

Chapter 12

Summary

In the chemical industry, the use of environmentally friendly processes is of great importance. The combination of fundamental and applied research is useful for the development of these processes. The fundamental research presented in this thesis, is part of a combined industrial-academic effort for cleaning-up an existing industrial process.

Besides the general introduction (chapter 1), the thesis consist of 3 parts. Part 1 (chapters 2-9) deals with the palladium catalyzed allylic alkylation, part 2 (chapter 10) deals with the palladium catalyzed carbonylation of allylic substrates and in the third part (chapter 11) the use of rhodium instead of palladium in these reactions is explored.

The industrial process of DSM to which our research is related, the carbonylation of dienes, involves palladium-allyl intermediates. To study the formation of side products resulting from nucleophilic attack, we used the allylic alkylation as a model reaction. Because of a special interest in the origin of the formation of regio-isomers of the side products, we focused on the topic of regioselectivity. First, we studied the structure of the Pd-allyl bond in detail by DFT calculations (chapter 3) and by X-ray crystal structures (chapter 7). Via stoichiometric and catalytic alkylation reactions we found a relation between the structure of the Pd-allyl bond and the regioselectivity. We succeeded in exploring the limits of the validity of the existing mechanistic theories. To explain the results, we developed a new model for the origin of the regioselectivity (chapter 9) (figure 1). Two reaction paths may be followed, leading to the opposite regio-isomer. In the first phase of the reaction, the electronically favored path leads to the branched product, whereas in the second phase, the sterically favored path leads to the branched product. We have determined a number of parameters influencing the rate and the regioselectivity of the reaction.

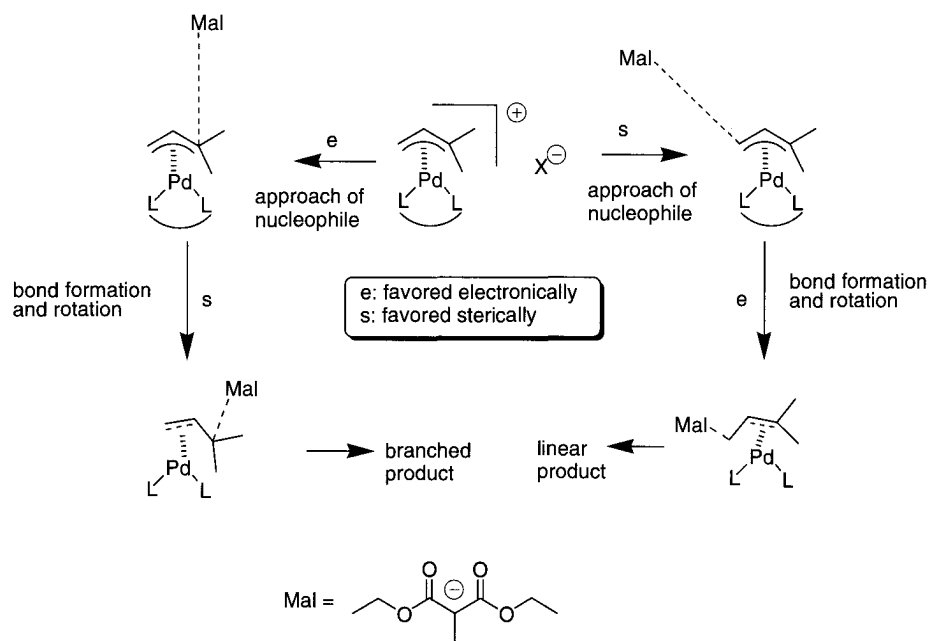


Figure 1: Proposed origin of the regioselectivity in the palladium catalyzed allylic alkylation.

For the industrial process under study by DSM, the catalytic reaction of the palladium-allyl complexes with CO and alcohol to form β - γ -unsaturated esters is highly important. We investigated the mechanism of the interaction of Pd(allyl) complexes with CO and found that two pathways are possible for the formation of the ester product (chapter 10). At high pressure, the well known migratory-insertion reaction leads to the formation of an acyl complex, which reacts with an alcohol to form the corresponding ester. In addition, we found a pathway involving the direct attack of methanoate to the coordinated CO to form an intermediate carbomethoxy species (figure 2). Reductive elimination of the carbomethoxy group and the η^3 -allyl leads to the formation of the ester product. Our results show that neither the insertion reaction nor the last step of the ester formation per se are slow, the overall low rate observed is due to relatively stable η^3 -intermediates.

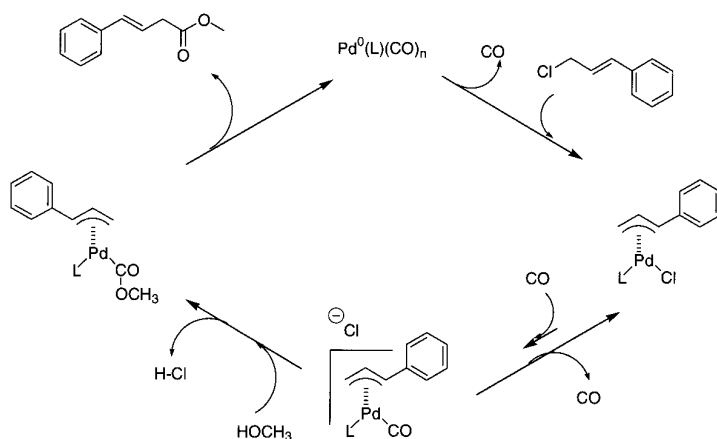


Figure 2: Proposed associative (carbomethoxy) pathway for the carbonylation of Pd(η^3 -allyl) complexes.

Finally, we conducted an exploratory study concerning the use of rhodium for the allylic alkylation and carbonylation reaction (chapter 11). To this end, a novel series of (diphosphine)-Rh(allyl)Cl₂ complexes has been prepared and studied in detail. It was found that depending on the ligand and the substitution pattern of the allyl, the hapticity of the Rh-allyl bond is either η^1 , η^1 - η^2 or η^3 . The Rh(allyl) complexes were tested in the allylic alkylation and in the reaction with CO. Although in literature the S_N2' nucleophilic attack on the η^1 -allyl moiety is the commonly accepted mechanism, we found that attack on complexes with other hapticities also takes place. As an additional novel mechanism for the rhodium catalyzed allylic alkylation, we proposed the direct nucleophilic attack on the η^1 - η^2 - or η^3 -allyl. Concerning the reaction of Rh(allyl) complexes with CO, we showed that at elevated pressures, migratory-insertion occurs to form the corresponding acyl complexes, thus forming a possible key intermediate in the rhodium catalyzed alkoxy-carbonylation.