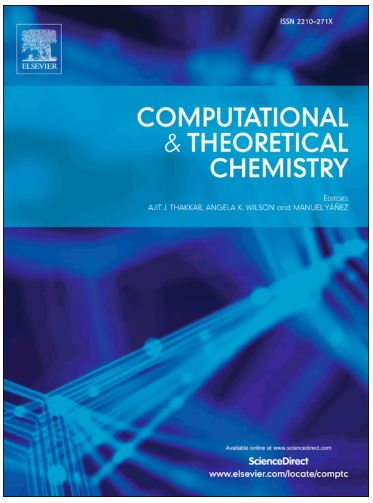

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Mechanistic Insights into the Chemoselectivity of $PtCl_n$ (n = 2, 4)-Catalyzed O–H Insertion and Cyclopropanation Compared to Rh- and Cu-Catalyzed Reactions

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ABSTRACT: Allyl alcohol could provide an interesting model for chemocontrol in transition metal-catalyzed insertion of carbenoid into O−H bond and olefin cyclopropanation. The chemoselectivity of $PtCl_2$- and $PtCl_4$-catalyzed (compared to Rh and Cu) reactions between methyl α-diazophenylacetate and unsaturated allyl alcohol has been carried out by DFT calculations. The potential energy profiles confirm that the intermediate free enol formed by intramolecular proton transfer is more favorable compared to the formation of the free ylide and cyclopropanation. The [1,3]-proton shift of the enol readily provides the final O−H insertion product, which has a barrier of 4.5 and 6.9 kcal/mol using metal-assisted two-allyl-alcohol clusters as a proton shuttle. Calculations provide a good explanation for the O−H insertion vs cyclopropanation of platinum, copper and rhodium catalysts have been used in these reactions. This study is expected to improve the understanding of platinum-catalyzed reactions for the C−X bond construction and provide guidance for the future design of new catalysts and new reactions.

Keywords: platinum, O−H insertion, cyclopropanation, chemoselectivity, enol

I. Introduction