

Catalytic Activities of Pd(II), Pd(I) and Pd(O)-diphosphine Complexes for Styrene Oxidation

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Received September 24, 1994

The catalytic activities of palladium(O, I, II)-diphosphine complexes were investigated in styrene oxidation using H₂O₂ as terminal oxidant. The rates showed a dependence on the chelate ring patterns of complexes (PdCl₂L); 5-membered ring (L=dppe: 1,2-bis(diphenylphosphino)ethane) < 6-membered ring (L=dppp: 1,3-bis(diphenylphosphino)propane) < 4-membered ring (L=dppm: bis(diphenylphosphino)methane). This sequence correlates with the ligand field strength and interactions between metal and phosphine ligands. Pd(II, I)-diphosphine complexes which are capable of making 4-membered chelate ring showed an enhancement of catalytic activities for styrene oxidation. The catalytic activities of Pd(O, I, II)-diphosphine complexes are described in terms of electronic and steric factors.

Introduction

Soluble transition metal complexes have been used extensively in industry to catalyze syntheses of organic compounds.¹ Especially, the phosphine complexes are used in the control of selective and partial oxidation of alkenes and olefins.² The direct oxidation of olefins with transition metal complexes has been attempted during the years.³ It is generally recognized that unsaturated ketones, aldehydes or other electronegatively substituted alkenes can be easily oxidized with H₂O₂ under basic conditions.⁴ The nucleophilic addition of hydroperoxide anion to carbon-carbon double bond can be promoted by the electron withdrawing substituents. From this point of view, transition metal ion is also capable of activating unsubstituted alkenes toward nucleophilic attack.⁵

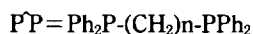
In this paper, the catalytic activities caused from the nature of metal complexes such as ring size, ring shape, oxidation state, steric and electronic structure of chelating diphosphine complexes are examined. This objective led us to the choice of palladium complexes with a wide variety of diphosphine ligands. The catalyst systems are designed to employ diphosphine ligands possessing appropriately selected electronic and steric properties. A discussion is also included concerning the origin of selectivity and yield in this class of catalysts based essentially on steric and electronic factors.

Experimental

Preparation of Compounds

[PdCl₂(P'P)]⁶ and [NiCl₂(P'P)]^{6,7a} Complexes. K₂-PdCl₄ (0.3 gr, 0.72 mmol) was dissolved in 1 mL hot water and 0.5 mL conc. HCl. n-Propanol (60 mL) was added and stirred for 15 min. The equimolar diphosphine ligand (0.72 mmol) was added and stirred for 30 min, and then the solution was refluxed for 2 hr. The pale yellow solid [PdCl₂(P'P)] formed was cooled and collected by vacuum filtration. The solid was washed with an ice-water and an ether and dried in vacuo for 12 hr. [NiCl₂(P'P)] complexes were prepared by

similar procedures. [MCl₂(P'P)] complexes (M=Pd or Ni) were air stable in the solid state and they all gave satisfactory elemental analyses (C, H) for the proposed structures.^{7a,b}

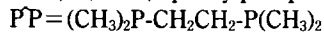


n = 1, bis(diphenylphosphino)methane (dppm)

n = 2, 1,2-bis(diphenylphosphino)ethane (dppe)

n = 3, 1,3-bis(diphenylphosphino)propane (dppp)

n = 4, 1,4-bis(diphenylphosphino)butane (dppb)



1,2-bis(dimethylphosphino)ethane (dmpe)



1,2-bis(diphenylphosphino)ethylene (dppety)

Pd(O) and Pd(I) Diphosphine Complexes. The complex of [Pd₂(μ-dppm)₃] was prepared according to literature method.^{7c,d,8} The complex of [Pd₂Cl₂(μ-dppm)₂] was obtained by the reaction of [Pd₂(μ-dppm)₃] with [PdCl₂(dppm)].^{7c} Samples of [Pd₂(dppm)₃] (0.2 g 0.088 mmol) and [PdCl₂(dppm)] (0.099 g 0.175 mmol) were dissolved in 10 mL of dichloromethane. After 2 hr of standing the solution was filtered and the product was precipitated through the addition of ether (yields 82%).

