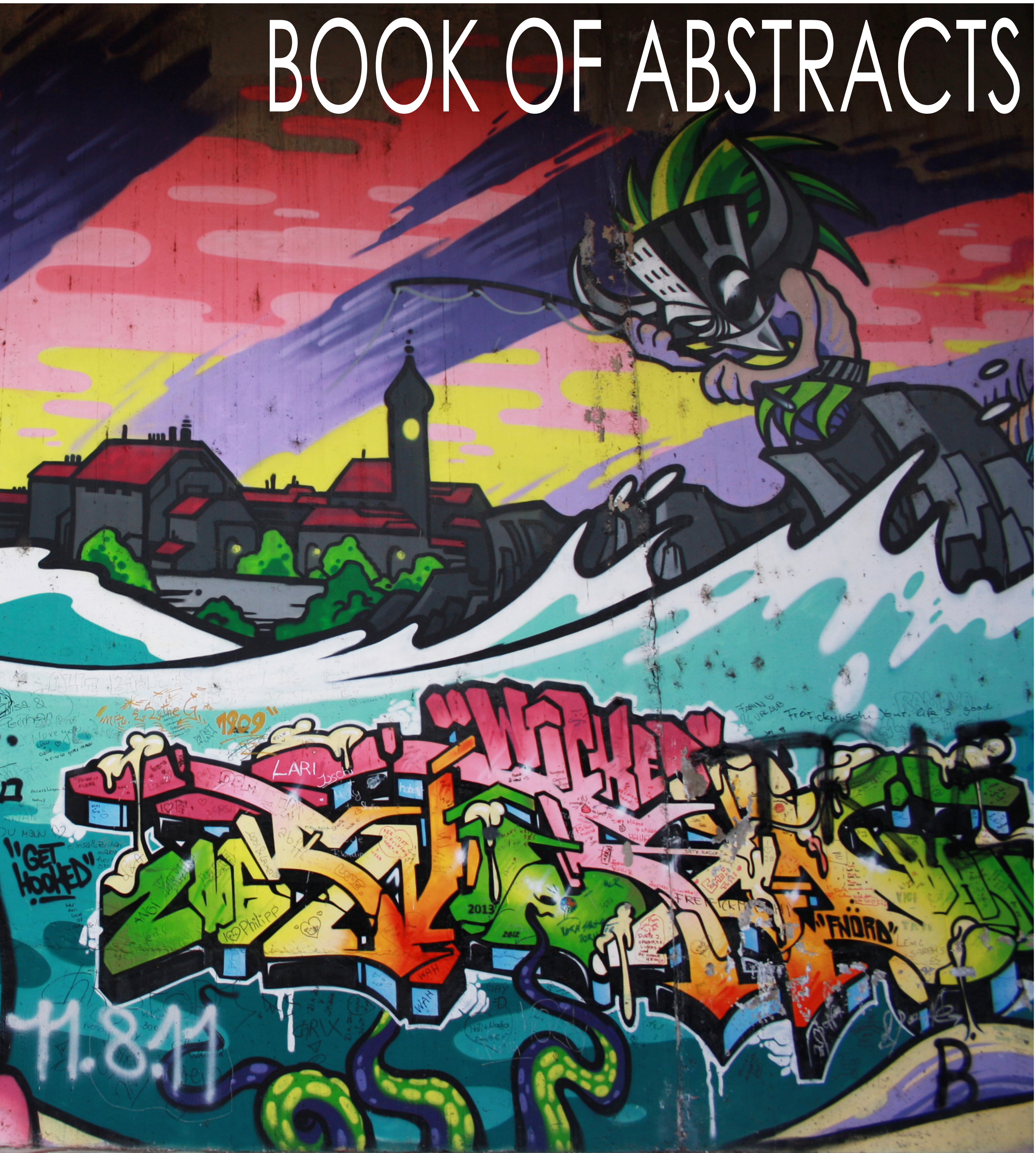
ISOMXXI

JULY 12-16, 2015 GRAZ, AUSTRIA

BOOK OF ABSTRACTS




So that you know
what to expect

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BOOK OF ABSTRACTS

of the 21st International Symposium
on Olefin Metathesis and Related Chemistry

edited by

Christian Slugovc

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21st International Symposium on Olefin Metathesis and Related Chemistry (ISOM XXI)

July 12-16 2015, Graz, Austria

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PROGRAMME

SUNDAY July, 12th

PL1 14:00-14:45

Richard R. Schrock

The Stereoselective Polymerization of Cyclic Olefins through ROMP by Molybdenum and Tungsten Catalysts

Massachusetts Institute of Technology

IL1 14:45-15:15

Kazushi Mashima

A Salt-free Reduction Protocol for Incorporating Redox-active Ligands to Early Transition Metals: Arylimido Tungsten Complexes as Catalysts for ROMP of Norbornene

Osaka University

IL2 15:15-15:45

Matthias Tamm

Catalytic Metathesis of Butadiynes

Technische Universität Braunschweig

Coffee-Break 15:45-16:10

IL3 16:10-16:40

C. Oliver Kappe

Process Intensification Applying Microwave and Continuous Flow Technologies – Metathesis and More

University of Graz

IL4 16:40-17:10

Karol Grela

New Structures and Applications in Ru-Catalysed Metathesis

University of Warsaw

IL5 17:10-17:40

Michael A. R. Meier

Metathesis with Renewables – From Sustainable Chemistry to Defined Polymer Architectures

Karlsruhe Institute of Technology

IL6 17:40-18:10

Ezat Khosravi

Design and Synthesis of Latent Catalysts for ROMP: Application in Adhesive Formulations in Electronics

Durham University

Welcome Mixer 18:10 -

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MONDAY July, 13th **Morning**

PL2 8:45-9:30

Alois Fürstner
Triple Bond Metathesis and Catalytic Alkyne Functionalization
Max-Planck-Institut für Kohlenforschung

IL7 9:30-10:00

Steven P. Nolan
The Catalytic Performance of an Olefin Metathesis Decomposition Product
University of St Andrews

L1 10:00-10:20

Bartosz Trzaskowski
Nitrenium Ions and Trivalent Boron Ligands as Analogues of N-Heterocyclic Carbenes in Olefin Metathesis
University of Warsaw

Coffee-Break 10:20-10:45

PT1 10:45-11:05

Richard Pederson
Materia – Innovations with Impact
Materia, Inc.

IL8 11:05-11:35

Olivier Baslé
Multicomponent Synthesis of Unsymmetrical Unsaturated *N*-Heterocyclic Carbenes (U_2-NHCs) And Their Applications in Olefin Metathesis
École Nationale Supérieure de Chimie de Rennes

L2 11:35-11:55

Raphael Reuter
Artificial Metalloenzymes for Ring Closing Metathesis Based on the Biotin-Streptavidin Technology
University of Basel

L3 11:55-12:15

Xavier Solans-Monfort
Computational Kinetics to Account for the Reactants Concentration Influence in Ru-Based Catalysed Olefin Metathesis
Universitat Autònoma de Barcelona

Lunch 12:15-13:45

at Restaurant Lebensgfyhl

MONDAY July, 13th **Afternoon**

IL9 13:45-14:15

Christian Bruneau
Cross Metathesis with Acrylonitrile
University of Rennes1

IL10 14:15-14:45

Hermanus C. M. Vosloo
Use of Metathesis in Alkene Feedstock Beneficiation
North-West University

L4 14:45-15:05

Annelies Dewaele
Valorization of Polybutadiene Waste Streams to Unsaturated Macrocycles with Ru Metathesis Catalysts
KU Leuven

L5 15:05-15:25

Sudheendran Mavila
Synthesis of Organometallic Nanoparticles via Intramolecular Cross-linking of ROMP-derived Polymers
Ben-Gurion University of the Negev

Coffee-Break 15:25-15:50

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IL11 15:50-16:20

Janine Cossy
Metathesis and Synthesis of Functionalized Heterocycles - Application to the Synthesis of Bioactive Natural Products
ParisTech/CNRS-UMR 8231/PSL Research University

IL12 16:20-16:50

Joëlle Prunet
Metathesis in the Synthesis of Taxol
University of Glasgow

L6 16:50-17:10

Sambasivarao Kotha
Applications of Olefin Metathesis to Polycycles and Cyclophanes
Indian Institute of Technology-Bombay

L7 17:10-17:30

Masamichi Ogasawara
Catalytic Enantioselective Synthesis of Planar-Chiral Zirconocenes and Their Application as Chiral Catalysts
Hokkaido University

Poster-Session 17:30-19h00

Including refreshments, nuts & chips

TUESDAY July, 14th **Morning**

PL3 8:45-9:30

Robert H. Grubbs
Olefin Metathesis Catalysts for the Controlled Synthesis of Large and Small Molecules
California Institute of Technology

IL13 9:30-10:00

Nathan C. Gianneschi
Seek, Destroy and Heal: Enzyme-Responsive Nanoparticles as *In Vivo* Targeted Delivery Systems
University of California

L8 10:00-10:20

Shigetaka Hayano
Stereoselective ROMPs of Norbornenes: Development of New Polymer Materials Based on Stereocontrol
Zeon Corporation

Coffee-Break 10:20-10:45

PT2 10:45-11:05

Christophe Le Ret
Industrial Examples of Ruthenium Based Metathesis Reactions
Umicore AG & Co. KG

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materials for a better life

IL14 11:05-11:35

Deryn E. Fogg
Compromising Situations: Decomposition of Ruthenium Metathesis Catalysts
University of Ottawa & Catalysis Center for Research and Innovation Ottawa

L9 11:35-11:55

Hans-Jörg Schanz
Ruthenium-Based Olefin Metathesis Catalysts Bearing pH-Responsive NHC Ligands for ROMP in Aqueous Media and Emulsions
Georgia Southern University

L10 11:55-12:15

Giovanni Occhipinti
How to Teach Z Selectivity to Grubbs Catalysts
University of Bergen

Lunch 12:15-13:45

at Restaurant Lebensgfyhl

Lebens
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TUESDAY July, 14th Afternoon

IL15 13:45-14:15

Jean-Marie Basset

Why Cyclooctane Metathesis does not give Polyethylene with Single Site W Based Catalysts?

King Abdullah University of Science and Technology

IL16 14:15-14:45

Odile Eisenstein

Learning on from Calculated NMR Chemical Shift Tensors of Alkylidene Complexes

CNRS-Université de Montpellier

L11 14:45-15:05

Victor Mougel

Quantitatively Analyzing Metathesis Catalyst Activity and Structural Features in Silica-Supported Tungsten Imido–Alkylidene Complexes

ETH Zürich

L12 15:05-15:25

Maxence Valla

Tailored Made Al-Doped Silica Dramatically Improves the Metathesis Activity of Re-Oxo-Alkylidene Supported Complexes

ETH Zürich

Coffee-Break 15:25-15:50

IL17 15:50-16:20

Bogdan Marciniec

Transformations of Vinylsubstituted Silsesquioxanes and Heterosilsesquioxanes *via* Metathesis vs. Metallative Coupling Procedures

Mickiewicz University in Poznan & Center for Advanced Technologies

IL18 16:20-16:50

Kenneth B. Wagener

Sulfur Functionalization of Polyolefins using ADMET

University of Florida

IL19 16:50-17:20

Der-Jang Liaw

Functional Polynorbornenes *via* Ring-Opening Metathesis Polymerization (ROMP) and Conjugated Polymers: Synthesis, Optoelectronic and Solar Energy Applications

National Taiwan University of Science and Technology

L13 17:20-17:40

André Mortreux

Advances in Alkyne Metathesis: Photochemical *vs* Thermal Activation Using *in situ* $Mo(CO)_6$-phenols and -silanols Catalysts

ENSCL-USTL

L14 17:40-18:00

Òscar Àrias

Challenges in Optimizing Alkyne Metathesis Catalysts

TU Braunschweig

Reception of the Governor of Styria 19:00-22:00

Das Land
Steiermark

WEDNESDAY July, 15th **Morning**

PL4 8:45-9:30
Amir H. Hoveyda
New Concepts, Catalysts and Methods for Stereoselective Alkene Metathesis
Boston College

IL20 9:30-10:00
Catherine S. J. Cazin
Phosphite Ligands in Ru-catalysed Olefin Metathesis
University of St Andrews

L15 10:00-10:20
Levente Ondi and Henrik Gulyas
High Activity, Stabilized Formulations, Efficient Synthesis and Industrial Use of Mo- and W-based Metathesis Catalysts
XiMo Hungary Ltd.

Coffee-Break 10:20-10:45

IL21 10:45-11:15
Luigi Cavallo
Looking Inside the Ru-NHC (N-Heterocyclic Carbene) Bond
King Abdullah University of Science and Technology

L16 11:15-11:35
Hsiao-Ching Yang
Carbene Rotamer Switching Controls the Stereoselectivity of Ring Opening Metathesis Polymerization by Ruthenium-Catalysts
Fu Jen Catholic University

L17 11:35-11:55
Katherine Paredes-Gil
Theoretical Characterization of Ruthenium Complexes with Potential Activity on Olefin Metathesis: Challenges and New Advances
Universidad Andrés Bello & Universidad de Chile

L18 11:55-12:15
Albert Poater
Playing with the Relative Stability of Olefin Metathesis Catalysts
King Abdullah University of Science and Technology & Universitat de Girona

L19 12:15-12:35
Jean I. Du Toit
Classification of Metal Carbene Catalyst Types for Activity as Alkene Metathesis Catalysis: a QSAR-type Approach
North-West University

Lunch 12:35-14:00
at Restaurant Lebensgfyhl

Excursion and Conference Dinner 14:00 - approx. 22:30
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THURSDAY July, 16th **Morning**

PL5 8:45-9:30

Michael R. Buchmeiser
N-Heterocyclic Carbene-High Oxidation State Molybdenum and Tungsten Alkylidene Complexes: Chiral Functional Group Tolerant Olefin Metathesis Catalysts
University of Stuttgart

IL22 9:30-10:00

Tien-Yau Luh
Polycyclopropene-Based Ladderphanes and Related Polymers
National Taiwan University

IL23 10:00-10:30

Felix R. Fischer
Ring-Opening Alkyne Metathesis Polymerization: Teaching Polymers the Meaning of Life
University of California Berkeley & Lawrence Berkeley National Laboratory

Coffee-Break 10:30-10:50

IL24 10:50-11:20

Andrea J. Robinson
Metathesis and Peptidomimetics
Monash University

L20 11:20-11:40

Shital K. Chattopadhyay
Modular Synthesis of Amino Acids and Cyclic Peptides Related to Histone Deacetylase Inhibition through Olefin Metathesis
University of Kalyani

L21 11:40-12:00

Francesca Ghirga
The Olefin Metathesis Reaction in the Synthesis of Resorc[4]Arenes with Intriguing Architectures
Istituto Italiano di Tecnologia & Università "La Sapienza"

L22 12:00-12:20

Subrata Ghosh
Substrate Specificity in Directing Ring Closing Metathesis of Trienes to Form Carbocycles or Oxacycles
Indian Association for the Cultivation of Science

Lunch 12:20-13:50

at Restaurant Lebensgfyhl

THURSDAY July, 16th **Afternoon**

L23 13:50-14:10

Michael Fuchs
Ring Closing Alkyne Metathesis And A *trans*-Selective Hydrogenation – On A Scalable Total Synthesis of (+)-Brefeldin A
Graz University of Technology

IL25 14:10-14:40

Lionel Delaude
Second-generation Ruthenium Catalysts for the Metathetical Ring-closure of Tetra-substituted Cycloolefins
University of Liège

L24 14:40-15:00

Grzegorz K. Zieliński
Formic Acid as an Alternative Hydrogen Source in Ruthenium Catalyzed Transfer Hydrogenation of Olefins
Polish Academy of Science

Coffee-Break 15:00-15:20

IL26 15:20-15:50

Kotohiro Nomura
(Imido)vanadium(V)-Alkylidene Complexes as Olefin Metathesis Catalysts
Tokyo Metropolitan University

PL6 15:50-16:35

Christophe Copéret
Bridging the Gap between Molecular Entities, Well-defined Surface Sites and Industrial Catalysts
ETH Zürich

Closing Ceremony & Farewell Party 16:35 - open end

Barbecue – pigling & more

Sponsored by

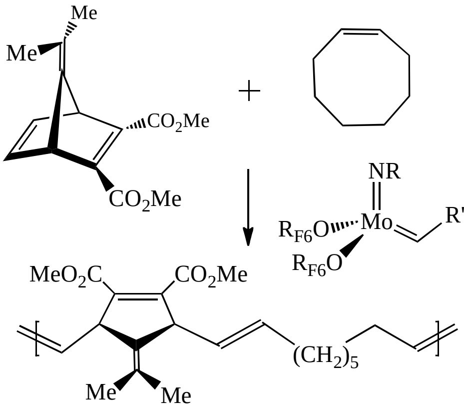
PLENARY LECTURES

The Stereoselective Polymerization of Cyclic Olefins through ROMP by Molybdenum and Tungsten Catalysts

Richard R. Schrock

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

It is now possible to prepare polymers that are stereoregular (*cis,isotactic* or *cis,syndiotactic*) through ring-opening metathesis polymerization (ROMP) with molybdenum and tungsten alkylidene initiators. *Cis,isotactic* polymers are prepared through enantiomorphic site control (ESC) with initiators that contain a biphenolate ligand, while *cis,syndiotactic* polymers are prepared through stereogenic metal control (SMC) with MAP (MonoAryloxidePyrrolide) initiators in which the metal is a stereogenic center. Hydrogenation of stereoregular *cis* polymers yields pure *isotactic* or *syndiotactic* polymers having a saturated backbone. In some cases the saturated polymers are crystalline and high melting, in contrast to atactic versions. A fifth stereoregular structure can be formed through SMC employing Mo catalysts and racemic chiral norbornenes or norbornadienes; the basic structure is *cis,syndiotactic*, but enantiomers are incorporated in an alternating fashion. This is a special type of AB copolymer. Alternating AB copolymers where A and B are different types of cyclic olefins have been prepared through ROMP with $Mo(NR)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ initiators (R = 2,6-$Me_2C_6H_3$ (**1**) or 2,6-*i*-$Pr_2C_6H_3$ (**2**)). An example of monomer **A** is cyclooctene and monomer **B** is 2,3-dicarbomethoxy-7-isopropylidenenorbornadiene. The >90% poly(A-*alt*-B) copolymers are formed with heterodyads (AB) that have the ***trans*** configuration. Evidence suggests that one *trans* hetero C=C bond is formed when A reacts with the *syn* form of the alkylidene made from B (*syn*-MB) to give *anti*-MA, while the other *trans* C=C bond is formed when B reacts with *anti*-MA to give *syn*-MB. *Cis* and *trans* AA dyads are proposed to arise when A reacts with *anti*-MA in competition with B reacting with *anti*-MA. Other recent results will be discussed as time permits.



AB Copolymer formed employing a molybdenum initiator.

Triple Bond Metathesis and Catalytic Alkyne Functionalization

Alois Fürstner

Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany;
e-mail: fuerstner@kofo.mpg.de

Schrock-alkylidyne complexes endowed with silanolate ligands represent a new generation of alkyne metathesis catalysts, which are cheap, readily prepared and now also commercially available. These complexes exhibit high catalytic activity and are distinguished by an exquisite functional group tolerance.[1] As will be shown in my presentation, they also allow substrates other than ordinary acetylene derivatives to be activated in a metathetic fashion.

Since alkynes are chemically more “expensive” than most olefins, their use as starting materials is justified only if advantage is taken from the peculiar reactivity inherent to the triple bond. One way to do so employs carbophilic pi-acid catalysts.[2] Furthermore, our group has recently reported that alkynes are amenable to *trans*-hydrogenation,[3] *trans*-hydroboration[4] and *trans*-hydrostannation.[5] Mechanistic aspects of these stereochemical unorthodox transformations will be discussed,[6] which seem to involve metal-carbene intermediates. Selected applications to target-oriented synthesis are meant to illustrate the scope and limitations of this emerging methodology.[7,8]

References:

1 Fürstner, A. *Angew. Chem. Int. Ed*. **2013**, *52*, 2794.
2 Fürstner, A. *Acc. Chem. Res*. **2014**, *47*, 925.
3 Radkowski, K.; Sundararaju, B.; Fürstner, A. *Angew. Chem. Int. Ed*. **2013**, *52*, 355.
4 Sundararaju, B.; Fürstner, A. *Angew. Chem. Int. Ed*. **2013**, *52*, 14050.
5 Rummelt, S. M.; Fürstner, A. *Angew. Chem. Int. Ed*. **2014**, *53*, 3626.
6 Rummelt, S. M.; Radkowski, K.; Rosca, D.-A.; Fürstner, A. *J. Am. Chem. Soc*. **2015**, in press
7 Fuchs, M.; Fürstner, A. *Angew. Chem. Int. Ed*. **2015**, *54*, 3978.
8 Rummelt, S. M.; Preindl, J.; Sommer, H.; Fürstner, A. *Angew. Chem. Int. Ed*. **2015**, *54*, in press.

Olefin Metathesis Catalysts for the Controlled Synthesis of Large and Small Molecules

Robert H. Grubbs

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA; e-mail: rhg@caltech.edu

Olefin metathesis catalysts have become one of the tools for the efficient synthesis of complex molecules. Until recently, the catalysts demonstrated poor catalyst controlled selectivity of the product double bond. Over the past several years, complexes based on molybdenum, tungsten and ruthenium have been discovered that will produce olefins with good to excellent selectivity for the generation of Z olefins both in cross and in ring closing metathesis. New ligands have been developed that result in different selectivities and open new applications of metathesis in the synthesis of an array of complex molecules. These catalysts are developed through design, computation and serendipity. Applications range from the preparation of pharmaceuticals to the control of the structure of polymeric materials.

References:

1 Mangold, S. L.; O'Leary, D. J.; Grubbs, R. H. *J Am. Chem. Soc.* **2014**, *136*, 12469.

2 MacFarlane, R. J.; Kim B.; Lee, B.; Weitekamp, R. A.; Bates, C. M.; Lee, S. F.; Chang, A. B.; Delaney K. T.; Fredrickson, G. H.; Atwater, H. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2014** *136*, 17374.

New Concepts, Catalysts and Methods for Stereoselective Alkene Metathesis

Amir H. Hoveyda

Boston College, Merkert Chemistry Center, Chestnut Hill, MA 02467, USA

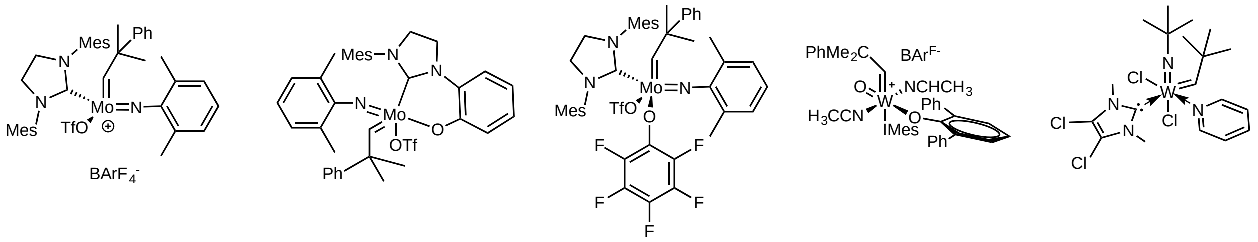
Concepts and mechanistic rationale that serve as the basis for the design and development of Ru-, Mo- or W-based complexes for efficient and stereoselective olefin metathesis reactions will be presented. The significance of the emerging catalysts in addressing difficult and compelling problems in chemical synthesis will be highlighted.

N-Heterocyclic Carbene-High Oxidation State Molybdenum and Tungsten Alkylidene Complexes: Chiral Functional Group Tolerant Olefin Metathesis Catalysts

Suman Sen, Roman Schowner, Katharina Herz, Dominik Imbrich, Christina Lienert,
Michael R. Buchmeiser*

Institute of Polymer Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany; michael.buchmeiser@ipoc.uni-stuttgart.de

N-Heterocyclic carbene (NHC) complexes of high oxidation state molybdenum imido alkylidene bis-triflates and tungsten oxo dichloro alkykidenes are reported. Both the Mo-imido alkylidene bistriflates and W-oxo dichloro alkykidenes serve as highly valuable progenitors to a variety of highly active neutral and cationic catalysts, which are accessible by simple replacement of the triflate or chloro-ligands by other coordinating or non-coordinating ligands. Single crystal x-ray structures of several representatives of this novel class of Schrock-type catalysts are presented and reactivity is discussed in view of their structural peculiarities. In the presence of monomer, the novel catalysts form cationic species and can be employed in the ring-opening metathesis polymerization (ROMP) of functional norbornenes, 7-oxanorbornenes and norbornadienes as well as in the cyclopolymerization of α,ω-hepta- and octadiynes. Monomers that contain functional groups that are not tolerated by the existing variations of Schrock's catalyst, e.g., nitrile, *tert*.- and *sec*-amine, thioether, hydroxyl and carboxylic acid moieties can be used with Mo-imido alkylidene bistriflates. Cationic Mo-imido alkyidene-NHC complexes are chrial at Mo and allow for turn-over numbers up to 240,000 in RCM. Equally important, high stereo- and regioregularity is achieved, too, offering access to highly tactic polymers and copolymers. In view of their high functional group tolerance and high regio- and stereoselectivity, the novel catalysts hold enormous potential in both organic and polymer chemistry, where they allow for the use of protic substrates and monomers, thereby offering access to functional (poly-) olefins.[1,2,3,4]



Structures of selected catalysts.

References:

1 Buchmeiser, M. R.; Sen, S.; Unold, J.; Frey, W. *Angew. Chem. Int. Ed*. **2014**, *53*, 9384.
2 Buchmeiser, M. R.; Sen, S.; Schowner, R. **2014**, patents pending.
3 Buchmeiser, M. R.; Sen, S.; Schowner, R., Herz, K., Lienert, C.; Imbrich, D. **2015**, unpublished results
4 Sen, S.; Schowner, R.; Buchmeiser, M. R. *Monatsh. Chem.* **2015**, *146*, 1037.

Bridging the Gap between Molecular Entities, Well-defined Surface Sites and Industrial Catalysts

Christophe Copéret

ETH Zürich, Department of Chemistry and Applied Biosciences
Vladimir Prelog Weg 1-5, 10 CH-8093 Zürich, Switzerland

Homogeneous and heterogeneous catalysts have, each, specific advantages. While homogeneous catalysts are typically associated with efficient chemical transformations at low temperatures (high selectivity), heterogeneous ones are typically preferred in term of processes (easier regeneration and separation processes).

Here, we will show how well-defined supported catalysts, prepared through the controlled functionalization of surfaces, can provide insightful information for both molecularly–defined homogeneous and classical heterogeneous industrial catalysts.

PROMOTION TALKS

Materia – Innovations with Impact

Richard Pederson

Vice President, R&D Materia, Inc. 60 N San Gabriel Blvd. Pasadena, CA 91107, USA

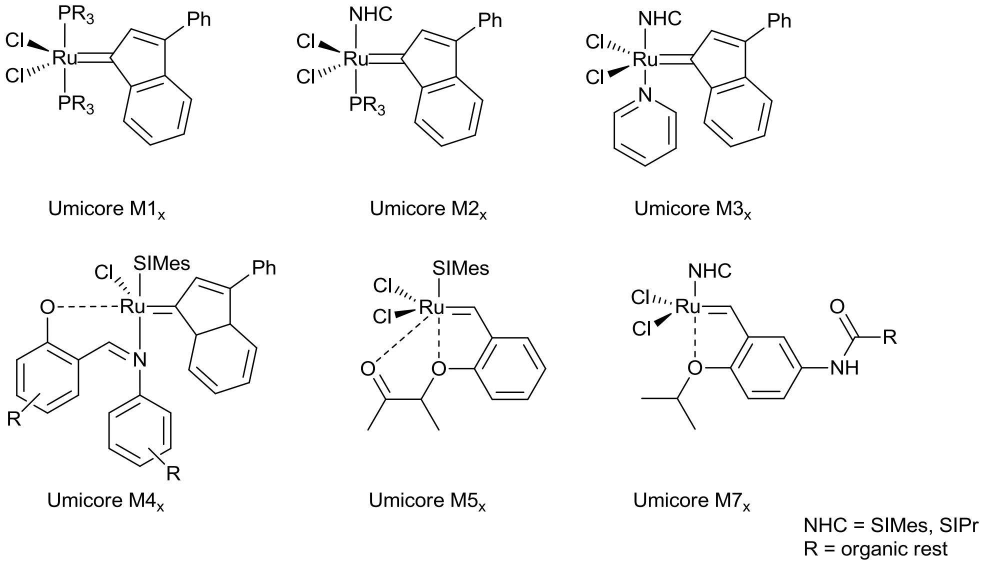
Materia commercializes the Grubbs Catalyst® technology, which enables chemical compounds to be synthesized with greater efficiency, under less stringent reaction conditions, and with reduced by-products and hazardous waste. Metathesis has been accepted as an emerging chemical technology platform and has been broadly adopted by the pharmaceutical, chemical, and polymer industries. This presentation will review commercial applications where metathesis has been implemented and discuss future opportunities. Examples of commercial successes have included Elevance Renewable Sciences' bio-refinery plant(s) and Lanxess' Therban® AT HNBR product lines. Future opportunities include stapled and macrocyclic peptides in the pharmaceutical arena, wind blade and automotive composites, and a variety of molded components for industrial and subsea and downhole oil & gas applications.

Industrial Examples of Ruthenium Based Metathesis Reactions

Christophe Le Ret,* Jessica Gomes-Jelonek

Umicore AG & Co. KG, Precious Metals Chemistry, Rodenbacher Chaussee 4, D-63457 Hanau-Wolfgang, Germany; e-mail: christophe.le-ret@umicore.com

Alkene metathesis has gained extensive use in industrial and academic synthetic chemistry as a powerful methodology for elegant, efficient and atom-economical formation of carbon-carbon double bonds.[1] Since its discovery in polymer chemistry in the early 1960s and the Nobel Prize in chemistry awarded in 2005 to Chauvin, Grubbs and Schrock,[2] this catalytic reaction has been used in a broad range of applications spanning from pharmaceuticals to agrochemicals, polymers, petrochemicals or renewables.



Umicore M Ruthenium based metathesis catalyst families

We aim to review and compare some of the Ruthenium based metathesis catalysts already available at commercial scale and to conclude with selected examples of industrial scale applications of metathesis reactions.

References:

1 a) Grubbs, R. H.; in *Handbook of Olefin Metathesis, Wiley VCH, Weinheim*, **2003**; b) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746; c) Michalak, M.; Gułajski, Ł.; Grela, K. "Alkene Metathesis" in *Science of Synthesis: Houben–Weyl Methods of Molecular Transformations*, Vol. 47a, Ed.: A. de Meijere; Georg Thieme Verlag, **2010**, p. 327

2 *http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2005/popular-chemistryprize2005.pdf*

INVITED LECTURES

A Salt-free Reduction Protocol for Incorporating Redox-active Ligands to Early Transition Metals: Arylimido Tungsten Complexes as Catalysts for ROMP of Norbornene

Kazushi Mashima,* Hiromasa Tanahashi, Hayato Tsurugi

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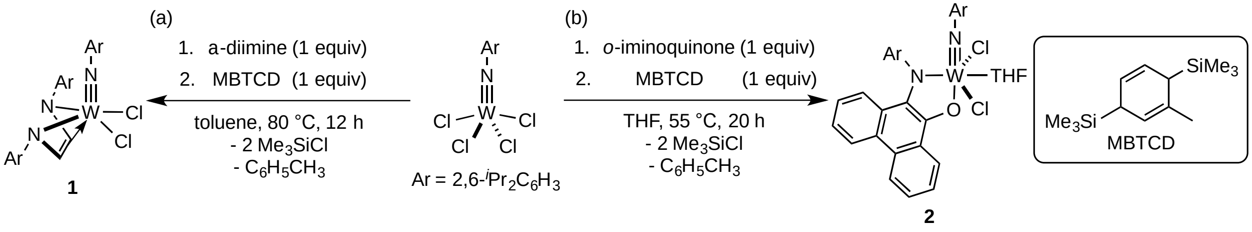
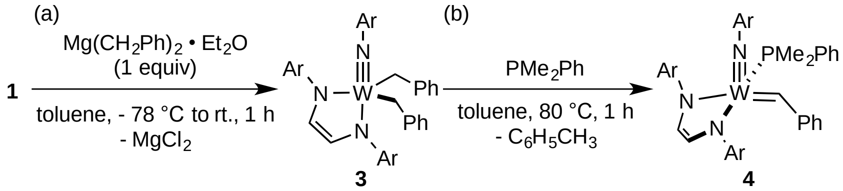
Low-valent early transition metal complexes have provided unique scaffolds for activating small molecules including olefin metathesis reactions. We have been interested in incorporation of redox-active ligands into early transition metals. We thus developed a salt-free reduction of high-valent early transition metal chlorides by 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (abbr. MBTCD).[1] In this contribution, we demonstrated that MBTCD and its nitrogen derivative, 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-dihydro-pyrazine (BTDP), reduced a wide variety of transition metals in salt-free manner, and we focused on synthesis of imido alkylidene complexes of tungsten bearing redox-active ligands as catalysts for ROMP of cyclic olefins.

Scheme 1 shows syntheses of tungsten imido complexes **1** and **2** by treating W(=NC_6H_3-2,6-$^i Pr_2$)Cl_4 and MBTCD in the presence of redox-active α-diimine and *N*-(2,6-diisopropylphenyl)phenanthren-*o*-iminoquinone. Treatment of **1** with 1 equiv of $Mg(CH_2Ph)_2 \cdot Et_2O$ resulted in the formation of a dialkyl complex **3** (Scheme 2 (a)). Thermolysis of **3** in the presence of PMe_2Ph at 80 °C afforded an alkylidene complex **4** (Scheme 2 (b)). Complexes **3** and **4** served as effective catalysts for the ring-opening metathesis polymerization (ROMP) of norbornene with 1 mol% of catalyst loading in toluene at 80 °C.

Scheme 1



Scheme 2



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Catalytic Metathesis of Butadiynes

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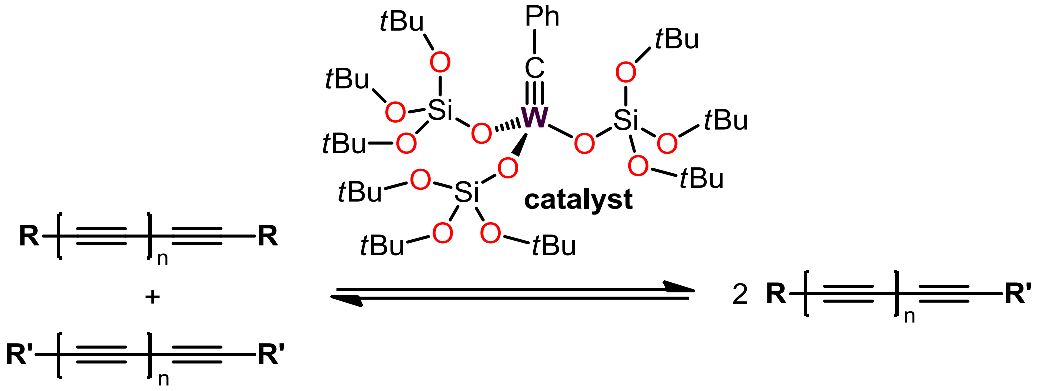
Catalytic alkyne metathesis involving the reversible cleavage and formation of carbon-carbon triple bonds still receives relatively little attention in comparison with the related Nobel prize-winning olefin metathesis technology. In recent years, however, the number of well-defined molybdenum and tungsten alkylidyne complexes that are able to catalyze alkyne metathesis reactions efficiently has been significantly expanded.[1] This lecture will present novel classes of alkyne metathesis catalysts and discuss their latest application in organic synthesis, polymer chemistry and materials science, with emphasis on recent developments in terminal alkyne metathesis[2] and, in particular, diyne metathesis (see Scheme).[3]



A representative alkyne (n = 0) and diyne (n = 1) metathesis catalyst.

