3] Thus, MMo_3S_4 (M = Pd, Ni) cubane clusters exhibit remarkable catalytic activity for some reactions of alkynes, including intramolecular cyclization of alkynoic acids to afford enol lactones.[4] Further, $M_2Mo_2S_4$ (M = Rh, Ir)[5a] and $RuMo_3S_4$[5b] cubane clusters are effective for the catalytic N–N bond cleavage of hydrazines. As an extension of these studies, we report here the intramolecular hydroamination of aminoalkynes catalyzed by $PdMo_3S_4$ cubane clusters.

Previously, we reported that the incomplete cubane-type cluster $[(Cp^*Mo)_3(\mu_2\text{-}S)_3(\mu_3\text{-}S)][PF_6]$ (**1**) serves as a versatile precursor for synthesis of heterobimetallic MMo_3S_4 (M = Ru, Ni, Pd) cubane clusters.[4d,6] Thus, the $PdMo_3S_4$ cluster bearing an alkene ligand dba on the palladium center, $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd(dba)][PF_6]$ (**2**), is readily available from the reaction of **1** and $[Pd(dba)_2]$ in 48% yield. In a similar manner, cluster **1** reacted with the Pd(0) η^2-alkene complex, [Pd(nbd)(ma)][7] (nbd = 2,5-norbornadiene), to afford the $PdMo_3S_4$ cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd(ma)][PF_6]$ (**3**) as dark brown crystals in 70% yield (Eq 1).



(1)

1

L = dba (**2**), ma (**3**)

The X-ray analysis of cluster **3** unambiguously shows the coordination of ma to the tetrahedral Pd site in a side-on fashion (Figure 1).[8] The C=C bond distance of the bound ma in cluster **3** (1.36(3) Å) is shorter than that in the Pd(0) alkene complex $[Pd(py)_2(ma)]$ (1.430(3) Å; py = pyridine),[7] however, almost comparable to or slightly shorter than those in Pd(II) alkene complexes such as $[PdCl_2(L)]$ (L = 1,4- or 1,5-cyclooctadiene; 1.37–1.39 Å)[9] and [PdClMe(L)(ma)] (1.410(7) Å; L = 2,9-dimethyl-1,10-phenanthroline).[10] This indicates that the palladium atom in cluster **2** or **3** behaves as an unique tetrahedral Pd(II)-like center. The Pd–Mo distances at 2.894(2)–2.949(2) Å as well as the Mo–Mo distances at 2.826(2)–2.848(2) Å are diagnostic of metal–metal bonds between these atoms, and the latter are slightly longer than those in cluster **1** (2.819(5) Å, average).[6] The core structure with six metal–metal bonds for **3** is consistent with its total electron count of 60 e^-.

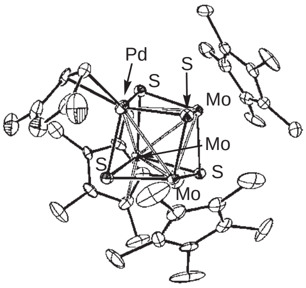
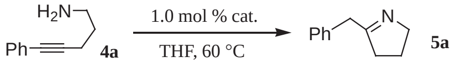


Figure 1. ORTEP drawing of the cationic part of cluster **3**.

Cluster **2** or **3** showed high catalytic activity for the intramolecular cyclization of aminoalkynes to afford cyclic imines (Table 1). Treatment of 5-phenyl-4-pentyn-1-amine (**4a**; 1.0 mmol) in THF in the presence of cluster **2** (0.010 mmol) at 60 °C for 0.5 h afforded the corresponding cyclic imine, 2-benzyl-1-pyrroline (**5a**) in almost quantitative yield (98% GLC). Cluster **3** can also promote the intramolecular cyclization with almost the same catalytic activity as cluster **2**. On the other hand, the $PdMo_3S_4$ cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd(PPh_3)][PF_6]$ prepared previously[6] exhibited low catalytic activity, which is probably owing to some difficulty in the substitution of substrate **4a** for the PPh_3 ligand. The cyclization did not proceed by using cluster **1**, $[Pd(dba)_2]$, or [Pd(nbd)(ma)].

