



# Rapid, room temperature oxidation of alcohols and C-H bonds

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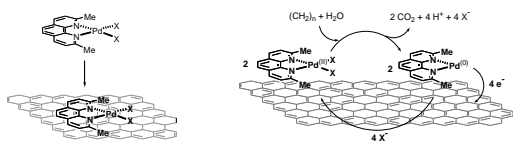


## Objective

Develop transition metal complexes for use as efficient catalysts in a low temperature, direct-hydrocarbon fuel cell.

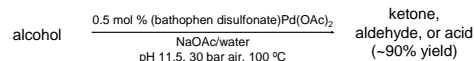
## Strategy

Synthesize homogeneous catalysts for the oxidation of hydrocarbons and other intermediates on the way to carbon dioxide. Adsorb or covalently attach catalysts on an electrode and demonstrate electrocatalytic activity.



## Pd catalysts for aerobic alcohol oxidation: a reasonable starting point

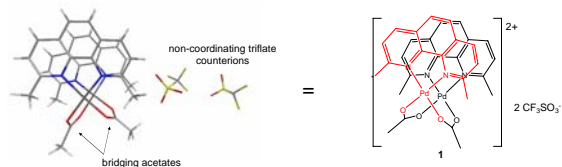
- Sheldon and coworkers have demonstrated that phenanthroline complexes of Pd(OAc)<sub>2</sub> will catalyze the aerobic oxidation of alcohols.



G.-J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, 287, 1636-1639.

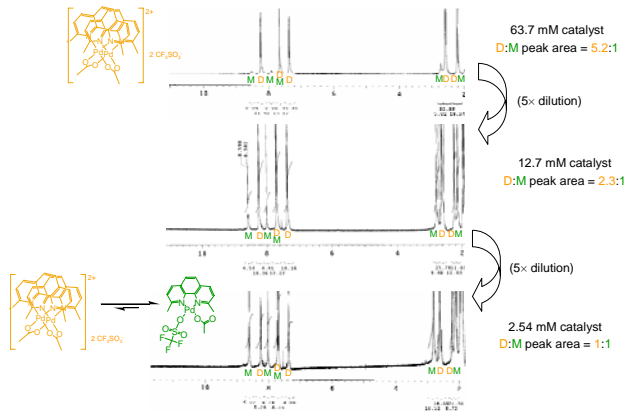
## Discovery of a new catalyst

- We have discovered a unique palladium coordination complex that oxidizes alcohols **at room temperature using air as the terminal oxidant**, with unprecedented initial turnover rates.

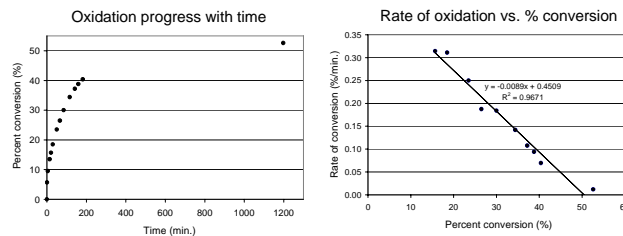
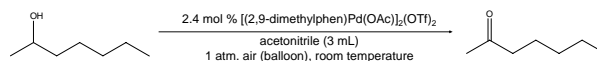


## Monomer-dimer equilibrium

- In solution, complex 1 exists in a **monomer-dimer** equilibrium. At high temperature and/or low concentration, the equilibrium shifts toward monomer. Below are <sup>1</sup>H NMR spectra of the catalyst at different concentrations.

