Mechanistic Investigations
of
Transition Metal Catalyzed Reactions

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Abstract

Transition metal catalyzed reactions have had a large impact on the human progress for the last century. Several extremely important areas, such as the agricultural industry and the plastic industry, have benefited from this development. The evolution of different transition metal catalysts has also been very important for the pharmaceutical industry. One vital factor when developing new and more effective catalysts is to obtain mechanistic insights. In this thesis, several different methods to investigate mechanisms for transition metal catalyzed reactions are presented.

The factors controlling regioselectivity for a palladium catalyzed allylic alkylation has been studied. Pre-formed (η^3-allyl)Pd complexes were used to minimize dynamic processes. In the study it was found that the regioselectivity depends mainly on steric interactions, rather than electronic effects. For complexes with less steric hindrance, the *trans* effect controlls the selectivity. Furthermore, the mechanism for a sulfinyl nucleophile, employed in the same type of reaction, has been studied and the mode of attack has been revealed. The importance of a fast Pd catalyzed Mislow-Braverman-Evans rearrangement to ensure that the correct product was formed, was also disclosed.

The important Mizoroki-Heck reaction has been investigated in two different studies. The first study revealed the mechanistic pathway for a Pd(II) catalyzed domino Mizoroki-Heck-Suzuki diarylation reaction. The dependence of benzoquinone as the re-oxidant, in order to achieve the diarylation product, was explained by its ability to coordinate to the palladium moiety, thereby allowing access to a new low-energy pathway to the product. In the second study, a new and mild nickel catalyzed variant of the Mizoroki-Heck reaction was presented and the mechanistic pathway for the reaction was introduced. In addition to this, the reasons for several unsuccessful conditions and additives were uncovered.

The development of new, environmentally more benign, catalysts for cross coupling reactions is important. Iron is one of the most promising metals for this purpose, but the mechanistic knowledge of this reaction is still not comprehensive. In this thesis, several mechanistic and computational studies reveal new insights into this reaction, paving the way to develop new and more effective catalysts and conditions for the reaction.

Keywords: alkene insertion, allylic alkylation, catalysis, cross coupling, density functional theory, free energy surface, iron, kinetic investigation, Mizoroki-Heck reaction, nickel, palladium reaction mechanism, sulfinylation, transition metal.

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