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Highly Selective Oxidation of Allylic Alcohols to α,β-Unsaturated Aldehydes Using Pd Cluster Catalysts in the Presence of Molecular Oxygen

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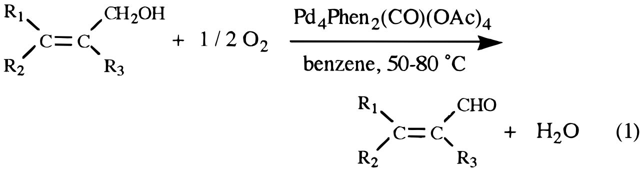
Much attention has been paid to metal cluster complexes having metal−metal bonds because unprecedented chemical reactions might occur on multimetallic centers of the cluster catalysts, and also because they are model compounds for heterogeneous metal catalysts.[1] Palladium complexes have unique catalytic activities and thus have been widely used in many organic syntheses.[2] However, little is known about selective organic transformations assisted by Pd cluster complexes.[3] We wish to report selective dehydrogenation of allylic alcohols to α,β-unsaturated aldehydes catalyzed by Pd_4 clusters in the presence of molecular oxygen (eq 1). To the best of our knowledge, this is the first example of selective oxidations with molecular oxygen *using metal cluster complex catalysts*.



(1)

Pd_4 clusters were prepared by known procedures.[4] Treatment of an acetic acid solution of $Pd(OAc)_2$ with CO gave $Pd_4(CO)_4(OAc)\cdot 2AcOH$ (PCA). Reaction of PCA (0.04 mmol) with 1,10-phenanthroline (Phen, 0.08 mmol) under a nitrogen atmosphere at room temperature for 0.5 h afforded a quantitative yield of $Pd_4Phen_2(CO)(OAc)_4$. [Anal. Calcd for $Pd_4C_{33}H_{28}N_4O_9$: C, 37.73; H, 2.67; N, 5.34. Found: C, 37.41; H, 2.98; N, 5.25.] $Pd_4Phen_4(CO)(OAc)_4$ was also obtained by a similar treatment of PCA with 4 equiv of Phen. A typical procedure for the oxidation reaction is as follows. Benzene (15 mL) and cinnamyl alcohol (0.61 g, 4.5 mmol) was first added to a reaction vessel containing $Pd_4Phen_2(CO)(OAc)_4$ (0.04 mmol). The mixture was then stirred at 50 °C under an oxygen atomsphere.[5] After 24 h, the reaction mixture was cooled, Pd clusters were removed by filtration, and the filtrate was subjected to column chromatography on silica (hexane:ethyl acetate (10:1)) to yield the product of cinnamaldehyde (0.56 g, 93%).

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

run	catalyst	conversion (%)	yield of cinnamaldehyde (%)	TOF[b]
1	$Pd_4Phen_2(CO)(OAc)_4$	100	quantitative	30
2	$Pd_4Phen_2(CO)(OAc)_4$[c]	18	14	4
3	$Pd_4Phen_4(CO)(OAc)_4$	1	1	0
4	$Pd_4(CO)_4(OAc)\cdot$ 2AcOH [PCA]	42	38	13
5	$Pd(OAc)_2$	30	28	8
6	Pd/C	39	29	9
7	$PdCl_2$	15	11	3

[a] Pd catalyst: 0.05 mmol, cinnamyl alcohol: 1.5 mmol, solvent: benzene, 5 mL, 50 °C, 24 h, O_2 atmosphere. [b] TOF = aldehyde[mol]/Pd[mol]. [c] N_2 atmosphere.

Oxidations of cinnamyl alcohol using various Pd compounds in a benzene solvent with oxygen yielded the results shown in Table 1. $Pd_4Phen_2(CO)(OAc)_4$ complexes had the highest catalytic activity for the dehydrogenative oxidation (a quantitative yield of cinnamaldehyde, run 1).[6] The use of $Pd_4Phen_4(CO)(OAc)_4$, PCA, and $Pd(OAc)_2$ resulted in low yields of cinnamaldehyde. Pd/C and $PdCl_2$ were poor catalysts for the selective oxidation. Other metal carbonyl clusters such as $Rh_6(CO)_{16}$, $Ru_3(CO)_{12}$, $Fe_3(CO)_{12}$, and $Os_3(CO)_{12}$ showed low catalytic activities for the oxidation of allylic alcohols under the present reaction conditions. In order to examine the additive effect of amines and pyridine derivatives, cinnamyl alcohol was oxidized by oxygen using mixtures of PCA and basic additives at 50 °C. Triethylamine and *N*,*N*,*N*′,*N*′-tetramethylpropanediamine additives were also effective. Both pyridine and bipyridine gave low yields of cinnamaldehyde.

