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Catalysis of Giant Palladium Cluster Complexes. Highly Selective Oxidations of *primary* Allylic Alcohols to α,β-Unsaturated Aldehydes in the Presence of Molecular Oxygen

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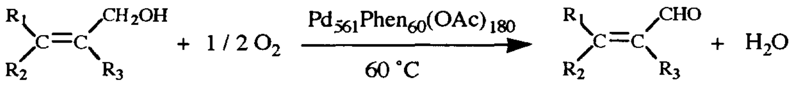
Abstract: A giant Pd cluster, $Pd_{561}phen_{60}(OAc)_{180}$, has high catalytic activity for the selective oxidations of various *primary* allylic alcohols to the corresponding α,β-unsaturated aldehydes in the presence of molecular oxygen under mild reaction conditions. A Pd cluster anchored on TiO_2 also catalyzes the above oxidations; the heterogeneous Pd_{561} cluster catalyst is easily separated from the reaction mixture and is reusable. © 1997 Elsevier Science Ltd.

Organic syntheses catalyzed by Pd compounds have been much interested both in academic and industrial areas because of their unique activities for many organic reactions and of convenient handling of the Pd compounds from the standpoints of stability and toxicity.[1] However, there is not extensive development in oxidations using molecular oxygen except for the Wacker-type reactions. Recently, much attention has been paid to the catalysis of metal cluster complexes due to their possibility to find new chemical reactions on their multimetallic centers, and also because they are model compounds for heterogeneous metal catalysts.[2] We have already reported that $Pd_4phen_2(CO)(OAc)_4$ cluster had high catalytic activity for the selective oxidations of allylic alcohols in the presence of molecular oxygen.[3]

Here, we wish to report that a giant Pd cluster, $Pd_{561}phen_{60}(OAc)_{180}$,[4] can smoothly catalyze selective oxidations of various *primary* allylic alcohols to give α,β-unsaturated aldehydes in the presence of molecular oxygen (eq.1). Further we tried to heterogenize the giant Pd_{561} cluster using TiO_2 as a support.[5] This solid compound also had high catalytic activity for the selective oxidations of *primary* allylic alcohols and was a reusable catalyst. To our knowledge, the giant Pd cluster system is one of excellent catalysts with the high selectivity for α,β-unsaturated aldehydes in the oxidations of *primary* allylic alcohols,[6] and have homogeneous particle size of *ca.* 30 Å, which can be model particles for many supported metal catalysts.



(1)

The giant Pd cluster of $Pd_{561}C_{1080}H_{960}N_{120}O_{360}$ was prepared by known procedure.[7] Reaction of AcOH solution of $Pd(OAc)_2$ with 1,10-phenanthroline (phen) under hydrogen atmosphere gave $[Pd_4phen(OAc)_2H_4]_n$ (n~100), which was further treated with O_2 in AcOH to afford a giant Pd cluster, $Pd_{561}phen_{60}(OAc)_{180}$. Anal. Calcd for $Pd_{561}C_{1080}H_{960}N_{120}O_{360}$: C, 16.4; H, 1.3; N, 2.1 %. Found: C, 16.12; H, 1.29; N, 2.64 %. The heterogeneous Pd_{561} cluster catalyst was obtained by the adsorption method of the Pd_{561} cluster on various titanium oxides (Japan Reference Catalyst, TIO 1~5) in AcOH solvent. A mixture of $Pd_{561}phen_{60}(OAc)_{180}$(0.025g), TiO_2(0.5g), and AcOH(5ml) was stirred at room temperature for 0.5 h under nitrogen atmosphere. The solid compound of 0.525g was obtained after filtration, washing with AcOH, and drying.[8] A typical procedure for the title oxidations is as follows. AcOH (15 ml) and cinnamyl alcohol (0.61 g, 4.5 mmol) were added to a reaction vessel containing the giant Pd complex (0.022 g ; 0.15 mmol of Pd atom). The mixture was then stirred at 60 °C for 3 h under oxygen atmosphere. After the usual work-up, the reaction mixture was subjected to column chromatography on silica gel (hexane : ethyl acetate,10:1) to yield cinnamaldehyde (0.49 g, 83 %).

Table 1 shows results of oxidations of cinnamyl alcohol using various kinds of Pd catalysts in the presence of molecular oxygen. $Pd_{561}phen_{60}(OAc)_{180}$ had the highest catalytic activity for the oxidative dehydrogenation to give cinnamaldehyde. Typical Pd compounds, $Pd(OAc)_2$ and $PdCl_2$ resulted in low yields of cinnamaldehyde, respectively. Further, supported Pd catalysts such as Pd/Carbon, Pd/Al_2O_3, and Pd/SiO_2 were also poor catalysts for the above oxidation. The yield of cinnamaldehyde was 28% when the reaction using the Pd_{561} cluster was carried out under nitrogen atmosphere instead of oxygen.