References:

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Process Intensification Applying Microwave and Continuous Flow Technologies – Metathesis and More

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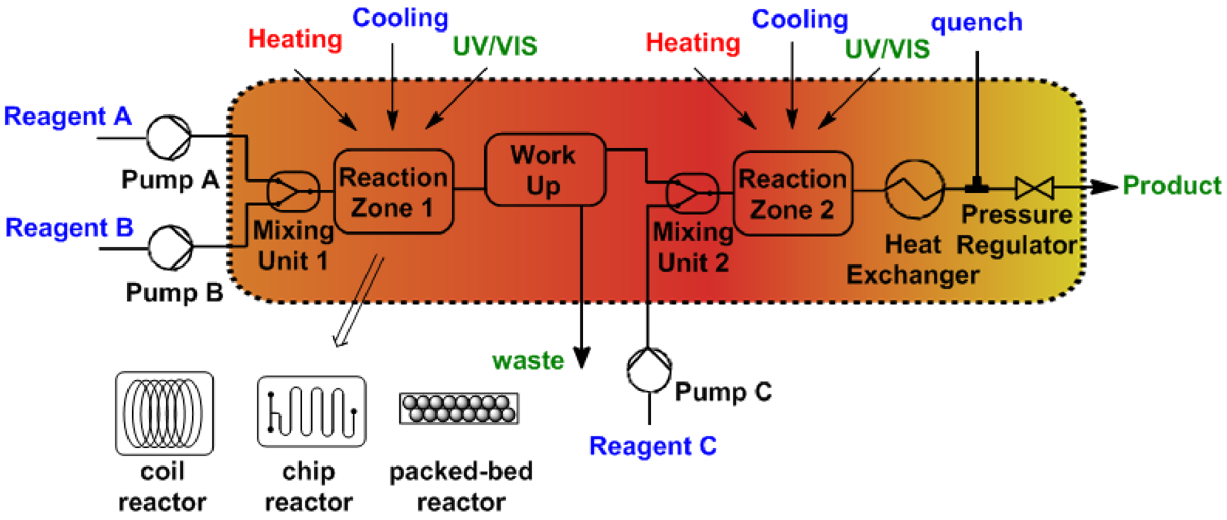
Continuous flow processes form the basis of the petrochemical and bulk chemicals industry where strong competition drives the need for highly performing, cost effective, safe and atom efficient chemical operations. Fine chemicals, such as drug substances and active pharmaceutical ingredients (APIs), are generally considerably more complex than commodity chemicals and usually require numerous, widely diverse reaction steps for their synthesis. The advantages of continuous flow processing are increasingly being appreciated also by the pharmaceutical industry Owing to the small reactor volumes, the overall safety of the process is significantly improved, even when harsh reaction conditions are applied. Thus, microreactor technology offers a unique way to perform ultrafast, exothermic reactions, and allows the execution of chemistries which proceed via highly unstable or even explosive intermediates (Figure).[1]



General Processing Scheme of Multistep Continuous Transformations

In this lecture, process intensification technologies related to Ru-catalyzed ring-closing metathesis and other transformations will be discussed involving both microwave batch and (conventionally heated) flow technologies. Special emphasis will be placed on how to translate microwave batch protocols to scalable continuous flow processes.

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New Structures and Applications in Ru-Catalysed Metathesis

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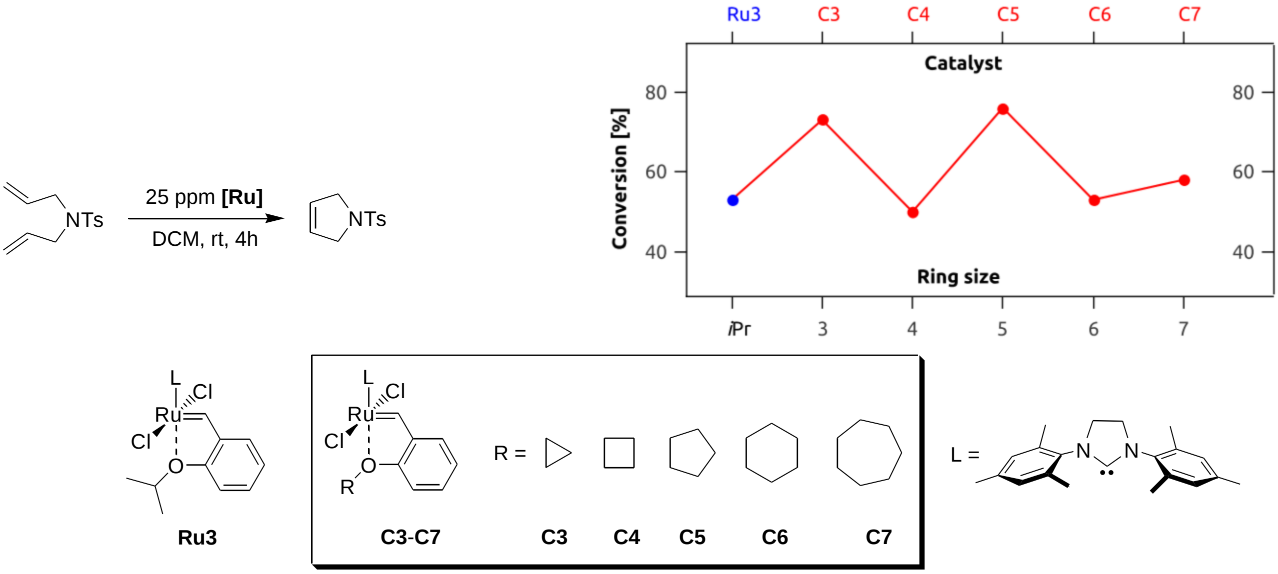
Ruthenium-catalyzed olefin metathesis reactions represent an attractive and powerful transformation for the formation of new carbon-carbon double bonds.[1] This area is now quite familiar to most chemists as numerous catalysts are available that enable a plethora of olefin metathesis reactions.[1] However, formation of substituted and crowded double bonds, decreasing the amount of metal, using metathesis in medicinal chemistry, etc. still remain a challenge, making industrial applications of this methodology difficult.[2] These limitations can be solved by designing new, more active and stable catalysts.



Structure-Activity Relationship in Selected Ether-Modified Hoveyda Catalysts

Sometimes even a small alteration of the catalyst's structure can lead to a visible change of its activity. This was the case in the ether-modified catalyst **C3 – C7** disclosed by us previously.[3] During the lecture a full account on this structural modification will be presented, accompanied by other examples.

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Metathesis with Renewables – From Sustainable Chemistry to Defined Polymer Architectures

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In ages of depleting fossil reserves and an increasing emission of greenhouse gases, it is obvious that the utilization of renewable feedstocks is one necessary step towards a sustainable development of our future. Especially plant oils bear a large potential for the substitution of currently used petrochemicals. Here, new approaches for the synthesis of monomers as well as polymers from plant oils as renewable resources will be discussed.[1] Moreover, lignin and carbohydrates offer the possibility to design novel renewable materials. Apart from striving for an increased sustainability, polymer science has always aimed for highly defined macromolecular architectures with one "holy grail" being the control over the monomer sequence.[2] Within this contribution, both aspects will be addressed and thus the synthesis of monomers and defined polymers from renewables via olefin metathesis will be discussed.

The preparation of a variety of monomers via olefin metathesis and the thereof derived polymers will be introduced.[3-5] For instance, the self-metathesis of highly unsaturated fatty acid methyl esters delivers long chain diesters for polyesters and polyamides and, as a highly valuable side product, cyclohexadiene, which can in turn be used for the synthesis of poly(caprolactone)s.[3] On the other hand, metathesis can be used to prepare a variety of defined renewable polymer architectures using both ROMP and ADMET. In this respect, a new ADMET procedure allows the synthesis of block- and star-shaped polymers by using a selective and irreversible chain transfer agent.[6] The thus obtained polymers can either be used for post-polymerization functionalization[7] or efficient polymer-polymer conjugation.[8] Ultimately, the combination of cross-metathesis and multicomponent reactions allowed the efficient synthesis of completely renewable dedrimers.[9]

In summary, the combination of renewable resources and olefin metathesis is very fruitful for the design of defined polymer architectures and for the development of a more sustainable polymer chemistry.

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Design and Synthesis of Latent Catalysts for ROMP: Application in Adhesive Formulations in Electronics

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The well-defined initiators based on molybdenum and ruthenium are very active and efficiently polymerize norbornene derivatives at room temperature. However, for some industrial processes such as adhesives using RTM (resin transfer moulding) and RIM (reaction injection moulding), it is desirable to control the initiation step in order to allow adequate mixing of monomer and initiator before polymerization occurs. For these applications, catalysts that are inactive at room temperature and initiate polymerization only upon heating would be desirable. The latent catalysts allow storing, transporting and polymerizing materials at desirable temperatures. We initiated a programme of work to develop a series of thermally switchable ruthenium catalysts generally for various applications and specifically for application in adhesive formulations for the electronic industry.

In this lecture, the synthesis and characterization of a series of latent ruthenium catalysts will be reported and their applications in homogenous ROMP reactions will be discussed. The results of ^{1}H-NMR and DSC investigations will be used to demonstrate that our designed ruthenium catalysts are inactive at room temperature and that they require elevated temperatures for their activation.

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The Catalytic Performance of an Olefin Metathesis Decomposition Product

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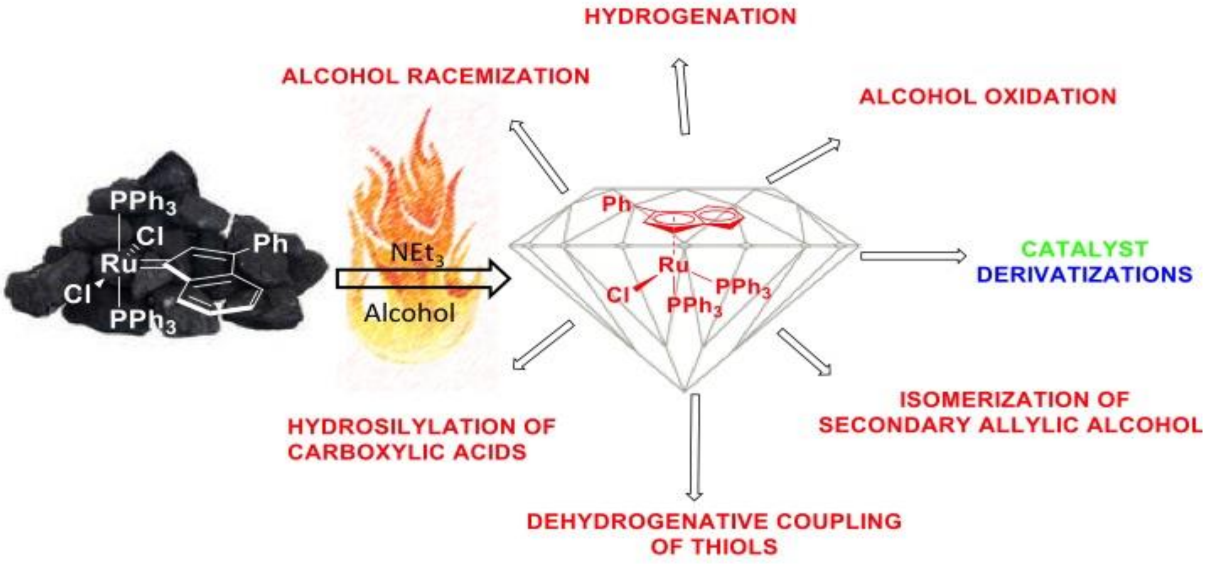
A fundamental study exploring the modes of decomposition of a ruthenium-based olefin metathesis catalyst has permitted the development of a novel and quite multipurpose pre-catalyst. This relatively simple organoruthenium complex facilitates a wide range of organic transformations. The reactive and catalytic versatility of this decomposition product will be the topic of this presentation.



Some Catalytic transformations enabled by the Manzini catalyst

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Multicomponent Synthesis of Unsymmetrical Unsaturated *N*-Heterocyclic Carbenes (U_2-NHCs) And Their Applications in Olefin Metathesis

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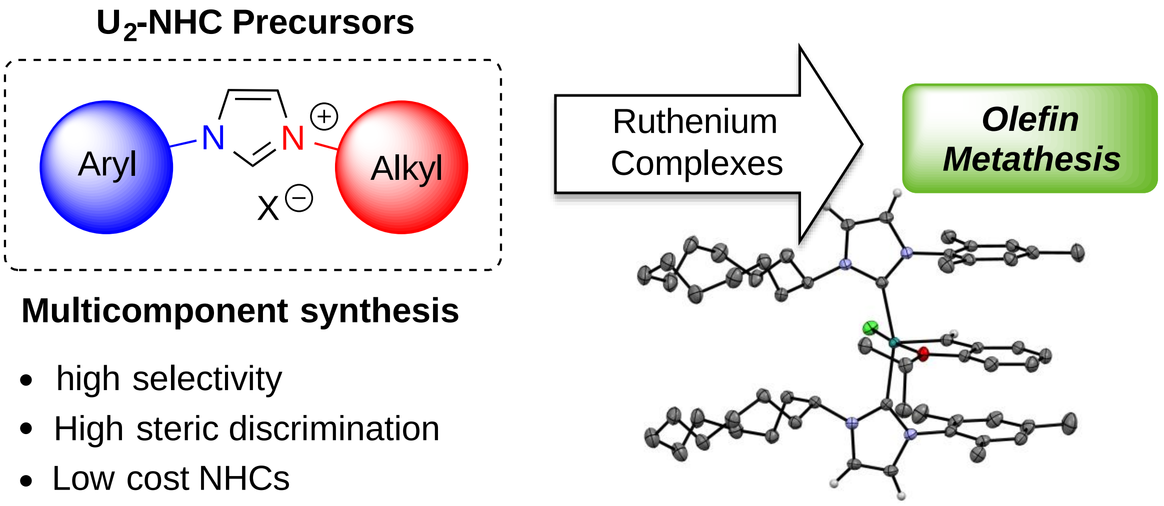
École Nationale Supérieure de Chimie de Rennes, CNRS UMR 6226, 11 allée de Beaulieu, CS50837, 35708 RENNES Cedex 7, France

The search for new low-cost practical and efficient (chiral) ligands synthesis is one of the most critical researches in modern organic chemistry. Recently, we disclosed a modular, selective and easily scalable multicomponent method affording access to a wide range of unsymmetrical unsaturated N-heterocyclic carbene (U_2-NHC) precursors.[1] Their application as ligands has allowed for the characterization of unprecedented ruthenium complexes with unique structures and interesting catalytic activities.[2,3]



Multicomponent synthesis

- high selectivity
- High steric discrimination
- Low cost NHCs

References:

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Cross Metathesis with Acrylonitrile

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F. Zagrouba[b]

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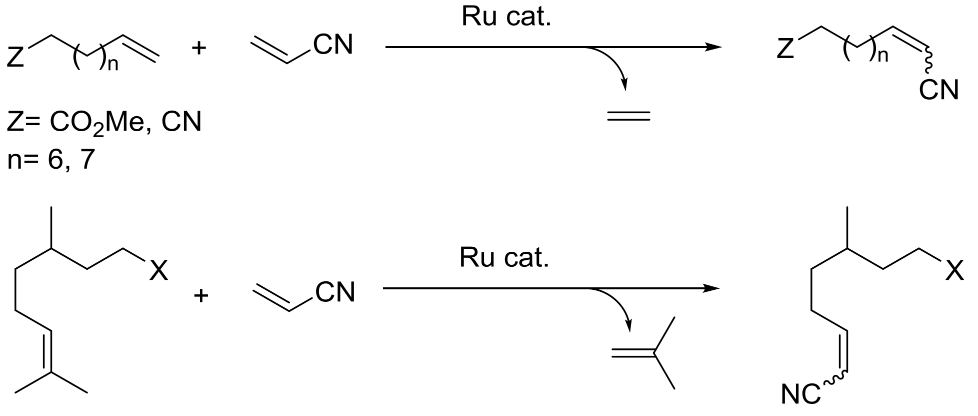
[b] *University of Carthage, Higher Institute of Sciences and Technology of Environment of Borj Cedria, B.P. 1003, 2050, Hammam-Lif, Tunisia*

Acrylonitrile is a cross metathesis partner of choice for the access to nitriles, amides and amines. However, its use in olefin metathesis is rather limited as it is considered to be a reluctant substrate which induces fast decomposition of the catalysts especially at low catalyst loading.

We will present some applications of cross metathesis reactions with various types of natural products aiming at preparing monomers for polyamide production[1,2] with high turnover numbers, and high added value products[3,4] from biomass.



Preparation of bifunctional monomers and terpene derivatives

References:

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Use of Metathesis in Alkene Feedstock Beneficiation

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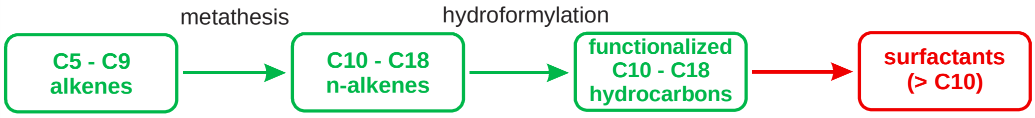
The RSA Olefins programme of the South African DST-NRF Centre of Excellence in Catalysis, c*change, aims to add value to the alkene feedstock obtained from *inter alia* syngas by converting shorter chain alkenes to longer chain alkenes in the detergent range. These alkenes can then be functionalized and subsequently converted to surfactants of the Guerbet-type, a commodity of very high value (see Figure). The reactions selected to achieve these conversions are the self-metathesis of shorter chain 1-alkenes to longer chain internal alkenes followed by the hydroformylation of the internal alkenes and further functionalization to surfactants.



Proposed beneficiation of lower value alkenes to high value surfactants.

Over the last number of years we investigated the possible industrial application of the alkene metathesis reaction using homogeneous precatalysts of the Grubbs-type. This motivated us to develop more thermally stable bidentate ruthenium carbene precatalysts. Grubbs-type precatalysts were modified by the addition of bidentate, hemilabile ligands to these complexes. The lifetime of the precatalysts was increased significantly using these ligands; similar selectivities, improved TON's and lower TOF's were obtained. A number of approaches and strategies were employed in our metathesis research. Experimental and theoretical results will be presented and the future application possibilities discussed.

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Metathesis and Synthesis of Functionalized Heterocycles - Application to the Synthesis of Bioactive Natural Products

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Metathesis has emerged as a powerful tool for the construction of C-C bonds and is now used to synthesize a great variety of products such as polymers, petrochemicals, pharmaceuticals as well as natural products. For our part, we will report that the ring-closing metathesis as well as the cross-metathesis can be utilized to functionalize heterocycles such as thiazoles and oxazoles and that these reactions can be utilized to synthesize myxobacterial antibiotics as well as antitumoral agents.

In addition, as pyridine, pyrimidine and imidazole moieties are present in a wide array of compounds, we will show that *N*-heteroaromatic-containing olefin substrates can be involved in cross-metathesis when a suitable substituent is present at C2.

Metathesis in the Synthesis of Taxol

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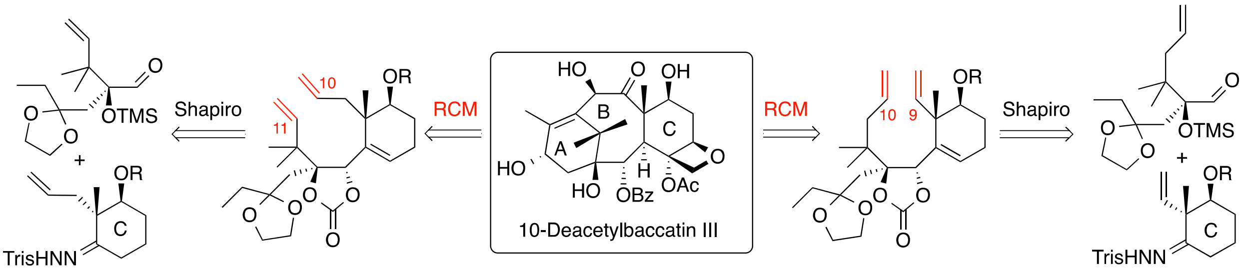
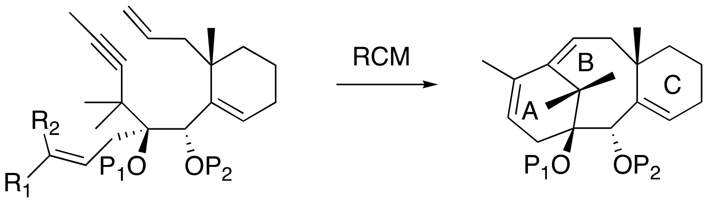
Taxol and taxotere are powerful antitumor agents that are used against a number of important human cancers. These two compounds can be prepared by hemisynthesis from 10-deacetylbaccatin III. We envisioned two retrosyntheses for this product, involving a ring-closing metathesis (RCM) to close the eight-membered B ring between C9 and C10[1] or C10 and C11,[2] and a Shapiro coupling to synthesise the RCM precursors.



Retrosyntheses of 10-deacetylbaccatin III employing RCM to form the eight-membered ring

A diastereoselective synthesis of RCM precursors will be shown, as well as the formation of cyclooctenes encompassing the BC-ring system of taxol. Emphasis will be put on influence of the diol protecting group on the outcome of the RCM step.

Finally, a route involving an ene-yne-ene RCM cascade directly forming the ABC tricycle of taxol will be presented.[3]



Direct formation of the ABC tricycle of taxol by an ene-yne-ene RCM cascade

References:

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Seek, Destroy and Heal: Enzyme-Responsive Nanoparticles as *In Vivo* Targeted Delivery Systems

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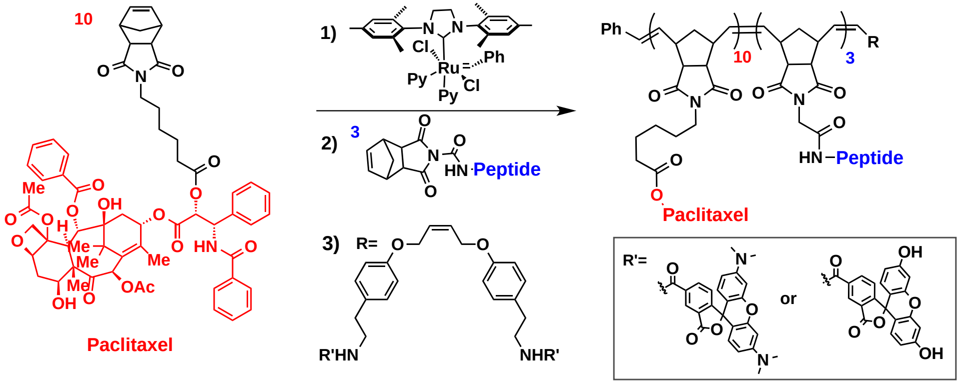
The goal of targeted therapeutics and molecular diagnostics is to accumulate drugs or probes at the site of disease in higher quantities relative to other locations in the body. To achieve this, there is tremendous interest in the development of nanomaterials capable of acting as carriers or reservoirs of therapeutics and diagnostics *in vivo*.[1] Generally, nanoscale particles are favored for this task as they can be large enough to function as carriers of multiple copies of a given small molecule, can display multiple targeting functionalities, and can be small enough to be safely injected into the blood stream. The general goal is that particles will either target passively via the enhanced permeability and retention (EPR) effect, actively by incorporation of targeting groups, or by a combination of both.[2] Nanoparticle targeting strategies have largely relied on the use of surface conjugated ligands designed to bind overexpressed cell-membrane receptors associated with a given cell-type.[3] We envisioned a targeting strategy that would lead to an active accumulation of nanoparticles by virtue of a supramolecular assembly event specific to tumor tissue, occurring in response to a specific signal. The most desirable approach to stimuli-induced targeting would be to utilize an *endogenous* signal, specific to the diseased tissue itself, capable of actively targeting materials introduced via intravenous (IV) injection. We present the development of nanoparticles capable of assembling *in vivo* in response to selective, endogenous, biomolecular signals. For this purpose, we utilize enzymes as stimuli, rather than other recognition events, because they are uniquely capable of propagating a signal via catalytic amplification. We will describe the preparation of highly functionalized polymer scaffolds utilizing ROMP, their development as *in vivo* probes and their utility as a multimodal imaging platform and as drug carriers capable of targeting tissue via a new mechanism.



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Compromising Situations: Decomposition of Ruthenium Metathesis Catalysts

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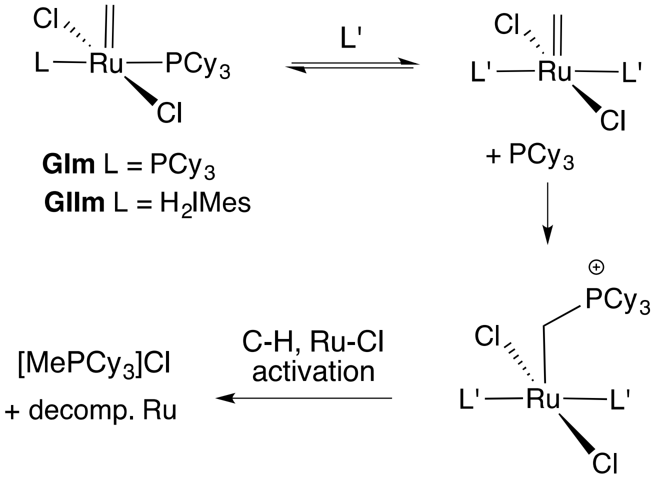
With industrial processes now beginning to emerge for molecular metathesis catalysts, improved understanding of their decomposition pathways is becoming increasingly important. Understanding the deleterious effect of contaminants offers the potential to reduce costs associated with feedstock purification, while also reducing overall catalyst consumption. Within the Grubbs catalysts, we have identified "donor-induced decomposition" [1] of the resting-state methylidene (**GIm**, **GIIm**; see Figure) as a key deactivation process, and have intercepted the σ-alkyl species in the first-generation system. We will discuss the generality of this pathway, which is enabled by phosphine attack on the metal species, as well as additional PCy_3-enabled pathways, and others arising from additional ligand loss. Contrasting behavior for phosphine-free catalysts will also be considered.



Donor-Induced Deactivation of the Grubbs Catalysts

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Why Cyclooctane Metathesis does not give Polyethylene with Single Site W Based Catalysts?

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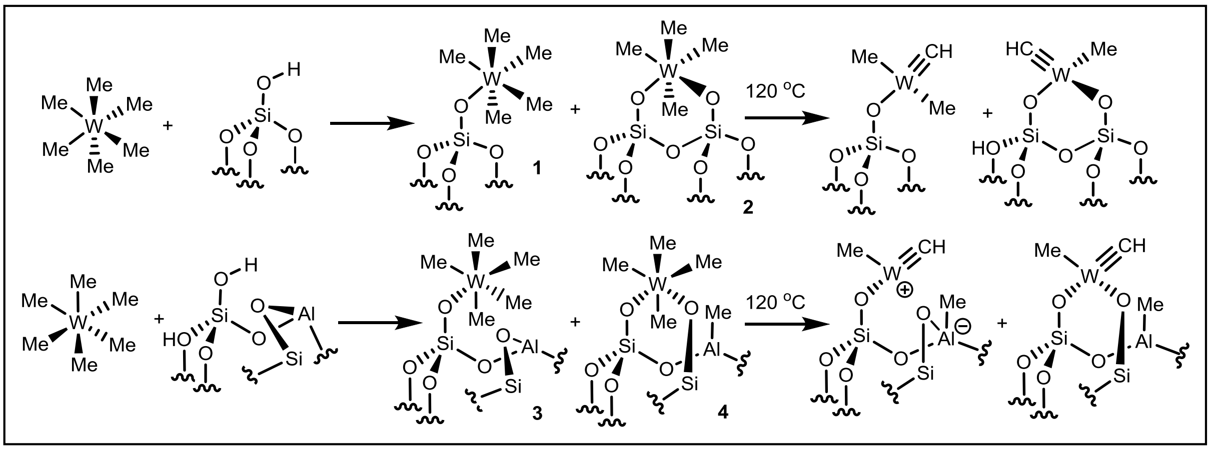
$W(CH_3)_6$ grafted on the surface of silica$_{(700)}$ gives a mixture of mono-podal[$\equiv$Si-O-WMe_5] (**1**) and bi-podal[$(\equiv Si\text{-}O)_2WMe_4$] (**2**) species and on the surface of silica-alumina$_{(500)}$, it produce **3** and **4** (with the migration of one methyl from W to Al). These complexes are transformed into various types of carbynic tungsten surface complexes at 120^{o}C (see Scheme).



*Various tungsten complex obtained after grafting of $W(CH_3)_6$ on silica-$_{700}$ (**1** & **2**) and silica-alumina-$_{500}$ (**3** & **4**) and after heat treatment of this complexes*

These complexes are efficient for metathesis of *n*-decane (TON=350) with a broad range of distribution of higher and lower hydrocarbons. Comparison with already synthesized silica supported neutral bi-podal tungsten indicates that the high increase in activity is due to the cationic character of one of the grafted tungsten complexes. Metathesis of cyclic alkanes in particular cyclooctane does not give any polymeric material but instead a wide distribution of cyclic paraffin’s ranging from cC5 to cC36. With cyclooctene using the same precatalyst a polymer is obtained. Linear olefin metathesis using the same catalyst and under the same reaction conditions gives a very striking different distribution of linear α-olefins and internal olefins. This shows that olefin and alkane metathesis processes occur via very striking different pathways.

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Learning on from Calculated NMR Chemical Shift Tensors of Alkylidene Complexes

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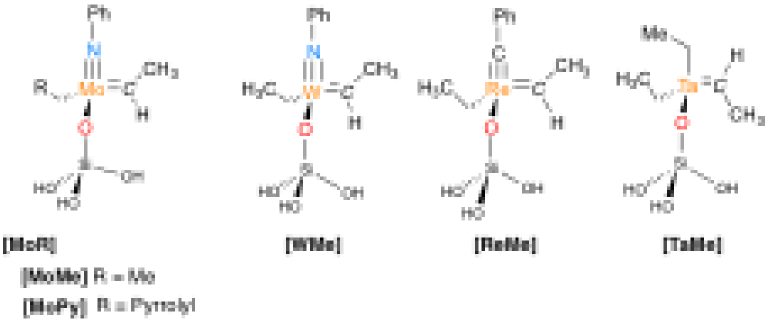
Establishing a relationship between chemical shifts and electronic/structural properties of NMR active atoms in molecules is challenging. For this purpose, the chemical shift tensors of the alkylidene carbon in several models of isostructural and isoelectronic Schrock type olefin metathesis catalysts differing by the metal and the ligands (see Fig.), were calculated. Relativistic calculations were first use to obtain accurate values of the chemical shift tensors for the ^{13}C of the alkylidene group. These calculations reproduce the experimental isotropic chemical shifts[1] in an essentially quantitative manner suggesting that the principal components of the chemical tensor for a static structure are also accurately determined. The calculations also provide the directions of these principal components. Non-relativistic calculations were carried out because they open the way for an NBO analysis of the chemical shifts. After assessing that relativistic and non-relativistic calculations gave qualitatively similar results, the NBO contributions to all bonds at the alkylidene carbon to the chemical shift tensors was analyzed. They show that the diamagnetic contributions to the chemical shifts are equal for the whole series and for the three directions of the tensors so that differences between chemical shifts arise from the paramagnetic contribution. The understanding of the various contributions of the chemical bonds to the paramagnetic contribution of the chemical shielding at the alkylidene carbon shed new light on the nature of the alkylidene metal carbon and in particular on the agostic M…CH interaction whose strength differs in these complexes. This methodology can open the route to the understanding of many related systems.



Complexes for which the ^{13}C (alkylidene) chemical shift tensors were calculated.

Acknowledgements: This study is carried out in collaboration with C. Copéret (ETH Zürich) and L. Emsley (ENS Lyon, France)

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Transformations of Vinylsubstituted Silsesquioxanes and Heterosilsesquioxanes *via* Metathesis vs. Metallative Coupling Procedures

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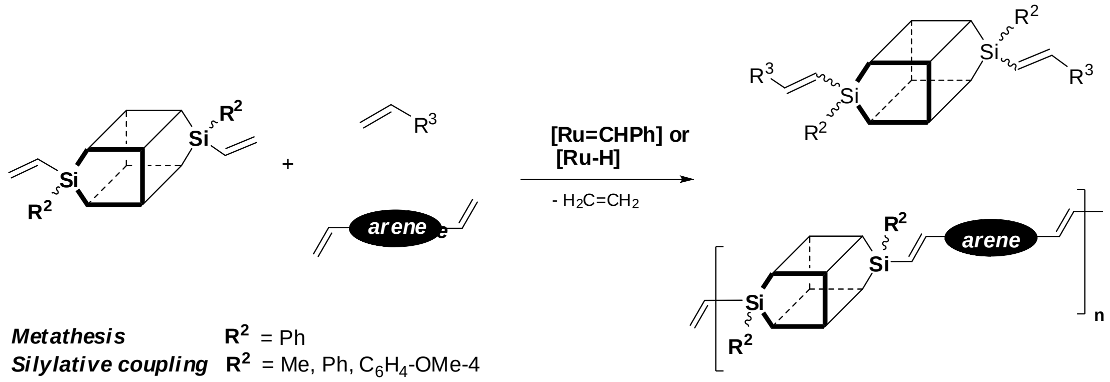
In the lecture, I focus on the application of metathesis and silylative coupling methodology to the synthesis of stereoregular dialkenyl substituted silsesquioxanes as well as novel silsesquioxylene-vinylene-arylene co-polymers according to the following general equation:[1,2]



Metathesis **R^2** = Ph
Silylative coupling **R^2** = Me, Ph, C_6H_4-OMe-4

R^3 = C_6H_5 (**a**), C_6H_4-Br-4 (**b**), C_6H_4-Cl-4 (**c**), C_6H_4-OMe-4 (**d**), C_6H_4-CF_3 -4 (**e**), C_6H_4-Me-4 (**f**), CH_2SiMe_3 (**k**), $CH_2C_6H_5$ (**l**), CH_2OH (**m**)

The fundamental thermal and mechanical properties (modulus of elasticity, friction, hardness and tensile strength) measured for selected polymer films are also discussed.
Our experience on metathesis and coupling of olefins with vinylsilicon derivatives has become a basis for extension of these procedures for functionalization of heterosilsesquioxanes containing boron or germanium[3] heteroatom which are studied as molecular and macromolecular models of new advanced materials.

