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Direct Epoxidations Using Molecular Oxygen*

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Abstract:

This poster summarizes our findings during the study of a novel homogeneous epoxidation catalyst system that uses molecular oxygen as the oxidant, a “Holy Grail” in catalysis. While olefins (alkenes) that do not contain allylic hydrogens can be epoxidized directly using heterogeneous catalysts, most olefins cannot, and so a general, atom-efficient route is desired. While most of the work performed on this project has been on pincer complexes of late transition metals, we also scouted out metal/ligand combinations that were significantly different, and unfortunately, less successful. Most of the work reported here deals with phosphorus-ligated Pd hydrides [(PCP)Pd-H]. We have demonstrated that molecular oxygen gas can insert into the Pd-H bond, giving a structurally characterized Pd-OOH species. This species reacts with oxygen acceptors such as olefins to donate an oxygen atom, although in various levels of selectivity, and to generate a [(PCP)Pd-OH] molecule. We discovered that the active [(PCP)Pd-H] active catalyst can be regenerated by addition of either CO or hydrogen. The demonstration of each step of the catalytic cycle is quite significant. Extensions to the pincer-Pd chemistry by attaching a fluorinated tail to the pincer designed to be used in solvents with higher oxygen solubilities are also presented.

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