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Stereoselective Addition of Carboxylic Acids to Electron Deficient Acetylenes Catalyzed by the $PdMo_3S_4$ Cubane-Type Cluster

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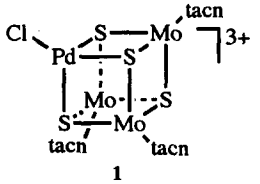
Abstract: The mixed-metal sulfide cubane-type cluster complex $[PdMo_3S_4(tacn)_3Cl][PF_6]_3$ (**1**; tacn = 1,4,7-triazacyclononane) was found to be a highly efficient and selective catalyst for the addition of carboxylic acids to acetylenes with electron-withdrawing groups. The corresponding trans addition products were exclusively obtained in good yields under mild reaction conditions in the presence of a catalytic amount of triethylamine.

Although the coordination chemistry of transition metal sulfide clusters with a cuboidal M_4S_4 core has been attracting intensive interest in recent years, catalytic activities of such clusters are still left undeveloped.[1] Recently we have prepared and characterized a novel cuboidal cluster $[PdMo_3S_4(tacn)_3Cl][PF_6]_3$ (**1**; tacn = 1,4,7-triazacyclononane), and revealed that cluster **1** is an active and highly selective catalyst for the addition of alcohols to alkynic acid esters.[2] Now we have found that cluster **1** also catalyzes the stereoselective addition of carboxylic acids to both terminal and internal acetylenes with electron-withdrawing groups.



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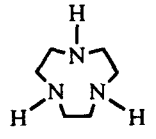
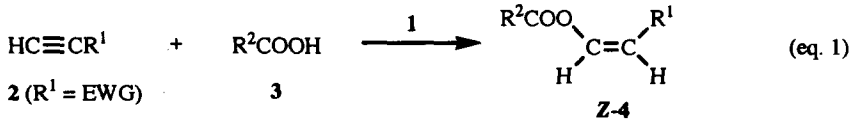
tacn =



Addition of carboxylic acids to acetylenes is a potential synthetic method for vinyl esters which is a versatile intermediate in organic synthesis.[3] Palladium,[4] ruthenium,[5] rhodium[6] and silver[7] compounds have so far been reported to catalyze such reactions, nevertheless examples of stereoselective intermolecular additions have still been limited. $Pd(OAc)_2$ was used as a catalyst for the stereoselective addition of acetic acid to 2-alkynic acid derivatives to give *Z*-vinyl esters,[4a] but this reaction is only applicable to internal acetylenes and addition to unsubstituted propiolates was claimed to be unsuccessful. Dixneuf et al. reported that ruthenium complexes $[Ru(p\text{-cymene})(PR_3)Cl_2]$ (R = Me, Ph)[5a] and $[Ru\{\eta^3\text{-}CH_2C(Me)=CH_2\}_2\{Ph_2P(CH_2)_4PPh_2\}]$[5b]



(eq. 1)

catalyze the selective addition of carboxylic acids to terminal acetylenes. However, these complexes failed to promote the addition of acetic acid to methyl propiolate (vide infra). To the best of our knowledge, there has been reported no effective catalyst for the reaction of carboxylic acids to terminal electron deficient acetylenes such as propiolic acid derivatives to give the corresponding Z-vinyl esters (eq.1).

When an acetonitrile solution (2 ml) of methyl propiolate (**2a**, 3 mmol), acetic acid (**3a**, 9 mmol), NEt_3 (0.15 mmol), and cluster **1** (9 μmol) was allowed to react at 40 °C for 8 h, 90% of the methyl propiolate was consumed and methyl 3-acetoxy-2-propenoate (**4a**, Z/E = 98 / 2) was formed in 65% yield (GLC). **4a** was isolated in 62% yield based on the starting **2a** after purification by column chromatography and bulb-to-bulb distillation. A similar reaction took place in the absence of NEt_3, but required much longer reaction time (97% conv., 66% isolated yield, Z/E = 98 / 2 after 72 h). On the other hand, prolonged reaction time in the presence of NEt_3 resulted in the isomerization of ***Z*-4a** to ***E*-4a**. Dilution of the reaction mixture with aqueous 1 N HCl followed by repeated washing with CH_2Cl_2 gave a blue solution, which exhibited characteristic absorptions of the cluster **1** in the UV-Vis spectrum. This indicated that the $PdMo_3S_4(tacn)_3$ cubane-type core was retained during the catalytic reaction.

