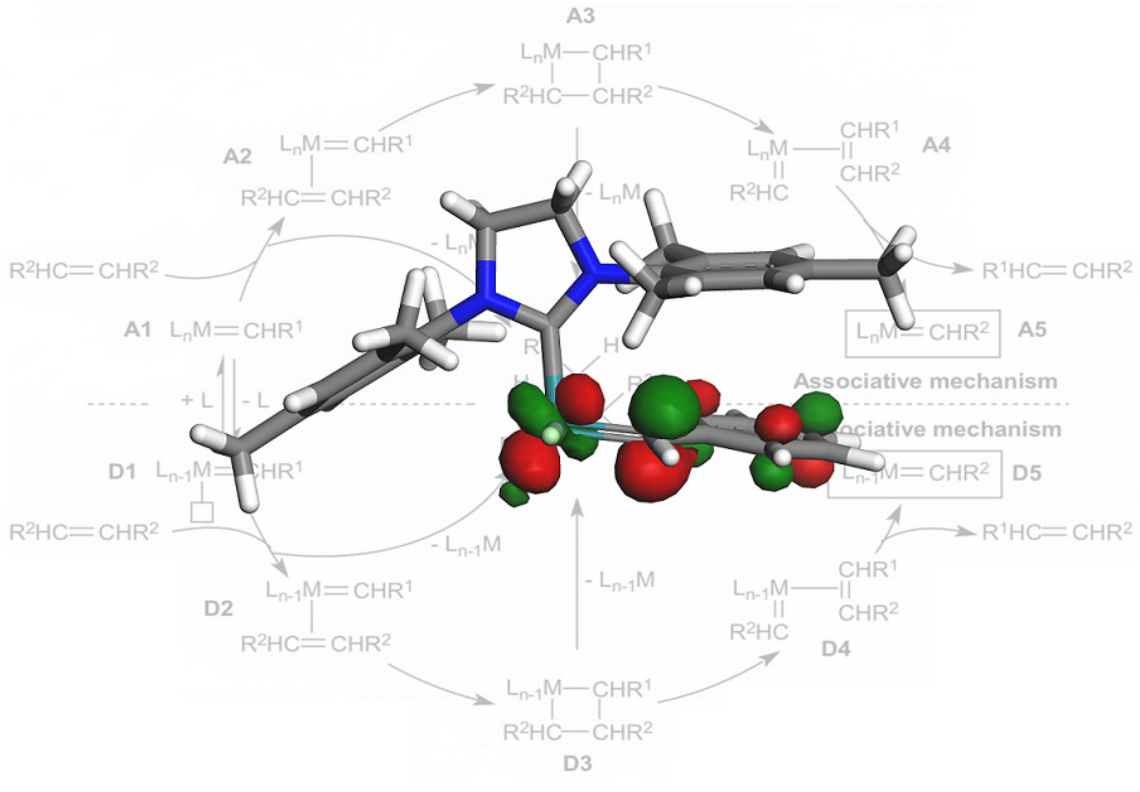
On the mechanism of homogeneous alkene metathesis – a computational study



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On the mechanism of homogeneous alkene metathesis – a computational study

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Thesis submitted for the degree
PHILOSOPHIAE DOCTOR in Chemistry
at the Potchefstroom campus of the North-West University

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November 2012

Acknowledgements

I just want to say thank you very much to the following persons:

- ✓ Dr CGCE van Sittert, promoter
- ✓ Prof HCM Vosloo, co-promoter
- ✓ The Catalysis and Synthesis group
- ✓ c*change for funding
- ✓ Prof HD Nelson for language editing
- ✓ The people at home

Soli Deo Gloria

"The full potential of olefin metathesis will be realized only when additional catalysts are discovered that are truly practical and afford exceptional selectivity for a significantly broader range of reactions."

A.H. Hoveyda, A.R. Zhugralin, Nature 450 (2007) 243.

