

Part 4: Conclusions and recommendations

Chapter 7: Conclusion and recommendations

Alkene metathesis is a powerful synthesis tool. The exchange of parts of two alkenes is achieved by catalysis through the breaking and rearranging of the carbon-carbon double bonds. A generally approved mechanism for alkene metathesis was proposed by Chauvin appointing metal carbenes as catalysts. The four main types of metal carbenes tested for metathesis activity are: Fischer- and Tebbe-type metal carbenes with low metathesis activity and the highly active Schrock- and Grubbs-type metal carbenes, based on tungsten, rhenium, molybdenum or ruthenium.

The results of a previous investigation [1] indicated that for the formation of metathesis products the LUMO orbital must be concentrated on the metal. It was also shown that the lower the energy of the LUMO orbital, the more favourable the formation of the alkene-catalyst bond. The hypothesis was formulated that for metal carbenes to show alkene metathesis activity, the LUMO orbital must be centred on the metal atom and the metal atom must have a positive atomic charge. The proposed general activity of alkene metathesis catalysts that increases from Fischer to Tebbe and then to Grubbs and Schrock was strongly supported by the formulated lowest-LUMO-energy hypothesis.

Therefore, in this study a molecular modelling investigation into the mechanism and products of the alkene metathesis reaction is continued by deeper investigation of the possibility of the frontier molecular orbital theory to be used as chemical reactivity indicator. Fischer- Tebbe- Grubbs- and Schrock-type metal carbenes are investigated in this regard.

The general activity trend of the four main metal carbenes to linear alkenes was used as a starting point. Building on prior knowledge, the frontier molecular orbital theory was used to gain further understanding in the activation step of the four types of metal carbenes and also four different types of ruthenium metal carbenes to investigate the effect of the ligands. The atomic orbital coefficients of each molecular orbital were calculated better to pin point the site of overlap and understand the contribution of

each atom to the LUMO. The objective to investigate the activity according to the catalyst activation step was thus successfully achieved in the study. By calculating the frontier orbital interaction in the initiation and activation step, the different activity of the metal carbene catalyst could be predicted and explained. The location and contribution of the atomic orbitals to the LUMO of the metal carbenes further elucidated the site of primary overlap.

To test the predictability and reliability of the frontier orbitals for chemical reactivity, experimental literature reactions of all the catalyst were calculated. The aim was to see if the yield, product distribution and difference in activity could be sufficiently explained by orbital interactions. In addition the natural population analysis (NPA) was also calculated to support the site of overlap in subsequent investigations. The objective to investigate the significance of the molecular orbital coefficients and natural population analysis in metathesis mechanism of homogeneous catalysed reactions was thus successfully achieved in the study. The location and size of the atomic orbital coefficients as well as the NPA charge support the formation of metathesis products.

From the literature we see that the four main types of metal carbenes all have different metal centres showing varying activities for alkene metathesis. This led to the question of what effect the metal has in the Gr2 framework. Can we modify the activity of the Gr2-type catalyst by simply changing the metal atom to a different transition metal? By screening all the transition metals as substitutes for ruthenium we calculated and compared the electronic properties of catalysts. The objective to investigate the effect of the metal was thus successfully achieved in the study. By exchanging ruthenium with all selected transition metals, it was found that only specific metals, including chromium, cobalt, rhodium, rhenium, osmium and iridium complied with the criteria defined for possible metathesis activity.

Subsequently, from the screening of the transition metals, rhenium and osmium were selected as possible metals for exchange with ruthenium in the Gr2 catalyst. Both

substituted catalysts were used for comparison to Gr2 by calculation of an alkene metathesis reaction known for Gr2. The reaction steps, from the activation of the catalyst to the formation of the metallacyclobutane, were calculated and the results compared. The objective to substitute the chosen metals in the Grubbs catalyst framework for designing new catalysts, was thus successfully achieved in the study. Both osmium and rhenium showed good potential with a bonding scheme and reaction energy profile similar to Gr2.

Alkene metathesis still has a long way to go before implementation of homogenous catalysis will be done on a large scale in industry. The way forward should start with looking back to what worked and what did not work and why. More investigations of key steps need to be done, before the development of new catalysts will yield truly useful results. Small steps do contribute, but we need to start thinking of more than just changing ligands.

By comparing different metal carbenes, this study proved the capability of using the frontier molecular orbital theory as a chemical reactivity indicator. Further studies on more complete reaction cycles and different reactions need to be done for additional verification, but a new computational route to better investigate the metathesis activity has been opened.

7.1 Recommendations

a) Further investigations of the Schrock catalyst system.

Schrock-type metal carbenes are highly active metal carbene catalysts. Results gained from this study show the calculated reaction energy profile to have a coordination energy barrier of 408 kcal/mol. For a reaction that runs at room temperature to completion in under two hours, the coordination energy barrier should be considerably lower. After coordination of the alkene the profile seems viable, only the initial approach of the alkene in the complete system leads to the high energy barrier. Using a different modelling approach, i.e. molecular simulation, may also lead to further insights.

b) Calculations including the solvent effect.

All calculations in this study have been done without considering the effect of the solvent. Including the solvent effect in the energy calculations should be the next step to further elucidate the complete electronic properties of the precatalyst and active catalyst species in the reaction mixture.

c) Complete catalytic cycle to test further the predictive quality of the atomic orbital coefficients of the bonding molecular orbitals.

In this study the alkene metathesis mechanism have only been investigated up to the formation of the metallacyclobutane intermediate. Moreover, it was found that the atomic orbital coefficients could be successfully used to predict the products of the reaction. However, only when the whole catalytic cycle can be successfully predicted by the atomic orbital coefficients, will effective catalyst design via the FMO theory be possible.

d) Experimental testing of the modified second generation Grubbs catalyst framework with Os and Re as substituted transition metals.

7.2 References

- [1] J.I. Du Toit, A modelling investigation into the mechanism of the homogeneous alkene metathesis reaction, NWU (Potchefstroom), (M.Sc. – dissertation), 2009. URL: <http://hdl.handle.net/10394/4408>.