Oxidations of various allylic alcohols with the $Pd_4Phen_2(CO)(OAc)_4$ cluster in benzene under an oxygen atmosphere yielded the results in Table 2. Many *primary* allylic alcohols were oxidized to yield the corresponding α,β-unsaturated aldehydes in high yields together with small amounts of hydrogenation products. Generally, the Pd_4 cluster catalyst oxidized allylic alcohols possessing disubstituted olefinic moieties at faster rates than trisubstituted allylic ones. When compared with other catalyst systems using molecular oxygen,[7] this Pd_4 cluster catalyst has the highest selectivity for dehydrogenation of allylic alcohols to α,β-unsaturated aldehydes. In oxidation to two *E*/*Z* iosmers (nerol and geraniol), we observed retention of the stereochemistry in the product α,β-unsaturated aldehydes (runs 13 and 14). Oxidation of nerol to neral was slower than that of geraniol. This might be explained by the steric congestion in active Pd intermediate species.[8] A (*E*,*E*)-dienol of sorbic alcohol was also oxidized stereoselectively to give (*E*,*E*)-2,4-hexadienal in high yield (eq 2). The $Pd_4Phen_2(CO)(OAc)_4$

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[1] (a) Gates, B. C. *Chem. Rev.* **1995**, *95*, 511. (b) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693. (c) Knozinger, H. *Cluster Models for Surface and Bulk Phenomena*; Plenum: New York, 1992. (d) Shriver, D. F.; Kaesz, H. D.; Adams, R. D. *The Chemistry of Metal Cluster Compounds*; VCH Publishers: New York, 1990.

[2] (a) Wilkinson, S. G.; Stone, F. G. A.; Abel, E. W., Eds. *Comprehensive Organometallic Chemistry II*; Pergamon Press Ltd.: New York, 1995; Vols. 7−9. (b) Tsuji, J. *Palladium Reagents and Catalysts*, John Wiley, New York, 1995. (c) Heck, R. F. *Palladium Reactions in Organic Syntheses*; Academic Press: London, 1985.

[3] (a) Moiseev, I. I.; Stromnova, T. A.; Vargaftig, M. N. J. *Mol. Catal.* **1994**, *86*, 71. (b) Vargaftik, M. N.; Zagorodnikov, V. P.; Storarov, I. P.; Moiseev, I. I. *J. Mol. Catal.* **1989**, *53*, 315. (c) Stolyarov, I. P.; Vargaftik, M. N.; Nefedov, O. M.; Moiseev, I. I. *Kinet. Katal.* **1982**, *23*, 376. (d) Blackburn, T. F.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1977**, 157.

[4] (a) Moiseev, I. I. *J. Organomet. Chem.* **1995**, *488*, 183. (b) Moiseev, I. I.; Stromnova, T. A.; Vargaftig, M. N.; Mazo, G. J. *J. Chem. Soc., Chem. Commun.* **1978**, 27.

[5] When scale up above the 15 mL reaction volume is carried out, the reaction vessel should be placed behind an appropriate shield.

[6] Moiseeve *et al.* have reported the catalysis of Pd_4 complexes for acetoxylation of olefins and toluene and for hydrogenation of olefins; the $Pd_4Phen_2(CO)(OAc)_4$ complex had the highest catalytic activity for the above reactions.[3c]

[7] (a) Bi−Pt/Alumina: Mallat, T.; Bodnar, Z.; Hug, P.; Baiker, A. *J. Catal.* **1995**, *153*, 131. (b) $Rh_6(CO)_{16}$: Kaneda, K.; Miyoshi, T.; Imanaka, T. *J. Mol. Catal.* **1991**, *64*, L7. (c) MnO_2: Xiao-yi, X.; Prestwitch, G. D. *Synth. Commun.* **1990**, *20*, 3125. (d) RuO_2: Matsumoto, M.; Watanabe, N. *J. Org. Chem.* **1984**, *49*, 3435.

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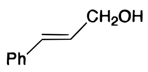
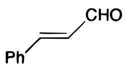
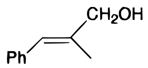
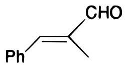
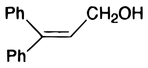
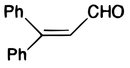
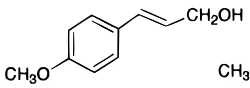
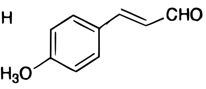
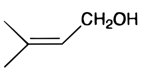
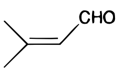
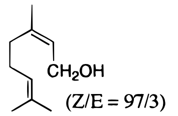
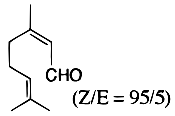
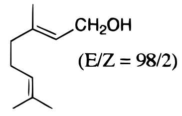
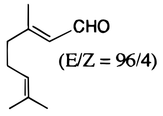
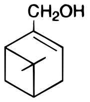
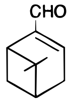
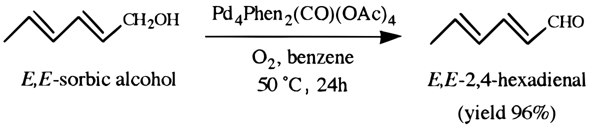
Table 2. Oxidation of Various Allylic Alcohols Catalyzed by $Pd_4Phen_2(CO)(OAc)_4$ in the Presence of Molecular Oxygen[a]

run	substrate	product	temp. (°C)	time (h)	convn (%)	yield[b] (%)
1			50	24	100	quantitative (93)
2[c]			50	3	100	quantitative
3			80	48	100	98(89)
4[c]			80	24	100	97
5			70	72	83	75
6[c]			70	72	100	98
7			50	24	100	97
8			50	24	100	98(91)
9[c]			50	6	100	79[d]
10			60	24	100	98
11[c]			60	12	100	53[e]
12[f]			60	12	100	93[g]
13			60	48	83	79
14			60	48	100	96(92)
15[c]			60	24	100	13[h]
16			50	48	100	94

