

Part 1: Introduction

Chapter 1: Introduction and objectives

1.1 Literature background

In alkene metathesis alkenes are converted to different alkenes in a catalysed reaction in which the alkylidene moieties interchange [1],[2]. In 1970 Herrison and Chauvin proposed a metal carbene catalysed mechanism [3],[4] for alkene metathesis. The general mechanism is shown in Fig. 1.

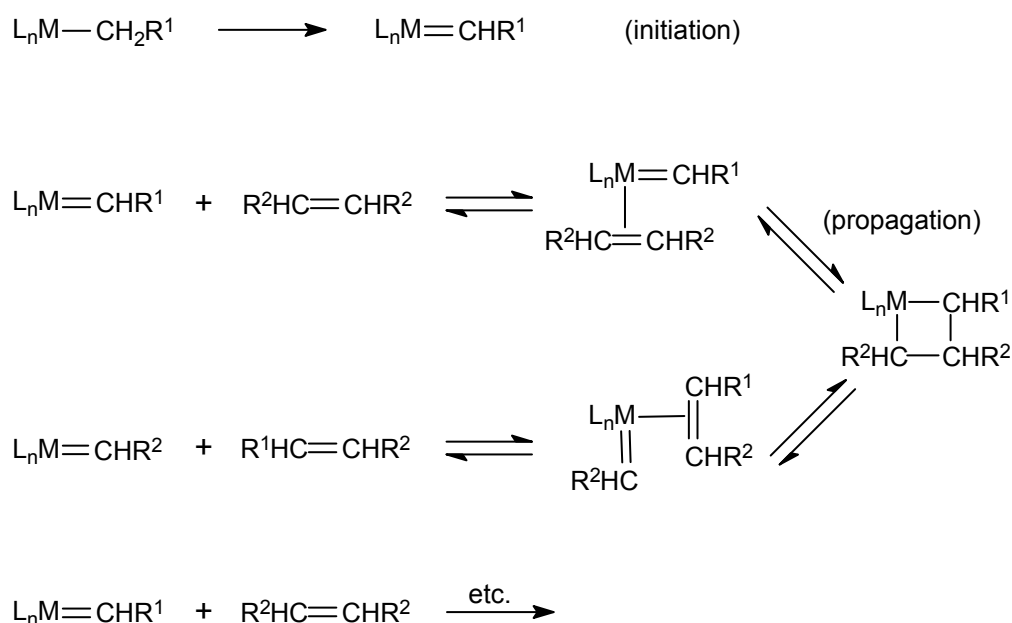


Fig. 1. Chauvin's metal carbene mechanism [2].

The mechanism can either be associative or dissociative; the difference being the dissociation of a ligand to form an open coordination site in the case of the dissociative mechanism. Furthermore, cyclopropane forms as the major side product with some of the catalysts. Since the proposal of Chauvin's metal carbene mechanism, the focus has been on finding a metal carbene that is active for homogeneous alkene metathesis. The first carbene that was tested was the Fischer-type metal carbenes [5],[6]. These metal carbenes [5], however, have low alkene metathesis reactivity. The discovery of the highly active Schrock- [7] and Grubbs-type [8] metal carbenes [2], based on tungsten, molybdenum or ruthenium [9], was the turning point in the development of active catalysts. From the literature the major metal carbenes can be

arranged according to a generalised trend for the metathesis reactivity for the self-metathesis of linear alkenes (Fig. 2.).

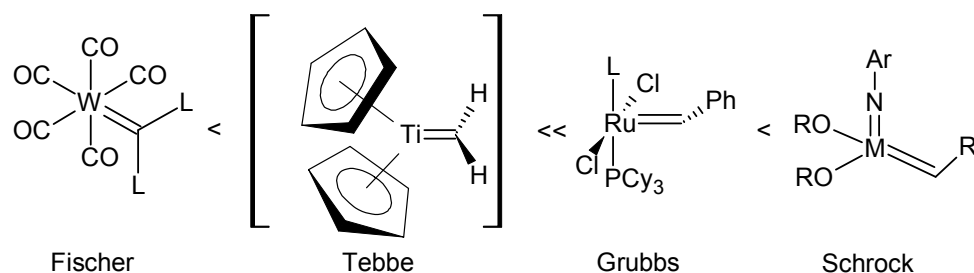


Fig. 2. Generalised trend for the metathesis reactivity for different metal carbenes.