Table 1 clearly shows the effectiveness of cluster **1** as the catalyst for the addition of **3a** to **2a**. With cluster **1**, turnover number as high as 2500 was achieved in 18 h without loss of the stereoselectivity. In contrast, the cuboidal aqua cluster $[PdMo_3S_4(H_2O)_9Cl]Cl_3$, mononuclear palladium, ruthenium and rhodium complexes, and silver salt failed to catalyze the reaction. It should be pointed out that [Ru(*p*-cymene) $(PR_3)Cl_2$] (R = Me, Ph)[5a] and $[Ru\{\eta^3\text{-}CH_2C(Me)=CH_2\}_2\{Ph_2P(CH_2)_4PPh_2\}]$[5b] were ineffective either under the reaction conditions described above or under those reported by Dixneuf.

Catalytic addition of various carboxylic acids **3a-3h** to **2a** by cluster **1** gave the corresponding Z-vinyl esters ***Z*-4a-4h** stereoselectively (Z/E > 94 / 6) in good yields (Table 2). In all cases, high stereoselectivities

Table 1. Catalytic Addition of **3a** to **2a**.[a]

Catalyst	Conversion (%)[b]	Yield of ***Z*-4a** (%)[b]
$[PdMo_3S_4(tacn)_3Cl][PF_6]_3$	90	65
$[PdMo_3S_4(tacn)_3Cl][PF_6]_3$[c]	98	89
$[PdMo_3S_4(H_2O)_9Cl]Cl_3$	0	0
$Pd(OAc)_2$	15	0
$PdCl_2(PhCN)_2$	22	0
$PdCl_2(PPh_3)_2$	41	0
$Pd(PPh_3)_4$	42	0
[Ru(*p*-cymene)$(PPh_3)Cl_2$]	4	0
[Ru(*p*-cymene)$(PMe_3)Cl_2$]	0	0
$[Ru\{\eta^3\text{-}CH_2C(Me)=CH_2\}_2\{Ph_2P(CH_2)_4PPh_2\}]$	3	0
$RhCl(PPh_3)_3$	0	0
Ag_2CO_3	9	6

[a]Reaction conditions: Catalyst (9 μmol), **2a** (3 mmol), **3a** (9 mmol), NEt_3 (0.15 mmol), MeCN (2 ml), 40 °C, 8 h.
[b]Determined by GLC based on **2a** charged.
[c]**2a** (26 mmol), **3a** (70 mmol), 18 h. Turnover number (**4a** / **1**) = 2570, isolated yield 85%.

Table 2. Addition of Carboxylic Acids **3** to **2a** Catalyzed by **1**.[a]

3 R^2		NEt_3 (mmol)	Reaction Time (h)	Conversion (%)[b]	Isolated Yield (%)[b]	Z/E[c]
Me	(**3a**)	0.15	8	90	62	98 / 2
		0	72	97	66	98 / 2
Ph	(**3b**)	0.15	5	92	76	98 / 2
		0	72	95	78	98 / 2
	(**3c**)	0.15	10	96	72	97 / 3
	(**3d**)	0.15	5	95	80	98 / 2
Et	(**3e**)	0.03	11	97	58	97 / 3
CH_2=C(Me)	(**3f**)	0.03	24	93	73	98 / 2
PhCH=CH	(**3g**)	0.03	30	94	73	96 / 4
^{t}BuOCONHCH_2	(**3h**)	0.03	17	90	48	94 / 6

[a]Reaction conditions: **1** (9 μmol), **2a** (3 mmol), **3a-3h** (9 mmol), NEt_3 (0-0.15 mmol), MeCN (2 ml), 40 °C.
[b]Determined by GLC based on **2a** charged. [c]Determined by GLC or ^{1}H NMR.

were observed up to 90% conversion of **2a**. In the reactions of **3e-3h**, it was necessary to use much smaller amounts of NEt_3 (0.03 mmol) than in others in order to suppress the *Z-E* isomerization of the products **4**.