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Sulfur Functionalization of Polyolefins using ADMET

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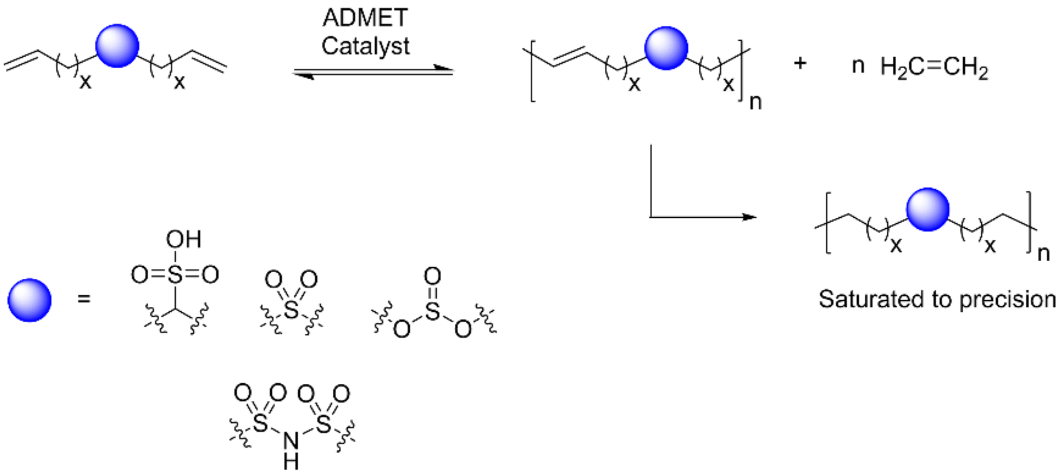
A series of oxidized sulfur-containing polyolefins has been synthesized via ADMET polymerization. Using the tolerant Grubbs' 1st generation metathesis catalyst to produce these polymers, we have further expanded our reach of precision functionalized materials. Sulfonate esters were synthesized by Opper et al. previously.[1] Building upon this, we devised "Reverse Solubilization Deprotection" as a strategy for quantitative deprotection of esters to acids, thus maintaining precision to create sophisticated ionomers. Sulfonimides containing acidic nitrogens within the backbone are also under investigation. Note the acidic backbone in comparison to the pendant sulfonic acid. Polysulfones display a thermal trend opposite other precision systems display: melting point of saturated polysulfones increase with increasing sulfone concentration from 115 ºC to 180 ºC. A more flexible, polar sulfite group may be introduced to lower the melting point slightly (38 °C). Sulfur functionalized displays a range of possible polymers and properties, while broadening the abilities of ADMET.



Representation of oxidized sulfur functionalities precisely placed via ADMET and subsequent saturation leading to symmetry and PE-type run-lengths

Acknowledgement: The authors would like to thank the US Army Research Office under grant #W911NF-13-1-0362. Also, we would like to thank Materia, Inc. for their gracious donation of catalysts used in this investigation

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Functional Polynorbornenes *via* Ring-Opening Metathesis Polymerization (ROMP) and Conjugated Polymers: Synthesis, Optoelectronic and Solar Energy Applications

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Polynorbornenes (PNBs) with various functional groups such as triarylamine, naphthalene, pyrene and hexaphenylbenzene (HPB) were synthesized *via* ring-opening metathesis polymerization (ROMP). PNBs showed excellent transparency at about 90% as well as thermal stability (T_gs from 160 to 245 ^oC) through incorporation of aromatic chromophores. Triarylamine-containing PNBs cast on flexible graphene displayed electrochromism and reversibility for multiple colour changes. The hexa-*peri*-hexabenzocoronene (HBC)-containing PNBs were prepared from HPB-containing precursors through cyclodehydrogenation. The PNBs with HBC moiety could be well dispersed in various organic solvents with exfoliated HBC emission in photoluminescence-excitation (PLE) maps. The conjugated polymers prepared *via* Suzuki coupling were used for wrapping single-walled carbon nanotubes (SWCNTs) to obtain semiconducting nanotubes. Their chiralities such as (6,5), (9,5) or (8,7) were confirmed by PLE maps as well as UV/Vis/NIR absorption spectra. In addition, polytriarylamine- or poly(triarylamine-fluorene)-based conjugated polymers possessed water/alcohol solubility, indicating that they are suitable materials for the hole-transporting layer of solar cells such as dye-sensitized solar cells (DSSCs) and organic photovoltaics (OPVs). When the alcohol soluble polytriarylamine-based conjugated polymer was used in perovskite solar cells, the overall power conversion efficiency (PCE) at 6.3% was higher than that of the PSS:PEDOT-based solar cell at 3.9%. These organo-soluble polymers can be used in large-scale solution processes to fabricate optoelectronic devices including organic light emitting diodes (OLED), solar cells, organic field effect transistors and for smart window applications.

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Phosphite Ligands in Ru-catalysed Olefin Metathesis

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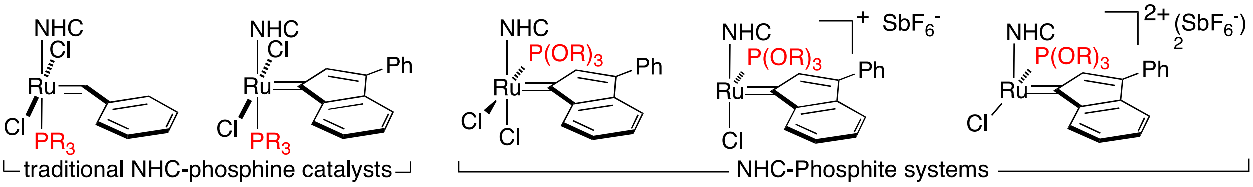
In this presentation, our recent work on the use of phosphite ligands in Ru-catalysed olefin metathesis will be discussed.[1-6] These studies led to the isolation of complexes having an unexpected behaviour and geometry, the bulky ligands NHC and P(OR)$_3$ being *cis* to each other (see Figure). Catalytic studies showed these systems to outperform state-of-the-art catalysts. The latest findings concerning these systems will be presented.



Phosphite-bearing alkene metathesis complexes.

The synergy of the mixed ligand system is clearly reflected by its catalytic activity compared to conventional systems. Further derivatisation of the system has led to cationic systems of high activity and unprecedented thermal stability, and to a rare example of Ru(III) 13-electron complex. Novel synthetic routes to well-defined mixed ligand systems and catalytic performance will be discussed, as well as the exact influence of this potential synergistic effect in olefin metathesis.

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Looking Inside the Ru-NHC (N-Heterocyclic Carbene) Bond

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Understanding the details of the nature of the interaction between NHCs with metal centres, and how these properties are influenced by the NHC structure, is of fundamental interest, since they impact the overall catalytic behavior. In this respect, selenourea and phosphinidene complexes have been used to measure the π-accepting ability of NHCs, independent of their σ-donating ability, via the collection of ^{77}Se or ^{31}P NMR spectra, respectively.[1,2] Herein, we will summarize our recent computational characterisation of the Se-NHC and P-NHC bonding with selenoureas and phosphinindenes derived from a range of imidazol-2-ylidenes, 4,5-dihydroimidazol-2-ylidenes and triazol-2-ylidenes ligands.[3] Bond energy decomposition analysis was used to quantify the ability of NHCs to accept π-electron density. Using the same techniques, we will present results aimed to achieve a better understanding of the Ru-NHC bond in prototype complexes representative of catalysts active in olefin metathesis.

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Polycyclopropene-Based Ladderphanes and Related Polymers

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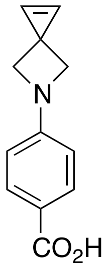
As part of our continuing interests in the chemistry of ladderphanes,[1] we are pleased to report poycyclopropene-based ladderphanes and related polymers. Monomeric cyclopropene-carboxylic acid was designed and synthesized. Through ester linkages, a range of different pendants and linkers were introduced to form the corresponding monomers **2** and **3**. ROMP of **2** and **3** using Schrock catalyst gave the corresponding polycyclopropenes **4** and ladderphanes **5** selectively. It is worth noting that the spacing separating the adjacent pendants or linkers in **4** and **5** would be less than those in polycyclobutene- and polynorbornene-based ladderphanes. The properties of these polycyclopropene–based polymers will be discussed.



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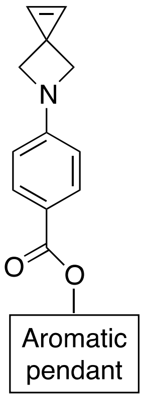

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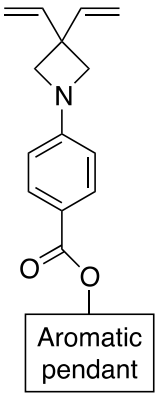

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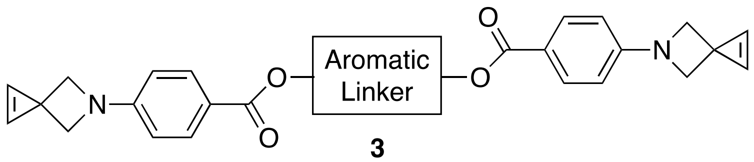

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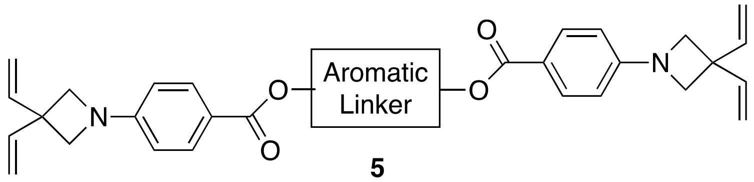

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Ring-Opening Alkyne Metathesis Polymerization: Teaching Polymers the Meaning of Life

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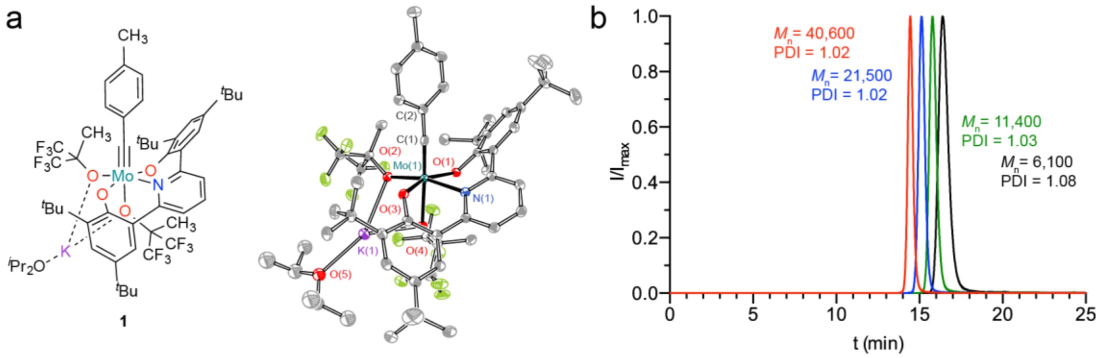

a) ORTEP representation of the X-ray crystal structure of ***1****; b) GPC traces for polymers produced through ROAMP with catalyst* ***1*** *at variable monomer/catalyst loadings*

Since its discovery in the mid-sixties, the development of stable, well defined, and functional group tolerant olefin metathesis catalysts has greatly influenced the fields of organic synthesis, polymer and materials science. Although alkene metathesis has found a wide range of applications, alkyne metathesis has only recently become the focus of attention. We have developed a pseudo-octahedral molybdenum benzylidyne complex [TolC≡Mo(ONO)(OR)]•KOR (R = $CCH_3(CF_3)_2$) (**1**), featuring a stabilizing ONO pincer ligand, initiates the controlled living polymerization of strained dibenzocyclooctynes at $T > 60$ °C to give high molecular weight polymers with exceptionally low polydispersities (PDI ~ 1.02). Kinetic analyses reveal that the growing polymer chain attached to the propagating catalyst efficiently limits the rate of propagation with respect to the rate of initiation ($k_p/k_i \sim 10^{-3}$). The reversible coordination of $KOCCH_3(CF_3)_2$ to the propagating catalyst prevents undesired chain-termination and -transfer processes. The ring-opening alkyne metathesis polymerization with **1** has all the characteristics of a living polymerization and enables, for the first time, the controlled synthesis of amphiphilic block-copolymers via ROAMP.

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Metathesis and Peptidomimetics

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Olefin metathesis has emerged as a powerful synthetic tool for the construction of peptidomimetics and there is little doubt that there will be high demand for peptides that have been modified *via* metathesis to provide enhancement of *in vivo* stability, elimination of *in vivo* S-S scrambling and reductase cleavage, enhancement of cell penetration and formulation stability, and oral availability. Our interest in this area has centered on exploiting homogeneous catalysis to control the replacement of metabolically and chemically unstable disulfide bridges within peptides. The native S-S motif, formed *via* oxidation of cysteine residues, performs both structural and functional (redox active) roles in peptides and significantly affects receptor binding, proteolytic degradation and formulation stability.[1] Replacement of cystine with the dicarba isostere (*S,S*)-2,7-diaminosuberic acid (and its unsaturated variants) has been applied by us and others to several naturally occurring and synthetic cyclic peptides, including vasopressin, oxytocin, octreotide and insulin superfamily molecules.[2] Significantly, our work on human insulin has provided much needed insight into the biological mechanism of receptor activation and has provided analogues with unrivaled biological selectivity and physical stability. There is also enormous opportunity to utilise metathesis to construct dicarba-based analogues of disulfide-rich peptides which include antimicrobial defensins, knottins, cyclotides, venom-derived toxins and ST enterotoxins. The complex architecture generated by multiple interlocked S-S bridges presents a formidable synthetic challenge and not surprisingly only a small number of attempts have been made to date.[3] Applying metathesis to large, polar biomolecules is not without its challenges! This presentation will present the latest results from our laboratory and highlight i) protecting-group free olefin metathesis, ii) a spectroscopic model for determining *E*/*Z*-geometry in installed dicarba bridges, iii) stereoselective bridge installation, and iv) regioselective multiple bridge installation *via* projects involving insulin, oxytocin and analgesic conotoxins.

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Second-generation Ruthenium Catalysts for the Metathetical Ring-closure of Tetrasubstituted Cycloolefins

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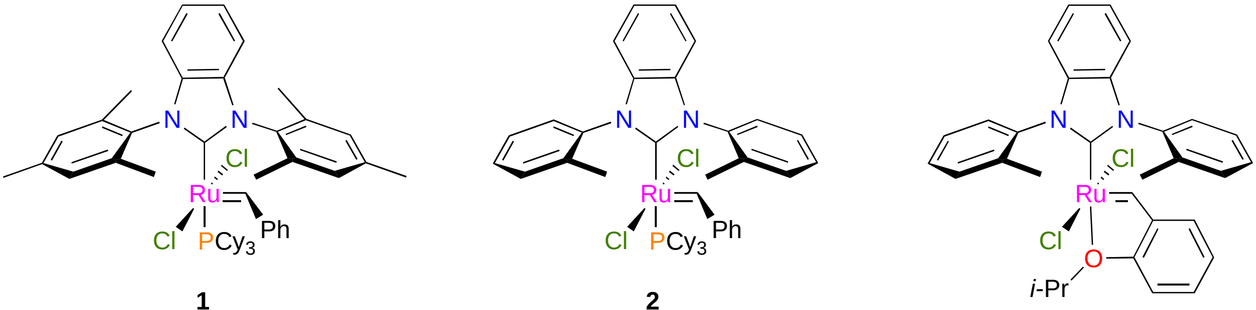
The introduction of N-heterocyclic carbene (NHC) ligands on well-defined ruthenium complexes has already afforded a wealth of highly active catalysts for olefin metathesis reactions.[1] However, the synthesis of tetrasubstituted alkenes remains a challenging task for most of these second-generation initiators, including the benzimidazolylidene derivative **1** that we developed in 2013.[2] Removing one of the *ortho*-substituents on the N-aryl groups of the NHC ligand is an efficient way to bypass this limitation and to ease the access of sterically hindered olefins to the catalytic center. This strategy was pioneered by Grubbs[3] and further implemented by other groups.[4] We have successfully applied it to the benzimidazolylidene family of ligands by replacing the mesityl-based NHC in complex **1** by it 2-tolyl analogue in catalysts **2** and **3**.[5]



1 **2** **3**

Second-generation ruthenium catalysts bearing benzimidazolylidene ligands

In this presentation, we shall discuss the stereochemical implications of the use of non-symmetrical aryl substituents on the NHC ligand of second-generation ruthenium-alkylidene complexes. We will also report on our latest investigations on this family of catalysts for the metathetical ring-closure of tetrasubstituted cycloolefins.

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(Imido)vanadium(V)-Alkylidene Complexes as Olefin Metathesis Catalysts

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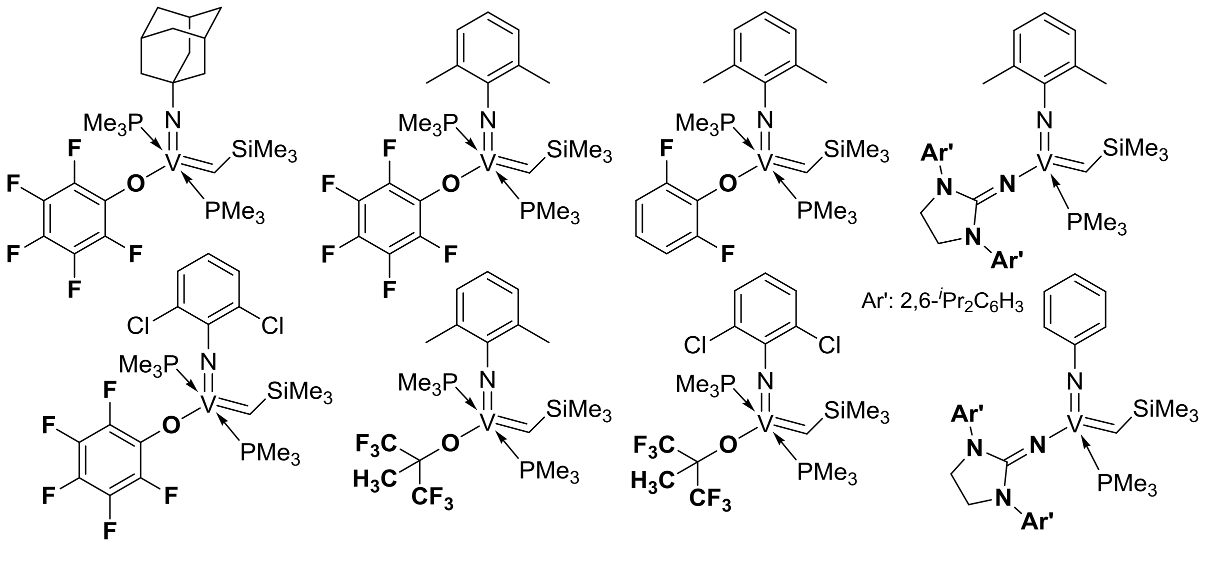
High-oxidation-state early transition metal alkylidene complexes are known to play essential key roles as catalysts in olefin metathesis. Our group focuses on synthesis and reaction chemistry of (imido)vanadium(V)-alkyl, alkylidene complexes because of fundamental importance in organometallic chemistry as well as of their potentials in catalysis.[1-3] We herein present that certain (imido)vanadium(V)-alkylidene complexes containing aryloxo ligands are highly active for (living) ring-opening metathesis polymerization (ROMP) of cyclic olefins and the activity can be tuned by the ligand modification.[2] Moreover, an efficient *cis* specific ROMP has been achieved by $V(CHSiMe_3)(N\text{-}2,6\text{-}X_2C_6H_3)[OCMe(CF_3)_2](PMe_3)_2$ (X = Me, Cl); both the activity and the selectivity increased upon addition of PMe_3 even at 50 ºC.[2d] We also present our results for synthesis and some reactions of (imido)vanadium(V)-alkylidene complexes containing imidazolidin-2-iminato ligands.[3b] Details will be introduced in the symposium.



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CONTRIBUTED LECTURES

Nitrenium Ions and Trivalent Boron Ligands as Analogues of N-Heterocyclic Carbenes in Olefin Metathesis

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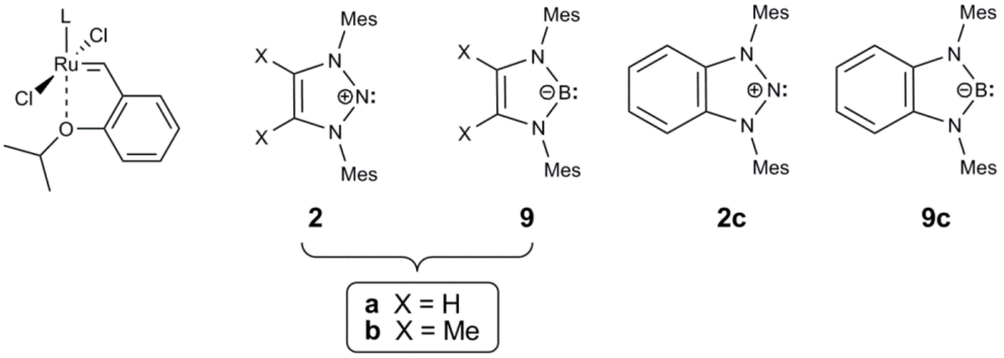
Unlike N-heterocyclic carbenes (NHCs), which are now commonly used in metal-based chemistry, the nitrogen-derived and boron-derived analogues, where either the nitrogen atom or the boron atom is attached directly to the metal center, has remained elusive as a ligand for metals. Recently, however, first stable complexes with such ligands has been prepared. Due to difficulties with the synthesis of ruthenium-based complexes of these ligands we decided to employ computational methods to asses, whether they are a viable option for new, potent metathesis catalysts. In this work we present a computational, density functional-based study of hypothetical Hoveyda-type Ruthenium catalysts with the original NHC group replaced by either nitrenium ions (NHNs) or trivalent boron NHC-like group (BHNs). We have analyzed the impact of the changes on the structural and electronic properties of six hypothetical catalysts: three bearing different NHN groups (**2a**, **2b**, and **2c**) and three with the BHN groups (**9a**, **9b**, and **9c**).[1] The structure of these precatalysts was based on the known Hoveyda- Grubbs catalyst (Figure 1). We also performed calculations for the initiation step of the catalytic cycle of these systems and compared them to the original Hoveyda catalyst.



Structure of investigated, hypothetical catalysts.

The results for all three precatalysts **2a-2c** clearly suggest that these hypothetical systems are poor candidates for potent and fast metathesis catalyst. The commonly used catalysts are characterized by energy barriers of approx. 19-20 kcal/mol, yielding fast initiation at ambient temperature. Our calculations for the NHN-modified precatalyst give us free energy barriers of 27-28 kcal/mol for the interchange mechanism. On the other hand for the BHN-modified the activation free energies are estimated at 13-15 kcal/mol. Such low values should in this case translate to a very low initiation rate constant and very fast reaction rates.

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Artificial Metalloenzymes for Ring Closing Metathesis Based on the Biotin-Streptavidin Technology

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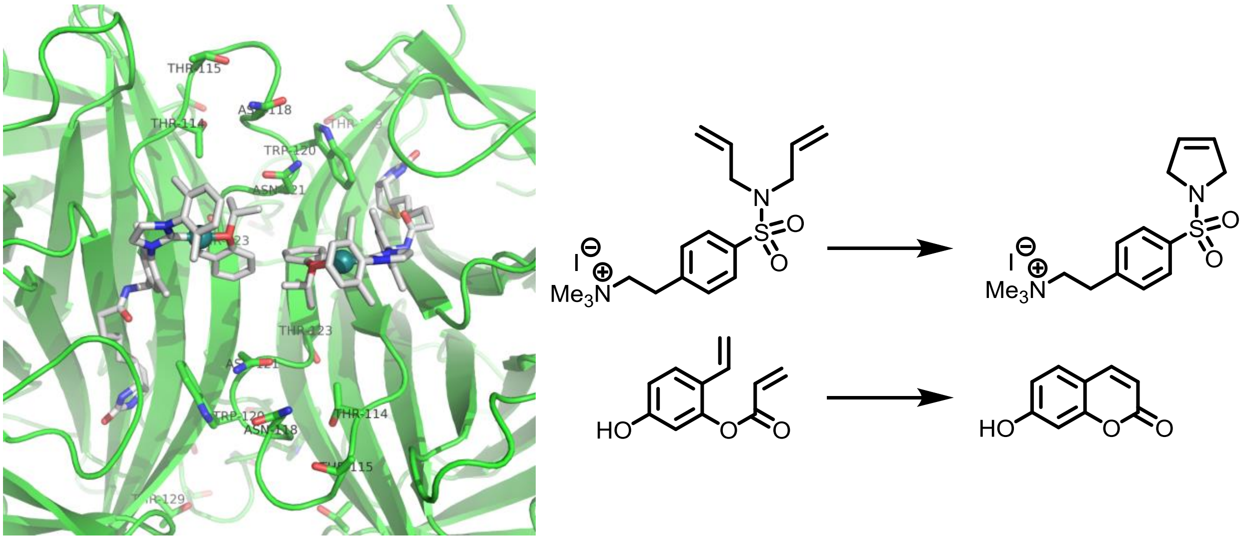
Artificial metalloenzymes consist of an abiotic metal cofactor anchored within a protein environment. Such hybrid catalysts combine beneficial features of biocatalysts with the diversity of chemical transformations available with transition metal catalysts.[1] While no enzyme is known to catalyse olefin metathesis, a variety of homogeneous catalysts have been developed for this versatile transformation. Relying on the biotin-streptavidin technology, biotinylated Hoveyda-Grubbs 2nd generation-derived catalysts were combined with streptavidin mutants to afford an artificial metathesaze for ring closing metathesis.[2,3] To accelerate the genetic optimization of the artificial metathesases, two complementary screening protocols have been developed: the first relies on screening within the periplasm of *E. coli* whereas the second is based on partially purified cell-free extracts.



X-Ray structure of K121N Sav –[Ru] complex and ring closing metathesis of model substrates.

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Computational Kinetics to Account for the Reactants Concentration Influence in Ru-Based Catalysed Olefin Metathesis

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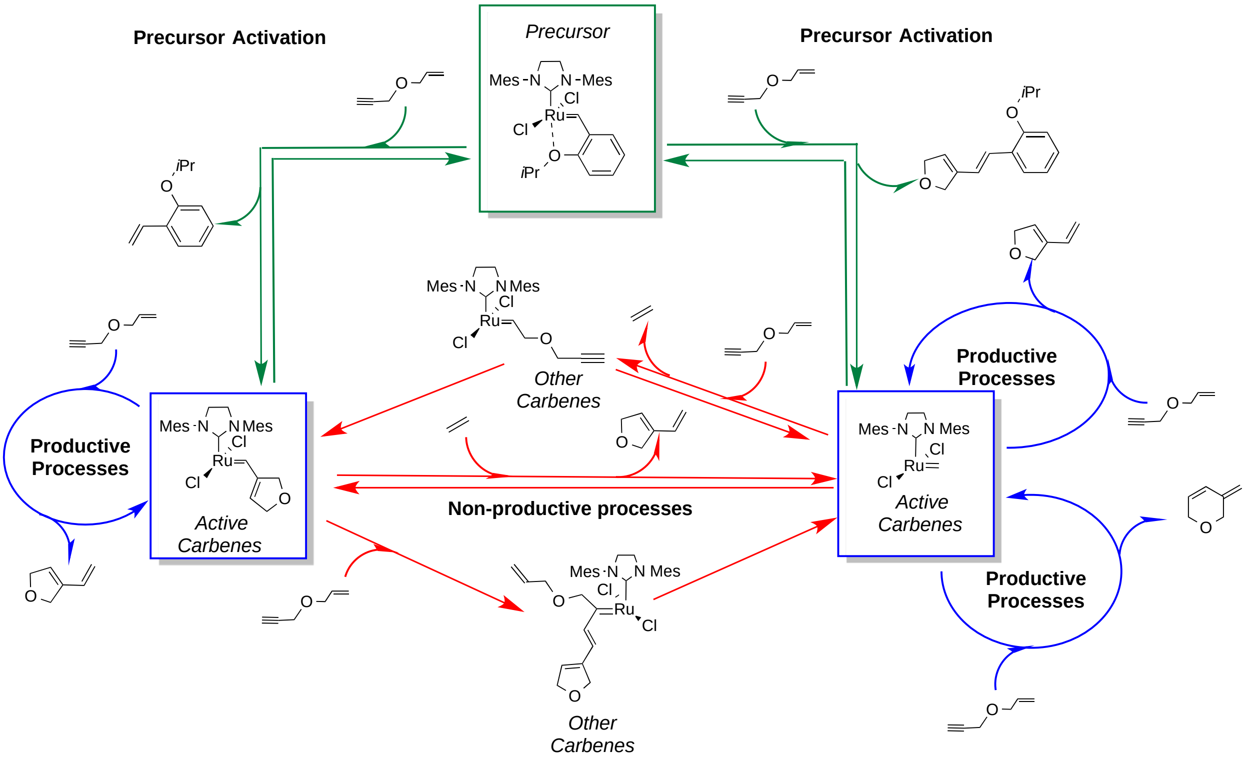
Kinetic models based on accurate QM methods can greatly enhance the understanding of complex catalytic systems.[1] Compared with studies based on the exploration of the potential energy surface, they allow a better determination of the nature of the rate determining intermediates and transition structures as well as to account for the influence of reactants and catalyst concentrations. This is important when several competitive pathways with very similar energetics are involved. In this sense the olefin metathesis is a paradigmatic example.

In this contribution, we will present a kinetic study based on previous DFT calculations on the *exo-/endo-* selectivity in Ring Closing Enyne Metathesis catalyzed by second generation Hoveyda-Grubbs catalysts.[2] For that, we will consider the full catalytic process: catalyst activation, productive cycle, non-productive processes and potential precursor regeneration. Results allow determining the role of reactants (specially ethene) concentrations on the applying reaction mechanism (*ene-then-yne* and *yne-then-ene*).



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Valorization of Polybutadiene Waste Streams to Unsaturated Macrocycles with Ru Metathesis Catalysts

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Large and unsaturated ring structures exhibit unique physical and chemical properties due to a dense conformation and the absence of chain ends. Industrially produced unsaturated ring structures include cyclooctadiene and cyclododecatriene (CDT). Because of a lack of feasible synthesis methods, larger macrocycles are not produced. The cyclo-depolymerisation of polybutadiene by metathesis however can herefore provide a worthy route. Since polybutadiene is produced on a large scale, waste streams are readily available and cheap. Previous research already showed interesting results with respect to the thermodynamic equilibrium.[1]

Here, we present an innovative process for the production of these larger macrocyclic structures with a ring size of C16-C44 carbon atoms. The obtained yield is greatly influenced by the type of the polybutadiene, reaction conditions and somewhat surprising the ligand environment of the Ru catalyst.

Study of the polybutadiene type highlighted the importance of a HMW polymer lacking vinyl groups. By this, high yields (93 %) of ring structures were obtained. Equilibrium distributions are dominated by *all-trans* CDT, which is economically less relevant. Although CDT is thermodynamically favored, it is a secondary reaction product from kinetically favored larger macrocycles, formed by tandem ring-opening ring-closing metathesis (RO-RCM). Further investigation of the reaction conditions on both equilibrium and kinetic product distributions clarified an optimal substrate concentration to maximize the kinetically formed C16-C44 macrocycles. Via variation of the ligand environment of the Ru catalyst, the secondary formation of CDT could be efficiently suppressed (Figure 1). Ru complexes lacking N-heterocyclic carbene (NHC) ligands (*e.g.* Grubbs I, Umicore I) seemed to be the success factor. A pseudo-equilibrium with a yield of 86 % macrocycles (C16-C44) was finally achieved.

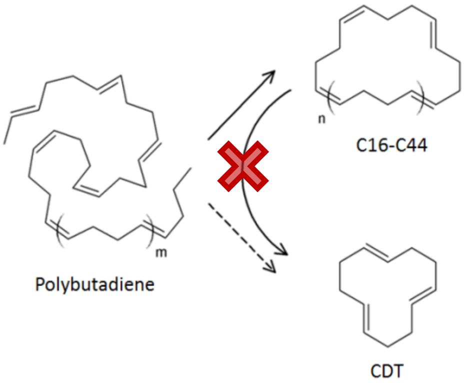

Figure 1: Proposed reaction scheme for the formation of cyclic oligomers from polybutadiene. C16-C44 macrocycles are produced directly from polybutadiene and subsequently converted to mainly CDT via RO-RCM, but this can be suppressed using Ru complexes lacking NHC-ligands.

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Synthesis of Organometallic Nanoparticles via Intramolecular Cross-linking of ROMP-derived Polymers

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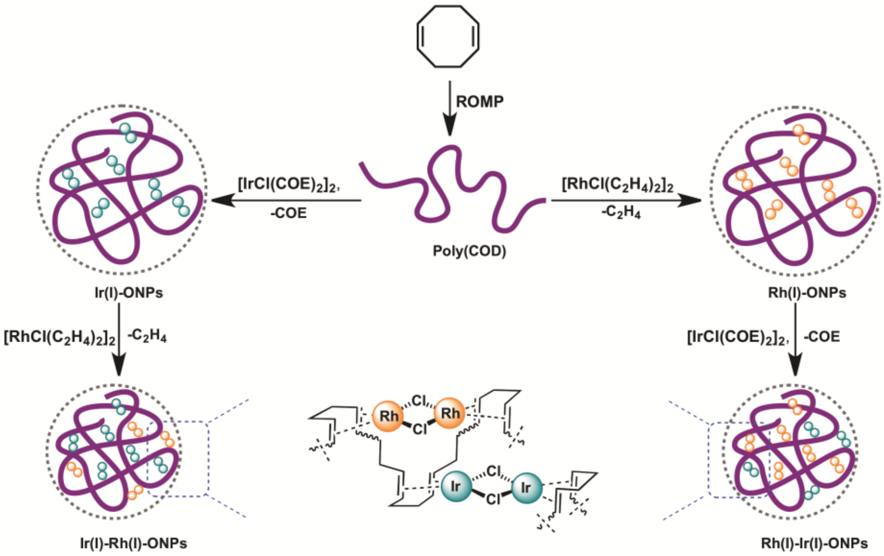
Department of Chemistry, Ben-Gurion University of the Negev,
Beer-Sheva 84105, Israel

Folding of single polymer chains is an appealing method for the synthesis of organic nanoparticles (ONPs) suitable for applications in nanomedicine, catalysis, imaging, recognition, etc.[1] Chain collapse involves the creation of an intramolecular cross-link between pendant functional groups on the polymer chain under dilute conditions. We have recently developed an approach to synthesize nanometric size mono- and bimetallic hybrid particles of ROMP-derived poly(COD) using various metal complexes such as $[RhCl(C_2H_4)_2]_2$ and $[IrCl(COE)_2]_2$ as cross-linkers.[2] The reaction of ROMP-derived poly(COD) with these complexes in dilute solutions produced well-defined π-bound polymeric complexes by direct exchange of labile ligands (ethylene or COE) by 1,5-hexadiene elements in poly(COD). The resulting polymer size, measured by DLS and SEC, was found to be inversely proportional to the amount of metal ions added due to concomitant intramolecular cross-linking. Moreover, the use of ROMP-derived copolymers such as polycyclooctadiene-*co*-polynorbornene carboxylate enabled the sequential folding of the single polymer chains with various metal ions utilizing orthogonal 1,5-diene and carboxylate functionalities. The synthesis, characterization, and intriguing properties of these nanometric size organometallic hybrid particles, as well as their application in selected metal catalyzed reactions will be presented.