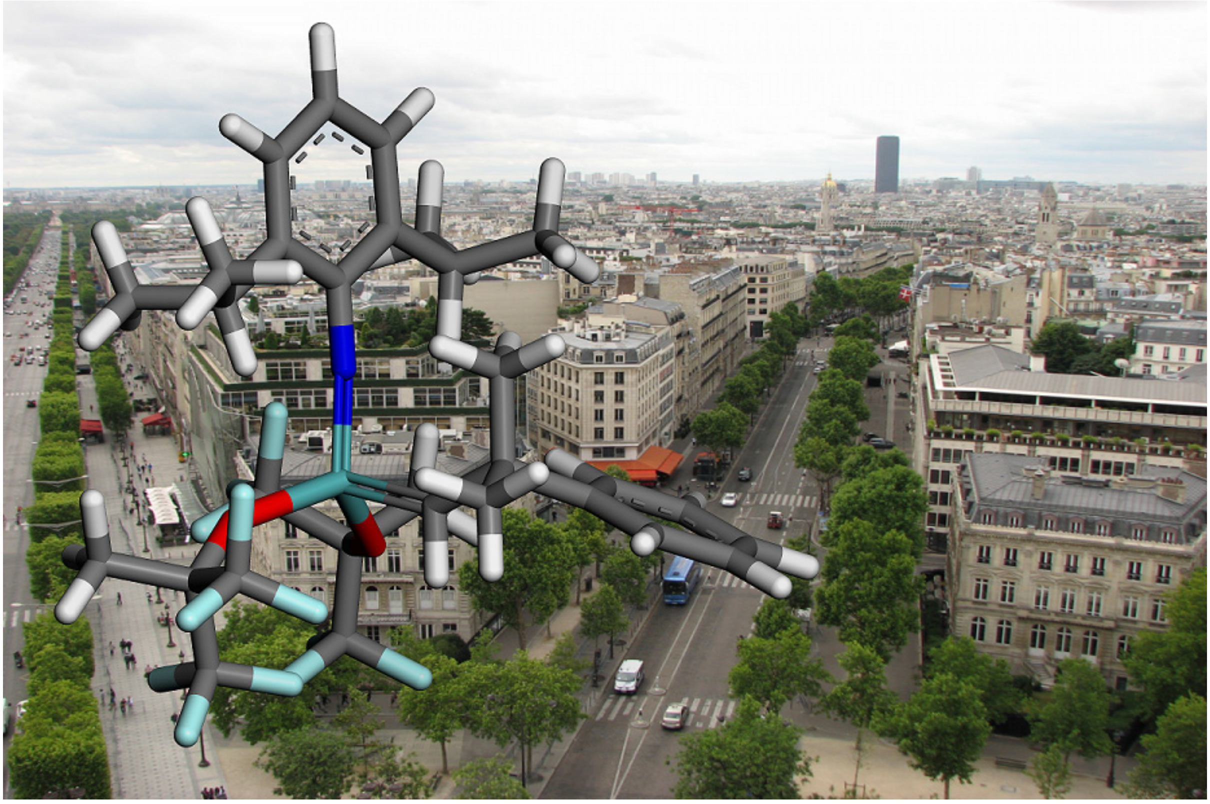

Table of Contents

Abbreviations

Ac	acetyl
alk	alkene
AO	atomic orbital
AOC	atomic orbital coefficient
Ar	aromatic
BDE	bond dissociation energy
CA	alkene carbon atom
cat	catalyst
CC	metal carbene carbon atom
Cp	cyclopentadienyl, C_5H_5
DFT	density functional theory
DNP	double numerical plus polarization
E_H	energy of HOMO
E_L	energy of LUMO
FA/FB	Fischer type catalyst reaction forming metathesis products (A) and cyclopropane (B)
FMO	Frontier molecular orbitals
G(M)	percentage of the metal M coordination sphere shielded by all ligands
GA/GB	Grubbs-type precatalyst reaction with reagent A or B
GGA	General Gradient Approximation
Gr2_indy	indenylidene-dichloro(tricyclohexylphosphine)(1,3-bis-(2,4,6-trimethylphenyl)-2-imadazolidinylidene)-ruthenium
Grubbs 1 (Gr1)	benzylidene-dichloro(bis(tricyclohexylphosphine))ruthenium
Grubbs 2 (Gr2)	benzylidene-dichloro(tricyclohexylphosphine)(1,3-bis-(2,4,6-trimethylphenyl)-2- imadazolidinylidene)ruthenium
H_2IMes	1,3-bis-(2,4,6-trimethylphenyl)-2-imadazolidinylidene

