

# ALKENE EPOXIDATION CATALYZED BY DIOXIDOMOLYBDENUM(VI) COMPLEXES SUPPORTED BY MULTIDENTATE AMINOBISPHENOLATO LIGANDS: ON THEIR ACTIVITY AND REACTION MECHANISM

Pasi Salonen<sup>a,b</sup>, Jörg A. Schachner<sup>c</sup>, Anssi Peuronen<sup>a,b</sup>, Nadia C. Mösch-Zanetti<sup>c</sup>, Ari Lehtonen<sup>b</sup>

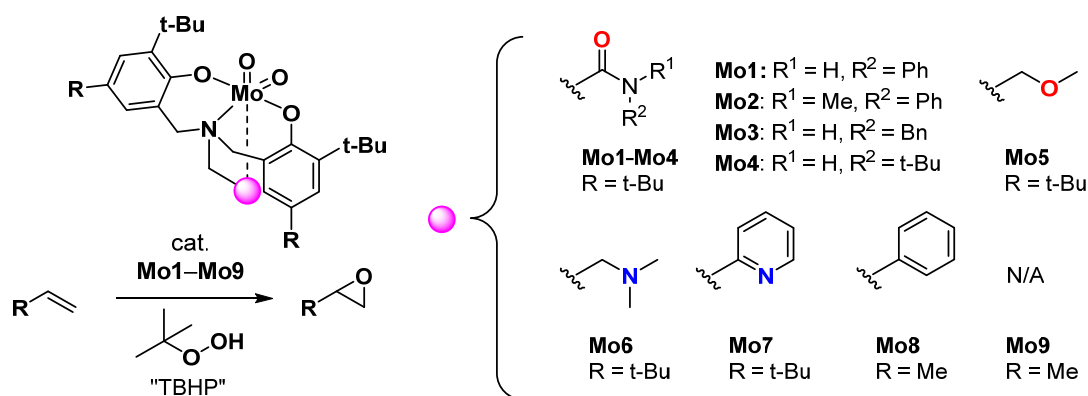
<sup>a</sup> University of Jyväskylä, Jyväskylä, Finland

<sup>b</sup> University of Turku, Turku, Finland

<sup>c</sup> University of Graz, Graz, Austria

Epoxides are versatile synthetic intermediates since they readily react with a variety of nucleophiles *via* ring opening and expansion reactions, yielding 1,2-difunctional compounds. Epoxides are most commonly obtained by alkene (ep)oxidation, which, in a laboratory setting, is often performed using peracids as stoichiometric oxidants. Industrially, molybdenum catalyzed alkene epoxidation is used instead. For example, in the industrial Halcon/ARCO hydroperoxide process, propene is epoxidized into propylene oxide in the presence of [Mo(CO)<sub>6</sub>] pre-catalyst and various organic hydroperoxides such as *tert*-butyl hydroperoxide (TBHP). Regardless of industrial adoption of Mo as the catalyst in alkene epoxidation, the precise mechanism(s) of epoxidation remain debated. Consequently, there is still academic interest in the matter.

Recently, we have engaged in studying the alkene epoxidation mechanism using various dioxidomolybdenum(VI) complexes supported by multidentate aminophenolato type ligands as pre-catalysts.[1,2] In the presented study, nine structurally diverse aminobisphenolato dioxidomolybdenum(VI) complexes (**Mo1–Mo9**, Scheme 1) were assessed in the epoxidation of various alkene substrates.[1] Experimental investigations reveal that all complexes are approx. one to two orders of magnitude more active in epoxidation catalysis than what is typically reported for structurally related complexes. A possible epoxidation mechanism invoking a partial ligand (pendant arm) dissociation from the Mo center prior to activation of the pre-catalysts by TBHP is suggested based on experimentally observed structure-activity relationships, as well as DFT calculations.



**Scheme 1.** Structures of various dioxidomolybdenum(VI) complexes **Mo1–Mo9** supported by tri- and tetradentate aminobisphenolato ligands used as epoxidation pre-catalysts. All coordinating atoms in the ligand pendant arm are colored. Bn = benzyl.

[1] P. Salonen, J.A. Schachner, A. Peuronen, M. Lahtinen, F. Belaj, N.C. Mösch-Zanetti, A. Lehtonen, *Mol. Catal.*, 540, 2023, 113034.

[2] N. Zwettler, J.A. Schachner, F. Belaj, N.C. Mösch-Zanetti, *Mol. Catal.*, 443, 2017, 209–219.