

Modification of Palladium (II) Catalysis for Selective Partial Oxidation of Alcohols with Multifunctional Pyridylsiloxane Ligands

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Introduction

Aerobic catalytic oxidation is much more environmentally friendly than oxidation using stoichiometric oxidants. The Pd(OAc)₂/pyridine system is active for the catalytic oxidation of primary and secondary alcohols to aldehydes and ketones, which are valuable for fine chemicals synthesis.¹ Pyridine stabilizes the monomeric Pd⁰ complex and promotes its aerobic reoxidation to Pd⁺² prior to the formation of Pd-Pd bonds.² Recently, a silica-supported Pd-bipyridyl complex was reported to be active for this catalytic process, and could be recycled several times.³

We have examined the use of bis(pyridyl)siloxane oligomers (Fig. 1) as ligands for Pd(OAc)₂. The presence of two pyridyl groups in the same molecule should increase the coordination strength of the ligand and, thus, the stability of the catalyst against formation of Pd particles. The siloxane backbone can be easily prepared with profunctional Si-H groups that can be converted quantitatively into silanol groups, enabling direct condensation of the bis-pyridyl oligomer into the silica structure. Since the pyridyl ligands prefer *trans* coordination in the square planar Pd complex, we hypothesize that the structure of the coordination complex depends strongly on the separation between the pyridyl groups. Here we report the synthesis and characterization of these bis(pyridyl)siloxane ligands, and their effect on the catalytic activities of Pd(OAc)₂ complex in the selective partial oxidation of benzyl alcohol.

Materials and Methods

The monomer (3-pyridyl)dimethylsilanol was prepared by metal-halogen exchange of 3-bromopyridine with *i*-PrMgCl, nucleophilic substitution with (CH₃)₂SiHCl, and catalytic oxidation of hydrosilane with H₂O over Pd(OH)₂/C. Higher oligomers were formed by a modified step growth process of Uchida et al. employing R(CH₃)SiHCl.^{4,5} Isolated yields for these transformations ranged from 70 to 95%.

Kinetics studies were performed under 1 atm of O₂ at 80 °C. Benzyl alcohol (1 mmol) dissolved in 1 mL of toluene was added quickly to a stirred solution of Pd(OAc)₂ (0.05 mmol), pyridylsiloxane ligand (0.2 meq pyridine), and molecular sieve 3A (0.5 g) in toluene (9 mL). The conversion of benzyl alcohol and formation of benzaldehyde were quantified by *ex situ* ¹H NMR analysis (10% in CDCl₃, 25 °C) at regular intervals.

Results and Discussion

Bis(pyridyl)siloxanes of the formula shown in Fig. 1 were synthesized for n = 0, 1, 2, and 3. When these ligands were added to a toluene solution of Pd(OAc)₂, binding of Pd was accompanied by new Si-CH₃ peaks in ¹H NMR. These peaks were assigned to various

coordination modes (linear, cyclic, etc.) based on the observed peak integrals. For comparison, a monofunctional (3-pyridyl)pentamethyldisiloxane ligand was also synthesized.

These Pd siloxane complexes were active in the oxidation of benzyl alcohol. The conversion data could be modeled using first-order kinetics up to about 70% conversion, beyond which noticeable deviations were observed, possibly due to product inhibition.² The first order rate constant for the monofunctional disiloxane-Pd(OAc)₂ complex decreased rapidly when the py: Pd ratio increased from 2 to 4 (Fig. 2). At py/Pd = 4, its rate constant was 0.020 min⁻¹, compared to 0.037 min⁻¹ when pyridine was used. The activities of the α,ω-bis(3-pyridyl)methylsiloxane Pd complexes were similar for n = 0, 1, and 2. These complexes were somewhat less active and the activity dependence on the py: Pd ratio was much less pronounced than the monofunctional ligand (Fig. 2). These ligands were too short to form stable *trans* bidentate complexes. Instead, they formed monodentate complexes and coordination chains. Blocking of the axial coordination site of benzyl alcohol by the auxiliary pyridyl group in these

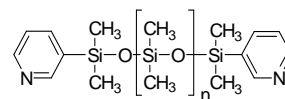


Figure 1. Structure of bis(pyridyl)siloxane ligands (n = 0, 1, 2, or 3).

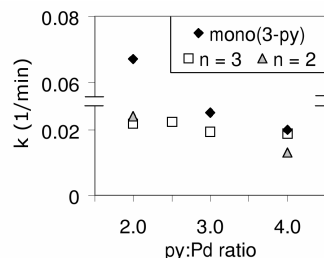


Figure 2. Effect of py: Pd ratio on rate constant for different bis(pyridyl)siloxane ligands.

ligands may be responsible for the reduced activity. In contrast, the ligand with n=3 can form the *trans*-bidentate complex. The activity of this complex was nearly independent of the py: Pd ratio. These results imply that cyclic coordination structures shield the active site against free pyridine molecules, which are responsible for suppressing catalytic activity.

Significance

We have demonstrated that Pd catalysts containing bis-pyridyl ligands exhibit a dramatically reduced dependence on ligand concentration than monopyridyl ligands due to their ability to form bidentate complexes. The bis-pyridyl ligands also could improve the stability of these catalysts. Since these ligands can be readily modified to react with silanols, they can be used to modify silica surfaces, act as anchoring points for Pd, and offer the possibility to form surface structures with optimal catalytic properties and with much better control than random functionalization can provide.

References

1. Nishimura, T., Onoue, T., Ohe, K., and Uemura, S., *Tetrahedron Lett.* 39, 6011 (1998).
2. Steinhoff, B. A., Guzei, I. A., and Stahl, S. S., *J. Am. Chem. Soc.* 126, 11268 (2004).
3. Karimi, B., Zamani, A., and Clark, J. H., *Organometallics* 24, 4695 (2005).
4. Uchida, H., Kabe, Y., Yoshino, K., Kawamata, A., Tsumuraya, T., Masamune, S., *J. Am. Chem. Soc.* 112, 7077 (1990).
5. Missaghi, M. N., Downing, C. M., Kung, M. C., and Kung, H. H., *Organometallics*, in press.