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Applications of Olefin Metathesis to Polycycles and Cyclophanes

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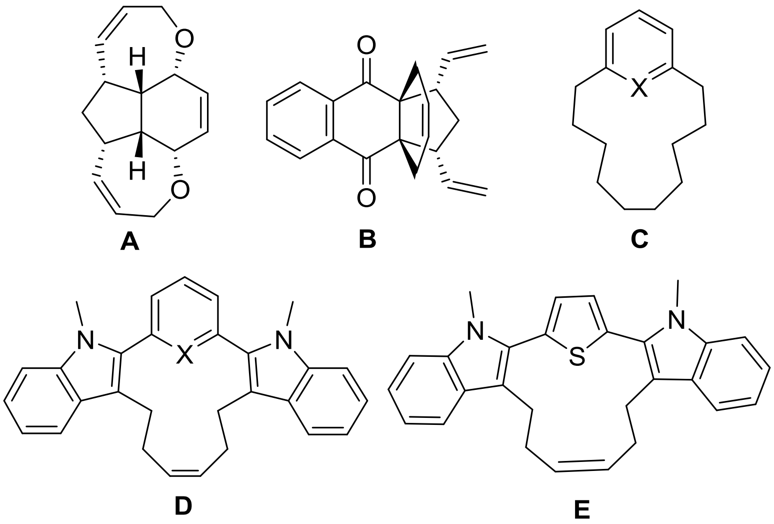
In this symposium we would like discuss the application of olefin metathesis to design polycycles by employing ring-rearrangement metathesis protocol. In this regard, carbocycles, oxacycles, and azacycles were reported from norbornene derivatives *via* Grignard reaction, Fischer indole cyclization, Diels–Alder reaction and ring-rearrangement metathesis as key steps.[1] A variety of cyclophane derivatives such as normuscopyridine and its analogues were reported *via* Grignard reaction, Claisen rearrangement and ring-closing metathesis as a key steps.[2]



Selected examples of polycycles and cyclophanes prepared by olefin metathesis

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Catalytic Enantioselective Synthesis of Planar-Chiral Zirconocenes and Their Application as Chiral Catalysts

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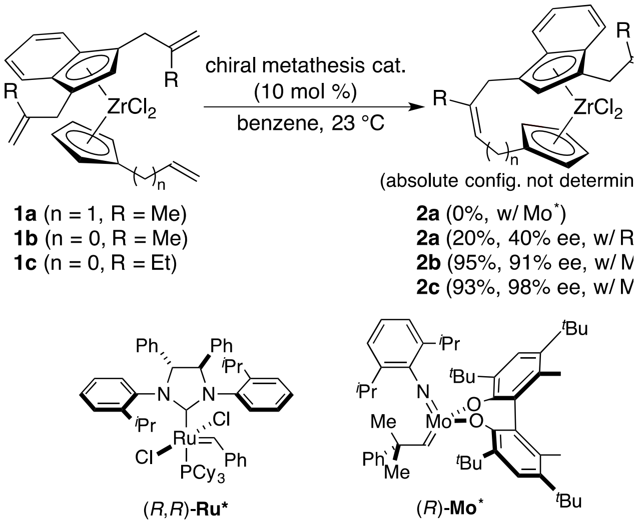
Planar-chiral metallocenes are important chiral scaffolds in organic/organometallic chemistry. However, *catalytic asymmetric synthesis* of such metallocenes has been rather unexplored. Recently, we have developed the asymmetric ring-closing metathesis (ARCM) protocols of preparing various planar-chiral complexes.[1] The substrates examined so far are 18-electron organometallics, such as ferrocenes[1a,c] and (π-arene)chromium complexes.[1b] Here we report the asymmetric synthesis of planar-chiral zirconocene species, which are 16-electron, Lewis acidic, and potential catalysts in further organic transformations.

Planar-prochiral C_s-symmetric triallyl-zirconocene **1a** was designed, and its ARCM reaction was examined. The **Mo***-catalyst[2] gave the undesired cross-metathesis dimer and the RCM product was not obtained. On the other hand, the **Ru***-catalyst afforded *ansa*-zirconocene **2a** only in 20% yield with 40% ee. In ARCM of the ferrocene/(π-arene)chromium substrates,[1] the length of olefinic tethers showed the dramatic effects in both chemical yields and the enantioselectivity of the RCM products. Whereas the bent metallocene structure of the Zr species puts the two η^5-ligands in closer proximity, the C_4-bridge in **2a** might be too long for the ARCM synthesis of *ansa*-zirconocenes. And indeed, zirconocenes **1b** and **1c**, which afford the C_3-bridged *ansa*-zirconocenes by RCM, are the excellent substrates for the ARCM reaction. Substrate **1b** reacted smoothly in the presence of **Mo*** to give **2b** in 95% yield with 91% ee. The enantioselectivity could be further improved to 98% ee by replacing the methyl groups of the methallyl side-arms with ethyl substituents in **1c**/**2c**.



Asymmetric Ring-Closing Metathesis Preparing Planar-Chiral ansa-Zirconocene Complexes

Applications of the planar-chiral C_1-symmetric zirconocene products as catalysts for the asymmetric carbometallation reactions are now under investigation, and additional results as well as details of the ARCM process will be presented at the symposium.

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Stereoselective ROMPs of Norbornenes: Development of New Polymer Materials Based on Stereocontrol

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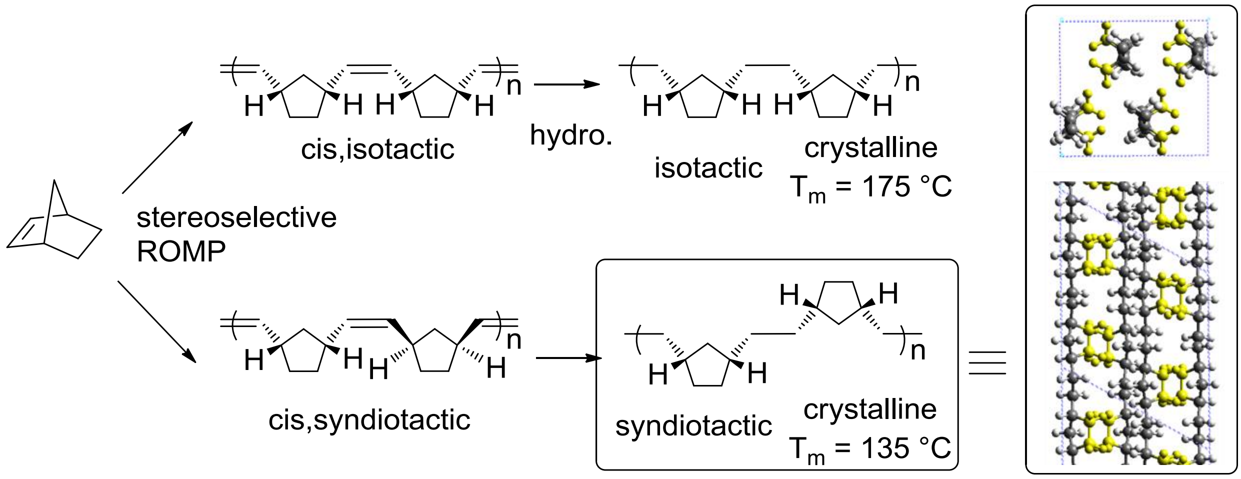
Stereospecific ring-opening metathesis polymerization (ROMP) of cycloolefins has been studied intensively in the past decades. Especially, iso- and syndio-specific ROMPs of various monomers have been attained by new monoalkoxide pyrrolide (MAP) Schrock catalysts in which the metal is stereogenic center.[1]

Recently, we have investigated isospecific- and syndioselective ROMPs of norbornenes such as norbornene (NB), dicyclopentadiene (DCP) and tetracyclododecene (TCD) by binary Mo- and W-based catalysts.[2] MoO(*rac*-5,5',6,6'-Me_4-3,3'-*t*-Bu_2-biphenolate)$_2$ gave cis,isotactic poly(NB) and poly(TCD), while $WNPhCl_4Et_2O$ provided cis,syndiotactic polymers. The following hydrogenation proceeded completely to form saturated polymers with retention of stereostructure of the backbone.

We found that control of stereostructure gave drastic influence on the properties of hydrogenated poly(NB), poly(DCP) and poly(TCD). For example, isotactic, atactic and syndiotactic hydrogenated poly(NB)s have different crystal structure, and in turn, different thermal performances such as melting point and crystallinity. Crystal structures of tactic and atactic hydrogenated poly(NB)s were determined by 2D-XRD measurement of monoaxially oriented polymers. Especially, hydrogenated isotactic- and syndiotactic-hydrogenated poly(DCP)s were characterized by extremely high melting and high crystallinity, suggesting potential application as engineering plastics.



Stereoselective ROMPs of NB: thermal properties and crystal structure of tactic polymers.

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Ruthenium-Based Olefin Metathesis Catalysts Bearing pH-Responsive NHC Ligands for ROMP in Aqueous Media and Emulsions

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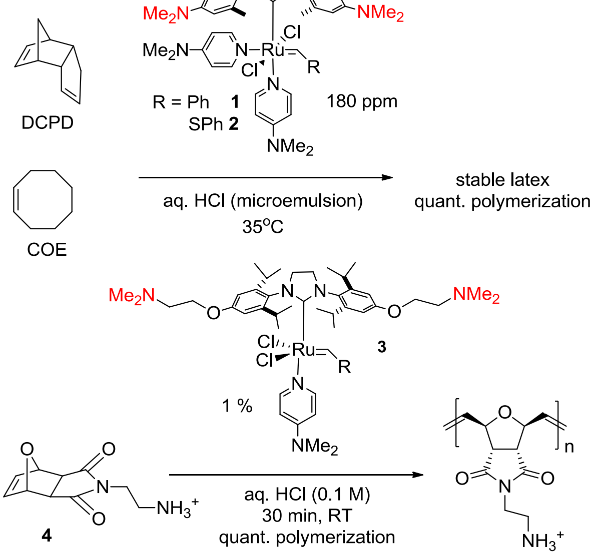
Despite the relative hydrolytic stability of the aqueous, Ru-based olefin metathesis reaction, today's known water-soluble catalysts are still lacking either due to their low relative metathesis activities in aqueous media or the rather cumbersome, multistep syntheses required for designs which actually exhibit moderately high activities.[1] In our efforts to develop highly active, water-soluble catalysts, we synthesized a series of catalysts bearing an NHC ligand (H_2ITap) bearing two aryl-NMe_2 groups.[2] The protonation of these groups in acidic aqueous media affords water-solubility, but also generates a species with low metathesis activity in aqueous media.[2a] However, complexes **1** and **2** accomplish quantitative conversions of DCPD and COE in micro-emulsion with acidic aqueous media using catalyst loadings as low as 180 ppm and in reaction times as low as 30 min, while forming stable latexes. To date, ring opening metathesis polymerization (ROMP) in emulsion have not been quantitative with neither such low catalyst loadings nor these low-reactive monomers.[3]



We have also addressed the low metathesis activity of the H_2ITap-bearing catalysts in aqueous media by developing a four-step, low cost synthesis to a small library of NHC-ligand precursors containing remote alkyl-NMe_2 groups which can be straightforwardly protonated with a variety of acids. Catalyst **3** performed quantitative ROMP of monomer **4** in aqueous acid in less than 15 min which rivals today's most active catalysts designs.[1]

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How to Teach Z Selectivity to Grubbs Catalysts

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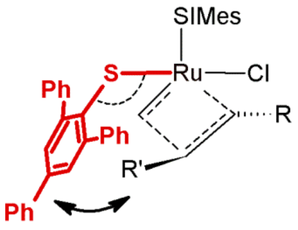
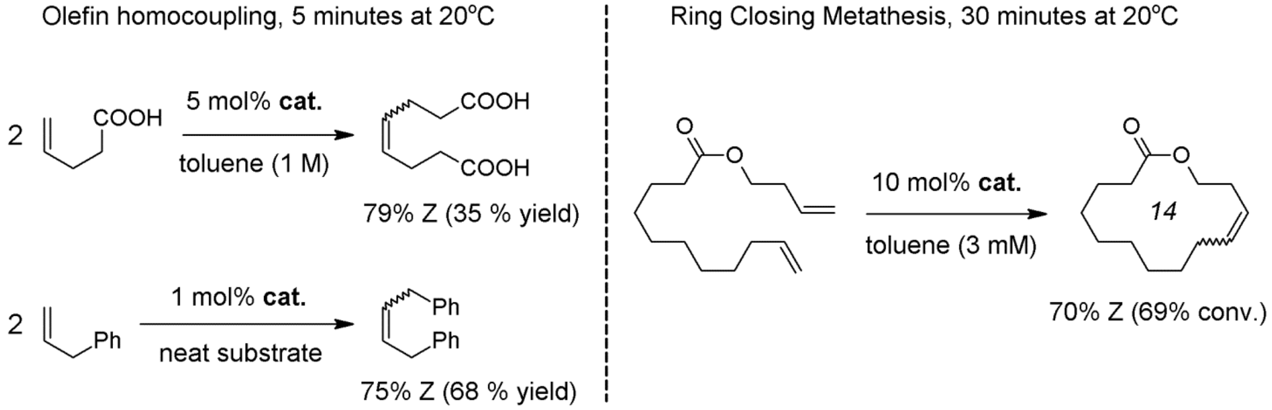
Ruthenium-based olefin metathesis catalysts of the general kind $RuCl_2(NHC)LCHR$ are known for their excellent activity, robustness and functional group tolerance, for example towards carboxylic acids, and they are tempting starting points for development of Z-selective olefin metathesis catalysts. A catalyst with >90 % Z-selectivity in metathesis homocoupling of terminal olefins can be obtained already by substituting a single chloride for a sterically demanding arylthiolate in the Hoveyda-Grubbs catalyst.[1,2] The selective catalyst metathesizes olefins following the same mechanism, with formation of the metallacyclobutane intermediate trans to the NHC (as shown to the right),[1,3] as the parent catalyst. Next, also the robustness (air, acid, etc.) of the parent catalyst may be "inherited" by the selective catalyst, via substitution of the second Cl by NCO.[4] Unfortunately, the application of these catalysts has so far been limited by their tendency to olefin isomerization, moderate activity, and poor performance in RCM.



We have now overcome these challenges (see scheme below). To illustrate: our most recent brand of thiolate-based catalysts reach appreciable yields after only a few minutes for most substrates, also at room temperature, and they are efficient at the high substrate dilutions of RCM, some even at temperatures >100°C. More importantly, these catalysts are the first Z-selective catalysts able to metathesize substrates with acidic functional groups, another property inherited from the parent $RuCl_2(NHC)LCHR$ catalysts.



Metathesis experiments using one of the new thiolate-based catalysts.

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Quantitatively Analyzing Metathesis Catalyst Activity and Structural Features in Silica-Supported Tungsten Imido–Alkylidene Complexes

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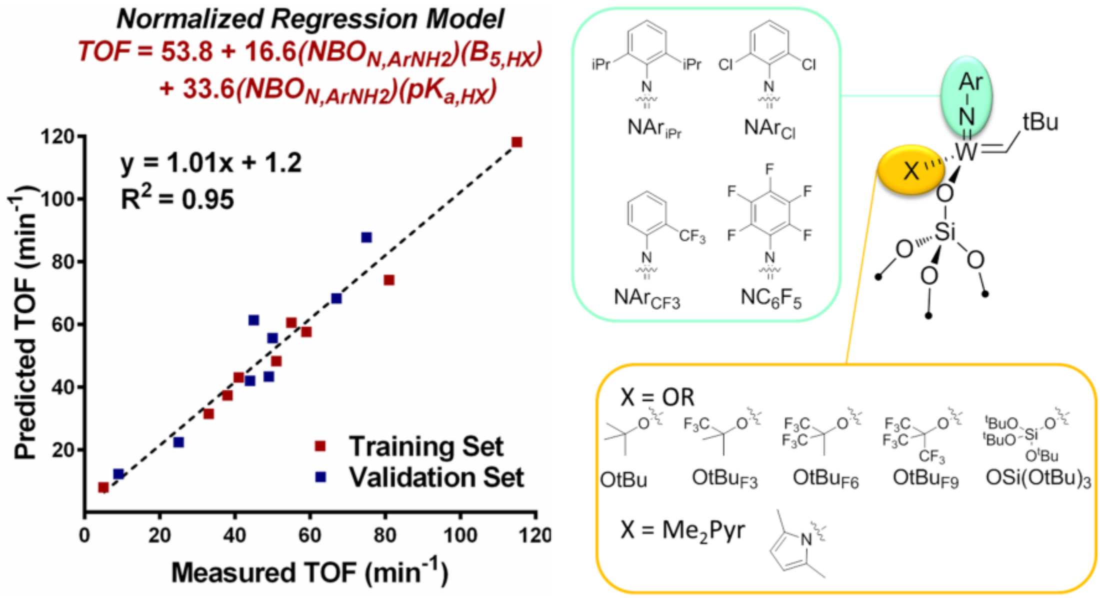
Over the past years, experimental and computational investigations of d^0 group 6–7 homogeneous and heterogeneous catalysts have provided insights allowing for tremendous advances in the understanding of active site structure and reactivity of metathesis catalysts.[1,2] However, the ligand effects and structural factors that influence the catalytic activity of these catalysts still remain unclear. We have here synthesized a broad series of fully characterized well-defined silica-supported W metathesis catalysts with the general formula $[(\equiv SiO)W(=NAr)(=CHCMe_2R)(X)]$ by grafting bis-X substituted complexes $[W(NAr)(=CHCMe_2R)(X)_2]$ on silica partially dehydroxylated at 700 °C, and evaluated their activity with the goal to obtain detailed structure–activity relationship (Figure 1). Quantitative influence of the ligand set on the turnover frequency (TOF) in self-metathesis of *cis*-4-nonene was investigated using multivariate linear regression analysis tools. We will describe here how the TOF of these catalysts can be predicted from simple steric and electronic parameters of the parent protonated ligands.



Multivariate linear regression model to predict TOF in cis-4-nonene self-metathesis

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Tailored Made Al-Doped Silica Dramatically Improves the Metathesis Activity of Re-Oxo-Alkylidene Supported Complexes

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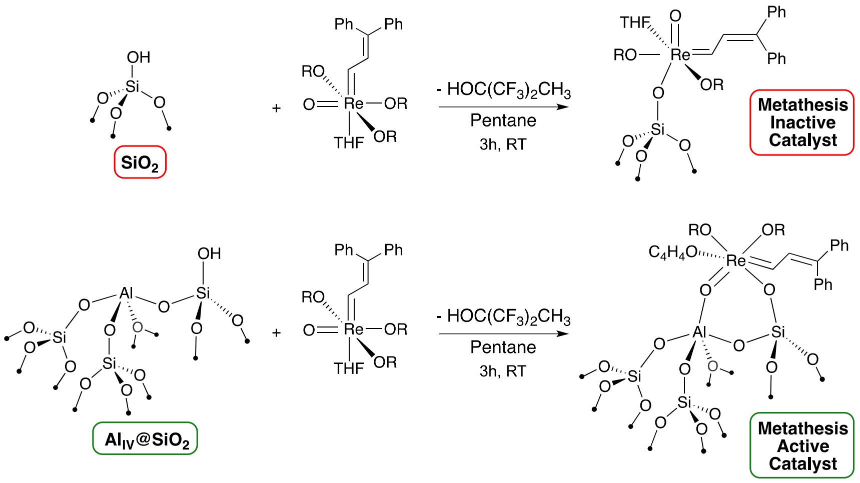
Re_2O_7/γ-alumina is the only heterogeneous alkene metathesis catalyst active at room temperature, and despite forty years of research the structure of the active sites and the intermediates are still unknown. Previous study on the model system CH_3ReO_3/Al_2O_3 allowed the observation of the metallacyclobutane metathesis intermediates for the first time for a Re catalyst.[1] However, the alkylidene species could not be observed on this system, and while probably generated in situ, their structures remains unknown.

The only example of well-defined supported Re^{VII} alkylidene is $(\equiv SiO)Re(\equiv C\text{-}t\text{Bu})(=CH\text{-}t\text{Bu})(CH_2\text{-}t\text{Bu})$, which was fully characterized by ^{13}C solid state NMR.[2] Nonetheless, its structure is far from the proposed active sites of the classical heterogeneous catalyst, in particular it has no oxo ligands. Worthy of note is the well-defined molecular compound having both oxo and alkylidene ligands, namely $Re^{VII}(=O)(=CH\text{-}CH=CPh_2)(\text{-}OC(CF_3)_2CH_3)(THF)$, which was reported in 1994 by Flatt and co-workers.[3] While inactive in metathesis, it could be activated by the addition of Lewis acids.

This work describes the transposition of this chemistry to well-defined Re oxo alkylidene supported systems. On partially dehydroxylated silica, a well-defined Re oxo-alkylidene was obtained and fully characterized, but it showed no metathesis activity catalyst (Figure1). In view of the activation of Re oxo alkylidene by Lewis acid, we will discuss here the development of a tailored made silica support containing both OH anchoring sites and Lewis acid site. The former allows the grafting of the molecular complex and the latter the activity of the Re alkyldene to provide a highly active metathesis catalyst (see Figure).



Grafting of $Re^{VII}(=O)(=CH\text{-}CH=CPh_2)(\text{-}OC(CF_3)_2CH_3)(THF)$ on SiO_2 and $Al@SiO_2$.

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Advances in Alkyne Metathesis: Photochemical *vs* Thermal Activation Using *in situ* Mo(CO)$_6$-phenols and -silanols Catalysts

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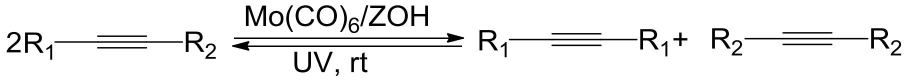
Molybdenum homogeneous alkyne metathesis was first reported using *in situ* generated catalysts consisting of Mo(CO)$_6$ and resorcinol as cocatalyst, as well as other phenols and silanols used in excess under thermal or photochemical activation.[1-3]
Microwaves activation has also proved to be an excellent way for producing Mo(CO)$_6$ based metathesis catalysts, using silanols as cocatalysts.[4]
Following our interest in the *in situ* synthesis of metathesis catalysts and our former experiments using UV irradiation at room temperature[2], we have been interested in this procedure to compare the activity of several Mo(CO)$_6$-ZOH systems.



$$2R_1\!-\!\equiv\!-\!R_2 \xrightleftharpoons[\text{UV, rt}]{\text{Mo(CO)}_6\text{/ZOH}} R_1\!-\!\equiv\!-\!R_1 + R_2\!-\!\equiv\!-\!R_2$$

ZOH = ArOH, Ar(R)$_2$SiOH, (Ar)$_2$RSiOH, Ph$_3$SiOH

The aim of this communication will be to describe data that will be focused on a comparison of the activity of these systems under thermal, or photochemical activation at room temperature, using 4-decyne and phenylpropyne as substrates.
Variations on the silanol $R^1R^2R^3$SiOH structures have been performed and have shown that mixed bis(alkyl)/aryl and bis(aryl)alkyl -silanols are at least as efficient as triphenylsilanol.[5]
It will be also shown that substitution of the hydroxyl group by the trimethylsilyl group leads to trimethylsilyl-phenoxy and trimethylsilyl-siloxy cocatalysts, which behave similarly as their unprotected precursors after an induction period.
Data relevant to the mechanism of the formation of the active species will also tentatively be exploited.
These results open a convenient and straightforward route to alkyne metathesis catalysts, and allow a rapid screening for comparing silanols as cocatalysts in this reaction, serving as a basis for the synthesis of new, well defined siloxy- based molybdenum carbyne complexes of higher or controlled reactivity.

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Challenges in Optimizing Alkyne Metathesis Catalysts

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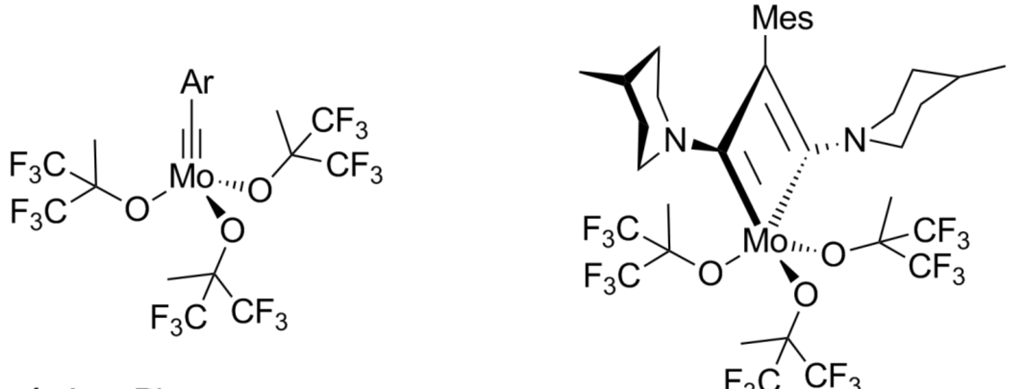
Alkyne metathesis - the catalytic cleavage and re-formation of a triple bond - has increasingly found applications in organic and polymer synthesis in the past decades.[1] Although several alkylidyne complexes of Mo and W have been reported as active catalysts for this reaction,[1–2] the functional group tolerance and substrate scope differ from one catalyst to another. For example, terminal alkynes are particularly challenging substrates, but our group recently reported a catalyst that is able to promote terminal alkyne metathesis (TAM).[3] On the other side, most of the catalysts are air-sensitive, which may be inconvenient regarding some applications.

To improve the catalyst stability and functional group tolerance is one of the goals of our research. On this basis, the established synthetic protocols have been modified in order to prepare new, otherwise inaccessible alkylidyne Mo complexes (**1**–**2**, see Scheme). Preliminary results concerning the stability and catalytic activity of these compounds will be presented in this contribution as well.

In addition, to gain a better insight into the mechanism and the deactivation pathways, we have explored the stoichiometric reaction of an alkylidyne complex with different substrates. In particular, the reaction with the electron-rich bis(4-methylpiperidino)acetylene led to the formation of the unusual, paramagnetic molybdenacylclobutadiene complex **3** (Scheme), an example for the well-established intermediates in the alkyne metathesis catalytic cycle.



1: Ar = Ph
2: Ar = 2,4,6-$(MeO)_3$Ph

3, Mes = 2,4,6-Me_3Ph

*Structure of the new alkylidyne complexes **1** and **2**,*
*and of the molybdenacyclobutadiene complex **3**.*

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High Activity, Stabilized Formulations, Efficient Synthesis and Industrial Use of Mo- and W-based Metathesis Catalysts

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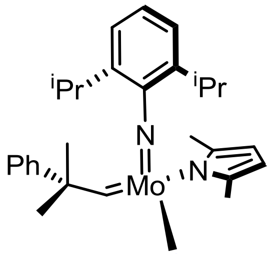
Despite scarce published evidence, Mo and W based metathesis catalysts excel at extremely low catalyst loadings. Feedstock quality granted loadings of 6 – 50 ppm (by mole) are common.

Regular industrial processes require large amount of catalysts, so the synthesis of kilogram quantities of MAP complexes (e.g. **1**) have been developed. The starting materials for the Mo- and W-catalysts, Na_2MoO_4 ($ 19 per kg) and WCl_6 ($ 60 per kg) are cheap. In the multistep synthesis[1] individual yields are high (82-97%) and the overall yield exceeds 60%. Use of industrial solvents and telescoping techniques which enabled the avoidance of sensitive intermediates' isolation renders a simple, scalable procedure and thus affordable priced catalyst.



1

ArO: *e.g.* tetraphenylphenoxy, subst. BINOL / octahydro-BINOL

Mo-based mono aryloxy pyrrolide (MAP) catalysts

Industrial use of our own complexes has been demonstrated with ton quantities in cross metathesis and with 20 kg in ethenolysis.

We have found different means to overcome moisture and oxygen sensitivity of these catalysts, which makes working without glove box a routine matter. It was discovered that several MAP catalysts are stable under atmospheric air in crystalline form for hours or even days. Others are protected as 10-20% paraffin solutions, giving pre-weighted, easy to use solid pellets. Again others are used as stable, chelated (Furstner kind)[2] complexes with an interesting new user friendly twist.

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Carbene Rotamer Switching Controls the Stereoselectivity of Ring Opening Metathesis Polymerization by Ruthenium-Catalysts

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Theory explained why the second-generation Ru-carbene catalyst is formed more slowly from the precatalyst.[1,2] An important mechanistic aspect is to uncover the role of multiple conformational structures in two steps of the catalytic mechanism. Computational analyses (M06-L DFT) reveal that the carbene rotamer acts as a toggle switch, triggering the dissociative mechanism to the active catalyst, also carbene rotamer energetic effects are responsible for the inverse relation between organophosphine dissociation rate and catalytic activity. Investigations detailed herein provide insight regarding the ring opening metathesis polymerization (ROMP) mechanism of stereochemical inversion of stereogenic at Ru carbene complexes through a carbene-rotamer relaxation and carbene-ligand rearrangement pathway. We illustrate how a better understanding in the propagation, where the norbornene is conjugated to the carbene ligand and the interaction with the consumption of next norbornene. Such interaction may also be important in directing the stereochemistry of the polymer during the course of the ROMP process of norbornenes with aryl pendant groups,[3] that serves as the basis for propagation of Ru-based E/Z isomer ratio as well as the tacticity for norbornene metathesis polymerization. The implications of the present studies regarding a more sophisticated knowledge of the role of asymmetric autocatalysis on the evolution of E/Z isomer with homotacticity of Ru-catalyzed ROMP reactions are discussed.

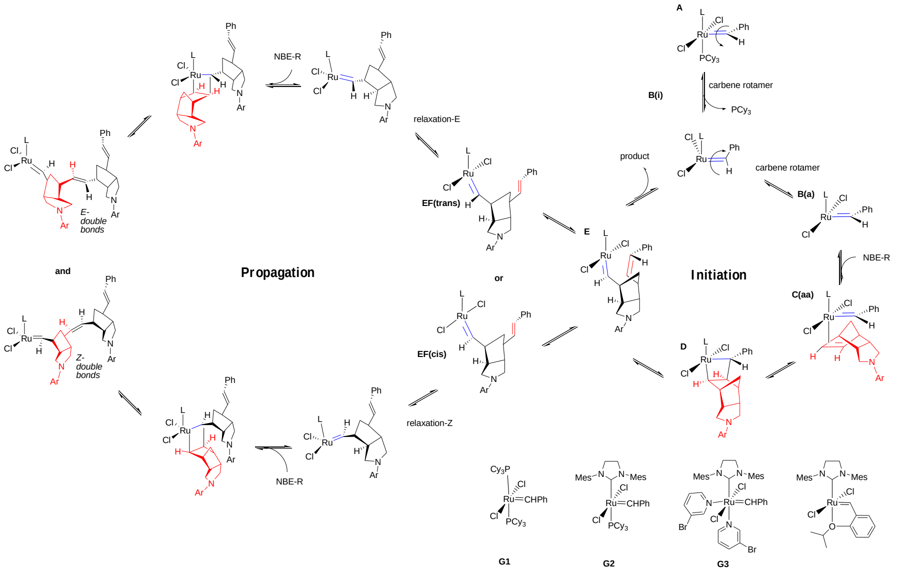

Figure. The schematic of Ru-based ring opening metathesis polymerization (ROMP)

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Theoretical Characterization of Ruthenium Complexes with Potential Activity on Olefin Metathesis: Challenges and New Advances

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Olefin metathesis is one of the chemical transformations most widely used in the synthesis of many organic compounds such as fine chemical, natural products and polymers. In this contribution, we present a summary of our latter computational results in four different topics. First, we address the different reactivity of the 1st and 2nd generation Grubbs catalysts in particular the ruthenacyclobutane formation. The calculations suggest that this event is easier from the second generation complexes than from the first one.[1] Secondly, we analyse the nature of the bonds and interactions involved in the initiation step by means of NBO theory and charge decomposition analysis.[2] These analysis allowed us to propose that the higher reactivity of the second generation catalysts arises from different effects: charge transfer, polarization and electron delocalization. The third study aims at understanding the different stabilities of the ruthenacyclobutane intermediate formed upon reaction with a terminal olefin as well as their interconversion pathways. The obtained theoretical results are in excellent agreement with the experimental evidence and they suggest that alkenes (**AR**) as well as carbene (**CR**) rotations are most likely interconversion pathways.[3] Finally, we have also performed a study on the factors influencing the *Z/E*-selectivity in Ru-based Grubbs type catalysts bearing chelating ligands. Results show that the constraints impose by the chelating group plays an important role in defining the *Z/E*-selectivity. However, the electronic nature of the ligands also plays an significant role.[4]

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Playing with the Relative Stability of Olefin Metathesis Catalysts

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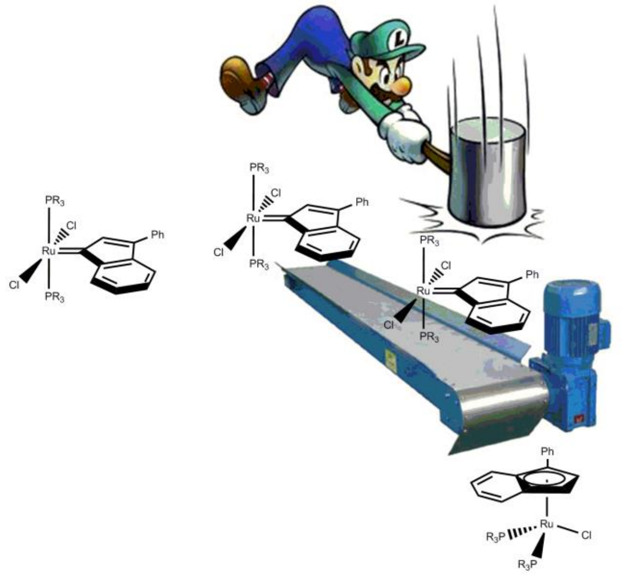
Olefin metathesis catalyzed by NHC ruthenium complexes still attracts remarkable attention as a versatile tool to form new C=C bonds,[1] and one recent example is the macrocycle active as a drug against hepatitis, requiring a Ru-based olefin metathesis catalyst for its synthesis.

We are try to unravel more mechanistic insights to improve the activity of the available olefin metathesis catalysts, modifying either the metal or the nature of the ligands.[2] However, understanding the decomposition routes of catalysts is extremely important as any insight gained in this area can guide catalyst design efforts. Take for instance, the well-defined and easily accessed [$RuCl_2(PPh_3)_2$(3-phenylindenylidene)], with poor performance as olefin metathesis catalyst, in solution under anaerobic and anhydrous conditions, exhibits rapid decomposition in the presence of alcohols. An unusual indenylidene to indenyl rearrangement has been uncovered,[3,4] DFT calculations are key to discover the mechanism and predict the decomposition reaction, and furthermore, explain the potential “innocent” role of the phosphanes.