The question now arises why the different metal carbenes display different alkene metathesis reactivity. Even if the general reaction mechanism scheme of the metathesis reaction are known, most of the important details like the rate-determining step, stereoselectivity, structure of the transition state and alkene-catalyst-complexes are not yet widely studied [10].

In a previous study [11] a molecular modelling investigation into the mechanism and products of the alkene metathesis reaction was done in an attempt to explain the general metathesis reactivity of metal carbene catalysts. Fischer- and Grubbs-type metal carbenes were investigated in this regard.

The results of the investigation indicated that for the formation of metathesis products the LUMO orbital must be concentrated on the metal. It was also clear 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 reactivity, the metal carbene must be a triplet carbene, the LUMO orbital must be centred on the metal atom and the metal atom must have a positive Mulliken charge. This was confirmed with Tebbe- and Schrock-type metal carbenes by additionally testing for these characteristics.

The proposed general reactivity trend of alkene metathesis catalysts that increases from Fischer to Tebbe and then to Grubbs and Schrock is strongly supported by the formulated lowest-LUMO-energy-hypothesis [11].

In this study we will investigate the suggested hypothesis further so that a model can be developed according to which new alkene metathesis catalysts can be designed through modelling. The method developed in a previous study [11] will be used as base for the modelling. This study can further play a significant role in the development of more active alkene metathesis catalysts.

1.2 Aim of the study

The aim of this study is to identify chemical reactivity indicators that predict alkene metathesis reactivity through a computational investigation of the alkene metathesis mechanism.

1.3 Objectives

Testing of the hypothesis model by

- a) doing a complete literature review of computational studies of metal carbenes used as metathesis catalysts;
- b) investigation into the activity according to the catalyst activation step;
- c) determining the significance of the molecular orbital coefficients and natural population analysis in metathesis mechanism of homogeneous catalysed reactions;
- d) investigation of the effect of the metal;
- e) substitution of chosen metals in the Grubbs catalyst framework for designing new catalysts.

1.4 Outline of thesis

The thesis is composed of five parts, namely: introduction, literature survey of alkene metathesis, computational modelling, conclusion and appendix. The chapters are presented in article format and cover the following aspects: a literature overview of computational studies in alkene metathesis, specifically pertaining to Fischer-, Tebbe-, Grubbs- and Schrock-type carbenes; frontier orbitals as chemical reactivity indicators; testing the frontier molecular orbital theory on experimental results; elucidating the effect of the metal by changing the ruthenium in the second generation Grubbs precatalyst framework and subsequently comparing the results of the two selected metals with the computational reaction of the ruthenium catalyst.

1.5 Methodology of the study

The main focus of the study is to determine the factor(s) that contribute to the reactivity of metal carbenes as alkene metathesis catalysts. This information can then be utilized to develop new catalysts. Fig. 3 shows the methodological overview.

