



# An air oxidizable bimetallic palladium(II) catalyst for asymmetric allylic oxidation of olefins in acetic acid

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**Abstract**—A bimetallic palladium(II) complex containing a triketone ligand and a bridging diphosphine ligand oxidizes olefins in acetic acid to allylic acetates by a direct air oxidation, which does not require intermediate redox systems. When the diphosphine is chiral, an asymmetric reaction occurs which gives enantioselectivities between 52 and 78% for cyclic olefins. © 2002 Elsevier Science Ltd. All rights reserved.

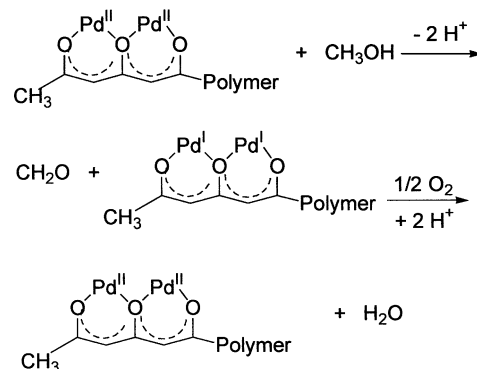
Industrially useful syntheses involving palladium(II) catalysis require that the process be a net air oxidation. Thus, the well-known Wacker process utilizes copper(II) chloride to reoxidize the Pd(0) formed back to Pd(II).<sup>1</sup> In turn, the copper(I) chloride that is formed, is oxidized to copper(II) chloride by molecular oxygen giving a net air oxidation. However, a serious problem in the use of this regeneration system in the oxidation of olefins in acetic acid to vinylic and allylic acetates is the fact that chloroacetates and diacetates become the main product.<sup>2</sup> Thus, a halide-free regeneration system is desirable for oxidation in acetic acid.

There are presently several systems available for the air oxidation of olefins in chloride-free acetic acid under mild reaction conditions (25°C and 1 atm O<sub>2</sub>). Two of these systems involve multistep electron transfer involving three redox systems. The first uses Pd(II)/Pd(0)–benzoquinone/hydroquinone–ML<sup>m</sup><sub>ox</sub>/ML<sup>m</sup> where ML<sup>m</sup> is an oxygen activating macrocyclic transition metal complex such as Co(salen).<sup>3</sup> The second reoxidation system uses the heteropoly acid H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·34H<sub>2</sub>O in place of the macrocyclic transition metal complex.<sup>4</sup> This latter system has the advantages over the previously employed metal macrocyclics of high stability, easy access to an active catalyst and simpler workup procedures. Only one type of system, palladium clusters in DMSO, involves direct oxidation of zerovalent palladium.<sup>5</sup> The present paper describes a bimetallic catalyst

for olefin oxidation, which is directly air oxidizable without the need for intermediate redox systems.

Previous papers describe the oxidation of organics by heterogeneous catalysts containing Pd(II) coordinated to surface triketone ligands attached to a polyphenylene polymer backbone.<sup>6</sup> These bimetallic surface species gave a net air oxidation with catalyst turnovers in the range of several hundred to more than a thousand. As shown in Scheme 1 using methanol oxidation as an example, the reason for this air oxidation capability is the fact the Pd(I)-dimer rather than Pd(0), is the reduced species. This Pd(I)-dimer is readily oxidized back to the Pd(II) dimer before Pd(0) can form.

Initial attempts to adapt this heterogeneous catalyst system to the oxidation of olefins in acetic acid produced complicated reaction mixtures containing both saturated and unsaturated esters.<sup>7</sup> However, bimetallic



**Scheme 1.** Oxidation of methanol by a bimetallic heterogeneous catalyst.

**Keywords:** palladium(II); olefins; air oxidation; allylic acetates; asymmetric; acetic acid; bimetallic.

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homogeneous catalysts **1** (Fig. 1) containing biphosphine bridging ligands such as 1,4-bis(diphenylphosphino)butane **1a**, gave only allylic and homoallylic esters. This result opened the possibility of an air oxidation system for allylic acetates. This bimetallic complex **1** is analogous to the catalysts previously employed for the asymmetric chlorohydrin synthesis.<sup>8</sup> Of course in the chlorohydrin synthesis the chelating bimetallic ligand was chiral as in **1b** or **1c**. Thus, the use of chiral bidentate ligands has promise for a synthesis of asymmetric allylic acetates which are useful reagents in natural product synthesis.

To test this new asymmetric synthesis, the oxidation of cyclic olefins was investigated in acetic acid at 25°C. These substrates have previously been studied using palladium(II) acetate at 60°C using benzoquinone–manganese dioxide as the reoxidation system.<sup>9</sup>

Initially the oxidation of cyclohexene was tested using the bimetallic catalyst **1a** containing a non-chiral bridging phosphine, 1,4-(diphenylphosphino)butane. It was found that the reaction proceeded catalytically under an oxygen atmosphere to give mainly 2-cyclohexenyl acetate with small amounts of 3-cyclohexenyl acetate. The catalysts turnovers were of the order of 50 and the yields of unsaturated acetates were >90% based on oxygen uptake. In some runs there was evidence of Pd(0) metal, but in these cases 90% of the initial catalyst could be recovered and used in another experiment. The precipitation of Pd(0) could be avoided by adding catalytic amounts of benzoquinone (1 mmol).

