FROM MECHANISM TO MATERIALS: TRANSLATING BISPIDINE-Cu TOSYLIMIDO CATALYSIS ONTO EPOXYACTIVATED AGAROSE BEADS

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Copper tosylimido complexes are highly reactive species and known as active intermediates in copper-catalyzed C–H amination and aziridination.[1,2] In this study, we investigated the reaction mechanism of a secondary-amine-containing bispidine-based copper complex in the selective aziridination of styrene, using [N-(p-toluenesulfonyl)imino]phenyliodinane as oxidant.[3] Our results demonstrate that product formation is accelerated by reversible deprotonation at the ligand throughout the catalytic cycle. Additionally, comparison of two complexes with pentadentate ligands containing secondary amines and two complexes with tertiary methyl-amine ligands revealed that placing the secondary amine trans to the nitrene group is crucial for increasing turnover frequency.[4]

To translate these insights into heterogeneous catalysis, we pursued immobilization of the copper–bispidine system on epoxy-functionalized agarose beads using a panel of nucleophilic linkers to covalently anchor the bispidine-based copper tosylimido catalyst at the bead surface. Although a range of linkers and functional groups was tested for covalent immobilization under standard epoxide-opening conditions, loading, loading rates, and catalytic yields were essentially unchanged. Together with spectroscopy and wash-out controls, this points to a mechanism dominated by noncovalent inclusion in the agarose pore network rather than true covalent immobilization. No leaching was detected over repeated washing and reaction cycles, and styrene aziridination proceeded with reproducible ~20% yields, consistent with mass-transport limitation as the dominant bottleneck rather than intrinsic catalytic inactivity.

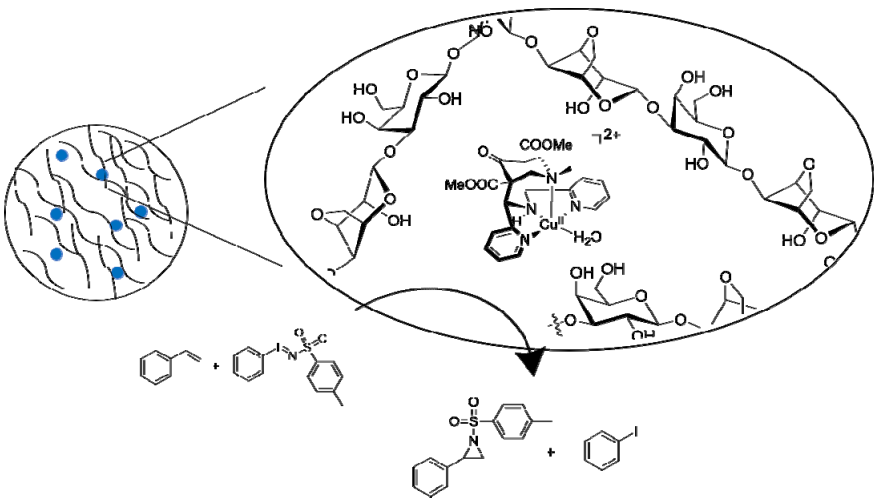

Figure 1: Schematic representation of the non-covalent immobilization of the copper complex within agarose pores.

[1] R.T. Gephart, T.H. Warren, Organometallics, 2012, 31, 7728–7752.

[2] H.J. Dequina, C.L. Jones, J.M. Schomaker, Chem, 2023, 9, 1658–1701.

[3] K. Bleher, P. Comba, M. Gast, S. Kronenberger, T. Josephy, Inorganica Chim. Acta, 2022, 532, 120752.

[4] T. Josephy, M. Heiduk, T. Saxl, K. Bleher, Inorganica Chim. Acta, 2025, 122587.