Materials and Instruments

Styrene (Aldrich) was purified by passing it through neutral alumina and distilled and stored under N₂ in the dark. Diphosphine ligands such as dppm, dppe, dppp, dppb, dppety, and dmpe (all from Aldrich) were commercial products and used without purification. Potassium tetrachloropalladate was prepared by adding potassium chloride in palladium chloride solution and used after recrystallization. Hydrogen peroxide (Junsei) was commercial product. GC measurements were taken on a Hewlett-Packard 5890 gas chromatograph equipped with a HP-FFAP capillary column and a Hewlett-Packard 3390A integrator. Identification of products was made with Hewlett-Packard 5970 GC-MASS. UV-visible spectra were recorded on a Shimadzu Model 2100 spectrophotometer. Elemental analyses were taken on a Hewlett-Packard Model

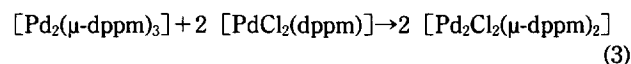
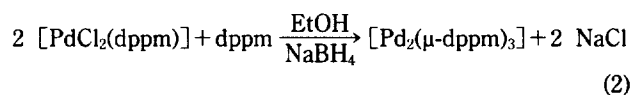
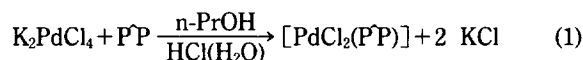
185B elemental analyzer.

Catalytic Reactions

Catalytic oxidations were carried out in a 25 mL round bottom flask equipped with side arm fitted with a screw capped silicon septum for periodic sampling. Constant temperature (25 °C) was maintained by water circulation through an external jacket connected with a thermostat. In a typical experiment, [PdCl₂(dppm)] (56 mg, 0.1 mmol) was put into a flask. Solvent (10 mL) was added and followed by a styrene (15 mmol). After stirring a few minutes, 35% H₂O₂ solution (0.5 mL, 5 mmol) was injected and the temperature was controlled and the time was started. The reaction was monitored with GC by periodic sampling.

Results and Discussion

The Pd-diphosphine complexes were prepared by adding diphosphine ligand to a suspension of K₂PdCl₄ in the distilled n-propanol as shown in equation 1. Binuclear complexes were also prepared according to a modified synthetic method outlined in the following sequence of reactions (2)-(3).



The prepared complexes have been characterized by ¹H NMR, ³¹P NMR, UV-visible spectroscopies and in most cases elemental analyses.^{7ab} When 35% H₂O₂ was added to a dichloroethane solution of Pd-diphosphine complex containing an excess of styrene, direct oxidation of olefin took place. Identification of oxidation products was made with GC-Mass and GC by comparison with authentic samples. It was plot-

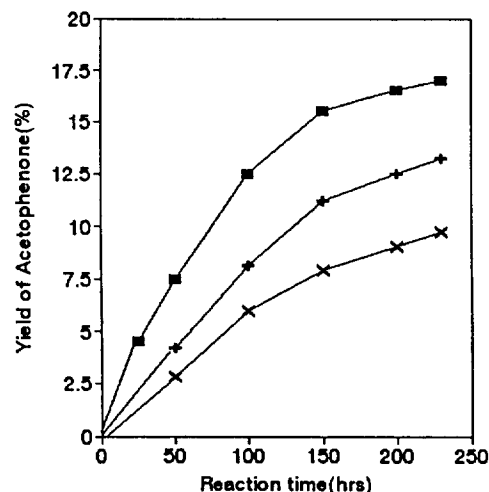


Figure 1. Reaction profiles for acetophenone formation catalyzed by Pd(II)-diphosphine complexes PdCl₂dppm (■—■), PdCl₂dppp (+—+) and PdCl₂dppe (×—×).

ted the conversion of styrene to main product, acetophenone vs. reaction time by varying complexes as shown in Figure 1. The reaction rates showed a dependence on the chelate ring patterns of complexes; 5-membered ring(dppe) < 6-membered ring (dppp) < 4-membered ring (dppm). For further investigation on catalytic activities of Pd-diphosphine complexes, the electronic and steric properties of these catalysts were considered in a systematic way by varying the substituents on phosphorus, chelate ring size and oxidation state of Pd metal.

Almost catalysts listed in Table 1 performed ketone selective oxidation. The rates of styrene oxidations were too slow in dichloromethane solution. The reaction rates were increased by using dichloroethane solvent at 83 °C (reflux temperature). Pd(II, I)-dppm complexes which have 4-membered chelate ring showed an enhancement of catalytic activities, while the complexes which are making 5-membered chelate