Recently, the catalytic hydroamination of alkynes based on early transition metals,[11] especially lanthanide metals,[12] has been extensively reported. In contrast, the hydroamination reactions using late transition metals have been relatively limited.[13,14] Mononuclear Pd(II) complexes such as $[PdCl_2]$,[14a] $[Pd(CH_3CN)_4][BF_4]_2$,[14b,14c] and $[Pd(triphos)][BF_4]_2$ (triphos = bis(diphenylphosphinoethyl)phenylphosphine)[14b,14c] are known to be effective for the intramolecular cyclization of aminoalkynes. Müller et al. reported that the intramolecular cyclization of **4a** by using $[Pd(CH_3CN)_4][BF_4]_2$ as catalyst at 90 °C for 2 h in THF gives imine **5a** in 48% yield (substrate/catalyst = 40).[14c] When these Pd(II) complexes were actually used as catalyst for the reaction of **4a** under the reaction conditions described in Table 1, the yield of **5a** was quite low. This indicates that the cat-

Table 1. Catalytic activity of several palladium complexes and clusters for intramolecular cyclization of **4a** to **5a**[a]



4a **5a**

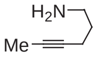
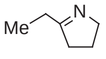
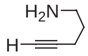
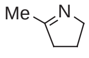
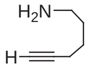
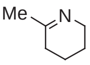
Run	Catalyst	Time/h	Conv./%[b]	Yield/%[b]
1	$[(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd(dba)][PF_6]$ (**2**)	0.5	98	98 (85)[c]
2	$[(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd(ma)][PF_6]$ (**3**)	1	96	95 (84)[c]
3	$[(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd(PPh_3)][PF_6]$	20	15	6
4	$[(Cp^*Mo)_3(\mu_2\text{-}S)_3(\mu_3\text{-}S)][PF_6]$ (**1**)	20	<1	<1
5	$[Pd(dba)_2]$	20	<1	<1
6	[Pd(nbd)(ma)]	20	<1	<1
7	$[PdCl_2]$	20	5	<1
8	$[Pd(CH_3CN)_4][BF_4]_2$	20	15	14
9	$[Pd(triphos)][BF_4]_2$	20	10	8

[a] All of the reactions of **4a** (1.0 mmol) with catalyst (0.010 mmol) were carried out in THF (8.0 mL) at 60 °C. [b] Determined by GLC. [c] Isolated yield.

alytic activity of cubane clusters **2** and **3**, which contain an unique Pd(II)-like center embedded in the Mo_3S_4 aggregate, is higher than that of conventional Pd(II) complexes.

Table 2 shows the results of the catalytic intramolecular cyclization of various aminoalkynes by using cluster **2**. Employment of an internal alkyne **4b** gave the corresponding cyclic imine **5b** in high yield after 3 h, while the reaction of a terminal alkyne **4c** proceeded relatively smoothly and **5c** was obtained in high yield after 0.1 h. When 6-aminohex-1-yne (**4d**) was employed, a six-membered cyclic imine, 2-methyl-1,2-dehydropiperidine (**5d**) was obtained.

Table 2. Intramolecular cyclization of several aminoalkynes catalyzed by **2**[a]

Run	Aminoalkyne		Time/h	Conv./%[b]	Yield/%[b]	Product	
1		**4b**	3	>98	96		**5b**
2		**4c**	0.1	>98	95		**5c**
3		**4d**	4	>98	96		**5d**

[a] All of the reactions of aminoalkynes (1.0 mmol) with **2** (0.010 mmol) were carried out in THF (8.0 mL) at 60 °C. [b] Determined by GLC.

To gain insight into the active species, the UV–vis spectra of the reaction solutions were measured. The UV–vis spectrum of a THF solution of cluster **2** showed two bands at λ_{max} 482 nm ($\varepsilon = 5600\,M^{-1}\,cm^{-1}$) and 608 nm (sh, $\varepsilon = 3250$), while that of cluster **3** also exhibited similar bands at 476 nm ($\varepsilon = 4050$) and 602 nm (sh; $\varepsilon = 750$). When cluster **2** or **3** was employed as catalyst for the hydroamination of aminoalkynes, analogous bands at λ_{max} 490 and 615 nm were observed in the UV–vis spectrum of the reaction solution during the reaction. These findings suggest that the $PdMo_3S_4$ cubane core is maintained throughout the catalytic reaction. On the basis of our previous investigations on the reactivities of $PdMo_3S_4$ cubane clusters toward alkynes,[4a–4c] the most plausible mechanism for this hydroamination reaction is considered as follows. The coordination of an aminoalkyne via the C≡C bond initially occurs at the unique Pd(II)-like atom in the cubane core, and the subsequent intramolecular nucleophilic attack of the amino group on the activated C≡C bond results in the formation of a cyclic imine.

In summary, we have found that $PdMo_3S_4$ cubane clusters containing an unique Pd(II)-like center show high catalytic activity for the intramolecular cyclization of aminoalkynes to afford cyclic imines. Studies aiming at optimization of the transformation and elucidation of the reaction mechanism are now in progress.

References and Notes

1 a) *Transition Metal Sulfur Chemistry*, ed. by E. I. Stiefel, K. Matsumoto, American Chemical Society, Washington, DC, **1996**. b) R. Hernandez-Molina, M. N. Sokolov, A. G. Sykes, *Acc. Chem. Res.* **2001**, *34*, 223. c) P. Venkateswara Rao, R. H. Holm, *Chem. Rev.* **2004**, *104*, 527.