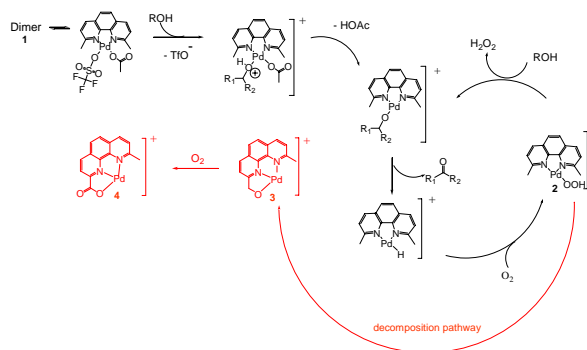


## Aerobic oxidation of 2-heptanol to 2-heptanone

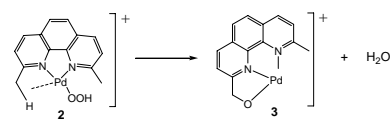


- Very fast initial turnover rates (>143 hr<sup>-1</sup>) are observed at room temperature using air as the terminal oxidant.
- After ~15 minutes, the rate of oxidation of 2-heptanol decreases *linearly* with percent conversion. Inactivation of the catalyst occurs before the reaction is complete.

## Proposed mechanism of aerobic alcohol oxidation



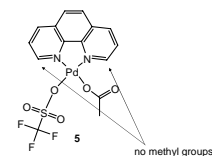
- Following aerobic alcohol oxidation, complex 4 was isolated from the reaction mixture and was determined to be the **catalyst decomposition product**.
- The palladium hydroperoxide species 2 is likely responsible for oxidation of the ligand by C-H activation as follows:



- Complexes 3 and 4 were also synthesized by adding H<sub>2</sub>O<sub>2</sub> directly to a solution of catalyst 1 in acetonitrile.
- When complex 3 was left in a solution exposed to air, the ligand was further oxidized to give 4.

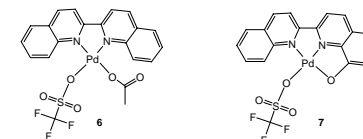
## Attempts to remedy ligand oxidation and preserve catalyst activity

- Since formation of complex 3 by oxidation of the methyl group was responsible for inactivation of the catalyst, complex 5—which contains the unsubstituted ligand—was synthesized.



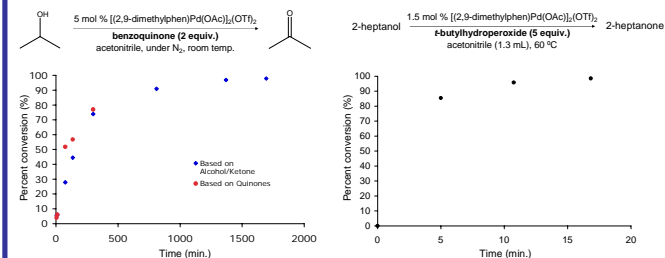
This complex showed no catalytic activity toward alcohol oxidation, indicating that the methyl groups play an important steric role in the catalysis.

- Complex 6, which has similar steric bulk to the catalytically active 3, but with no methyl groups, was also synthesized. When used as a catalyst in aerobic alcohol oxidation, 6 was oxidized almost immediately to the phenolate 7.



## Excluding O<sub>2</sub>: alternative oxidants

- To avoid ligand oxidation and concomitant catalyst inactivation, other oxidants were studied in the absence of molecular oxygen.



- Benzoquinone and *t*-butylhydroperoxide are both suitable oxidants for the reduced palladium catalyst under the conditions shown above.
- Our success with benzoquinone, an outer-sphere oxidant, suggests that **this oxidation could also be achieved electrochemically**.

## Methanol oxidation

- When catalyst 1 is placed in a DMSO/methanol solution, palladium black precipitates from the solution. This indicates oxidation of some other species, likely methanol.
- Complex 1 is a competent catalyst for the oxidation of methanol and formaldehyde in the presence of benzoquinone in acetonitrile-d<sub>3</sub>, implicating its potential as an anode catalyst in a methanol fuel cell.

## Future work

- Immobilize catalyst 1 on an electrode surface for use as an oxidation electrocatalyst.
- Synthesize complex 8 and test it as a catalyst for alcohol oxidation.