Table 1. Catalytic activities of Pd-diphosphine complexes for styrene oxidation

Run	Complexes	Solv.	T (°C)	Turn Over Number					time (hr)	selectivity of D (%)
				A	B	C	D	T		
1	PdCl ₂ dppm	dcm	25	5.8	0.1	0.2	15.0	21.1	72	71.1
2	PdCl ₂ dppe	dcm	25	4.0	0.5		6.5	11.0	72	59.1
3	PdCl ₂ dppp	dcm	25	6.0	1.5	0.1	9.1	16.7	72	54.5
4	PdCl ₂ dppety	dcm	25	0.8			0.1	0.9	72	
5	PdCl ₂ dppb	dcm	25	1.7	0.3	0.1	2.2	4.3	72	51.2
6	PdCl ₂ dppm	dce	83	5.1	0.1	0.1	18.2	23.5	2	77.4
7	PdCl ₂ dppe	dce	83	3.8	0.5		6.4	10.7	2	59.8
8	PdCl ₂ dppp	dce	83	4.1	2.1	0.5	8.0	14.7	2	54.4
9	PdCl ₂ dppety	dce	83	2.5	0.9		0.6	4.0	2	
10	PdCl ₂ dmpe	dce	83	0.7				0.7	2	
11	Pd ₂ Cl ₂ (μ-dppm) ₂	dce	83	5.1	0.2	0.7	26.8	32.8	2	81.7
12	Pd ₂ (μ-dppm) ₃	dce	83	0.9	0.9	0.1	1.4	3.4	2	44.1

Experimental conditions: complex, 0.1 mmol; styrene, 15 mmol; H₂O₂, 5 mmol; solv., dcm = dichloromethane, dce = dichloroethane, TON = product mmol/Pd mmol; A; benzaldehyde, B; styreneoxide, C; phenylacetaldehyde, D; acetophenone, T; total amount of product

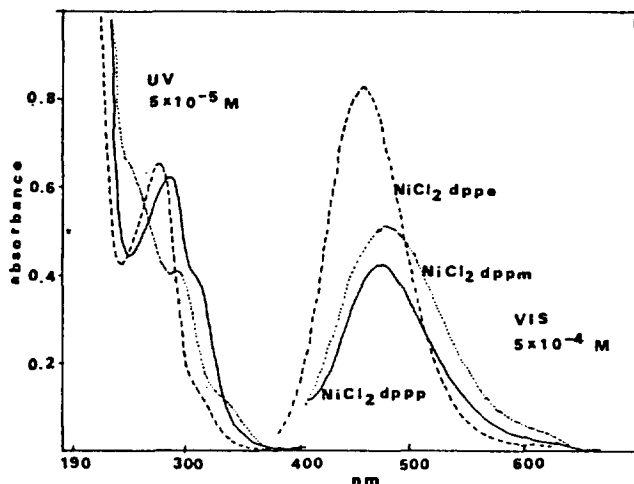


Figure 2. UV-visible spectra of NiCl_2dppm (···), NiCl_2dppp (—) and NiCl_2dppe (---) in acetonitrile solution.

ring found to be worst catalysts. The catalytic activities depend on the steric and electronic parameters of the transition metal complexes which react with olefin. The electronic and steric effects are intimately related and difficult to separate in any pure way. For example, increasing the chelate ring and bulkiness of alkyl substituent will decrease the percentage of s character in phosphorus lone pair, changing the electronegativity of atoms can also affect bond distance and angle. One can consider the ring size effect of catalytic activities which is ascribed mainly to steric reasons, because a more hindered site for the coordination of olefin is more difficult to form the activated complex. In a point of steric view, the catalytic activity should be decreased in a sequence of dppm , dppe , dppp , and dppb . On the contrary the chelating patterns are extremely important to olefin activation. In forming chelate complexes, the optimum ring size for metal having natural bond angle is five. It has long been known that the dppe is an excellent chelate ligand. The dppm can chelate but the four membered ring so formed is strained. The chelating tendency also decreases as the chain length increases, so that for the ligands $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ the tendency to chelation is greatest for $n=2$.⁹ One can consider that the complex having higher electron density on the metal is much available for back donation ($\text{M} \rightarrow \text{olefin}$) in the metal-olefin complex formation, so that the olefin is less activated for nucleophilic attack. However, for the Pd-diphosphine complexes, electron density on the metal are rare in literature. X-ray crystallographic data on P-M bond distances for homologous series of metal complexes have been reported by Steffen and coworkers.¹⁰ On square planar $[\text{PdCl}_2(\text{P}^*)_2]$ complexes, where $\text{P}^* = \text{dppm}$, dppe and dppp , P-Pd bond distances were 2.234, 2.233, and 2.244 Å, respectively. The electronic transitions of phosphine complexes are affected by chelating pattern, ligand field strength and the length of P-M bonds. Unfortunately, the electronic spectra of Pd-diphosphine complexes are difficult to assign because the d-d bands are obscured by intense charge transfer band. However the electronic spectra of Ni(II)-diphosphine complexes clearly showed d-d transition bands in the range of 460-477.5 nm (Figure 2). From these electronic transition spectra, the ligand field