HOMO	highest occupied molecular orbital
L	ligand
LUMO	lowest unoccupied molecular orbital
M	metal
MCB	metallacyclobutane intermediate
Me	methyl group, CH_3
Mes	$C_6H_2Me_3$
MO	molecular orbital
Mo(Ph)	$Mo(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$
NBO	natural bond orbital
NHC	N-heterocyclic carbene
NPA	natural population analysis
PCy_3	tricyclohexylphosphine
PES	potential energy surface
Ph	phenyl group, C_6H_5
PHC	P-heterocyclic carbene
pre	precatalyst
Ru(H)	$H_3Ru{=}CH_2$
SA/SB	Schrock-type precatalyst reaction with reagent A or B
SP	square-pyramidal
TA/TB	Tebbe-type precatalyst reaction with reagent A or B
TBP	trigonal-bipyramidal
Tebbe	(μ-Chloro)(μ-methylene)bis(cyclopentadienyl)(dimethylaluminium)titanium
Tol	toluene, $C_6H_5CH_3$
TS	transition state
W(Tol)	(ditoluenecarbene)pentacarbonyltungsten

Summary

On the mechanism of homogeneous alkene metathesis – a computational study

Key words : Alkene metathesis, mechanism, DFT, frontier orbitals, chemical reactivity

A mechanism for alkene metathesis has been proposed by Chauvin, wherein metal carbenes act as catalysts for the reaction. The use and discovery of Fischer-, Tebbe-, Grubbs- and Schrock-type metal carbenes have to a certain extent proven the general mechanism. These metal carbenes showed different activity for alkene metathesis. Only Grubbs- and Schrock-type carbenes proved to be highly active for metathesis. A lot of studies have been done on the reasons for the activity, but still the main factors are unknown.

In this study a molecular modelling investigation into the mechanism of the alkene metathesis reaction is done in an attempt to identify a factor(s) that can predict activity. By defining and knowing factors that contribute to activity, new catalysts can be designed that are truly active and selective. Fischer-, Tebbe-, Grubbs- and Schrock-type metal carbenes are investigated in this regard.

The results of the investigation indicate that the frontier molecular orbital theory shows a possibility for prediction of alkene metathesis activity. By observing the size and location of the atomic orbital coefficients of the molecular orbital, the site of primary overlap for formation of metathesis products could be identified. The largest atomic orbital coefficient of the LUMO should be located on the metal atom. An atomic orbital coefficient should also be present on the carbene carbon for secondary overlap for formation of the metallacyclobutane intermediate. By exchanging the ruthenium in the second generation Grubbs catalyst framework the effect of the metal could be elucidated. The results clearly showed the important influence the metal atom has on the electronic properties of the catalyst complex.

The results of frontier molecular orbital calculations supported the general activity trend of the four main types of metal carbenes for the metathesis of linear alkenes. By changing the metal in known catalyst frameworks a deeper understanding can be gained for the design of new alkene metathesis catalysts.