[a] Pd catalyst: 0.05 mmol, substrate: 1.5 mmol, solvent: benzene, 5 mL, O_2 atmosphere. [b] Determined by GC, and values in parentheses were isolated yields. In isolation of products, the reaction scale was three-fold. [c] AcOH (5 mL) in acetate and 9% of 1-hexanol were also formed. [e] 30% of 3-methyl-2-butenyl acetate and 17% of 3-methyl-2-butanol. [f] A mixed solvent of benzene (4.5 mL) and AcOH (0.5 mL) was used. [g] 6% of 3-methyl-2-butenyl acetate. [h] 87% of geranyl acetate.

catalyst had low activity for oxidation of seconary allylic alcohols and benzyl alcohol.[9]



(2)

The use of acetic acid in place of benzene increased the rate of formation of α,β-unsaturated aldehydes. However, in the case of aliphatic allylic alcohols, such as 3-methyl-2-penten-1-ol and geraniol, use of acetic acid led to some esterification and hydrogenation of allylic alcohols under our reaction conditions (runs 11 and 15).[10] 1,2-Dichloroethane and toluene solvents were also effective. Acetonitrile and ethanol were poor solvents for the oxidation.

When nitrogen was used instead of oxygen, the $Pd_4Phen_2(CO)(OAc)_4$ cluster did not form the dehydrogenation product (run 2 in Table 1). While we have not yet studied the mechanism of these reactions, we speculate that this selective oxidation might occur *via* the following reaction pathway.[11] First, oxidative addition of allylic alcohol to the Pd cluster could occur, giving an allylic alkoxide and hydride species. β-Hydrogen elimination would then lead to an α,β-unsaturated aldehyde. Molecular oxygen reaction with the hydrides so formed could then yield H_2O and regenerate the active catalytic species. These hydride species might also be responsible for the observed hydrogenation of allylic alcohols. Details of the mechanism for the present oxidation are under investigation in our laboratory.

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(8) A similar reactivity between two regioisomers has been observed also in other oxidizing reagents. (a) References 7b–d. (b) $NiSO_4/K_2S_2O_8$: Yamazaki, S.; Yamazaki, Y. *Chem. Lett.* **1989**, 1361. (c) $Co(OAc)_3$: Hirano, M.; Morimoto, T.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3749. (d) Pyridinium Dichromate: Kanemoto, S.; Matsubara, S.; Takai, K.; Oshima, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3607. (e) MnO_2: Zhang, N.; Mann, C. M.; Shapley, P. A. *J. Am. Chem. Soc.* **1988**, *110*, 9591. (f) Cp_2ZrH_2: Ishii, Y.; Nakano, T.; Ogawa, M. *J. Org. Chem.* **1987**, *52*, 4855.

(9) There are few oxidation catalysts having higher activity for primary alcohols. For examples, see: (a) $ZrO(OAc)_2$: Kaneda, K.; Kawanishi, Y.; Teranishi, S. *Chem. Lett.* **1984**, 1481. (b) $RuCl_2(PPh_3)_3$: Kanemoto, S.; Oshima, K.; Matsubara, S.; Takai, K.; Nozaki, H. *Tetrahedron Lett.* **1983**, *24*, 2185. (c) $RuH_2(PPh_3)_4$: Murahashi, S-I.; Ito, K-I.; Naota, T.; Maeda, Y. *Tetrahedron Lett.* **1981**, *22*, 5327. (d) Pt/O_2: Lansbury, P. T.; Hangauer, D. G.; Vacca, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 3964. Generally, effective reagents for the selective oxidation of allylic alcohols also give high activity for oxidation of benzylic alcohols. However, benzyl alcohol was not readily oxidized to benzaldehyde (16% for 48 h) under the present reaction conditions.

(10) Using a mixed solvent of benzene and AcOH could depress the esterification and hydrogenation to give high yields of the α,β-unsaturated aldehydes (run 12 in Table 2).

(11) For reviews of the mechanism of alcohol oxidations see: (a) Simandi, L. I. *Catalytic Activation of Dioxygen by Metal Complexes*; Kluwer Academic Publishers: Netherlands, 1992. (b) Hudlicky, M. *Oxidations in Organic Chemistry*; ACS Monograph: Washington, DC, 1990. (c) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: London, 1981.