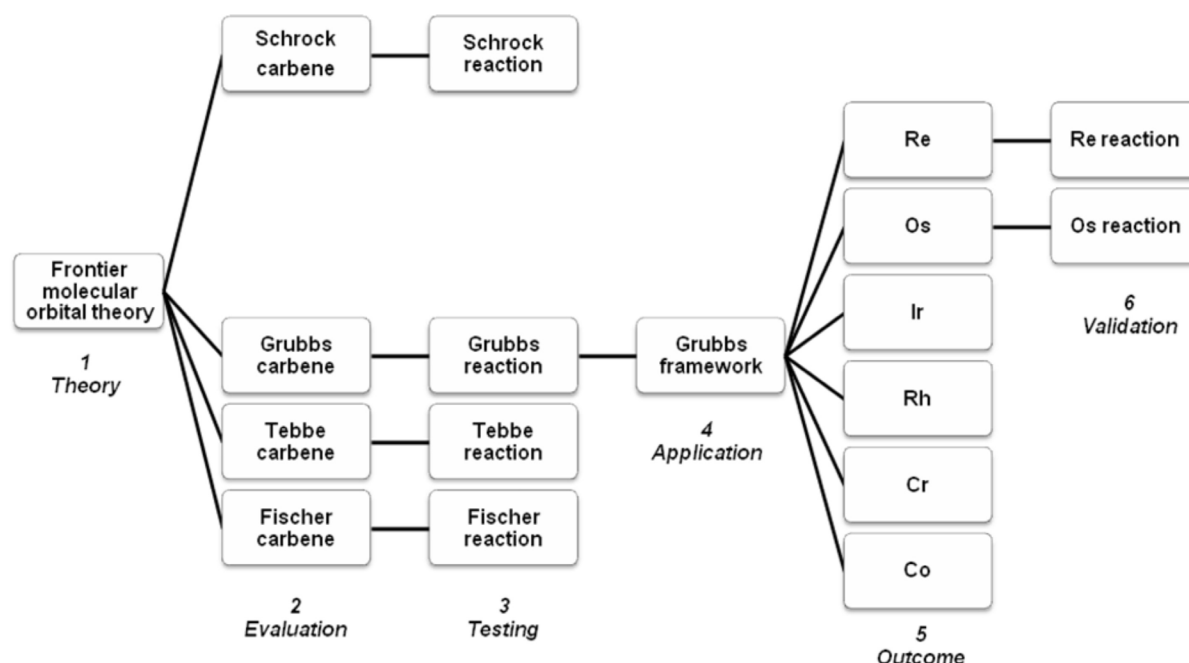


Fig. 3. Methodological overview of study.

The first step was to decide which theory to apply and use for alkene metathesis. The perturbation theory [12] describes the energy interaction between two molecules as the sum of the charge interaction and the frontier orbital interaction. The mechanism of alkene metathesis is a [2+2] cycloaddition type reaction. In cycloaddition reactions the reaction occurs because of the overlap of the frontier orbitals. Therefore, the frontier molecular orbital theory was selected. The next step was to evaluate the theory by calculating the electronic properties of the four major types of metal carbenes used as alkene metathesis catalysts. This was done to see whether we could predict via modelling calculations the generalised reactivity trend for linear alkenes. Thereafter, the theory was tested with known literature reactions [13-16] of the four metal carbene types. To apply the theory to develop new catalysts all the transition metals were substituted into the second-generation Grubbs precatalyst- and catalyst frameworks. The outcome of the investigation identified six possible transition metals which complied to the criteria for metathesis activity, as Ru does. The last step was validating the theory by recalculating the known literature reaction [15] of the ruthenium carbene with the two replacement metals, Re and Os, as substitutes in the precatalyst- and catalyst framework.

1.6 References

- [1] M.B. Smith, J. March, March's advanced organic chemistry, fifth ed. John Wiley & Sons Inc, New York, 2001.
- [2] P. Ahlberg, Development of the metathesis method in organic synthesis, Advanced information on the Nobel Prize in Chemistry 2005, http://nobelprize.org/nobel_prizes/chemistry/laureates/2005/chemadv05.pdf, Accessed 7 March 2008
- [3] K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreissl, U. Schubert, K. Weiss, Transition metal carbene complexes, Verlag Chemie GmbH, Weinheim, 1983.
- [4] K.J. Ivin, Olefin metathesis, Academic Press Inc, London, 1983.
- [5] R.H. Grubbs, Handbook of metathesis, vol 1. Wiley-VCH, Weinheim, 2003.
- [6] T.J. Katz, T.H. Ho, N.Y. Shih, Y.C. Ying, V.J. Stuart, J. Am. Chem. Soc. 106 (1984) 2659.

-
- [7] R.R. Schrock, J.S. Murdzek, G.C. Bazan, J. Robbins, M. DiMare, M. O'Regan, *J. Am. Chem. Soc.* 112 (1990) 3875.
- [8] S.T. Nguyen, L.K. Johnson, R.H. Grubbs, *J. Am. Chem. Soc.* 114 (1992) 3974.
- [9] V. Dragutan, I. Dragutan, A.T. Balaban, *Platinum Met. Rev.* 50 (2206) 35.
- [10] M.A. Tlenkopatchev, S. Fomine, *J. Organomet. Chem.* 630 (2001) 157.
- [11] 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>.
- [12] I. Fleming, *Molecular Orbitals and Organic Chemical Reactions*, Reference Ed. WILEY, Chichester, 2010.
- [13] C.P. Casey, H.E. Tuinstra, M.C. Saeman, *J. Am. Chem. Soc.* 98 (1976) 608.
- [14] F.N. Tebbe, G.W. Parshall, D.W. Ovenall, *J. Am. Chem. Soc.* 101 (1979) 5074.
- [15] A.K. Chatterjee, T. Choi, D.P. Sanders, R.H. Grubbs, *J. Am. Chem. Soc.* 125 (2003) 11360.
- [16] W.E. Crowe, Z.J. Zhang, *J. Am. Chem. Soc.* 115 (1993) 10998.