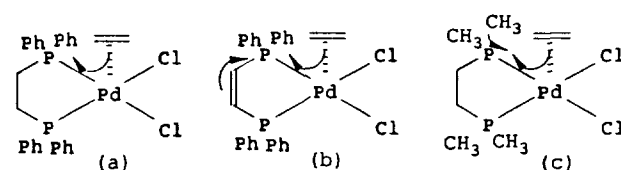
Table 2. Catalytic activities of Ni-diphosphine complexes for styrene oxidation

Run	Complexes	Turn Over Number					selectivity of	
		A	B	C	D	T	A (%)	B (%)
1	NiCl_2dppm	6.5	5.8	0.5	0.3	13.1	49.6	44.3
2	NiCl_2dppe	3.0	0.9			3.9	76.9	23.1
3	NiCl_2dppp	4.3	2.2	0.4	0.2	7.1	60.6	31.0
4	$\text{NiCl}_2\text{dppety}$	2.6	0.4			3.0	86.7	13.3

Experimental conditions: complex, 0.1 mmol; styrene, 15 mmol; H_2O_2 , 5 mmol; solvent; dichloroethane, temp.; 83 °C, reaction time; 2 hr, A; benzaldehyde, B; styreneoxide, C; phenylacetaldehyde, D; acetophenone, T; total amount of product

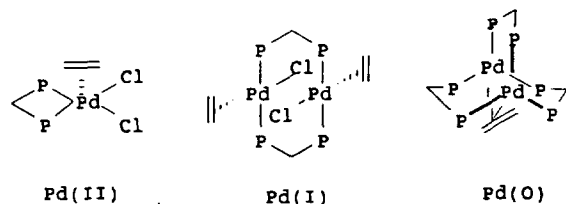
strength goes in the order; dppe ($21,739 \text{ cm}^{-1}$) > dppp ($21,168 \text{ cm}^{-1}$) > dppm ($20,942 \text{ cm}^{-1}$). The sequence of catalytic activities of Ni(II) complexes observed in Table 2 was consistent with the reverse sequence of ligand field strength; $\text{dppe} < \text{dppp} < \text{dppm}$. Therefore, the five membered ring complexes (MCl_2dppe , $\text{M} = \text{Pd, Ni}$) which might have higher electron density on metal was found to be worst catalysts.

A second observation can be made when different pattern in five membered ring is considered. To compare the catalytic activities, the turn over rates (TON/hr) of these five membered ring complexes for styrene oxidation in dichloroethane at 83 °C were calculated. According to the shape of ligand, the turn over rates were varied in a sequence of $\text{PdCl}_2\text{dppe} = 5.4 > \text{PdCl}_2\text{dppety} = 2.0 > \text{PdCl}_2\text{dmpe} = 0.35$, respectively. This trend strongly suggests that the rich π -electron in unsaturated ligand results in a higher electron density on the metal. The complexes of dppety (b) and dmpe (c), therefore, have lower activities for the nucleophilic attack. These results offer some interesting insight into the origin of activity in the oxidation of olefin.



It is generally known that tertiary phosphine ligands act as a π -acceptor, with the strength of back bonding ($\text{M} \rightarrow \text{phosphine}$) increasing in the series of $\text{L} = \text{Et}_3\text{P} < \text{Ph}_3\text{P} < (\text{CF}_3)_3\text{P} < (\text{PhO})_3\text{P}$.¹¹ Based on π -acceptor property of phosphine ligands, one can deduce the catalytic activities for olefin oxidation. The phosphorus atom of activated species(a) act as a π -acceptor, which can increase the back donation ($\text{M} \rightarrow \text{phosphine}$). Therefore, the π -electron of olefin readily transfer through metal to phosphine, while the π -electron of unsaturated ligand(b) and electron donating methyl group(c) prevent metal from back donating ($\text{M} \rightarrow \text{phosphine}$). Thus the electron density on the metal is increased.

A third observation can be made when the binuclear complexes^{7a,8} are considered. The results of acceleration for olefin oxidation by binuclear complexes (run 11 in Table 1) are reasonable. Especially it is interesting to compare the catalytic activity with oxidation state; the sequence of Pd(II), Pd(I) and Pd(O).