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Classification of Metal Carbene Catalyst Types for Activity as Alkene Metathesis Catalysis: a QSAR-type Approach

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It is a well-established fact that the difference in the activity of the main types of metal carbenes[1-5] has a major influence on the efficiency and application of these metal carbenes as metathesis catalysts. The focus of a previous study[6] was to determine the effectiveness of frontier orbitals as chemical reactivity indicators in the alkene metathesis reaction, especially focusing on the generalized trend for alkene metathesis reactivity, the ligand effect on ruthenium metal carbenes, the bonding in the transition state of a Grubbs-type metal carbene catalyzed alkene metathesis reaction and the initialisation steps of the reaction up to the formation of the metallacyclobutane. FMO theory showed promising potential for clarifying the cause for the difference in the activity of the main types of metal carbenes catalysts.

Therefore, the method was further developed to a QSAR-type approach to examine the properties of the major metal carbene catalyst types in order to identify descriptors to classify the major metal carbene catalyst types with relation to the general activity trend. A comparative investigation of the foremost Fischer-, Tebbe-, Grubbs- and Schrock-type metal carbenes were done using computational methods and principal component analysis. The effect of the change in metal atom as well as the change in ligands was specifically considered. The results showed that the components obtained from the extracted principal component analyses could successfully reproduce or match the generalized trend for metathesis activity, highlighting the importance of the frontier orbitals in the metathesis reaction. The model was further tested by comparison of the known commercially available catalysts for alkene metathesis.[7]

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Modular Synthesis of Amino Acids and Cyclic Peptides Related to Histone Deacetylase Inhibition through Olefin Metathesis

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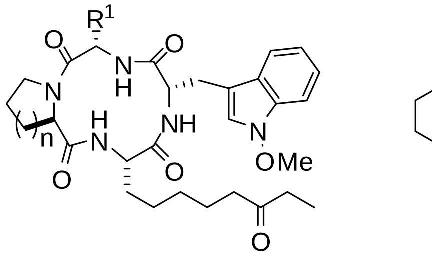
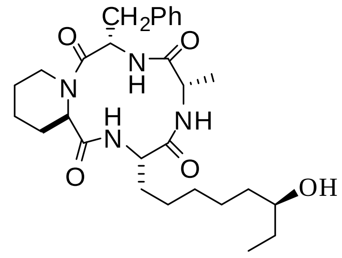
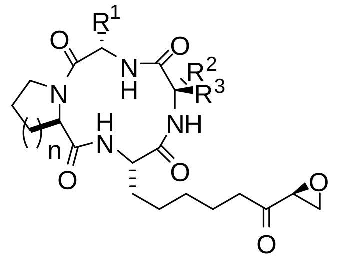
Inhibitors of Histone Deacetylase enzymes (HDAci) have attracted notable attention in the area of anti-cancer drug design from chemists and biologists.[1] A sub-class of such agents is the cyclic tetrapeptides having a pendant eight-carbon chain containing a keto (as in apicidines **1-2)**, a hydroxyl (as in microsporin B, **3**), or an epoxy ketone (as in trapoxins **4-5**) moiety required for reversible or irreversible metal binding as a prelude to their biological activity. Inspired by their potential as drug candidates, synthetic ramification of the two modules within these structures has remained important for the last three decades and occasionally such analoguing efforts have resulted in the identification of a better candidate.[2] A key to the success of such efforts is the design and synthesis of the unusual lipophilic amino acid component 2-amino-8-oxodecanoic acid (Aoda) or (2S, 9S)-2-amino-8-oxo-9,10-epoxydecanoic acid (Aoe) and modifications thereof. Several elegant methodologies have indeed been emerged for such purpose.[3] We have recently reported[4] a short synthesis of Aoda, Aoe and an analogue from a common precursor using cross-metathesis between the two terminal olefins of the type **6** and **7**. A modular approach towards the synthesis of natural products trapoxin and microsporin has been developed following our developed methodology. The results will be presented along with the scope and limitations.



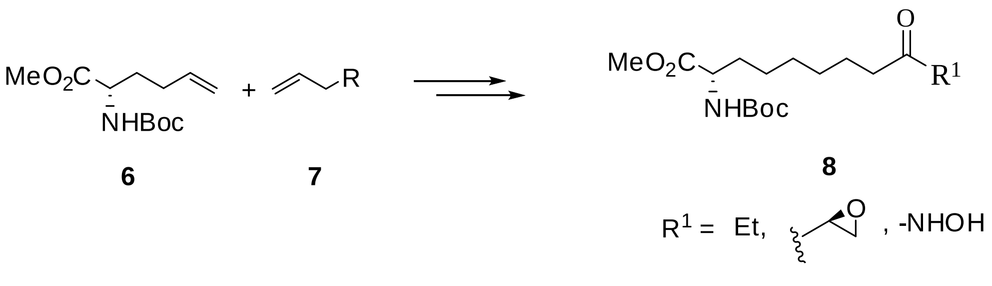
1, Apicidin B, n = 1, R^1=CH(CH_3)Et
2, Apicidin C, n = 2, R^1=$CHMe_2$



3, Microsporin A



4, Trapoxin A, $R^1 = R^2$ = Bn, R^3 = H
5, HC-Toxin C, $R^1 = R^3$ =Me, R^2 = H



6 **7** **8**

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The Olefin Metathesis Reaction in the Synthesis of Resorc[4]Arenes with Intriguing Architectures

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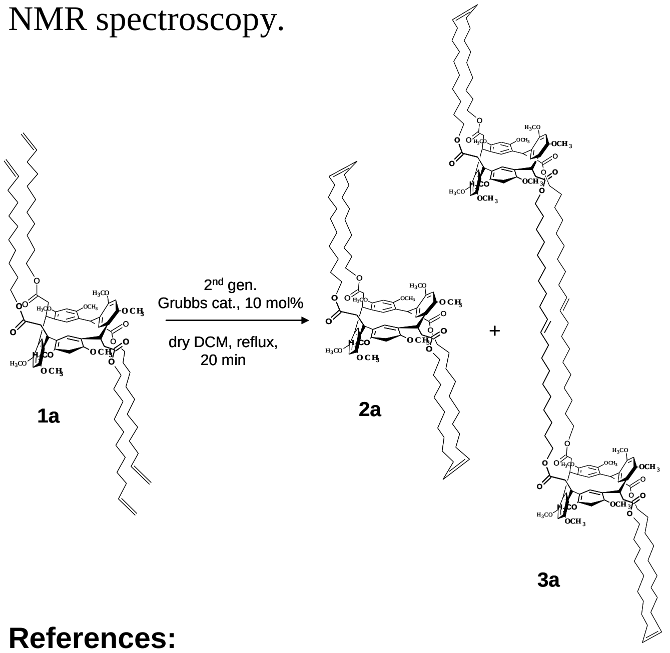
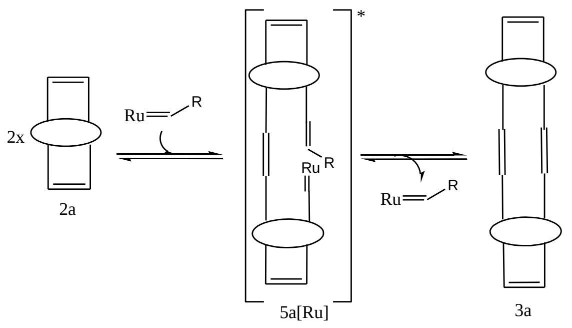
Tetramerization of (E)-2,4-dimethoxycinnamic acid ω-undecenyl ester with ethereal BF3 gave the three resorc[4]arene stereoisomers **1a**, **1b**, and **1c**, which were assigned a chair, cone, and 1,2-alternate conformation, respectively.[1] The *chair* stereoisomer **1a**, which featured the simplest pattern of substituents, was submitted to olefin metathesis, using the second-generation Grubbs complex as the catalyst. Depending on reaction conditions, different products were isolated: bicyclic alkene **2a** (46%), the linear dimer **3a** (5%), and a cross-linked homopolymer **P1a** (44%).

The synthesis of compound **2a** occurs by two almost contemporary ring-closing metathesis (RCM) reactions, driven by the elimination of two molecules of ethylene, passing through the isolated intermediate **[4a]**. With regard to the mechanistic pathway for the dimerization of **2a** leading to **3a**, we envisaged a series of reversible ring-opening-cross metathesis (ROM-CM) reactions passing through the not isolated intermediate [**5a**]Ru, which can be considered as the metallated form of a product proposed in the literature for the synthesis of cylindrocyclophanes.[2] Studies of the ROM-CM mechanism were carried out on compound **2a**, in comparison with similar macrocyclizations described in the literature.[3] The formation of intermediate [**5a**]Ru was monitorated by ^{1}H-NMR spectroscopy.



1a **2a** **3a**



2a 5a[Ru] 3a

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Substrate Specificity in Directing Ring Closing Metathesis of Trienes to Form Carbocycles or Oxacycles

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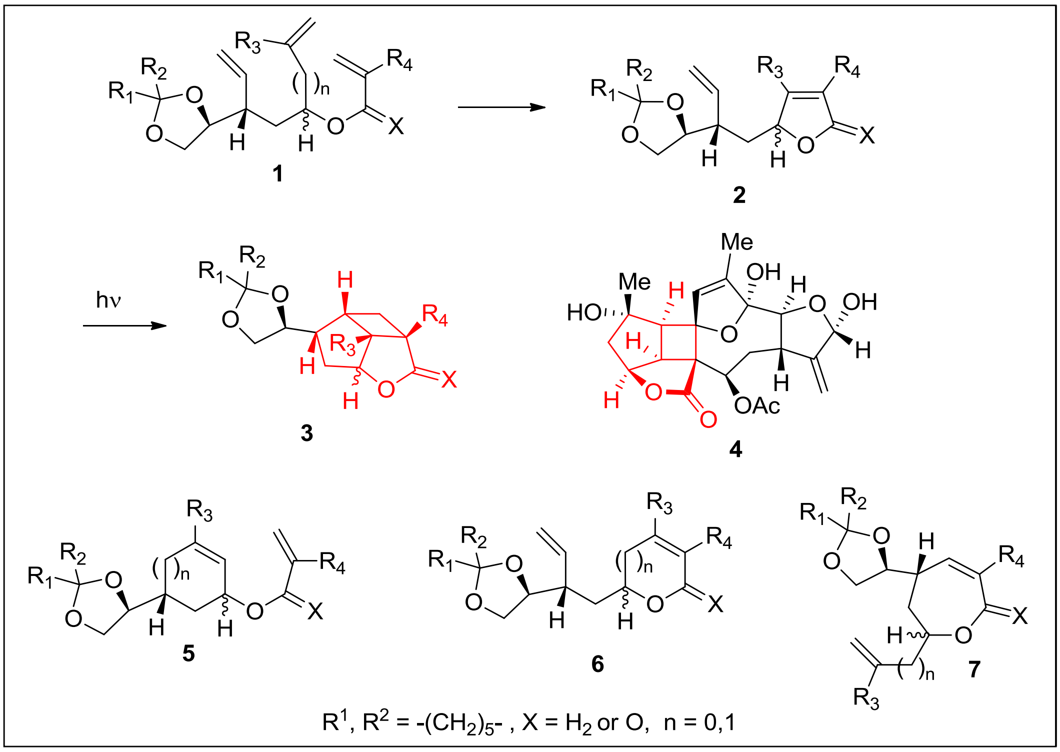
In connection to a program aimed at the synthesis of the antiplasmodial and anticancer diterpene beilschowskysin **4**,[1] we required the synthesis of the butenolide **2** (X=O), photocycloaddition of which is expected to provide the tricyclic bridged lactone **3** (X=O), the core structure present in **4**. Butenolide ring systems can be conveniently prepared through ring closing metathesis (RCM) of appropriate dienes.[2] We chose to employ RCM of the triene **1** (X=O, n=1) to provide **2** (X=O). RCM of **1** can lead to three different products-the cycloalkenes **5**, the oxa-cycles **6** and **7**. Although tandem RCM of alkene chains having tetra-and hexa-olefinic units has been studied,[3] there is no report on RCM of the triene systems such as **1**. We noticed that RCM of **1** can lead exclusively either to the cycloalkenes **5** or the oxacycles **6** or **7** by changing steric and electronic properties of the reacting alkene centers. The results of this investigation along with an approach towards the synthesis of **4** will be presented.



R^1, R^2 = -$(CH_2)_5$- , X = H_2 or O, n = 0,1

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Ring Closing Alkyne Metathesis And A *trans*-Selective Hydrogenation – On A Scalable Total Synthesis of (+)-Brefeldin A

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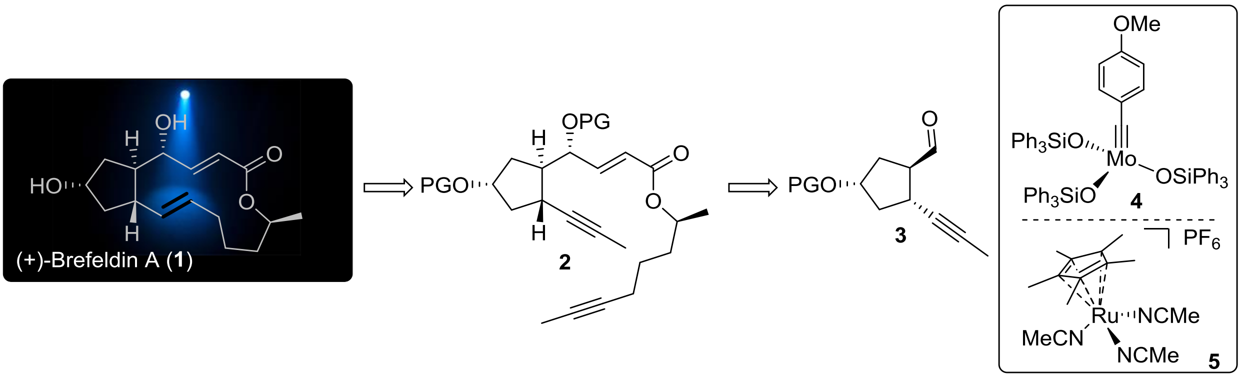
Alkyne Metathesis – without any doubt – has emerged as an extremely potent tool in the construction of macrocyclic compounds and an illustrious number of natural products has shown the outstanding tolerance towards very sensitive structural motifs and the smooth application of this versatile chemical reaction.[1] Especially with the regard to subsequent transformations the formed alkyne moiety depicts a tremendously good starting point in terms of chemical selectivity and the variety of the available chemical methodologies.



Brief retrosynthetic draft and RCAM catalyst ***4*** *and trans-hydrogenation catalyst* ***5***

Within these methods, a *trans*-selective hydrogenation of an alkyne to the *E*-configured double bond under mild reaction condition has been still problematic until very recently. A new methodology involving ruthenium catalyst **5** has been established, which can directly add hydrogen onto an alkyne to form the desired *E*-alkene.[2a] To prove the applicability of the elaborated methodology, (+)-Brefeldin A (**1**, BFA) has been synthesized *via* a short and concise route, which transformed the dialkyne **2** smoothly into the natural product. Particularly, we found an imposing selectivity for the alkyne (neither the double bond nor the ester moiety were harmed by the reduction step) and were able to show the scalability of both methods, as the two reactions were performed on gram scale.[3] Additionally, the complexity of the molecule has given more insight into the chemistry behind the recently developed, ruthenium catalyzed *trans*-addition processes[2] and has emerged new questions about the mechanistic course.

References:

1 Fürstner, A. *Angew. Chem. Int. Ed.* **2013**, *52*, 2794.
2 a) *trans*-hydrogenation: Radkowski, K.; Sundararaju, B.; Fürstner, A. *Angew. Chem. Int. Ed.* **2013**, *52*, 355; b) *trans*-hydroboration: Sundararaju, B.; Fürstner, A. *Angew. Chem. Int. Ed.* **2013**, *52*, 14050; c) *trans*-hydrostannation: Rummelt, S. M.; Fürstner, A. *Angew. Chem. Int. Ed.* **2014**, *53*, 3626.
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Formic Acid as an Alternative Hydrogen Source in Ruthenium Catalyzed Transfer Hydrogenation of Olefins

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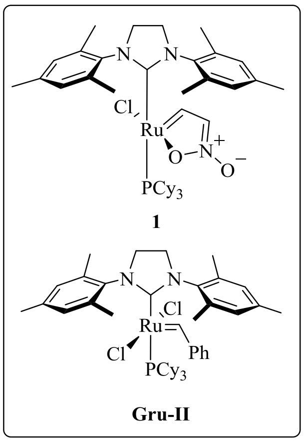
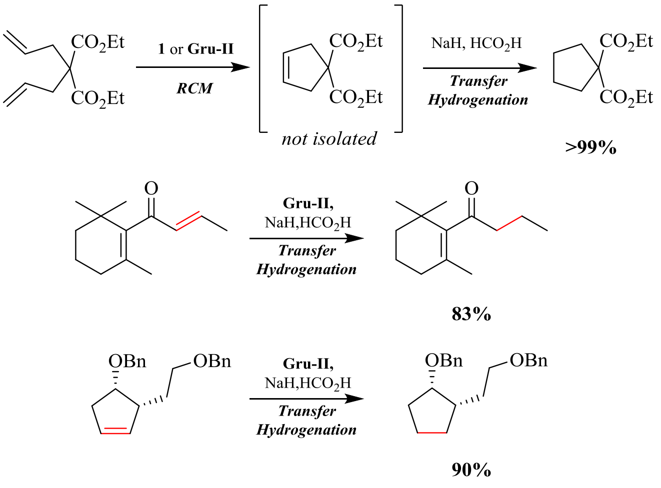
Catalytic olefin metathesis, as one of the most important methodologies of C-C double bond formation, does not need a particular introduction. Furthermore ruthenium alkylidene complexes were found not only as a great olefin metathesis catalysts[1] but they are well known in literature as active catalysts of numerous non-metathetic reactions.[2]
During our recent study on application of a new nitronate ruthenium complex **1** in olefin metathesis, we have noticed its unexpected non-metathetic activity. Depending on the conditions applied, the same complex promoted efficiently olefin metathesis, cycloisomerization, reduction of a carbonyl group, as well as isomerization of a C-C double bond.[3]
The interesting further results confirmed that complex **1** can also catalyze metathesis and transfer hydrogenation in one-pot sequence without isolation of the metathesis product. Moreover we proved that in this conditions many commercially available ruthenium alkylidene complexes (like **Gru-II**) can catalyze metathesis and transfer hydrogenation sequence or transfer hydrogenation depending on used substrate (see Scheme). Methodology was tested on several olefins and more interesting results appeared. The methodology that was developed in our group allows for selective hydrogenation in mild conditions using formic acid instead of dangerous hydrogen gas and does not cleave the benzyl groups.[4]



1

Gru-II



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POSTER PRESENTATIONS

Phase Transfer Activated Metathesis Catalyst

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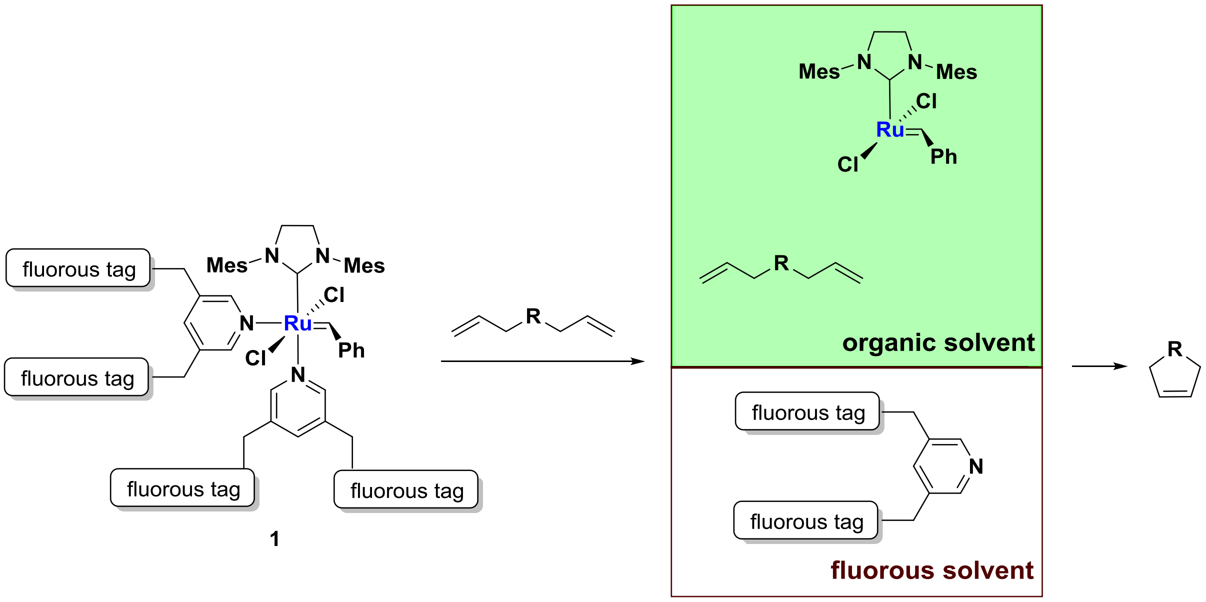
A novel concept of catalyst design will be discussed, using a metathesis catalyst as an example. Unlike most of the past catalyst modifications focusing on the balance of ligand binding affinities and catalyst stabilities, the new catalytic rate was improved through phase transfer. This "Phase Transfer Activation" protocol is based on the use of two orthogonal phases: one phase is used to scavenge the dissociated ligand, while the other provides the locus for the catalytic cycle. When the dissociated ligand with the phase label has much higher affinity in the orthogonal phase, the remained active specie does not deactivated by ligand rebinding and shows higher catalytic efficiency.

A fluorous analogue of Grubbs third-generation catalyst **1** was designed with this concept. This catalyst was prepared from a pyridine complex precursor and a fluorous pyridine, which was synthesized via a two-step procedure. This new catalyst shows dramatic rate accelerations in ring-closing metathesis reactions under fluorous/organic liquid/liquid biphasic conditions (see Scheme) as compared to monophasic organic conditions.



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High-value Alcohols and Higher-oxidation-state Compounds by Catalytic *Z*-selective Cross-Metathesis

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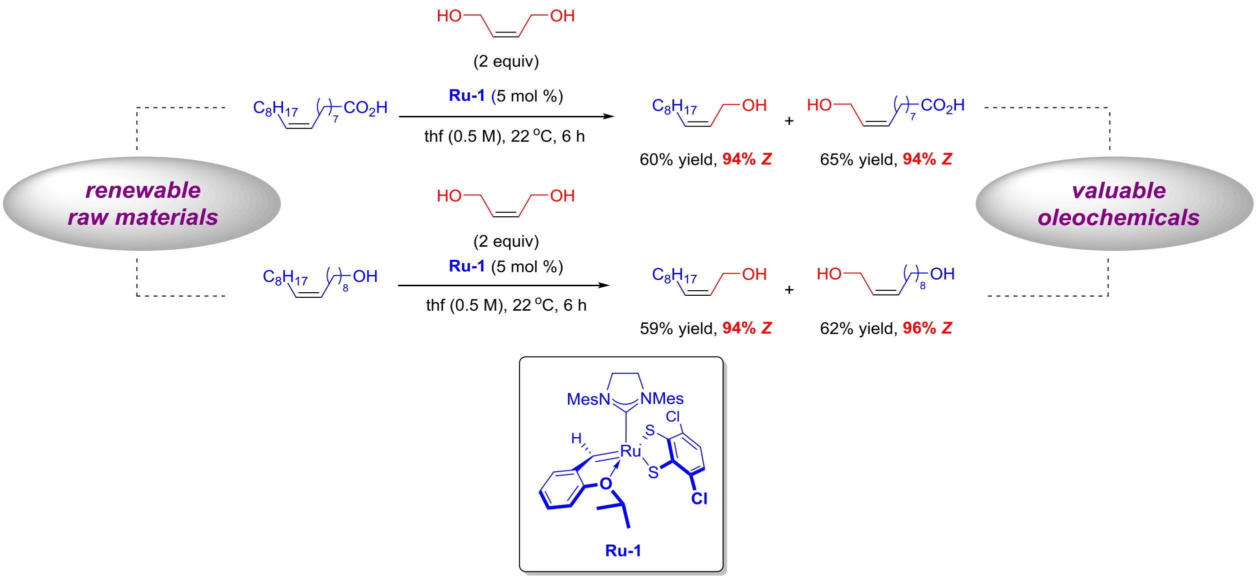
Olefin metathesis catalysts provide access to molecules that are indispensable to physicians and researchers in the life sciences.[1,2] A persisting problem, however, is the dearth of chemical transformations that directly generate acyclic *Z* allylic alcohols, including products that contain a hindered neighboring substituent or reactive functional units such as a phenol, an aldehyde, or a carboxylic acid. Here we present an electronically modified ruthenium–disulfide catalyst that is effective in generating such high-value compounds by cross-metathesis. The ruthenium complex is prepared from a commercially available precursor and an easily generated air-stable zinc catechothiolate. Transformations typically proceed with 5.0 mole per cent of the complex and an inexpensive reaction partner in 4–8 hours under ambient conditions; products are obtained in up to 80 per cent yield and 98:2 *Z*:*E* diastereoselectivity. The use of this catalyst is demonstrated in the synthesis of the naturally occurring anti-tumor agent neopeltolide and in a single-step stereoselective gram-scale conversion of a renewable feedstock (oleic acid) to an anti-fungal agent. In this conversion, the new catalyst promotes cross-metathesis more efficiently than the commonly used dichloro–ruthenium complexes, indicating that its utility may extend beyond *Z*-selective processes.



Conversion of renewable feedstock to valuable oleochemicals via Ru-catalyzed Z-selective cross-metathesis

Acknowledgement: R. Kashif M. Khan, S. Torker, M. Yu, M. S. Mikus

References:

1 Hoveyda, A. H.; Zhugralin, A. R. *Nature* **2007**, *450*, 243.
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Cross Metathesis of Terminal Alkynes

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Over the time, alkyne metathesis[1] – including alkyne cross metathesis (ACM)[2] – became a useful tool for organic and natural product synthesis. However, the efficient metathesis of terminal alkynes (TAM) was achieved only lately by Tamm and coworkers using the well-defined molybdenum pre-catalyst [MesC≡Mo($OCCH_3(CF_3)_2)_3$] (**1**). It had been shown that terminal alkynes can be metathesized at room temperature with short reaction times and low catalyst loading in high yields.[3] The molybdenum complex **1** is also capable of performing cross metathesis of terminal alkynes, as shown in figure 1.

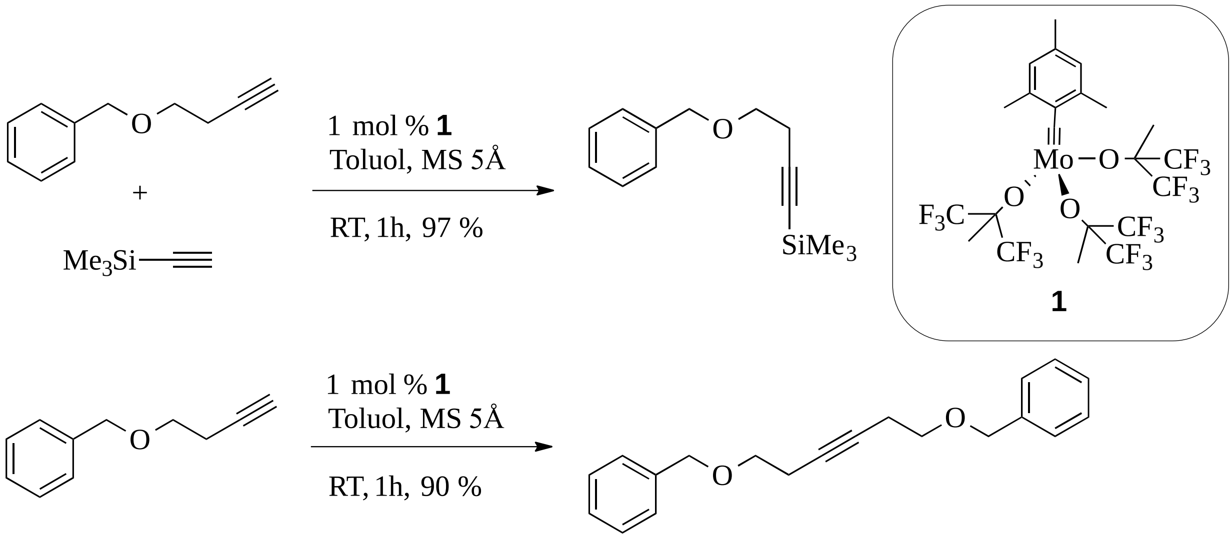

*Fig. 1: TAM and ACM introducing a trimethylsilyl group to terminal alkynes using the molybdenum complex **1** as pre-catalyst.*

Cross metathesis of terminal alkynes is of interest regarding the introduction of protecting groups into organic compounds. The introduction of a silyl group via alkyne cross metahesis takes place in a neutral environment avoiding the use of nucleophiles SiX (X = halide). Thus, base sensitive and electrophilic compounds can easily be silylated without the prior introduction of proper protecting groups.

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Development of One-pot Ring-closing Metathesis (RCM) / 1,3-Dipolar Reaction Using Ru Carbene Catalysts and Its Application to the Synthesis of Novel Polycyclic Heterocycles

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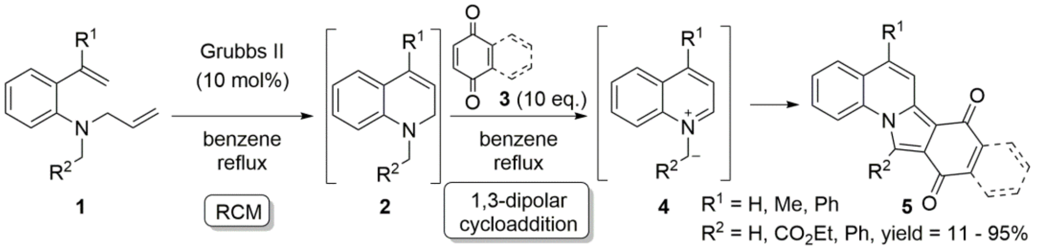
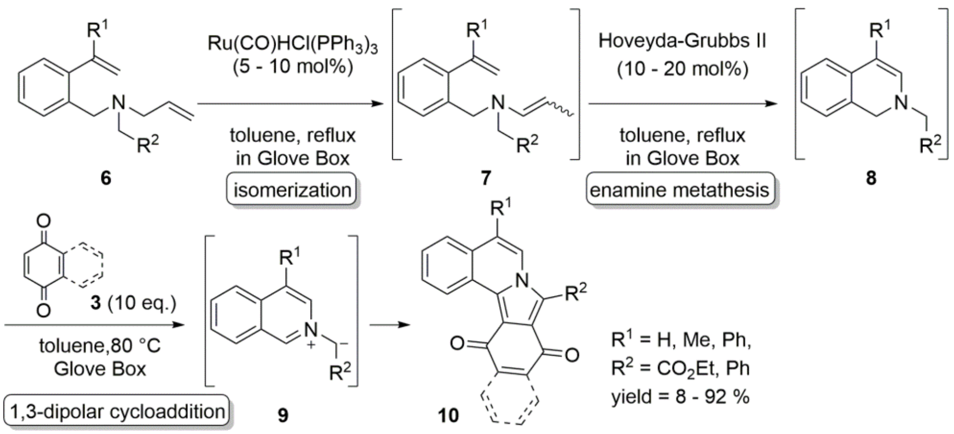
Over the past decade, several reaction sequences consisting of an olefin metathesis step and a subsequent non-metathesis transformation of the newly generated carbon-carbon double bond were developed with using ruthenium alkylidene catalysts. For example, recently, we developed a one-pot ring-closing metathesis (RCM) / oxidation methodology.[1] Herein, we discovered two novel tandem catalysis, a one-pot RCM / 1,3-dipolar cycloaddition[2] (Scheme 1) and a one-pot isomerization / enamine metathesis[3] / 1,3-dipolar cycloaddition (Scheme 2). The trigger of catalysis was the conversion of RCM intermediates **2** and **8** into other active spices **4** and **9**. In particular, quinones worked as not only dipolarophiles but also suitable oxidants. The color of novel polycyclic heterocycles **5** and **10** was dramatically changed up to only one substituent group R^1 or R^2. These compounds were useful for photosensitive or fluorescent dyes.



Scheme 1. One-pot RCM / 1,3-dipolar cycloaddition



Scheme 2. One-pot isomerization / enamine metathesis / 1,3-dipolar cycloaddition

References:

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3 Recently reported an example of enamine metathesis; S. Xu, F. Haeffner, B. Li, L. N. Zakharov, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2014**, *53*, 6795.

Interchain Cross-metathesis as a Novel Approach to Multiblock Copolymer Synthesis

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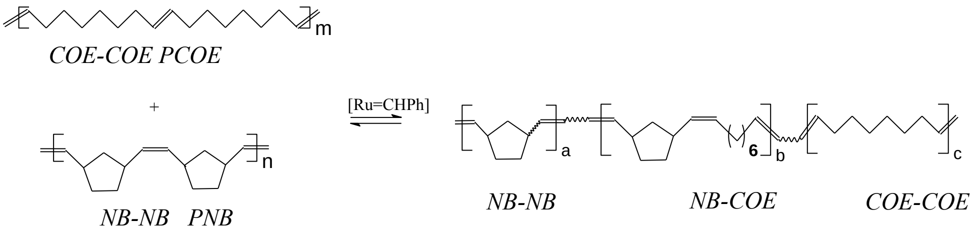
Cross-metathesis reactions involving polymers were mostly studied with regard to intramolecular or intermolecular degradation.[1] There are only a few examples of cross-metathesis between polymers.[2] In this study, we carried out the cross-metathesis between polynorbornene (PNB) and poly(1-octenylene) (PCOE) using the 1st generation Grubbs' catalyst. product.[3]



In this way, the multiblock copolymers of different structure can be obtained using Gr-1 catalyst, though it is not suitable for effective ring-opening copolymerization of NB and COE. New NB-COE multiblock copolymers were identified and characterized by NMR, GPC, and DSC methods. ^{1}H NMR spectroscopy was also used to monitor the interaction of Gr-1 with macromolecules. It was found that, contrary to the ROMP process, COE units form Ru-carbene complexes much faster than NB ones, presumably due to steric reasons. On the whole, the cross-metathesis reaction proceeds slowly and decreasing the average lengths of PNB and PCOE blocks from more than 200 to 2 units takes of the order of a day. The obtained copolymers possess a statistical multiblock chain structure, which can be controlled by altering the reaction time and catalyst concentration. During the reaction course a decrease in the copolymer molecular weight and crystallinity takes place. The crystallinity of resulting copolymers is lost when the average crystallizable COE block length approaches 2 units. The glass transition temperature also depends on the average length of COE blocks, ranging from -44 to -32 ^{o}C for the copolymers as compared to -79 ^{o}C for the PCOE. Our study opens broad perspectives for the controlled synthesis of statistical multiblock copolymers via the cross-metathesis reactions between polymers with carbon–carbon double bonds in their backbone.

The study was partially supported by RFBR (project 14-03-00665). Yu. D. also thanks the RF President grant for young Russian scientists (MK-7525.2015.3).