Opsomming

Oor die meganisme van homogene alkeenmetatese
- ’n berekeningstudie

Sleutelwoorde: Alkeenmetatese, meganisme, DFT, grensorbitale, chemiese-reaktiwiteit

ʼn Meganisme vir alkeenmetatese is voorgestel deur Chauvin, waarin metaalkarbene as katalisatore vir die reaksie optree. Die gebruik en ontdekking van Fischer-, Tebbe-, Grubbs- en Schrock-tipe metaalkarbene het in ʼn sekere sin die algemene meganisme bewys. Hierdie metaalkarbene toon verskillende reaktiwiteite vir alkeenmetatese. Dit het geblyk dat slegs die Grubbs- en Schrock-tipe karbene hoogs reaktief is vir metatese. Baie studies is gemaak oor die redes vir die reaktiwiteit, maar die hooffaktore is nog onbekend.

In hierdie studie word ʼn modelleringsondersoek na die meganisme van die alkeenmetatesereaksie gemaak in ʼn poging om ’n faktor(e) te identifiseer wat reaktiwiteit kan voorspel. Deur faktore te ken en te definieer wat ’n bydrae tot reaktiwiteit lewer, kan nuwe katalisatore wat werklik reaktief en selektief is, ontwerp word. Fischer-, Tebbe-, Grubbs- en Shrock-tipe metaalkarbene is in hierdie verband ondersoek.

Die resultate van die ondersoek dui daarop dat die grens molekulêre-orbitaalteorie die moontlikheid toon vir voorspelling van alkeenmetatese-reaktiwiteit. Deur die grootte en plek van die atoomorbitaalkoeffisiënte van die molekulêre orbitaal waar te neem, kan die plek van primêre oorvleueling vir die vorming van metateseprodukte geïdentifiseer word. Die grootste atoomorbitaalkoeffisiënt van die LUMO moet op die metaalatoom gelokaliseer wees. ʼn Atoomorbitaalkoeffisiënt moet ook teenwoordig wees op die karbeenkoolstof vir sekondêre oorvleueling vir die vorming van die metallasiklobutaantussenganger. Deur die rutenium in die tweede-generasie Grubbs-katalisatorraamwerk te vervang, kan die effek van die metaal verklaar word. Die resultate toon duidelik die belangrike invloed van die metaalatoom op die elektroniese eienskappe van die katalisatorkompleks.

Die resultate van die grens molekulêre-orbitaalberekeninge ondersteun die algemene reaktiwiteitstendens van die vier hooftipes metaalkarbene vir die metatese van lineêre alkene. Deur die metaal in die bekende katalisatorraamwerke te verander, kan ’n dieper begrip van die ontwerp van nuwe alkeenmetatesekatalisatore verkry word.

Preface

- This is to state that I, Jean I du Toit, have chosen the article format for submitting my thesis.

- The thesis was written in South African English. All articles were written in American English, because of submission to American Journals.

- All the articles were written by

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  The work was done by myself, Jean I du Toit, with editing done and suggestions given by Dr CGCE van Sittert and Prof HCM Vosloo as respectively promoter and co-promoter of my PhD.

- I, Cornelia GCE van Sittert, hereby give my permission that Jean I du Toit may submit the article(s)/manuscript(s) for degree purposes.

- I, Hermanus CM Vosloo, hereby give my permission that Jean I du Toit may submit the article(s)/manuscript(s) for degree purposes.

- The review article (Ch 2) : *Metal carbenes in homogeneous alkene metathesis: computational investigations* was accepted by the Journal of Organometallic Chemistry. Article in press: J.I. du Toit, et al., Journal of Organometallic Chemistry (2013), http://dx.doi.org/10.1016/j.jorganchem.2013.03.041

- All articles have been formatted for submission to the Journal of Organometallic Chemistry. Guide for Authors available at http://www.elsevier.com/journals/journal-of-organometallic-chemistry/0022-328X/guide-for-authors

- Acknowledgements for all articles: (omitted for ease of reading)

We thank the North-West University for its financial support of our Laboratory for Applied Molecular Modelling and the South African Department of Science and Technology - National Research Foundation's Centre of Excellence in Catalysis (c*change) for their financial contribution towards the studies of JIDT.