2 *Catalysis by Di- and Polynuclear Metal Cluster Complexes*, ed. by R. D. Adams, F. A. Cotton, Wiley, VCH, New York, **1996**.

3 a) M. Hidai, S. Kuwata, Y. Mizobe, *Acc. Chem. Res.* **2000**, *33*, 46. b) M. Hidai, Y. Ishii, S. Kuwata, in *Modern Coordination Chemistry*, ed. by G. J. Leigh, N. Winterton, Royal Society of Chemistry, Cambridge, **2002**, p. 208. c) M. Hidai, in *Perspectives in Organometallic Chemistry*, ed. by C. G. Screttas, B. R. Steele, Royal Society of Chemistry, Cambridge, **2003**, p. 62. d) M. Hidai, Y. Mizobe, *Can. J. Chem.* **2005**, *83*, 358.

4 a) T. Murata, Y. Mizobe, H. Gao, Y. Ishii, T. Wakabayashi, F. Nakano, T. Tanase, S. Yano, M. Hidai, I. Echizen, H. Nanikawa, S. Motomura, *J. Am. Chem. Soc.* **1994**, *116*, 3389. b) T. Wakabayashi, Y. Ishii, T. Murata, Y. Mizobe, M. Hidai, *Tetrahedron Lett.* **1995**, *36*, 5585. c) T. Wakabayashi, Y. Ishii, K. Ishikawa, M. Hidai, *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2123. d) I. Takei, Y. Wakebe, K. Suzuki, Y. Enta, T. Suzuki, Y. Mizobe, M. Hidai, *Organometallics* **2003**, *22*, 4639.

5 a) H. Seino, T. Masumori, M. Hidai, Y. Mizobe, *Organometallics* **2003**, *22*, 3424. b) I. Takei, K. Dohki, K. Kobayashi, T. Suzuki, M. Hidai, *Inorg. Chem.* **2005**, *44*, 3768.

6 I. Takei, K. Suzuki, Y. Enta, K. Dohki, T. Suzuki, Y. Mizobe, M. Hidai, *Organometallics* **2003**, *22*, 1790.

7 A. M. Kluwer, C. J. Elsevier, M. Bühl, M. Lutz, A. L. Spek, *Angew. Chem., Int. Ed.* **2003**, *42*, 3501.

8 A synthetic procedure and crystallographic data for cluster **3** are described in the Supporting Information.

9 a) L. Benchekroun, P. Herpin, M. Julia, L. Saussine, *J. Organomet. Chem.* **1977**, *128*, 275. b) M. F. Rettig, R. M. Wing, G. R. Wiger, *J. Am. Chem. Soc.* **1981**, *103*, 2980.

10 V. G. Albano, C. Castellari, M. E. Cucciolito, A. Panunzi, A. Vitagliano, *Organometallics* **1990**, *9*, 1269.

11 a) A. M. Baranger, P. J. Walsh, R. G. Bergman, *J. Am. Chem. Soc.* **1993**, *115*, 2753. b) F. Pohlki, I. Bytschkov, H. Siebeneicher, A. Heutling, W. A. König, S. Doye, *Eur. J. Org. Chem.* **2004**, *2004*, 1967.

12 a) Y. Li, T. J. Marks, *J. Am. Chem. Soc.* **1996**, *118*, 9295. b) A. Zulys, T. K. Panda, M. T. Gamer, P. W. Roesky, *Chem. Commun.* **2004**, 2584. c) S. Hong, T. J. Marks, *Acc. Chem. Res.* **2004**, *37*, 673.

13 a) T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675. b) M. Tokunaga, M. Eckert, T. Wakatsuki, *Angew. Chem., Int. Ed.* **1999**, *38*, 3222. c) T. Kondo, T. Okada, T. Suzuki, T. Mitsudo, *J. Organomet. Chem.* **2001**, *622*, 149. d) S. Burling, L. D. Field, B. A. Messerle, P. Turner, *Organometallics* **2004**, *23*, 1714. e) C. G. Hartung, A. Tillack, H. Trauthwein, M. Beller, *J. Org. Chem.* **2001**, *66*, 6339.

14 a) Y. Fukuda, S. Matsubara, K. Utimoto, *J. Org. Chem.* **1991**, *56*, 5812. b) T. E. Müller, A.-K. Pleier, *J. Chem. Soc., Dalton Trans.* **1999**, 583. c) T. E. Müller, M. Grosche, E. Herdtweck, A.-K. Pleier, E. Walter, Y.-K. Yan, *Organometallics* **2000**, *19*, 170.