Next, the oxidation of cyclohexene was carried out using the chiral catalyst, **1b**. A reaction mixture containing 25 mL of acetic acid containing 0.12 mmol of catalyst **1b**, 0.7 M sodium acetate and 10 mmol of cyclohexene at 25°C placed under an atmosphere of pure oxygen. The oxygen uptake was measured by gas burets.<sup>10</sup> Over 5 days a total of 2 mmol of oxygen was consumed. A total of 3.8 mmol of 2-cyclohexenyl acetate was recovered which corresponds

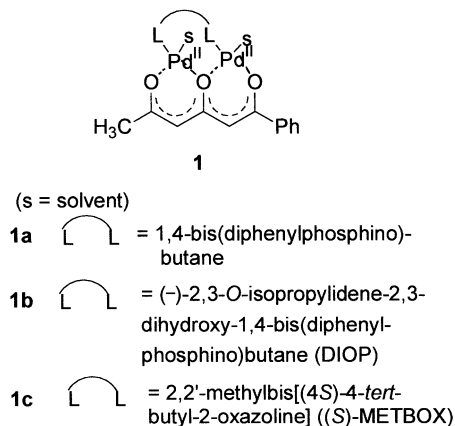


Figure 1. Structure of the bimetallic catalysts.

to a 95% yield assuming oxygen behaves as a four-electron oxidant. The reaction mixture also contains 2% 3-cyclohexenyl acetate. This yield represents a catalyst turnover of 30. At the conclusion of the run there was no evidence of Pd(0) metal. A pure sample of the allylic acetate was obtained by column chromatography. The % ee, which was determined by chiral Eu(hfc)<sub>3</sub>, was found to be 52%.

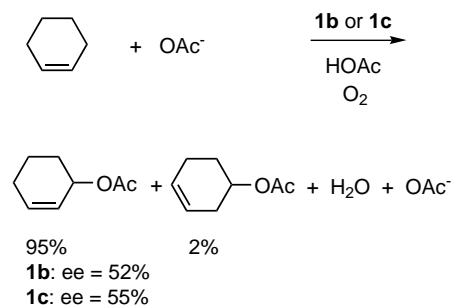
The oxidation of cyclohexene was also carried out with catalyst **1c** (0.12 mmol) under the same conditions as above, but the oxygen uptake was not measured. In 6 days 6 mmol of unsaturated acetates were formed for a catalyst turnover of 50. The yields based on unreacted cyclohexene were >90%. The % ee of the 2-cyclohexenyl acetate was 55%. The results are summarized in Scheme 2. It is noteworthy that the two catalysts gave almost the same ee even though one contained phosphine ligands and the nitrogen ligands.

Cyclopentene was also oxidized under the same conditions as cyclohexene using catalyst **1b**. A total of 100 mL (4.6 mmol) of oxygen was consumed in 4 days. A total of 8.3 mmol of 2-cyclopentenyl acetate was recovered which corresponds to a 92% yield based on oxygen uptake. A 2% of 3-cyclopentenyl acetate was also obtained. The % ee of a pure sample of 2-cyclopentenyl acetate, which was obtained by column chromatography, was 78%.

Cycloheptene was oxidized by catalyst **1c** (0.12 mol) under the same conditions, but the oxygen uptake was not measured. In 4 days a 70% conversion of the starting olefin to 2-cycloheptenyl acetate was achieved in 85% yield. No homoallylic acetate was observed. The % ee of the 2-cycloheptenyl acetate was 70%.

Finally, the oxidation of cyclooctene was attempted using catalyst **1c**. In the run the oxidation uptake was monitored by gas burets. In 5 days no oxygen uptake was observed and no acetated octenes were detected after workup of the reaction mixture.

The above results correspond well with the results obtained previously by the palladium(II) acetate–ben-



Scheme 2. Oxidation of cyclohexene by a bimetallic Pd(II) catalyst.

zoquinone–manganese dioxide reoxidation system.<sup>9</sup> The ease of oxidation was in the order: cyclopentene>cycloheptene>cyclohexene>cyclooctene. Although the oxidation of cyclooctene was observed in the prior study at 60°C, it was not observed under the milder conditions of the present study. Small amounts of the homoallylic acetates were also noticed in the previous study. The smallest quantities were observed with cycloheptene that no gave no homoallylic acetates in the present study.

This communication describes a catalytic bimetallic palladium(II) air oxidation system which is the simplest one proposed to date since it does not require an intermediate reoxidant and does not involve the oxidation of Pd(0). Only catalytic amounts of benzoquinone are added to prevent the precipitation of Pd(0) after many catalytic cycles.

This is made even more valuable because the catalyst can be chiral, and provided an asymmetric synthesis of allylic acetates. The initial results were very encouraging: the % ee ranged from 52% for cyclohexene to 78% for cyclopentene. Previous attempts at asymmetric allylic oxidation of cyclohexene using chiral Pd(II) catalysts gave ee's of less than 5%.<sup>11</sup>

Future work will concentrate on improving the optical yields, rates and catalyst turnover numbers.

#### Acknowledgements

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