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Applications of Olefin Metathesis in Developing Macrocycles

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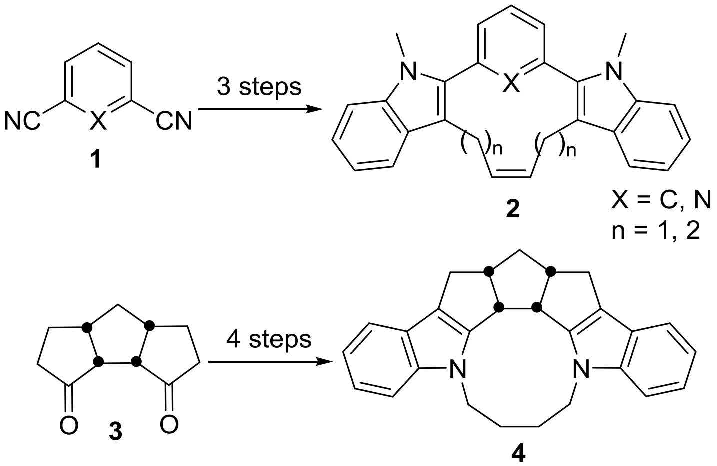
Musk is an important component of the perfumery industry. It is obtained from musk deer (*Moschus moschiferus*). Muscone and muscopyridine are the major products whereas musk xylene, musk ambrette, musk ketone, diphenhydramine, and imipramine are minor products of musk.[1] Although, several efforts have been directed toward the preparation of these products synthetically, only a few reports are available for the synthesis of normuscopyridine and its analogues.[2,3]



Indole-based macrocycles

In view of our interest in devising new strategies for assembling cyclophanes[4]and different macrocycles,[5] we have developed a simple methodology for the synthesis of normuscopyridine and its analogues with commercially available starting materials such as pyridine-2,6-dicarbo nitrile **1** or isophthalonitrile to indole-based macrocylic derivative **2** via Grignard reaction, Fischer indolization and ring-closing metathesis as key steps. Various indole-based macrocycles derivatives have also been assembled.[6] In another sequence, to transform *cis*-*syn*-*cis*-triquinane derivative **3** into the diindole based macrocycle **4** Fischer indolization and ring-closing metathesis were involved as the key steps.[7]

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Synthesis and Reactivity of Molybdenum Alkylidene Complexes with Chelating N-Heterocyclic Carbene Ligands

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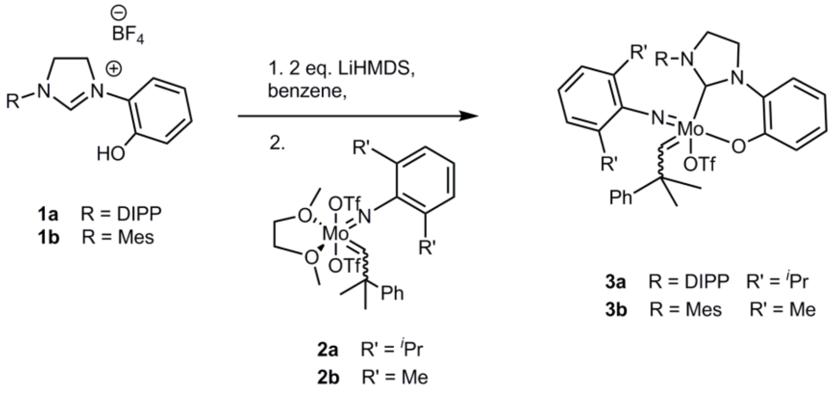
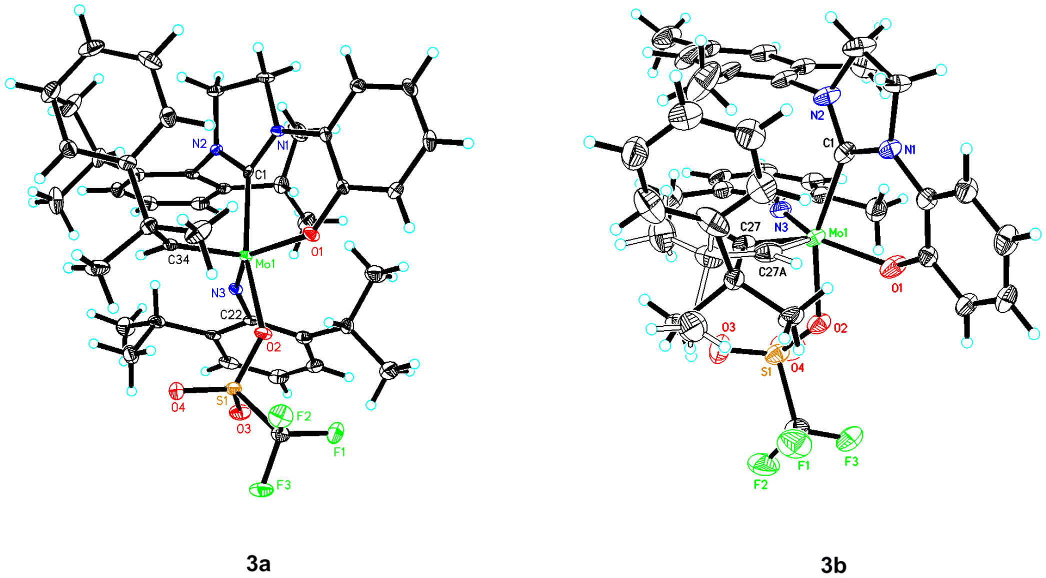
Using the BF_4-salts of imidazolium compounds that feature a phenolic unit[1] we have synthesized new high oxidation state molybdenum imido alkylidene complexes with chelating N-heterocyclic carbene ligands (NHCs). The proposed structures have been confirmed by single-crystal X-ray diffraction. Reactivity and functional group tolerance as well as results in the stereospecific polymerizations based on the bidentate nature of the ligand that has influence on the reorientation of the ligands around the molybdenum center during the polymerization will be presented.[2]



Scheme 1. Synthesis of catalysts ***3a*** *and* ***3b****.*



3a **3b**

Figure 1. Single-crystal X-ray structures of catalysts ***3a*** *and* ***3b****.*

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Regio- and Stereoselective Cyclopolymerization of Diynes with Chiral Mo Imidio Alkylidenen N-Heterocyclic Carbene Complexes

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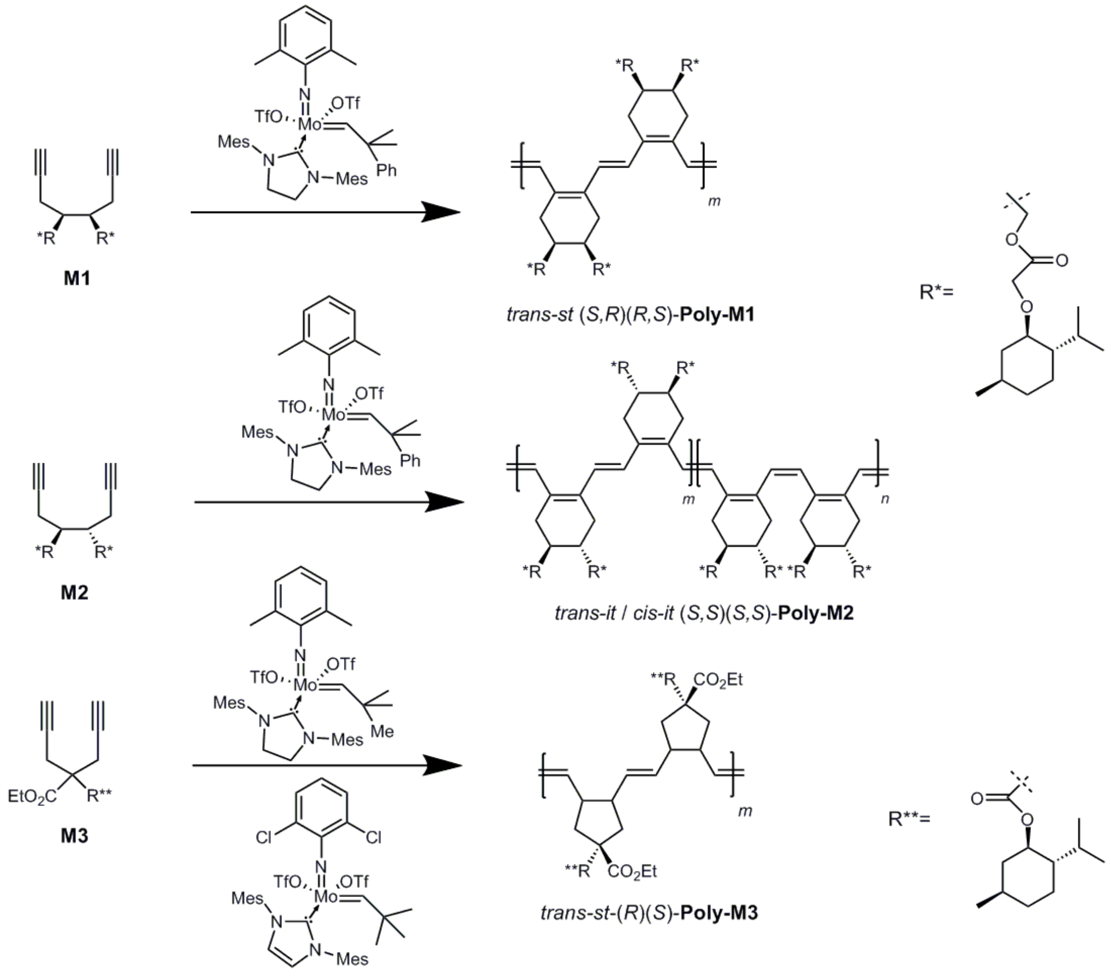
N-heterocyclic carbene (NHC) complexes of Schrock's molybdenum imido alkylidene bis(triflate) complexes[1] have been used in the regio- and stereoselective cyclopolymerizations of chiral 1,6-heptadiynes[2] and 1,7-octadiynes.[3] With the help of NMR spectroscopy, IR spectroscopy, GPC and UV-Vis measurements we could analyze the microstructure of these conjugated polymers, which was either syndio- or isotactic with predominantly *trans*-configured double bonds. On the base of these data we propose a polymerization mechanism for this new type of Schrock catalysts.[4]



Monomers and initiators used in cyclopolymerization.

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Zr (IV) and Hf (IV) Complexes Bearing the 6-(2-(Dialkylboryl)phenyl)-pyrid-2-ylamido Motif for Tandem Ring-Opening Metathesis/Vinyl-Insertion Polymerization

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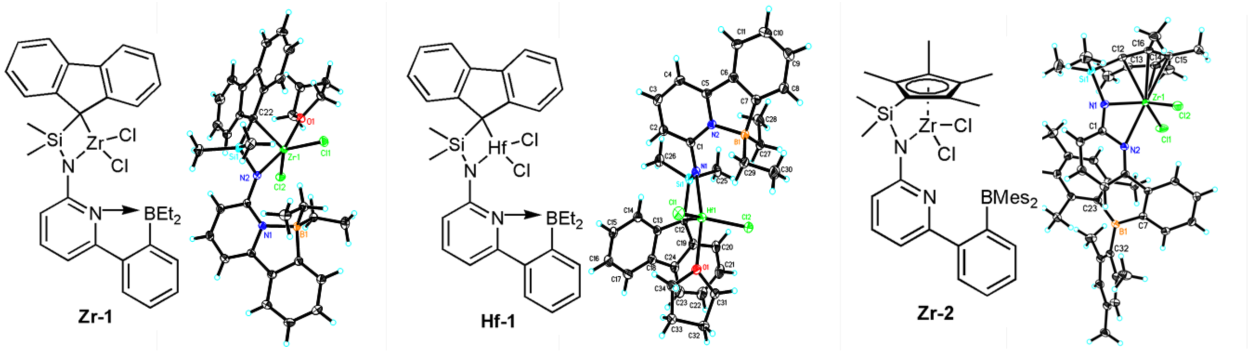
Ti^{IV}-, Zr^{IV}- and Hf^{IV}-complexes bearing the 6-(2-(dialkylboryl)phenyl)-pyrid-2-ylamido motif can switch from vinyl insertion polymerization (VIP) to ring-opening metathesis polymerization (ROMP) through an α-H elimination process.[1] This way, copolymers containing both VIP- and ROMP-derived structures within one single polymer chain are obtained. These provide the potential of functionalization through polymer analogous conversions.[2] In order to shed light on the mechanism of this switch, group 4 transition metal complexes **Zr-1**, **Hf-1** and **Zr-2** bearing an aminoborane motif were designed and synthesized. Their performance in the copolymerization of ethylene (E) with norborn-2-ene (NBE) was explored and the structural prerequisites that allow for the above-mentioned switch from VIP to ROMP have been elucidated.



*Structures of pre-catalysts **Zr-1**, **Hf-1** and **Zr-2**.*

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Guiding Chemistry with Light: From Regioselective RCM to New Concepts in Selective PPGs Removal

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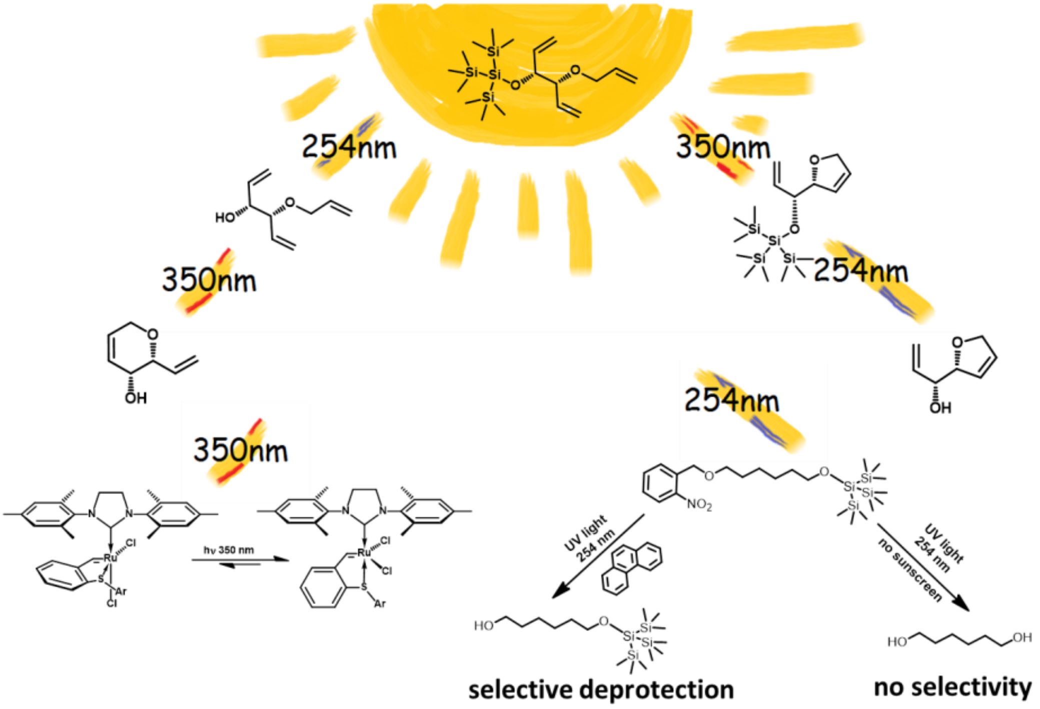
The ability to selectively guide consecutive chemical processes towards a preferred pathway by using light of different frequencies is an appealing concept. In this example we couple two photochemical reactions, one, the photo-isomerization and consequent activation of a sulfur-chelated latent olefin metathesis catalyst at 350 nm and the other the photo-cleavage of a super-silyl protecting group at 254 nm. Depending on the steric stress exerted by a photo-removable neighboring chemical substituent, we demonstrate the selective formation of either five or six membered ring frameworks by light-triggered ring-closing metathesis. An interesting outcome of this study was the discovery of a new type of chromatic selectivity. By exploiting differences in molar absorption coefficients, we developed a protocol for the selective removal of different photolabile protecting groups (PPG's) using an internal or external auxiliary chromophores that function as "sunscreens" for one of the PPG's, prompting the selective deprotection using a single light source. Thus, in this initial study, a proof of concept for catalytic chromatic orthogonal processes and an applicable concept for selective protecting group removal is presented.



Guiding chemistry with light

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Amino Acids as Chiral Anionic Ligands in Ruthenium Based Asymmetric Olefin Metathesis

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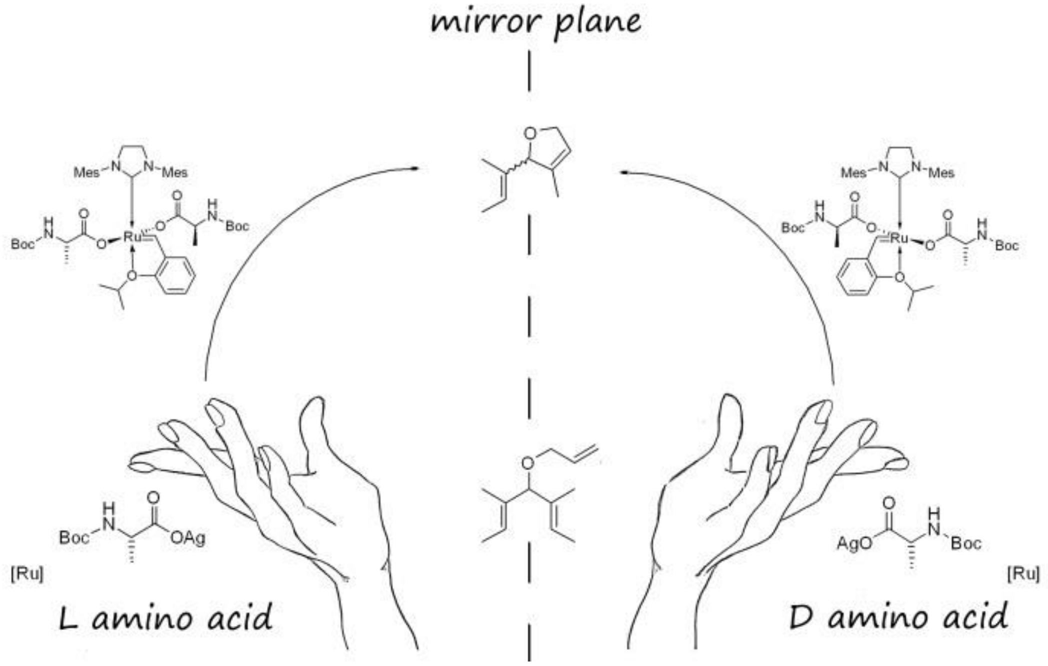
The vast development of the metathesis reaction over the years have enabled the promotion of asymmetric metathesis by chiral ruthenium pre-catalysts.[1] Notwithstanding the efficiency observed for these ruthenium chiral complexes, they all require intricate and expensive syntheses of chiral NHC ligands. Thus, straightforward and low cost synthesis protocols of ruthenium pre-catalysts for asymmetric metathesis are a sought after goal. Furthermore, due to usually required reaction optimization, a tunable chiral catalyst is highly desirable. Extensive studies discussing the replacement of the commonly used chloride ligands in the known ruthenium alkylidenes by different halides and pseudo-halides, showed that fine-tuning of the anionic ligands can lead to different reactivity and selectivity of the pre-catalysts.[2] As a first approach to these challenges, we present a new concept for the synthesis of benzylidene type ruthenium pre-catalysts, bearing amino acids as chiral anionic ligands, and their application to asymmetric metathesis. The use of amino acids as ligands enables a most facile protocol as well as easily tuned properties. In this study, reduction of the lability of the carboxylate ligands was found to be crucial in improving the observed enantioselectivity.[3]



Tunable ruthenium pre-catalysts with amino acid anionic ligands for asymmetric metathesis

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Latent Olefin Metathesis Catalysts for Tetra-Substituted Alkenes

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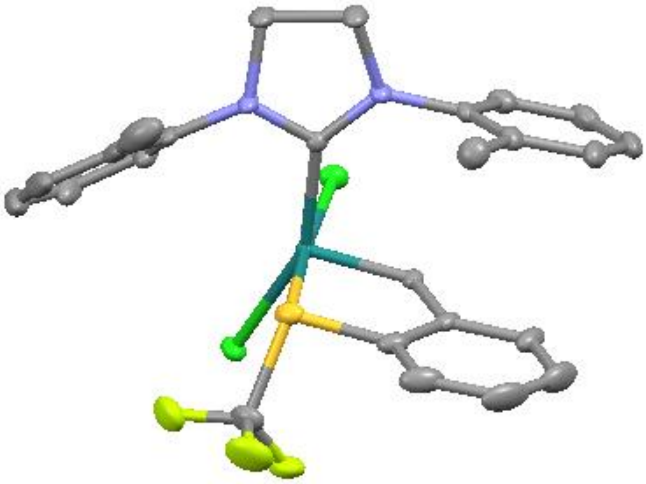
[b] *Department of Chemical Engineering, Sami Shamoon College of Engineering, 77245 Ashdod, Israel*

N-Tolyl substituted NHCs have been used in ruthenium complexes by Grubbs[1] and Grela[2] for the cross-metathesis of hindered olefins as well as ring-closing metathesis of olefins to afford tetra-substituted alkenes. Based on our previous work on latent S-chelated ruthenium olefin metathesis catalysts,[3] we now expand the scope of latent reactions by using N-Tolyl NHCs. Preliminary results show that while latency is conserved (no reaction at room temperature), the stimulation of the reaction by heat or light leads to very efficient production of tetra-substituted olefins by olefin metathesis reactions. Latent catalysts are particularly useful for the synthesis of polymers;[4] thus, our initial results on novel polymers formed by olefin metathesis of hindered olefins will be shown.



New o-tolyl-NHC Complex

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Jojoba Oil Olefin Metathesis: A Valuable Source for Bio-renewable Materials

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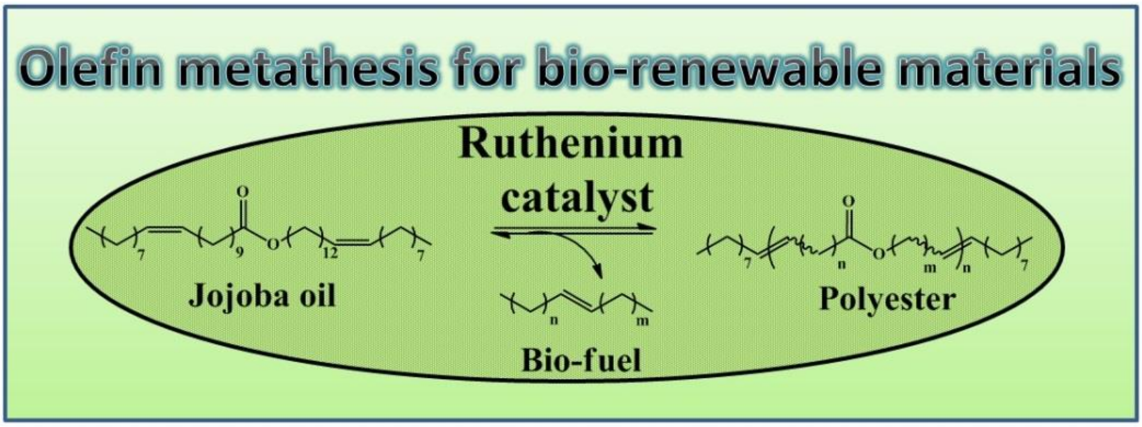
Jojoba oil is a diene composed of two monounsaturated hydrocarbon chains linked by an ester moiety. Ruthenium catalysed cross-metathesis reactions (CM) of the oil produced ADMET oligomers and hydrocarbon by-products under various conditions. Both the polyester oligomers and the hydrocarbon distillates were analysed by several analytical techniques. The oligomers were also hydrolysed under basic conditions to assess potential degradability. Oligomerisation of the starting material by an alternative thiol-ene 'click' reaction was also probed. A high atom economy is expected for this catalytic process given that all products obtained may be used either as sources for bio-fuel (hydrocarbons), or as potential renewable and degradable materials (polyester chains). In addition, a novel methodology for a concise preparation of synthetic jojoba oil will be presented.



Olefin metathesis of jojoba oil

References:
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Silica-Supported Molybdenum NHC Imido Alkylidene Bistriflate Complexes

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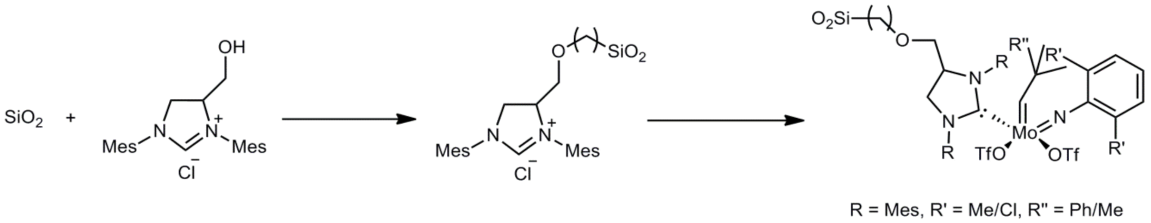
Molybdenum NHC-imido-alkylidene-bistriflate-complexes offer new possibilities in olefin metathesis.[1] Due to their 16-electron structure and the resulting high functional group tolerance these new complexes are a promising alternative to the currently used Grubbs- and Grubbs-Hoveyda-catalysts.[2,3,4] Immobilization of these catalysts could result in higher turn-over numbers (TONs) and the possibility of creating low metal content products, like for pharmaceutical applications. With this strategy the advantages of both, homogenous and heterogeneous catalysis are combined.

The possibility of immobilization via the NHC-ligand is an advantage over the immobilization of known Schrock-catalysts.[5,6] For example immobilization via the imido ligand implies the introduction of an additional substituent throughout the whole synthesis of the parent bistriflate imido precursors. On the contrary, introduction of the NHC ligand is the last step of the catalyst synthesis. Another advantage of immobilization via the NHC ligand is that the possibility of changing the alkoxide ligands is preserved, therefore allowing the fine-tuning of reactivity and enantioselectivity in olefin metathesis reactions.



Scheme 1. Immobilization of NHC-imido-alkylidene-bistriflate-Schrock-complexes.

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An Enantioselective Formal Synthesis of (-) Vinigrol

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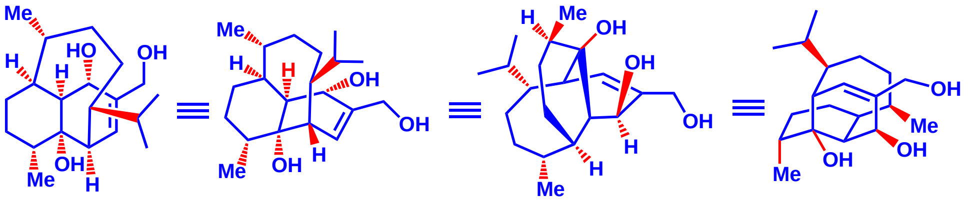
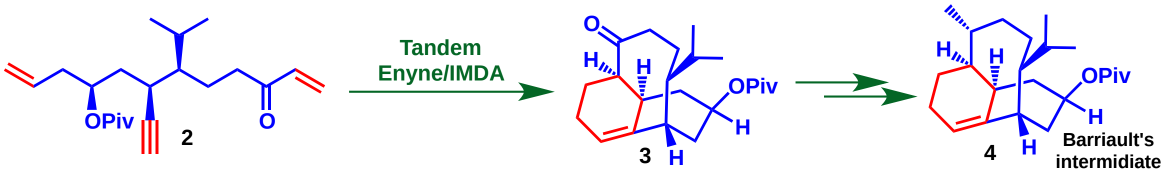
Vinigrol (**1**),[1] a unique diterpene encompassing the decahydro-1,5-butanonaphthalene carbon skeleton, was isolated by Hashimoto and co-workers in 1987 and has been shown to exhibit a broad spectrum of biological activity.[2] Besides the multiple sites of oxygenation, vinigrol contains a tricyclic core having a *cis*-fused [4.4.0] system bridged by an eight-membered ring with eight contiguous stereocenters made it a formidable challenge for synthetic chemists for nearly four decades.[3] Till date, two total syntheses[4] and one formal syntheis[5] of this molecule have been reported.



*Structure of Vinigrol (**1**)*

It was evident from the earlier approaches that the construction of an eight membered ring on pre-existing *cis*-decalin framework is difficult. To circumvent this problem, we envisaged a conceptually simple, one-pot, domino enyne metathesis - IMDA reaction for the construction of all three rings (*6-6-8*) of vinigrol from its stereochemically well-defined open chain precursor **2**. In this presentation our efforts[6] culminating in the first enantioselective formal synthesis of vinigrol, based on a domino enyne metathesis followed by an IMDA reaction, will be discussed.



Strategy for core structure of vinigrol

References:

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Synthesis of *Z*-enoates and Dienoates through Catalytic *Z*-selective Cross-metathesis

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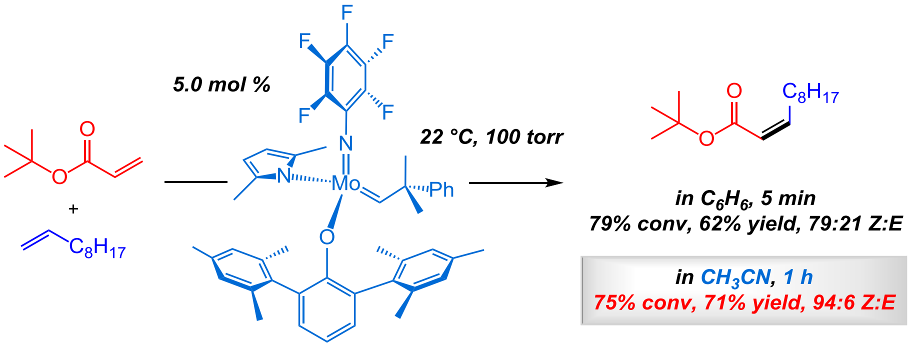
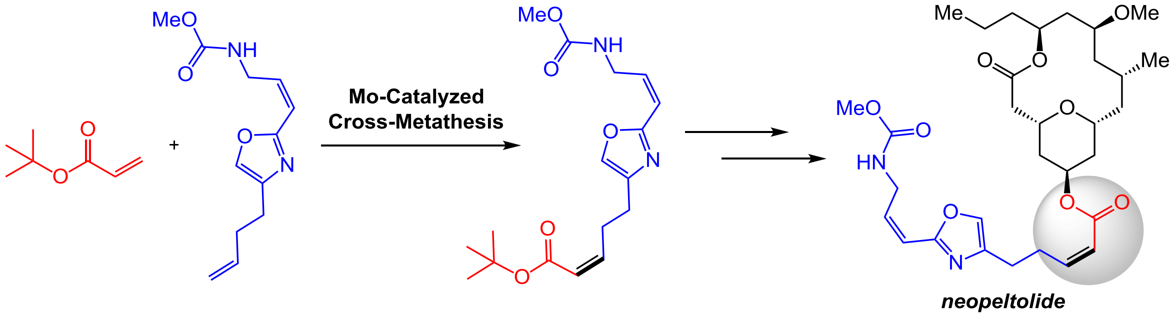
The first catalytic cross-metathesis method for synthesizing acyclic *Z*-enoates and (*E*,*Z*)-dienoates is presented. Dienoates are generated efficiently with Mo-based monoaryloxide monopyrrolide (MAP) complex with high selectivity (up to 87% yield and >98:2 *Z*:*E*). Transformations to *Z*-enoates are afforded in the presence of Mo-based MAP complex in Lewis basic solvents with yields up to 71% and >98:2 *Z*:*E*. Aliphatic, homoallyl, allyl, vinyl olefins and dienes serve as suitable substrates. Investigation of a Mo-MAP complex in the presence of different Lewis basic solvents through spectroscopic studies indicate new solvent-coordinated species involved in enhanced reactivity and selectivity.



Effect of Lewis basic solvents for Mo-catalyzed cross-metathesis of acrylates to Z-enoates

The utility of this approach will be demonstrated in the synthesis of the side chain of anti-tumor agent neopeltolide.[1]



Synthesis of neopeltolide side-chain through Mo-catalyzed cross-metathesis

Acknowledgements: Brett Johnson, Erik Townsend, Elizabeth Kiesewetter.

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Rapid Assembly of Polycyclic Carbon Networks through a Domino Process Involving RO-RCEM-CM-DA Reaction of Norbornene Derivatives

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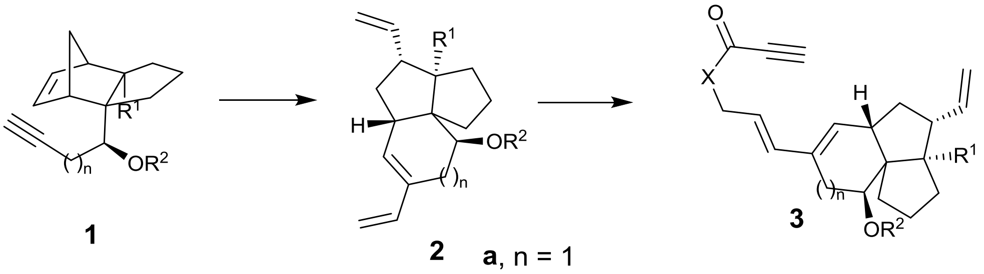
Domino processes involving ring opening-ring closing metathesis of norbornene derivatives having alkene chain at C-2 have been exploited extensively by us and others for rapid construction of a variety of ring systems present in natural products.[1] In contrast little attention has been paid on domino ring opening (RO)-ring closing enyne metathesis (RCEM) of norbornene derivatives with alkyne chain at C-2.[2] We thought of a domino RO-RCEM of the norbornene derivatives **1a**,**b** followed by selective cross metathesis (CM) of the vinyl group of the conjugated diene **2** and Diels-Alder reaction of the resulting trienone **3** to construct pentacyclic structures related to retigeranic acid **4** (Scheme 1). While the domino protocol worked efficiently for **1a**, the norbornene derivative **1b** remained unchanged. However, the expected ROM product **5**, prepared from **1b** through a non-metathetic path, underwent smooth RCEM to give **2b**. The latter was transformed to **3b** through selective CM. An IMDA of **3b** led to a pentacyclic structure related to **4**. The result of this investigation along with a rationale for the difference in reactivity between **1a** and **1b** towards metathesis will be presented.