Table 1. Oxidations of Cinnamyl Alcohol with Various Pd Catalysts in the Presence of Molecular Oxygen[a)]

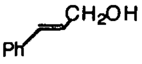
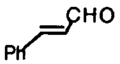
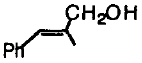
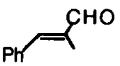
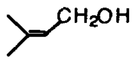
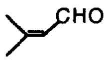
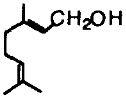
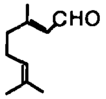
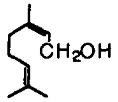
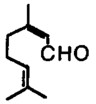
catalyst	conv. (%)	yield of cinnamaldehyde (%)	TOF[b)]
$Pd_{561}phen_{60}(OAc)_{180}$	100	94	26
$Pd_{561}phen_{60}(OAc)_{180}$ [c)]	64	28	8
$Pd(OAc)_2$	35	10	3
$PdCl_2$	32	6	3
Pd/Carbon	27	8	2
Pd/Al_2O_3	39	34	11
Pd/SiO_2	20	8	2

[a)] Cat.: [Pd atom : 0.05 mmol], substrate : cinnamyl alcohol : 1.5 mmol, solvent : AcOH 5.0 ml, 60 °C, 1 h, O_2 atmosphere. [b)] TOF=aldehyde [mol] / Pd atom [mol]. [c)] N_2 atmosphere .

Results of oxidations of various allylic alcohols with $Pd_{561}phen_{60}(OAc)_{180}$ are shown in Table 2 together with the heterogeneous systems (*vide infra*). Many *primary* allylic alcohols were oxidized to give the corresponding unsaturated aldehydes in high yields accompanied with small amounts of hydrogenation products. In the case of geraniol, esterification occurred to some degree. However, use of benzene solvent in place of AcOH depressed the undesired side reaction, leading to α,β-unsaturated aldehydes in high yields at the expense of slow rates. Further, when the oxidation of geraniol was carried out in a mixed solvent of AcOH and benzene, the reaction rate could be increased keeping high chemoselectivity. Oxidation of an *(E, E)*-dienol, sorbic alcohol gave stereoselectively *(E, E)*-2,4-hexadienal in a high yield. Notably, the giant Pd cluster showed low catalytic activity for oxidations of *secondary* allylic alcohols and benzyl alcohols.[9]

Use of metal clusters heterogenized on supports could lead to easy separation from the reaction mixture after the reaction and to reuse of catalysts. Table 2 also shows the heterogeneous catalysis of TiO_2-anchored Pd_{561} cluster for the oxidations of allylic alchohols. The Pd_{561} cluster on TiO_2 had high catalytic activity for the oxidations of various allylic alcohols, *e.g.*, cinnamyl alcohol and sorbic alcohol. This catalyst was easily separated from the reaction mixture by a filtration, and then subjected to reuse for the oxidations of various allylic alcohols. As shown in Table 3, it is confirmed that this heterogeneous catalyst was reusable without an appreciable loss of the activity and selectivity.

Table 2. Oxidations of Various Allylic Alcohols with $Pd_{561}phen_{60}(OAc)_{180}$ and TiO_2-Anchored $Pd_{561}phen_{60}(OAc)_{180}$ in the Presence of Molecular Oxygen[a]

substrate	product	homogeneous time (h)	 conv. (%)	 yield (%)	 selectivity (%)	heterogeneous time (h)	 conv. (%)	 yield (%)	 selectivity (%)
		1 24[b]	100 97	94 97	94[d] 100	1	100	99	99
		24 24[b]	100 78	99 78	99 100	2	99	94	95
		1 24[b]	100 98	79 97	79 98	4	100	91	91
		2	100	100	100	5	100	98	98
		1 24[b]	100 100	89 99	97 99	24[b]	96	96	100
		24 24[b] 24[c]	94 40 100	57 39 95	61[e] 97 95	24[b]	70	70	100
		24[b] 24[c]	35 100	35 100	100 100	24[b]	52	52	100

[a] Cat. $Pd_{561}phen_{60}(OAc)_{180}$ [Pd atom : 0.05 mmol], $Pd_{561}phen_{60}(OAc)_{180}/TiO_2$: 0.30 g, substrate : 1.5 mmol, solvent : AcOH 5.0 ml, O_2 atmosphere, 60 °C. [b] Solvent : benzene 5.0 ml. [c] Solvent : benzene 4.5 ml+AcOH 0.5 ml. [d] 3-Phenylpropanol was also formed. [e] Geranyl acetate was also formed.

Table 3. Heterogeneous Oxidations of Cinnamyl Alcohol with TiO_2-Anchored $Pd_{561}phen_{60}(OAc)_{180}$[a]

catalyst	time (h)	conv. (%)	yield. (%)	selectivity (%)
$Pd_{561}phen_{60}(OAc)_{180}/TiO_2$	1	100	99	99
Reuse 1	1	100	92	98
Reuse2	1	100	90	97

[a] Cat.: $Pd_{561}phen_{60}(OAc)_{180}/TiO_2$: 0.30g [Pd atom : 0.10 mmol], substrate : cinnamyl alcohol 1.5 mmol, solvent : AcOH 5.0 ml, O_2 atmosphere, 60 °C.

A possible path for the oxidation is as follows.[10] First, allylic alcohol is dehydrogenated on the Pd cluster surface to give α,β-unsaturated aldehyde and hydride species on the Pd surface. Attack of molecular oxygen to the Pd hydride regenerates the active Pd species together with the formation of H_2O. Remained hydride species on the Pd cluster may induce hydrogenation and isomerization of allylic alcohols to give by-products. Details of the mechanism for the present oxidation are under investigation in our laboratory.

In conclusion, the Pd_{561} cluster had high catalytic activity for the selective oxidations of various *primary* allylic alcohols to give α,β-unsaturated aldehydes in the presence of molecular oxygen. The heterogeneous TiO_2-anchored Pd_{561} cluster also efficiently catalyzed the above oxidations. This fixation of the metal cluster with metal oxides might be clue to design for a new heterogeneous metal cluster catalyst, *e.g.*, homogeneous distribution of metal cluster sizes on the support surface without structural destruction of the cluster.

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