



# Rapid, low temperature catalysts for the oxidation of organic molecules

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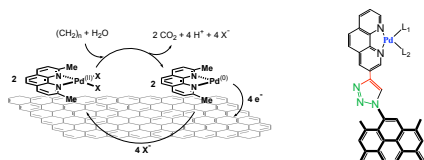


## Objective

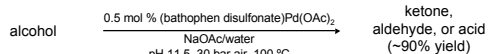
Our goal is to develop low-temperature molecular oxidation catalysts that can be supported on graphite electrodes as candidates for novel fuel cell catalysts. A specific objective was to identify molecular catalysts that can oxidize alcohols and other hydrocarbon fuels rapidly at low temperatures.

## Approach

Our approach involved: (1) the design of mononuclear palladium complexes containing labile coordination sites that can bind and activate alcohols toward oxidation, and (2) the development of methods to support these complexes on graphite electrodes either by absorption or covalent attachment of the catalyst to the graphite surface. Initial studies focused on aerobic oxidation in solution to illuminate the design criteria for generating active, low-temperature oxidation catalysts.



- Sheldon and coworkers demonstrated that phenanthroline complexes of Pd(OAc)<sub>2</sub> catalyze the aerobic oxidation of alcohols, but these catalysts were only active at high temperatures (100 °C) and 30 bars of air.

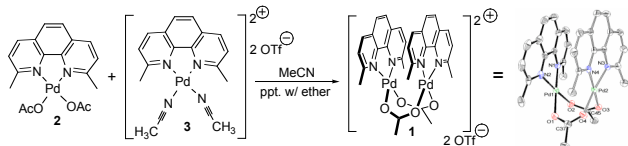


G.-J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **200**, 287, 1636-1639.

## Discovery of a new catalyst

- We discovered that a mono-cationic palladium complex containing a labile acetonitrile ligands served as a very active catalyst that oxidized alcohols **at room temperature using air as the terminal oxidant**, with a high initial turnover rate.

## Preparation of catalyst 1

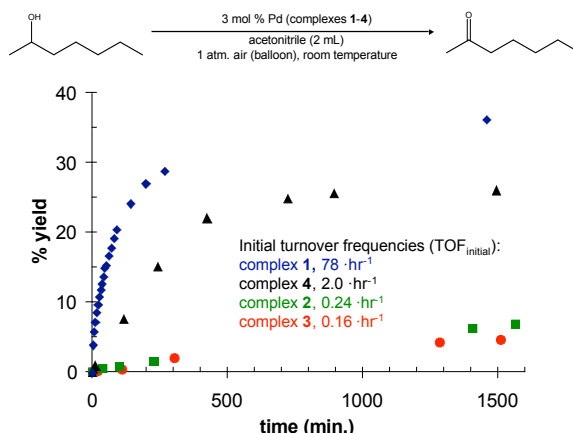


## Catalyst 1 monomer-dimer equilibrium



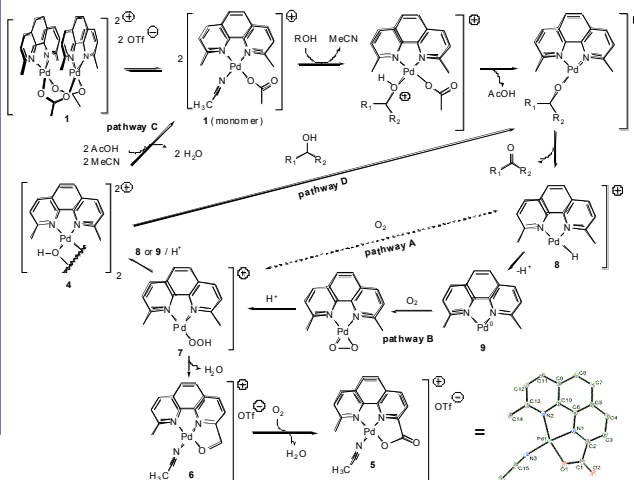
- Mechanistic studies reveal that in coordinating solvents, **1** exists in equilibrium with its solvate monomer.

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



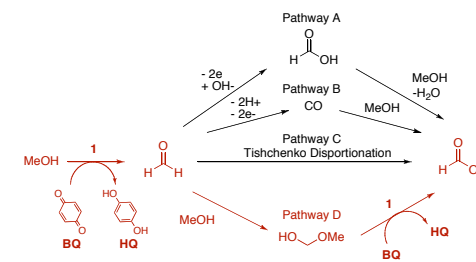
- For catalyst **1**, we observed high initial turnover rates (78 ·hr<sup>-1</sup>) at room temperature using air as the terminal oxidant.
- Catalyst **1** is much more active than catalysts **2-4**. Key feature: **1** contains both a labile coordination site and a coordinated acetate base.
- Despite fast initial rates, the turnover numbers are modest due to catalyst decomposition.
- Mechanistic studies revealed that catalyst decomposition was due to the generation of partially-reduced oxygen species (PROS) generated during the re-oxidation of palladium by the terminal oxidant O<sub>2</sub>.

## Proposed mechanism of aerobic alcohol oxidation



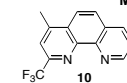
## Methanol oxidation

- Methanol is an attractive liquid fuel for fuel cells for mobile applications. Conventional Pt/Ru electrocatalysts are poisoned by CO, an intermediate generated during methanol oxidation by heterogeneous Pt or Pt/Ru catalysts.
- The use of more selective benzoquinone (**BQ**) oxidants enabled the quantitative oxidation of methanol to methyl formate at 50 °C with catalyst **1** without catalyst decomposition.
- Mechanistic studies revealed that methanol is oxidized to methyl formate by a mechanism which does not involve CO as an intermediate (path D). This implies that molecular catalysts can oxidize methanol without CO poisoning.



## Mechanistic Insights lead to improved catalysts

- Mechanistic studies revealed that catalyst decomposition was due to oxidation of methyl groups of the dimethyl phenanthroline ligand (**7**→**5**).
- A novel synthetic route was devised to a monotrifluoromethyl phenanthroline ligand, **10**. A palladium catalyst analogous to **1** bearing this ligand exhibited similar rates to **1** with twice the catalyst lifetime. Preliminary studies reveal that the ligand is not oxidized, implicating that higher turnover numbers can be obtained with these catalysts.
- The synthesis of this ligand provides a strategy for attachment to graphite electrodes to investigate the electrocatalytic behavior of the supported catalysts.



## Platinum dimers: A new approach to electro-oxidation catalysts

- Solution studies reveal that oxidation of the molecular catalysts is critical to achieving long lifetimes.
- Preliminary studies suggest that mononuclear catalysts oxidized inefficiently at electrode surfaces.
- We have recently generated binuclear Pt complexes that exhibit facile and reversible oxidation behavior at electrode surfaces.
- These complexes exhibit a variety of organic oxidation reactions, are stable in the acidic media typical of fuel cells, and retain their activity when supported on surfaces.
- Future studies will focus on the use of these complexes as dimeric analogues of successful methane oxidation catalysts such as **11**.