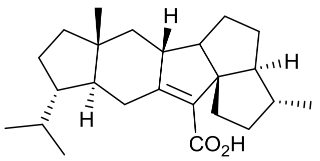


1

2

3

a, n = 1
b, n = 0



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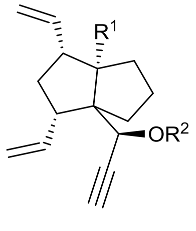

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Synthesis of (Imido)Niobium(V)-Alkyl, -Alkylidene Complexes and Some Reactions

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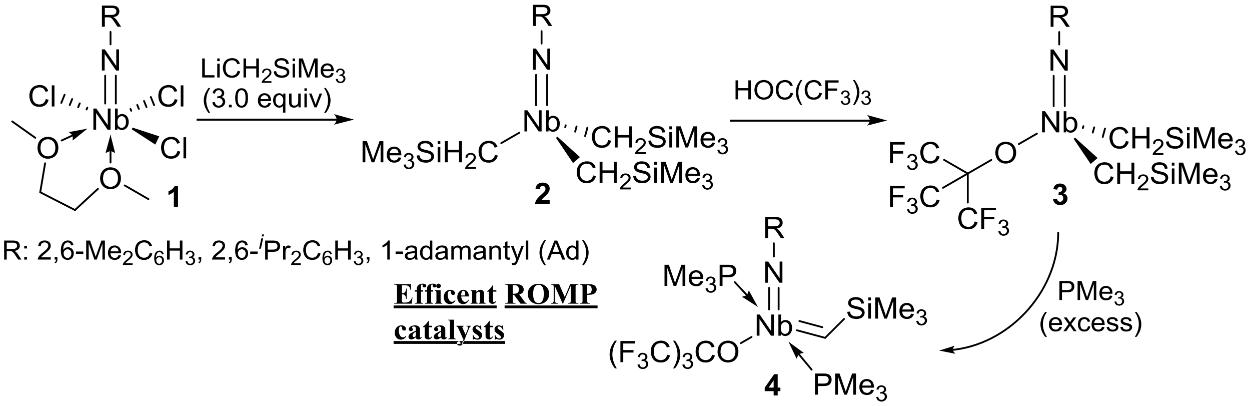
High oxidation state early transition metal alkylidene complexes are important intermediates in olefin metathesis, as demonstrated by molybdenum, tungsten. Synthesis and reaction chemistry of organo-vanadium(V) complexes are also considered not only of fundamental importance, but also of their potentials in catalysis, because of unique characteristics (notable reactivity toward olefins etc.) observed in classical Ziegler type vanadium catalysts.[1] Although certain vanadium complexes are known to exhibit notable activities for ring-opening metathesis polymerization (ROMP),[2] however, successful examples with the niobium(V)-alkylidenes still have been limited so far.

We herein present our preliminary results for synthesis of (imido)niobium(V)-alkyl and -alkylidene complexes and some reactions including ROMP with the isolated alkylidenes. A series of (imido)niobium(V) trialkyl complexes, $Nb(NR)(CH_2SiMe_3)_3$ [**2**, R = 2,6-$Me_2C_6H_3$, 2,6-$^i Pr_2C_6H_3$, 1-adamantyl (Ad)], were prepared from $Nb(NR)Cl_3(dme)$ (**1**) by treating with 3 equiv of $LiCH_2SiMe_3$. Treatment of the trialkyl complexes with $HOC(CF_3)_3$ afforded the corresponding dialkyl analogues (**3**), whereas the similar reactions with phenols afforded a mixture of mono- and bis-phenoxides. These complexes (**3**) were identified by NMR spectra, elemental analysis. Niobium(V)-alkylidene complexes, $Nb(CHSiMe_3)(NR)[OC(CF_3)_3](PMe_3)_2$ (**4**), could be prepared from the dialkyl analogues (**3**) by α-hydrogen abstraction upon heating in the presence of PMe_3 (excess). These complexes (**4**) exhibited high catalytic activities for ROMP of norbornene, affording high molecular weight polymers with unimodal molecular weight distributions.[3] Details will be introduced in the symposium.



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Synthesis of End-Functionalized Poly(arylene vinylene)s by ADMET Polymerization and Chain Transfer/ Wittig-type Coupling

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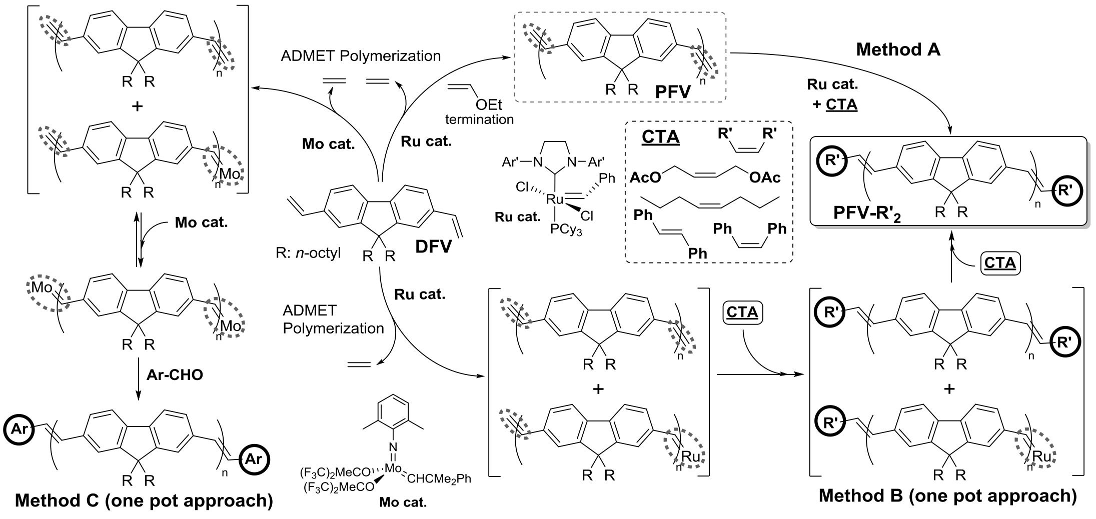
Synthesis of structurally regular, chemically pure π-conjugated polymers attracts considerable attention in terms of better/advanced device performances. We demonstrated syntheses of *defect-free*, all-*trans*, high molecular weight poly(fluorene-2,7-vinylene)s (PFVs) by acyclic diene metathesis (ADMET) polymerization,[1] and their exclusive end-functionalization by combined olefin metathesis and Wittig-type coupling.[2] However, rather excess (>2 equiv) amount of Mo-alkylidene catalyst (reagent) is required for completion of the end functionalization. We herein present the “catalytic” one pot synthesis by ADMET polymerization in the presence of chain transfer agent[3] using Ru catalyst.[4] We also present our another approach using Mo catalyst.[4]

Three approaches have been considered for this purpose (Scheme shown below). Catalytic chain transfer of once prepared PFVs (vinyl group at the chain ends) using Ru catalyst gave end-functionalized PFVs (Method A) under optimized conditions. Note that the PFVs could also be obtained (Method B, one-pot approach), when the ADMET polymerization of DVF using Ru catalyst was conducted in the presence of chain transfer agent (CTA); an additional CTA at the final stage was quite effective for completion of the end-functionalization. Various end-functionalized PFVs have thus been obtained by adopting this approach. The ADMET condensation of DFV using Mo catalyst followed by Wittig-type cleavage with aldehyde (Method C, one-pot approach) also afforded end-functionalized PFVs. More details will be introduced in the symposium.



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4 submitted for publication.

N-Heterocyclic Carbene Molybdenum Alkylidene Complexes: Functional Group-Tolerant Metathesis Catalysts

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We synthesized the first N-heterocyclic carbene (NHC) complexes of Schrock's molybdenum imido alkylidene bis(triflate) complexes. Unlike existing bis(triflate) complexes, the novel 5-fold coordinated 16 e^- Mo complexes contain two carbenes, i.e. a Schrock carbene and an NHC. Single crystal x-ray analysis revealed trigonal bipyramidal complexes with one triflate (OTf) ligand *trans* [O(1)-Mo(1)-C(1)~152^{O}] to the NHC. In course of the metathesis reactions this triflate leaves the complex and generates a cationic 14 e^- Mo complex. The most important observation is that catalysts of this type are active in ring-closing metathesis (RCM), the cyclopolymerisation of α,ω-diynes and ring opening metathesis polymerisation (ROMP). Monomers containing functional groups, which are not tolerated by the existing variations of Schrock's catalyst, e.g., *sec*-amines, hydroxy, and carboxylic acid moieties, can be used. These catalysts therefore hold great promise in both organic and polymer chemistry.

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Cationic Imido Alkylidene-NHCs Complexes: Staggering Catalysts for the Homo-metathesis of 1-Alkenes

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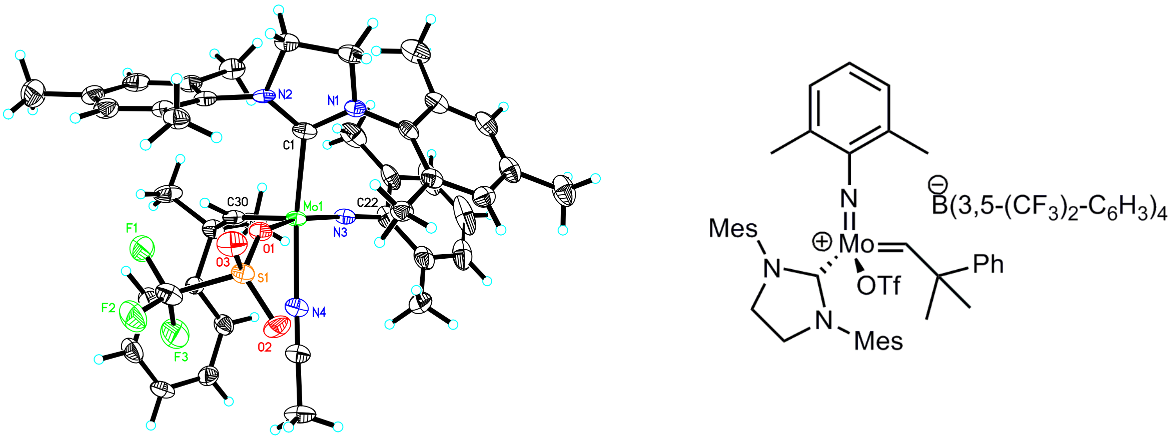
We recently reported on the first N-heterocyclic carbene (NHC) complexes of Schrock's molybdenum imido alkylidene bis(triflate) complexes, which can be prepared through the addition of free NHCs to a universal precursors. Reaction of these compounds with $AgB[3,5\text{-}(CF_3)_2C_6H_3]_4$ in dichloroethane afford the cationic imido alkylidene-NHCs complex $[Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CHCMe_3)(CH_3CN)(OTf)(IMesH_2)^+\ B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4^-]$. The solid-state structure of this compound has been determined by *X-ray* diffraction, and its reactivity with 1-alkene, α,ω-dienes and ethenolysis has been explored. In these reactions, turn-over numbers up to 140,000 have been reached.



Cationic imido alkylidene-NHCs catalyst

References:

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Reactivity of Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_3$)(OTf)($IMesH_2$)(OR): Controlling Metathesis Activity Through the Choice of Different Fluorinated Alkoxides Ligands

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We recently reported on the first N-heterocyclic carbene (NHC) complexes of Schrock's molybdenum imido alkylidene bis(triflate) complexes, which can be prepared through the addition of free NHCs to a universal precursors.[1] Reaction of these compounds with one equivalent of different fluorinated alkoxides (i.e. $OCH(CF_3)_2$, OC_6F_5, $OCCH_3(CF_3)_2$) in dichloroethane afford the desired complexes. Here we provide a comprehensive insight about this new class of metal alkylidenes, both in terms of their structure and reactivity in various metathesis reactions.[2]

R = -Mes
Ar = -2,6-$Me_2C_6H_3$

R = -Mes
Ar = -2,6-$Me_2C_6H_3$

[Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_3$)(OTf)($IMesH_2$)(OR) **)** *catalysts*

References

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Development of Enyne Metathesis / Isomerization / Diels-Alder One-Pot Reaction for Novel NIR Dye

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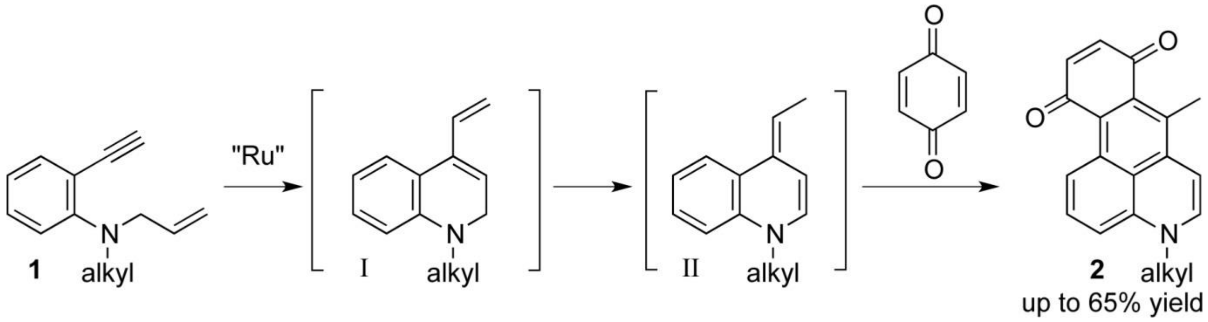
Over the past decade, several reaction sequences consisting of an olefin metathesis step and a subsequent non-metathesis transformation of the newly generated carbon-carbon double bond were developed with using ruthenium alkylidene catalysts. For example, recently, we developed a one-pot ring-closing metathesis (RCM)/ oxidation methodology[1] and RCM/1,3-dipolar cycloaddition methodology.[2]

Herein, we discovered a novel tandem catalysis, a one-pot ring-closing enyne metathesis / isomerization / Diels-Alder cycloaddition (Scheme). In practice, the acyclic enyne in the presence of the ruthenium alkylidene first undergoes a RCM to generate cyclic 4-vinyl-1,2-dihydroquinolines **I**; following diene isomerization and then upon the addition of a dienophile, **I** are selectively converted to a 7-methyl-4*H*-naphtho[3,2,1-*de*]quinoline-8,11-dione core **2**. Compound **2** are blue solids and novel solution-processable π-conjugated nitrogen-containing heterocycle and have characteristic absorption in near-infrared (NIR) region.



Enyne metathesis/isomerization/[4+2] cycloaddition one-pot reaction

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Chain-Growth Copolymerization of Ethynylarenes into Functionalized Conjugated Porous Networks

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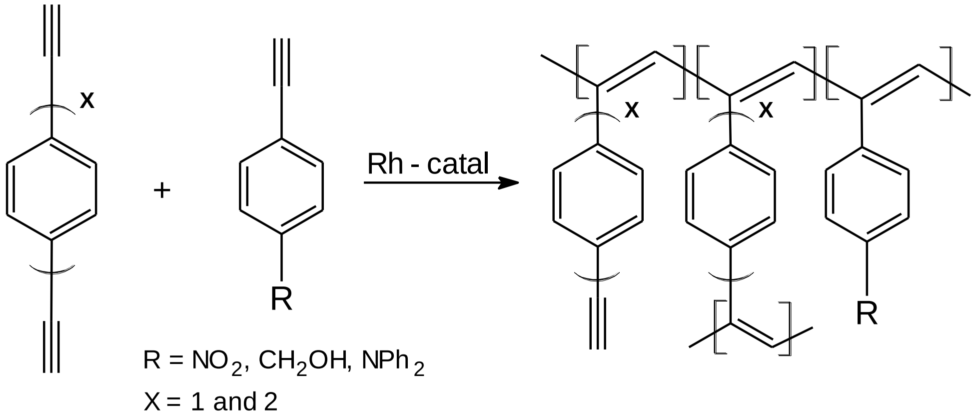
Chain-growth polymerization of diethynylarenes (1,4-diethynylbenzene, DEB, and 4,4´-diethynylbiphenyl, DEBPh) with [Rh(nbd)acac] catalyst has recently been reported as an efficient tool for the synthesis of densely cross-linked conjugated polyacetylene microporous networks.[1] In this contribution, we report the synthesis of networks with heteroatomic groups, which should exhibit increased sorption capacity for special sorbates. Two series of networks have been prepared by copolymerization of either DEB or DEBPh with functionalized phenylacetylenes: (4-nitrophenyl)acetylene, [4-(hydroxymethyl)phenyl]acetylene and [4-(diphenylamino)phenyl]acetylene (comonomer ratio in the feed = 1:1, see Scheme 1). Despite low average comonomer ethynyl functionality in the feed (*f* = 1.5) the densely cross-linked functionalized networks (degree of branching up to 35 %) with comonomeric composition equal or close to the composition of the feed and S_{BET} values up to 460 m^2/g were obtained in high yields. The microporosity of networks was governed by size of the substituents of the linear units and length of cross-links of the branching units.[2]



R = NO_2, CH_2OH, NPh_2
X = 1 and 2

***Scheme 1.** Synthesis of functionalized polyacetylene-type networks*

Acknowledgement: Financial support from the Czech Science Foundation (15-09637S) and the Science Foundation of CU (No. 580214) is gratefully acknowledged.

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Synthesis of a Basket-Resorc[4]Arene *via* Metathesis Reaction and Encapsulation Studies of Fullerenes C_{60} and C_{70}

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Tetramerization of (*E*)-2,4-dimethoxycinnamic acid ω-undecenyl ester with ethereal BF_3 gave three resorc[4]arene stereoisomers which were assigned a *chair*, *cone*, and *1,2-alternate* conformation.

The *cone* stereoisomer **1a** (Fig. 1a) was submitted to olefin metathesis,[1] using the second-generation Grubbs complex $[(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh)]$ as the catalyst, yielding resorc[4]arene derivative **2a** endowed with a large solvophobic basket-like cavity defined by two C_{20} hydrocarbon chain loops.

Here we present an exhaustive study aimed at investigating the type of supramolecular recognition between resorc[4]arene **2a** and fullerenes **C_{60}** and **C_{70}**. Molecular modeling studies (namely, Docking[2] and Molecular Dynamics) showed that **2a** is able to efficiently encapsulate the fullerenes (Fig. 1b). Therefore, encapsulation studies were carried out by UV spectroscopy and the equilibrium constants of the relative complexes were determined, providing a satisfactory agreement with molecular modeling data.

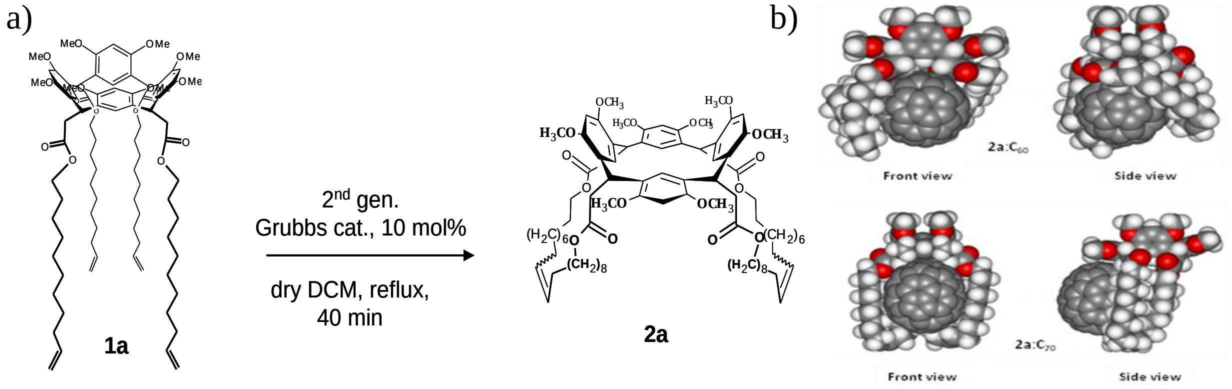

*Figure 1. a) Olefin metathesis reaction on undecenyl resorc[4]arene **1a**;*
*b) Computed structures of **$2a{:}C_{60}$** (up) and **$2a{:}C_{70}$** (down) complexes.*

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Ruthenium Metathesis Pre-catalysts with Unsymmetrical N-Heterocyclic Carbene Ligands

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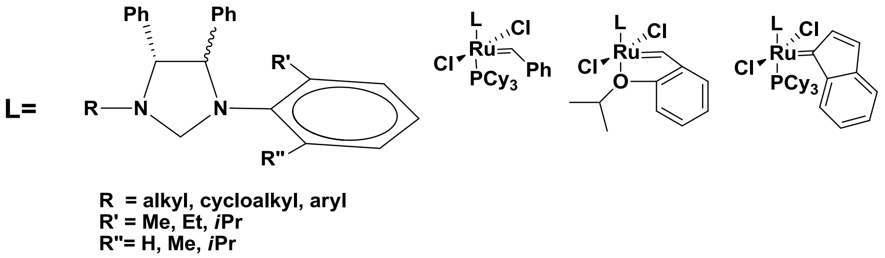
Catalytic olefin metathesis has become a very powerful tool in organic synthesis, polymer chemistry and transformation of renewable resources.[1] The advent of ruthenium catalysts bearing N-heterocyclic carbene (NHC) ligands represents a turning point in olefin metathesis because of their tolerance towards oxygen, moisture and many polar functional groups.[2]

During the last years many efforts have been directed to the design of new NHC ligands, in order to increase the efficiency of the corresponding metal complexes. Among these, due to their high level of dissymmetry and increased flexibility, unsymmetrical NHC (u-NHC) ligands represent very attractive structural motifs to directly modulate catalyst properties.[3]

Recently, we focused on the preparation of new u-NHC ruthenium based metathesis pre-catalysts and on the study of their catalytic behavior. Preliminary results suggest that the nature of *N*-substituents, combined with different configuration of the NHC backbone, can strongly modify stability, reactivity and selectivity of the catalysts.[4]



New u-NHC ruthenium metathesis pre-catalysts

The synthesis of a series of new Ru-complexes having u-NHCs will be presented and their catalytic performance in a set of standard metathesis reactions[5] as well as in more recent applications of green chemistry detailed. Suitable balance between the nature of *N*-substituents and the backbone configuration of the NHC should allow for the design of even more performing catalysts.

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Grubbs-Hoveyda Type Catalysts Bearing a Dicationic *N*-Heterocyclic Carbene for Biphasic Olefin Metathesis Reactions in Ionic Liquids

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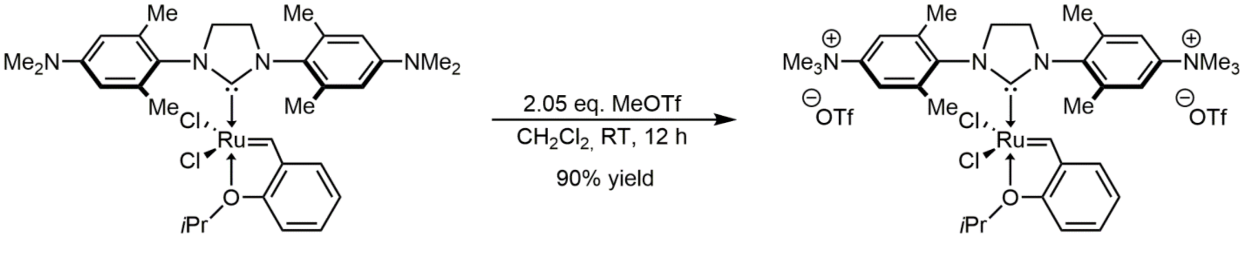
One remaining challenge in olefin metathesis is the removal of the catalyst after the reaction.[1] Our group[2] and others[3] reported on biphasic metathesis reactions using an ionic liquid (IL) and a nonpolar organic solvent to gain access to products with unprecedented low metal contamination. Crucial property of the catalyst for biphasic reactions is the selective solubility in the IL. Therefore, new catalysts containing ionic moieties have to be designed and tested on their reactivity.

A new dicationic ruthenium alkylidene, $H_2ITapMe_2(OTf)_2Cl_2Ru{=}CH–(C_6H_4–O–i\text{Pr})$ (**2**) ($H_2ITapMe_2$=1,3-bis(2‘,6‘-dimethyl-4‘-trimethylammoniumphenyl)-4,5-dihydroimidazol -2-ylidene), was prepared in high yield using the neutral precursor **1** reported by Schanz *et al.*[4] This is, to the best of our knowledge, the first example of a Grubbs-Hoveyda type catalyst bearing a permanent dicationic *N*-heterocyclic carbene ligand.



1 **2**

Preparation of the dicationic catalyst $H_2ITapMe_2(OTf)_2Cl_2Ru{=}CH–(C_6H_4–O–i\text{Pr})$.

The reactivity of **2** was tested in ring closing metathesis (RCM), ring opening metathesis (ROMP) and acyclic diene metathesis (ADMET) under biphasic conditions using a nonpolar organic solvent and the ionic liquid 1-butyl-2,3-dimethylimidazolium tetrafluoroborate $[BDMIM^+][BF_4^-]$.

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Preparation and Reactivity of Schrock-type Catalysts Bearing Ionic Ligands

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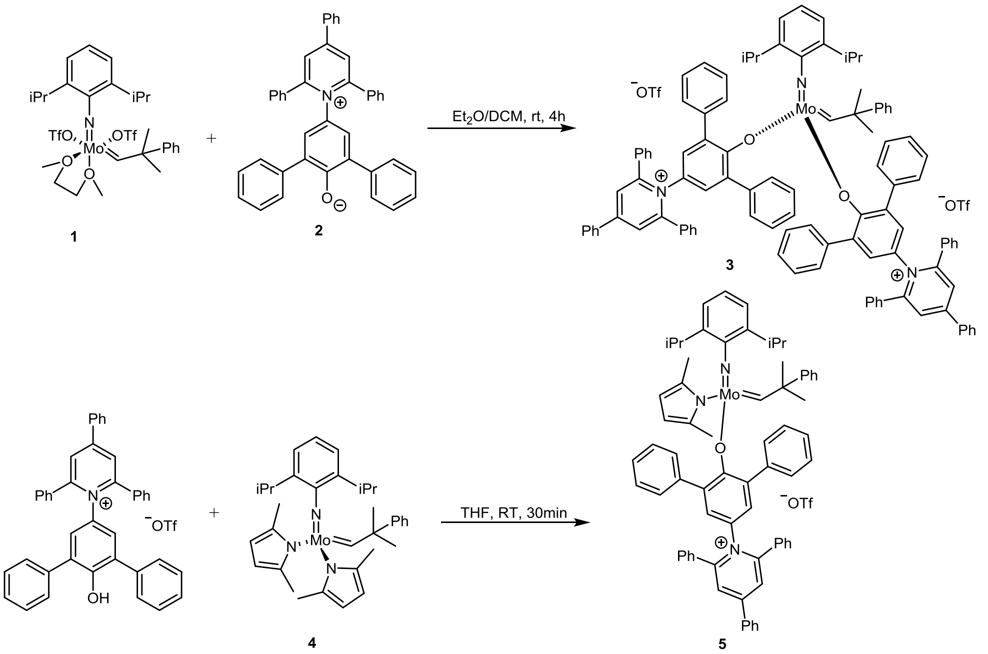
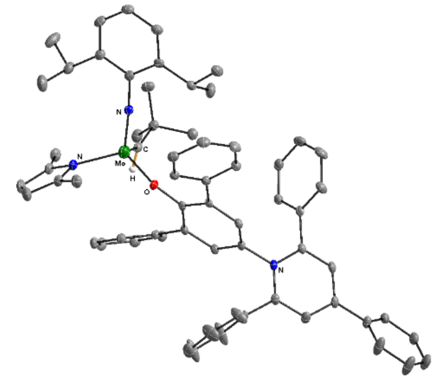
Here we report on the synthesis and reactivity of novel Schrock-type catalysts bearing bulky ionic ligands. Mo-imido alkylidenes coordinated by ionic ligands can be prepared by reaction of bistriflate **1** with betaine **2**. The dicationic complex **3** is formed in high yield. The monoaryloxide pyrrolide (MAP) type complex **5** is formed in a similar manner from bispyrrolide **4.** The new catalysts show high reactivity and stability towards a number of substrates. TONs of up to 170000 have been reached. These complexes are potentially suitable for biphasic catalysis. Current efforts focus on reactions in ionic liquids.



*Synthesis of ionic catalysts **3** and **5**.*



*Single Crystal X-Ray Structure of **5**.*

NHC-Ligated Tungsten Oxo Alkylidenes: Highly Active Catalysts for Olefin Metathesis Reactions

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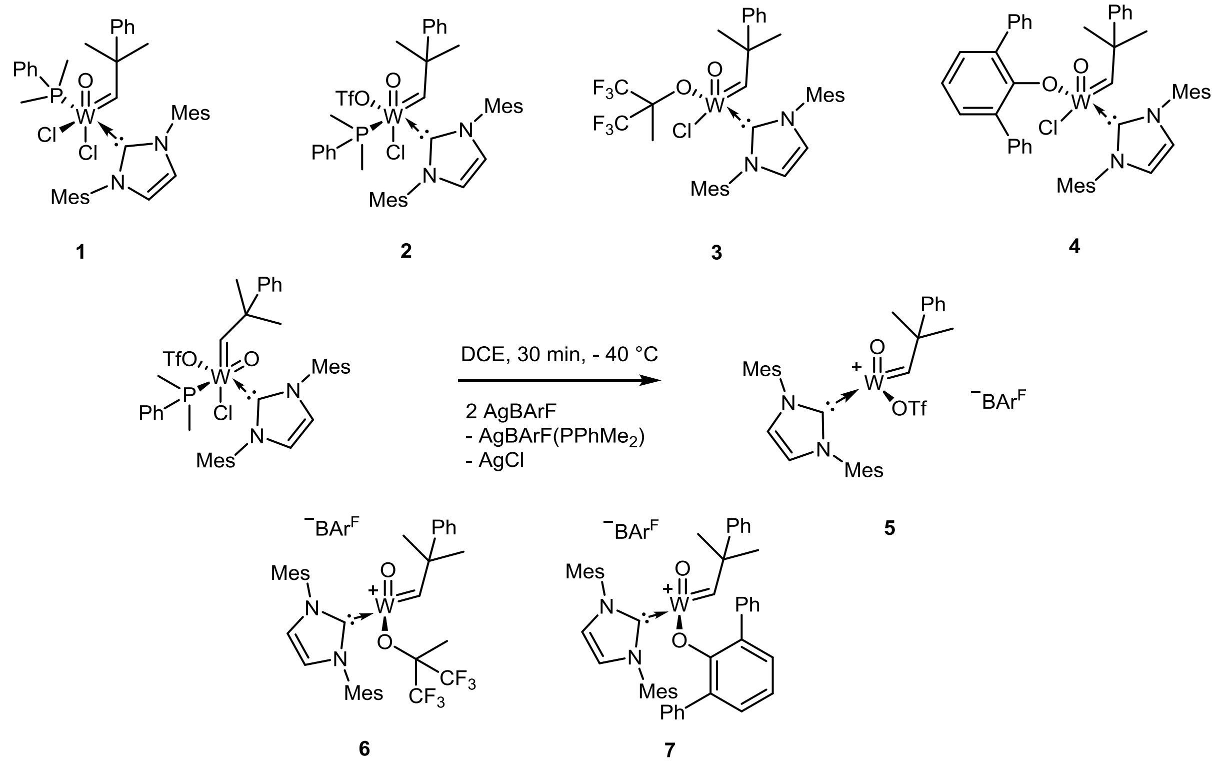
In this contribution we report on the synthesis and reactivity of novel Schrock-type catalysts bearing NHC ligands (see Fig.). Recently, we reported on the unique reactivity and stability of Mo-imido alkylidenes coordinated by NHCs[1]. Now we are extending the scope to W-oxo-alkylidenes and show the variability of the synthetic methods. The new catalysts show high reactivity and stability towards a number of substrates. TONs of a few thousand have been reached upon activation of suitable precursors with silver salts and/or Lewis acids. Ring closing metathesis, cross metathesis and self-metathesis activity has been investigated in detail. Remarkably, our catalysts are potential candidates for metathesis reactions in the presence of functional groups like amines or alcohols.[1]



*NHC coordinated W-oxo alkylidenes **1-7**.*

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1 Sen, S.; Unold, J.; Frey, W.; Buchmeiser, M. R. *Angew. Chem.* **2014**, *126*, 9538; *Angew. Chem. Int. Ed.* **2014**, *53*, 9384.

2 Schowner, R.; Frey, W.; Buchmeiser, M. R. submitted.

Synthesis and Reactivity of Ionic High Oxidation State Mo and W Imido NHC Alkylidene Complexes

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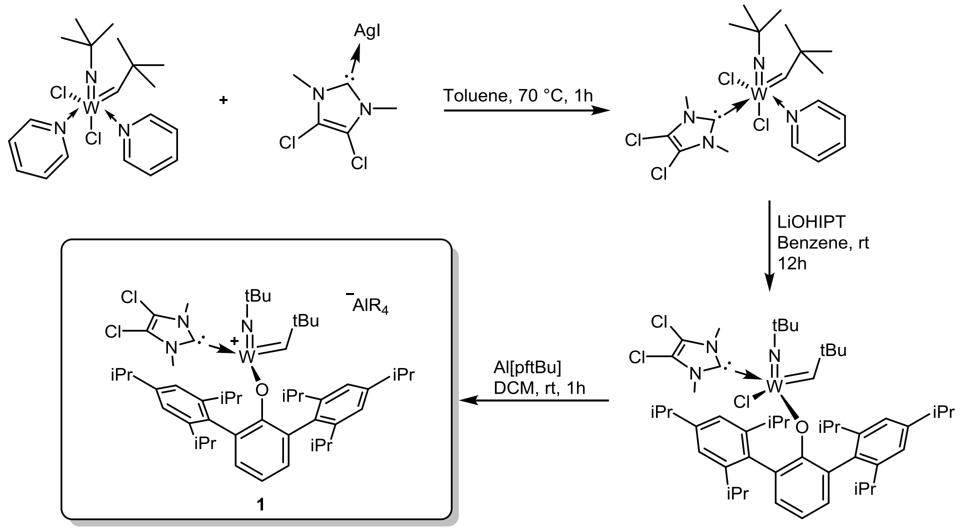
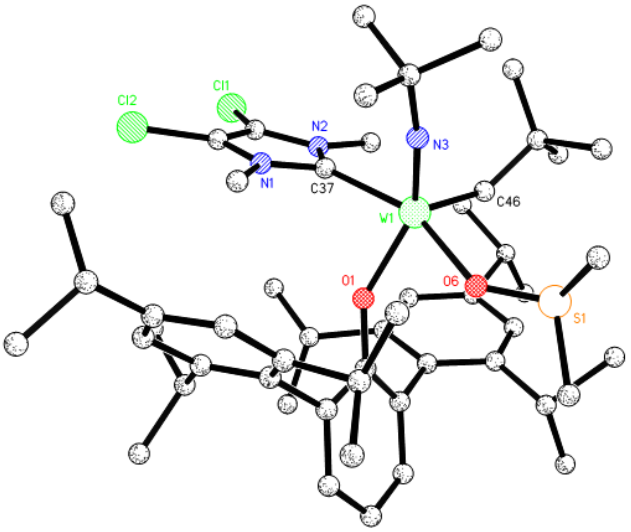
We have developed a synthetic route to highly active, ionic Schrock-type catalysts bearing N-heterocyclic carbenes as neutral ligands. Our catalysts show similar behavior to known MAP (Mono Aryloxide Pyrrolide) catalysts in terms of Z-selectivity when a small imido and NHC ligand are combined with a very bulky terphenoxide ligand. The reactivity and stability to a number of substrates and functional groups is evaluated under different conditions.