Cluster **1** also effected the catalytic addition of **3a** to terminal acetylenes with electron-withdrawing groups including propiolic amide **2k** and ethynyl sulfone **2l** to give *Z*-vinyl esters (Table 3). However, the reaction of ethynyl ketone **2m** led to the exclusive formation of ***E*-4m** and no ***Z*-4m** was obtained. This difference probably stems from the facile isomerization of ***Z*-4m** to ***E*-4m**.[8] Reactions of internal acetylenes **2n** and **2o** with **3a** took place similarly to form the corresponding *Z*-vinyl esters in 81% and 65% yields,

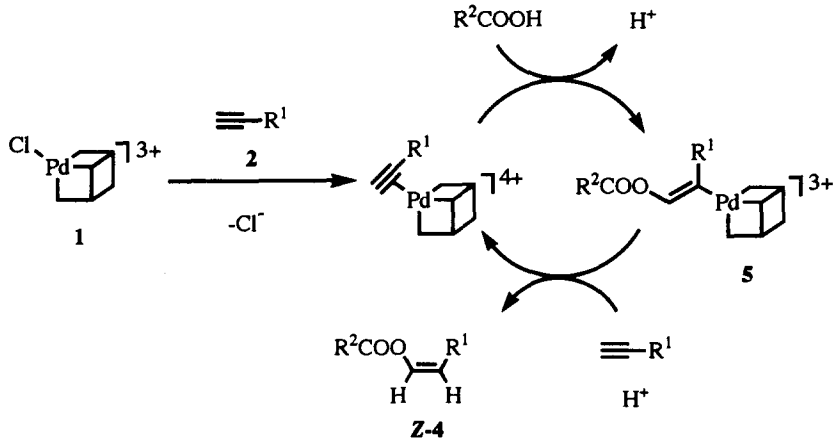
Table 3. Catalytic Addition of **3a** to **2** by Using **1**.[a]

2		NEt_3 (mmol)	Reaction Time (h)	Conversion (%)[b]	Isolated Yield (%)[b]	Z/E[c]
HC≡CCOOEt	(**2i**)	0.15	11	97	58	97 / 3
HC≡CCOO^{t}Bu	(**2j**)	0.15	12	95	71	99 / 1
HC≡CCON 	(**2k**)	0.15	9	97	85	97 / 3
HC≡CSO_2Tol	(**2l**)	0	2.5	-	51	97 / 3
HC≡CCOPh	(**2m**)	0	36	93	57	0 / 100
MeC≡CCOOMe	(**2n**)[d]	0.15	10	91	81	100 / 0
MeOOCC≡CCOOMe	(**2o**)	0.15	48	94	65	100 / 0

[a]Reaction conditions: **1** (9 μmol), **2i-2o** (3 mmol), **3a** (9 mmol), NEt_3 (0-0.15 mmol), MeCN (2 ml), 40 °C.
[b]Determined by GLC based on **2** charged. [c]Determined by GLC or ^{1}H NMR. [d]Under MeCN reflux.

respectively, although the former reaction required a higher reaction temperature (MeCN reflux). In contrast, the addition of **3a** to phenylacetylene did not proceed under the same reaction conditions.

A plausible mechanism for the present catalysis is shown in Scheme 1. The initial coordination of the acetylene to the Pd site of **1** and the following nucleophilic attack of carboxylate anion at the terminal acetylenic carbon atom from the outer coordination sphere lead to formation of the vinylpalladium intermediate **5**. The Pd-C bond in **5** is then cleaved by protonolysis with retention of the stereochemistry around the double bond to afford the trans addition product ***Z*-4**. In this catalytic cycle, the cuboidal $PdMo_3S_4^{4+}$ core plays a critical role in effectively activating the acetylenic carbon toward the nucleophilic attack without accompanying side-reactions of **2** such as oligomerization and polymerization. Further studies on the catalytic stereoselective additions across carbon-carbon multiple bonds by cluster **1** are now in progress.



Scheme 1.

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