The way that an olefin binds to a Pd-diphosphine complex has substantial differences in coordination number and orientation.⁸ Pd(I) has some advantage to accelerate the olefin oxidation in comparison with Pd(II) analogue; i) there are two active metal centers ii) Pd(I) has three coordination number, and thus the four coordinate activated species are easily formed through vacant orbital. However, Pd(I) also has the steric hindrance between two metal centers and bridging ligands. The results of run 11 in Table 1 seem to be compensated for these two aspects. Pd(I) accelerated the oxidation while Pd(0) was less active under the same experimental conditions (run 12 in Table 1). It has been reported that electron-withdrawing substituent on the metal promotes nucleophilic addition to the olefin.¹² Activity decline in Pd(0)-phosphine complex occurs due to the loss of chloride ligand. In binuclear complexes, the role of diphosphine ligand is to prevent dissociation of dimer to monomer and to promote binuclear reactions involving the formation and cleavage of metal-metal bonds. Unfortunately these properties of $[\text{Pd}_2(\mu\text{-dppm})_2]$ complex suppressed the styrene activation for the nucleophilic attack. It appears that there is a substantial back donation ($M \rightarrow \text{olefin}$) when the activated species, $[\text{Pd}(\text{PP})(\text{olefin})]$, is formed.

Acknowledgment. This work has been supported by Korea Science & Engineering Foundation and Basic Science Research Institute Program, Ministry of Education, Korea.

References

- (a) Dargo, R. S. *Coord. Chem. Rev.* **1992**, *117*, 185. (b) Akhrem, I. S.; Volpin, M. E. *Russ. Chem. Rev.* **1990**, *59*, 1906. (c) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1990.
- (a) Nogradi, M. *Stereoselective Synthesis*; VCH: New York, 1986. (b) Pignolet, L. H. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum Press: New York, 1983.
- (a) Drent, E. *Pure & Appl. Chem.* **1990**, *62*, 661. (b) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidation of Organic Compounds*; Academic: New York, 1981.
- Plesincar, B. *Oxidation in Organic Chemistry*; Trahanovsky, W. S. ed.; Academic: New York, 1979.
- Sacaki, S.; Maruta, K.; Ohkubo, K. *Inorg. Chem.* **1981**, *20*, 1374.
- (a) Appleton, T. G.; Bennet, M. A.; Tomkins, I. B. *J. Chem. Soc. Dalton.* **1976**, 439. (b) Stern, E. W.; Maple, P. K. *J. Catal.* **1972**, *27*, 134. (c) Cooper, S. J.; Brown, M. P.; Puddephatt, R. J. *Inorg. Chem.* **1981**, *20*, 1374.
- (a) Park, Y. C.; Cho, Y. J. *Bull. Kor. Chem. Soc.* **1989**, *10*, 220. (b) Park, Y. C.; Kim, K. C.; Cho, Y. J. *J. Kor. Chem. Soc.* **1992**, *36*, 5, 685. (c) Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 2267. (d) Muir, L. M.; Gossel, M. C.; Brown, M. P. *J. Chem. Soc. Dalton.* **1986**, 1955.
- Kirss, R. U.; Eisenberg, R. *Inorg. Chem.* **1989**, *28*, 3372.
- Puddephatt, R. J. *J. Chem. Soc. Rev.* **1983**, *12*, 99.
- Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432.
- Wilkinson, G.; Gillard, R. D.; McCleverty, J. A. *Comprehensive Coordination Chemistry*; Pergamon Vol. 5, 1987.
- (a) Zanarado, A.; Pinna, F.; Michelin, R. A.; Strukul, G. *Inorg. Chem.* **1988**, *27*, 1966. (b) Gosling, R.; Tobe, M. L. *Inorg. Chem.* **1983**, *22*, 1235. (c) Eisenstein, O.; Hoffmann, R. J. *Amer. Chem. Soc.* **1981**, *103*, 4308.

Passive Films on Chromium Studied by Three-parameter Ellipsometry

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Received September 30, 1994

Passive films formed on chromium surface in citrate buffer solution were investigated by means of three-parameter ellipsometry. The citrate buffer was found to be a suitable medium in which oxide film on chromium could be removed by cathodic treatment, providing a reference surface for the optical study. The passive film effectively protecting the chromium surface from corrosion was found to have thicknesses in the range 0.65 to 1.25 nm depending on the potential in the range of -0.20 to 0.60 V (0.1 M KCl calomel electrode). The complex refractive index of the passive film did not show significant potential-dependent changes, indicating that the composition of the film material does not depend on potential.

Introduction

Chromium is an extremely corrosion resistant metal due

to its passivating property. The corrosion resistance of many chromium containing alloys including the stainless steel is due to the chromium content in the surface region. However, studies on the passivating film on the chromium surface have not been very extensive. Ellipsometry,¹⁻³ Auger spectroscopy,²

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