*Synthetic Route to ionic catalyst **1***



*Single crystal X-ray structure of **1·DMSO***

Layered Double Hydroxides as Tunable Olefin Metathesis Catalyst Supports

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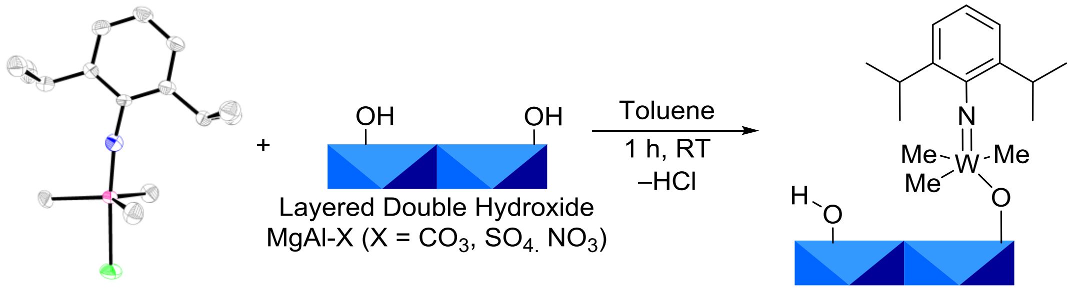
Chemistry Research Laboratory, University of Oxford, 12 Mansfield Road, Oxford, OX1 3TA, United Kingdom

Heterogeneous olefin metathesis has been exploited by industry for decades,[1] however there is still fundamental interest in the exact nature of the active species on the surface as well as the role the support plays. Recent work in our group has focused on exploiting layered double hydroxides (LDHs)[2] as efficient catalyst supports *e.g.* for ethylene polymerisation.[3,4] Utilising the principles of surface organometallic chemistry (SOMC)[5] these tunable, high surface area, highly dispersible materials are capable of supporting tungsten imido complexes which are active for the metathesis of olefins.



Supporting procedure utilising surface hydroxyl groups

We have synthesised a tungsten imido complex bearing methyl substituents, which when supported on LDHs of the type MgAl-X (where X = CO_3, SO_4 or NO_3) is active for the metathesis of ethylene and 2-butenes to form propylene in the slurry phase. The active site is postulated to be a tungsten methylidene species formed *in situ* with concomitant loss of methane observed by ^{1}H NMR spectroscopy. The reactivity of this complex with propylene and other substrates is under investigation and attempts to form a defined alkylidene derivative will also be presented.

We have also demonstrated that the reaction pathway of this catalyst can be altered by employing alkyl aluminium reagents as cocatalysts, making it active for the selective dimerisation of ethylene to 1-butene at a range of temperatures with minimal complex decomposition.

Finally, the commercially available Hoveyda-Grubbs 2nd generation catalyst has been supported LDHs. The activity of this catalyst towards metathesis of a range of olefinic substrates is currently being evaluated.

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Cyclic Alkane Metathesis Reactions via Surface Organometallic Chemistry

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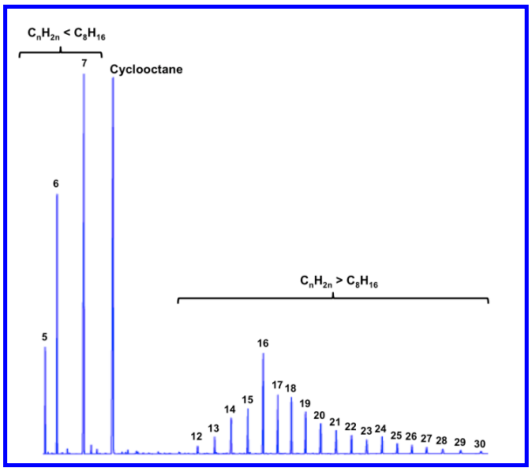
Macrocyclic alkanes are a class of molecules with high value interest in industry because they serve as building blocks in the synthesis of macrolides. Thus, it was envisaged that cyclooctane metathesis would offer a rapid and facile access to these cyclic structures using surface organometallic chemistry.[1] In the following work,[2] we employ a single multifunctional silica-supported catalyst for synthesis of wider distribution of macrocyclic alkanes.



GC chromatogram of cyclooctane metathesis products catalyzed by 1. Conversion= 70%, TON= 450. The turnover number (TON) is the number of mol of cyclooctane transformed per mole of W.

We have demonstrated that the cyclic alkane metathesis catalyzed by a multifunctional supported W single catalytic system lead to an unprecedented distribution of macrocyclic alkanes in the range of C12 to C40.[3] The main advantage of our catalyst system is the fact that we used a W single catalyst able to promote different elementary steps. Furthermore, no polymeric products were detected.

Acknowledgement: The financial assistance of this research has been fully supported by the King Abdullah University of Science and Technology.

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Theory-Assisted Discovery of Z-selective Olefin Metathesis Catalysts

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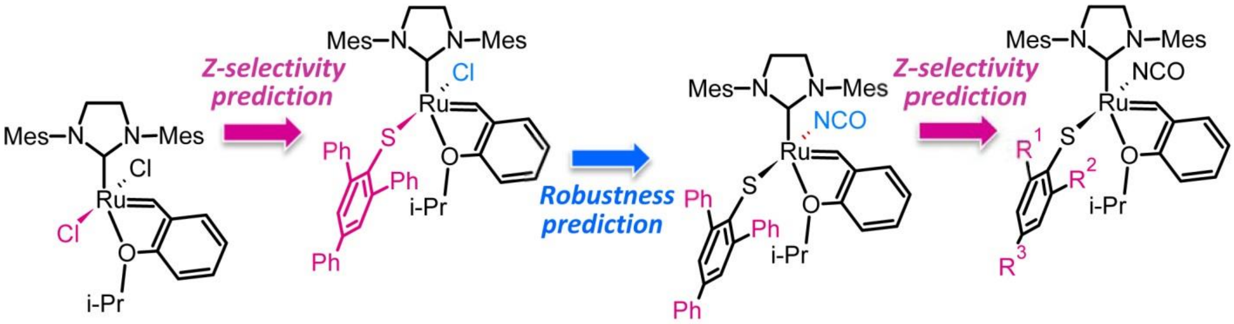
Traditional catalyst discovery is largely driven by chance and serendipity and improving the design of a catalyst usually involves costly and time-consuming experimental trial-and-error. However, little by little the tedious experiment-only approach is being replaced by a powerful new strategy in which computational chemistry identifies the most interesting subset of candidate catalysts. In this way, fewer candidate catalysts need to be synthesized and the discovery process is accelerated.

To illustrate, here we describe the pivotal role that theory has played in the development of Z-selective analogues of Grubbs and Hoveyda-Grubbs catalysts (see Figure); first by identifying sterically demanding thiolates as a selectivity-inducing scaffold that could replace one of the chlorides in the parent, symmetric catalyst,[1] next by singling out isocyanate as a ligand that would be better bonded to ruthenium and thus offer a more robust catalyst,[2] and, recently, by improving the Z-selectivity *via in silico* screenings of candidate bulky thiolate ligands, thus achieving catalysts with near-perfect Z-selectivity.[3] Optimization to such high selectivity requires accurate computational methods that are able to discriminate between “selective” and “highly selective” catalysts. This kind of quantitative prediction, confirmed by experiment, turned out to be achievable only with accuracy settings and approaches (convergence criteria, integration grids, etc.) that are not standard in common computational chemistry packages such as Gaussian 09.



The role of computational prediction in the development of Z-selective olefin metathesis catalysts from the unselective Hoveyda-Grubbs second-generation catalyst

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1 a) Nelson, J. W.; Grundy, L. M.; Dang Y.; Wang Z.-X.; Wang X. *Organometallics* **2014**, *33*, 4290; b) Occhipinti, G.; Hansen, F. R.; Törnroos K. W.; Jensen V. R. *J. Am. Chem. Soc.* **2013**, *135*, 3331; c) Jensen V. R.; Occhipinti G.; Hansen F. Novel Olefin Metathesis Catalysts. *Int. Patent Appl. WO* 2012032131, **2012**.

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Carbonization of Macroporous poly(Dicyclopentadiene)-foams

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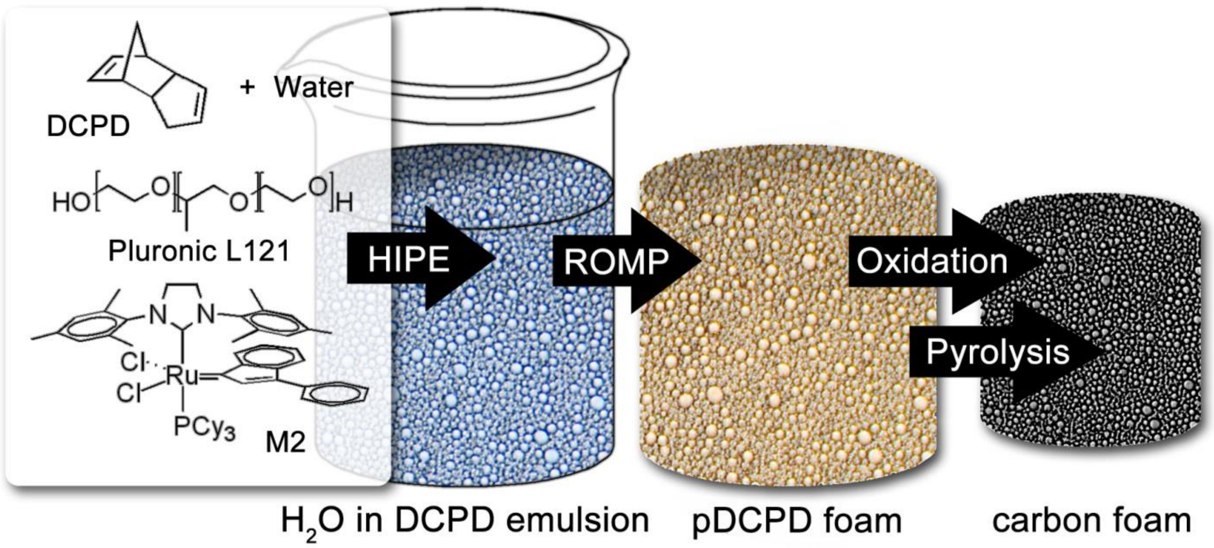
High internal phase templating of surfactant stabilized dicyclopentadiene-water mixtures and subsequent curing via Ring-opening Metathesis Polymerization yields throughout opened macroporous poly(dicyclopentadiene) foams[1] which, upon oxidation, can be pyrolysed yielding macroporous carbon foams of conductivities of up to 2800 Sm^{-1}.[2] When the pyrolysis is conducted in the presence of carbon dioxide, micro- and mesoporosities are additionally created leading to increased specific surface areas of up to 1100 m^2g^{-1}. Similarly, Fe_3C/C-foams can be prepared starting from macroporous poly(dicyclopentadiene) $\gamma Fe_2O_3/Fe_3O_4$ nanocomposite foams.[3]



Schematic way of preparing macroporous carbon from dicyclopentadiene

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New Star-Shaped Polymer Based on Porphyrin-Core and NBE

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Porphyrins are a group of organic compounds with high conjugated structure, which have received considerable attention due to their interesting excited state chemical properties, electron-transfer processes and photo-physical properties.[1]

In this work, we focused on the synthesis of a star-shaped polymer with a porphyrin-core by ROMP, trying to combine the properties of a star-shaped polymer such as impact-resistant plastics, different, thermoplastic elastomers and variety of morphologies.

The synthesis[2] is described below (Figure 1), and the absorption and emission spectra of isolated porphyrin (TPPF$_{20}$); functionalized with norbornene (**7**) (NBE-TPPF$_{20}$) and the polymer (polyNBE-TPPF$_{20}$) are compared in Figure 2.Polymerization was done in a 10 NBE : 1 NBE-TPPF$_{20}$ ratio using the Grubbs 2ndgeneration as catalyst in CHCl$_3$.

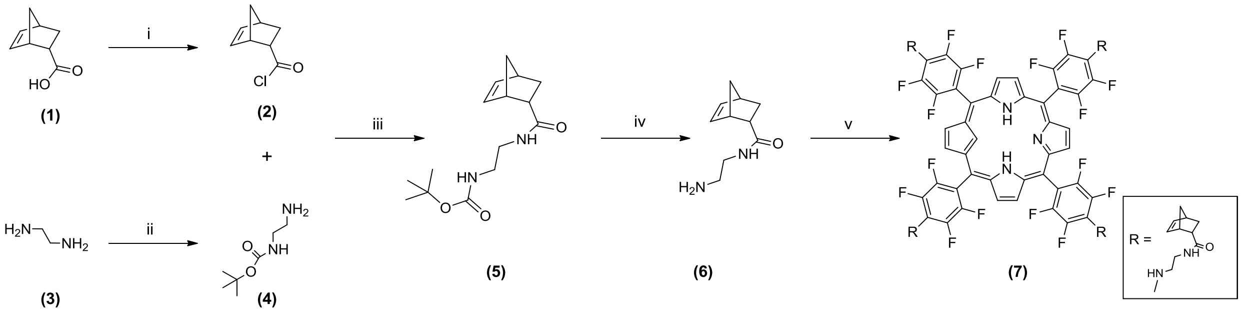

Figure 1. Synthetic route: i) (COCl)$_2$,DMF$_{(cat)}$,DCM. ii) (Boc)$_2$,DCM, ref 12h. iii) TEA, DMAP$_{(cat)}$, DCM. iv) TFA,DCM. v)TPPF$_{20}$, K$_2$CO$_3$, NMP, ref 12h.

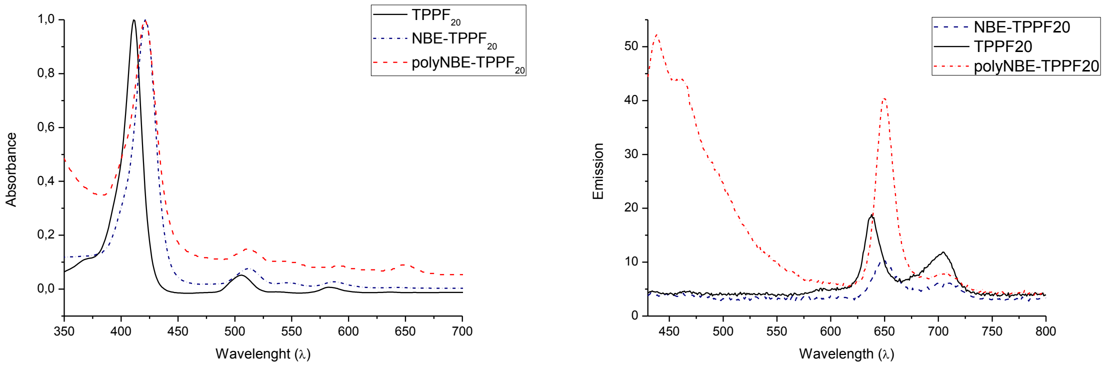

Figure 2. Absorption and emission spectra of TPPF$_{20;}$ NBE-TPPF$_{20}$ and polyNBE-TPPF$_{20}$

Acknowledgement: This work was supported by FAPESP (2012/24617-4, 2013/06532-4), CNPq and CAPES.

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Quinones as Anti-Isomerization Agents in Metathesis Reactions

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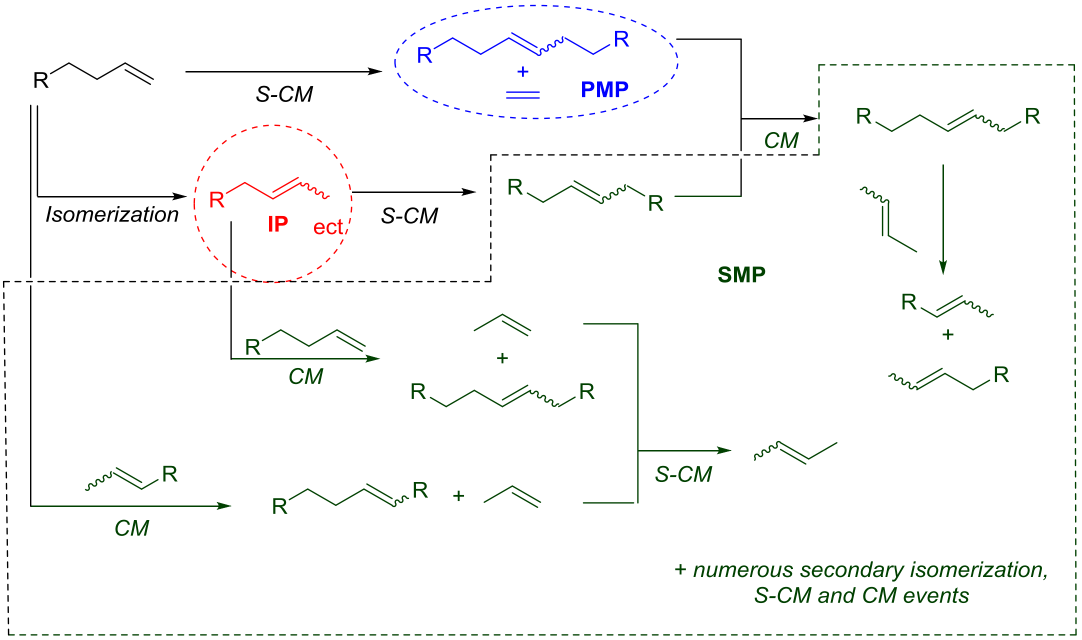
Olefin metathesis, catalyzed by transition metal complexes, has emerged as a unique and powerful transformation for the inter-conversion of olefins in both organic and polymer chemistry.[1] Unfortunately, this methodology is not free from some drawbacks. One of them is the possibility of isomerization of the double bond in the obtained products mainly caused by products of decomposition of catalysts. This undesired side reaction can significantly alter the product distribution and decrease the yield of the desired product, and in some cases it can even entirely prevent its formation.[2] Additionally, the side products resulting from unwanted isomerization are frequently difficult to remove via standard purification techniques.[3]

In our work we have developed new olefin metathesis complexes which contain quinone moiety as well as investigating their activity and influence on isomerization process.



Possible reactions of linear alkenes in the presence of a metathesis catalyst.

Acknowledgement: This work has been supported by NCN/2011/03/D/ST5/06079.

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1 a) Grubbs, R. H. Handbook of Metathesis; Wiley-VCH: Weinheim, Germany, **2003**; b) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592; c) Grela, K. Olefin Metathesis: Theory and Practice, John Wiley & Sons, Inc., Hoboken, NJ, USA, **2014**.

2 a) Michalak, M.; Wicha, J. *Synlett* **2005**, 2277; b) Michalak, M.; Wicha, J. *J. Org. Biomol. Chem.* **2011**, *9*, 3439.

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Ruthenium Nanoparticles as Unsuspected, Isomerization-active Participants during Olefin Metathesis

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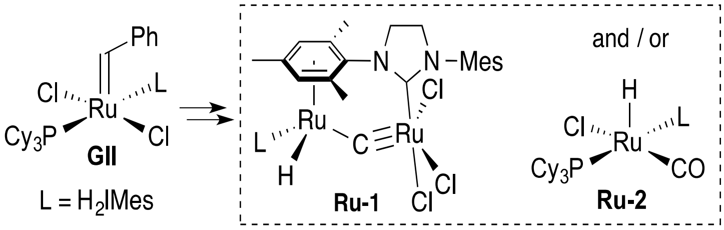
Unwanted olefin isomerization represents a long-standing challenge in olefin metathesis.[1] Adventitious isomerization can precede or follow metathesis, thus affecting the integrity of both the reagents and the reaction products.[2] The species responsible for metathesis have been the subject of much debate. To date, however, proposed culprits focus exclusively on molecular ruthenium complexes (see Figure).[3]



Commonly cited culprits for isomerization.

Here we examine the role of metal nanoparticles (NPs), formed via a previously unrecognized decomposition pathway. The evidence for formation and operation of NPs will be presented, and the implications for catalysis will be explored.

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New Chemoswichable Carbamatoalkylidene Ruthenium Catalysts for Olefin Metathesis

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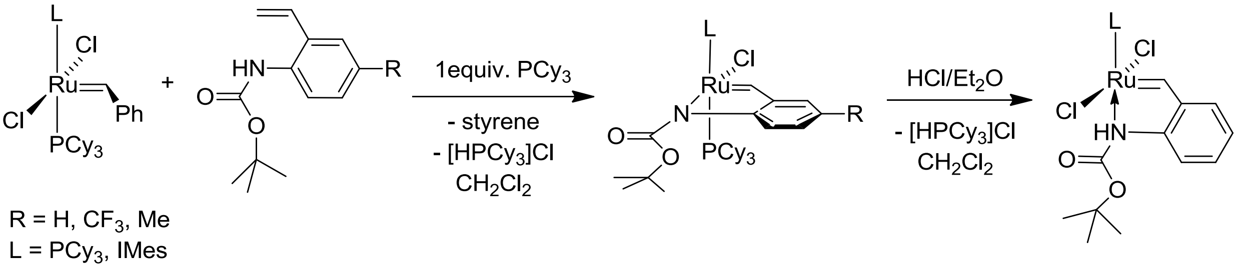
Despite large progress of olefin metathesis,[1] efforts are still made to prepare new improved catalysts. One of the most intensively studied groups of olefin metathesis complexes are latent catalysts, which are inactive in the standard conditions and they can be activated by chemical or thermal methods.[2] We recently reported synthesis of ruthenium carbamato- and amidobenzylidene complexes which behave like latent, chemoswitchable catalysts of olefin metathesis.[3] In this communication we report preparation, characterization, catalytic performance and mechanism of chemical activation of new representatives of carbamatobenzylidene ruthenium chelates.



It was demonstrated in a series of test reactions that the catalysts are inactive in their dormant forms and dramatically increase their catalytic activity after addition of such activators as HCl (Et_2O) or other Bronsted acids. The mechanism of activation of ruthenium carbamatobezylidenes in the presence of HCl was found to involve protonolysis of the Ru-N bond, asociacion of the chloride to coordination sphere accompanied by dissociation of PCy_3 and structural rearrangement.

Acknowledgement: Financial support from the National Science Centre (Poland), (project No. UMO-2011/03/B/ST5/01047) is gratefully acknowledged.

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1 *Handbook of Metathesis*, (Grubbs, R. H.; Wenzel, A.G.; O'Leary, D.J.; Khosravi, E. eds.), Wiley-VCH, Weinheim, **2015**; *Olefin Metathesis: Theory and Practice, (Grela K. ed.),* Wiley & Sons, 2014.
2 Vidavsky Y.; Anaby A.; Lemcoff N. G. *Dalton Trans.* **2012**, *41*, 32.
3 Pietraszuk C.; Rogalski S.; Powala B.; Mietkiewski M.; Kubicki M.; Spolnik G.; Danikiewicz W.; Wozniak K.; Pazio A.; Szadkowska A.; Kozowska A.; Grela K. *Chem. Eur. J.* **2012**, *18*, 6465.

New Latent Ruthenium Catalysts Bearing Aryloxybenzylidene Ligands and Their Application in Olefin Metathesis

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The availability of well-defined ruthenium-based catalysts tolerant of moisture, oxygen, the majority of functional groups and typical processing conditions has made olefin metathesis widely used in synthesis.[1] Latent catalysts belong to intensively studied groups of olefin metathesis catalysts especially due to their applicability in ROMP.[2] Recently, we have reported aryloxybenzylidene ruthenium chelates which behave like latent catalyst of olefin metathesis.[3] In this communication we report preparation, characterization and catalytic performance of new latent ruthenium catalysts bearing aryloxybenzylidene ligands (see Figure):

R = C_6H_5, C_6H_4-Me-4, C_6H_4-CF_3-4

R' = H, NO_2, t-Bu

New aryloxybenzylidene ruthenium chelates

Efficient synthetic procedures were described. All synthesized ruthenium complexes were characterized by spectroscopic methods. Their catalytic activity was screened in selected test reactions including ring opening metathesis polymerization of 1,5-cyclooctadiene and cross-metathesis of allylbenzene with Z-1,4-bis(acetoxy)but-2-ene. It was demonstrated that the catalysts are inactive in their dormant forms and dramatically increase their catalytic activity after addition of such activators as HCl (Et_2O) or other Bronsted acids.

Financial support from the National Science Centre (Poland), (project No. UMO-2011/03/B/ST5/01047) is gratefully acknowledged.

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1 *Handbook of Metathesis*, (Grubbs, R. H.; Wenzel, A.G.; O'Leary, D.J.; Khosravi, E. eds.), Wiley VCH, Weinheim, **2015**; *Olefin Metathesis: Theory and Practice,* (Grela, K. ed.), Wiley & Sons, 2014.
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3 Żak, P.; Rogalski, S.; Przybylski, P.; Kubicki, M.; Pietraszuk, C. *Eur. J. Inorg. Chem.* **2014**, 1131.

Synthesis and Application of a Family of Specialist Olefin Metathesis Catalysts

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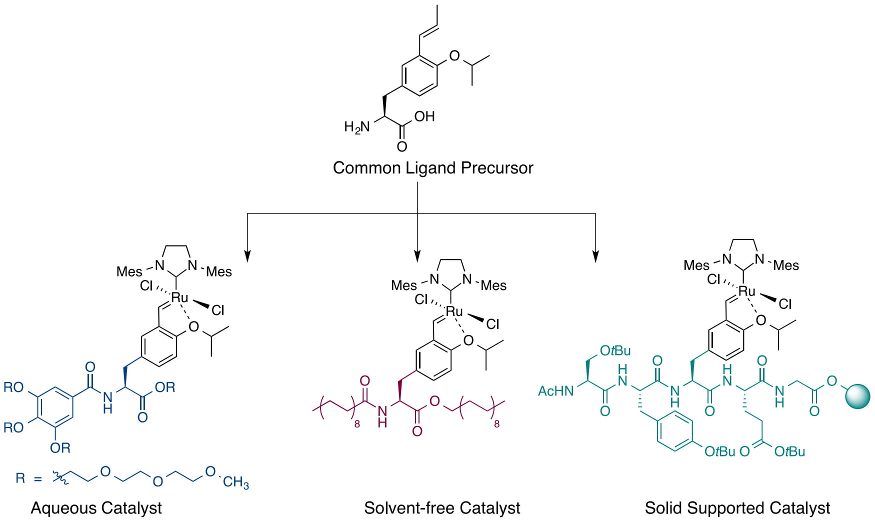
There is a need for specialist olefin metathesis catalysts to address specific synthetic needs such as activity in highly polar solvents and solvent-free conditions, and removal of Ru-residue from the reaction mixture.[1] Numerous catalysts have been designed to address these challenges, although their development has had a narrow focus towards one specific property.[2] As part of our study on the improvement of olefin metathesis technology,[3] we recently investigated a divergent strategy which allows the preparation of a family of functionalised Ru-alkylidene based catalysts. Beginning with a common ligand precursor derived from commercially available L-tyrosine, catalyst analogues with a range of different properties can be synthesised.

Mum and three joey catalysts



Three catalysts from one family

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1 Vougiokalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746.

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Acrylate Metathesis: Origin of the Superior Performance of Phosphine-Free Ruthenium Catalysts

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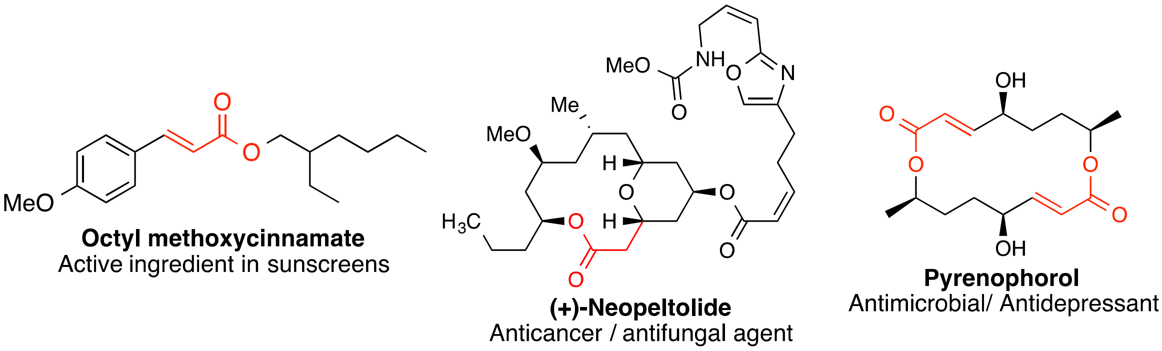
Acrylate metathesis, as a technology enabling direct access to α,β-unsaturated esters, has enormous potential in "renewable metathesis",[1] as well as organic synthesis (Chart 1).[2] Recent advances in this area have been achieved largely through use of the second-generation Hoveyda catalyst, **HII**. In numerous reports, **HII** has been shown to outperform **GII** in acrylate cross-metathesis reactions.[3] This disparity does not hold true for olefin substrates in general, suggesting that the observed deactivation may be particular to the electron-deficient acrylate.



Octyl methoxycinnamate
Active ingredient in sunscreens

(+)-Neopeltolide
Anticancer / antifungal agent

Pyrenophorol
Antimicrobial/ Antidepressant

Chart 1. *High-value targets in acrylate cross-metathesis.*

Here we demonstrate that the superiority of **HII** originates in its phosphine-free nature. We show that a new deactivation mechanism is involved. Literature precedents suggest that this mechanism is operative for a range of alkenes, including acrylates, acrylonitriles, vinyl ketones, acrylamides, and acroleins. This pathway is thus of broad relevance to the metathesis of electron-deficient olefins.

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Competing Pathways in Equimolar Reactions of the Second and Third Generation Grubbs Catalyst with Vinylsilanes – Computational and Experimental Approach

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Among the various functionalised olefins, vinylsilanes are group of reagents exhibiting particularly diverse reactivity towards ruthenium-based olefin metathesis catalysts.[1] Factors determining observed differences in reactivity have not been fully investigated. Understanding the factors that determine the regioselectivity of stoichiometric metathesis of vinylsilanes with ruthenium benzylidene complexes and better understanding of the competitive processes leading to decomposition of alkylidene complexes in the presence of vinylsilanes can be crucial for better use of metathesis transformations in silicon chemistry.

In the communication we report on the computational studies of the regioselectivity of cycloaddition of selected vinylsilanes to the second generation Grubbs' catalysts. Moreover, mechanism of decomposition of the second generation Grubbs' catalyst in the presence of trimethylvinylsilane was examined. The results of DFT studies were complemented by using experimental methods. Reactivity of selected vinylsilanes were examined in reactions with equimolar amounts of the second and third generation Grubbs' catalysts. On the basis of computational and experimental studies a general scheme of reactivity of vinylsilanes toward ruthenium alkylidene complexes was proposed.[2]

Acknowledgement: Financial support from the National Science Centre (Poland), (project No. N 204 1851 40*) is gratefully acknowledged.*

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2 Rogalski, S.; Żak, P.; Wyrzykiewicz, B.; Pietraszuk, C.; Sliwa, P.; Handzlik, J. submitted.

Phosphine-Based Z-Selective Ruthenium Olefin Metathesis Catalysts

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Vidar R. Jensen*

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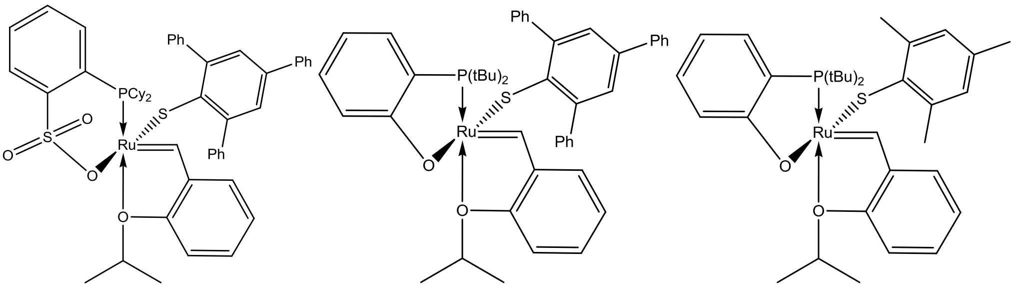
Only in recent years have catalysts selective for the Z-isomer product been developed.[1-6] For ruthenium, highly selective catalysts have been obtained for catalysts that bind the incoming olefin cis to an N-heterocyclic carbene (NHC) ligand, in contrast to the standard first- or second-generation catalysts that bind the substrate trans to the phosphine or NHC ligand. Trans-binding and Z-selective analogues of the second-generation catalysts could, however, be obtained via substitution of a single chloride by a sterically demanding arylthiolate ligand.[5-6]

The above-mentioned advancements of Z-selective NHC-based ruthenium catalysts have not been matched by first-generation analogues, and the selectivities reported for phosphine complexes have so far been disappointing.[7-8] Here, we report the first phosphine-based olefin metathesis catalysts showing significant Z selectivity, developed using a strategy consisting of computational prediction and experimental follow up, and with bulky arylthiolates as the selectivity-inducing ligands. We show that it is possible to achieve true trans-binding Z-selective analogues of the first-generation catalysts, based on both monodentate phosphine and various P-O phosphine chelates (see Figure).



1 **3** **2**

Z-selective catalysts constructed using L-X phosphine chelates.

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Tri(dimethylamido)tungsten Benzylidyne as a Precursor for Novel Tungsten Alkylidyne Complexes

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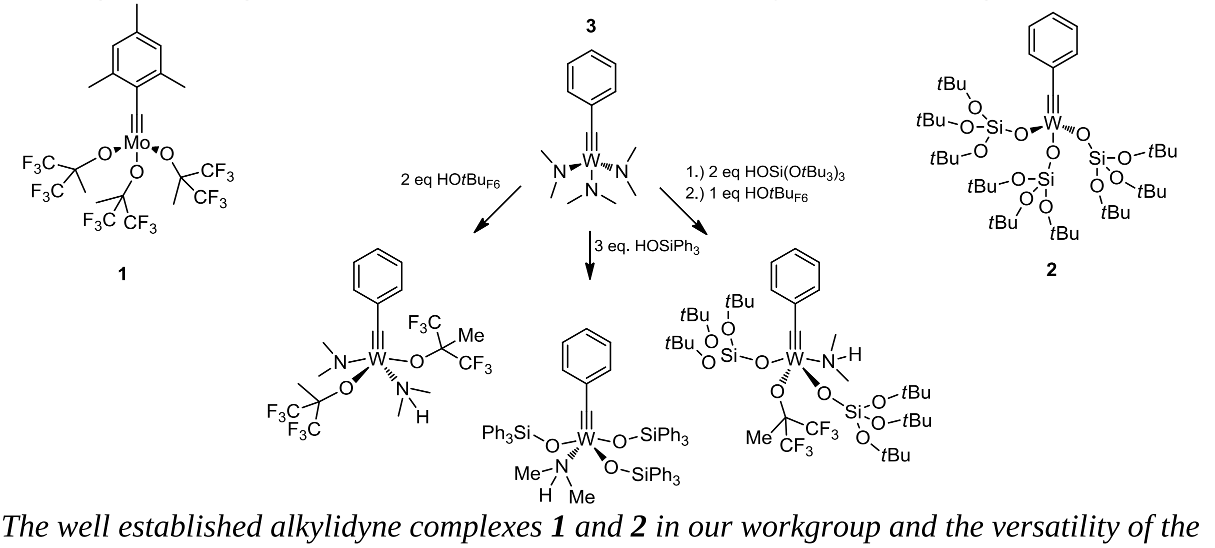
Lately our workgroup could show that the 2,4,6-trimethylbenzylidyne molybdenum complex [MesC≡Mo{OC(CF_3)$_2$Me}$_3$] (**1**) is an efficient catalyst for metathesis of internal and terminal alkynes[1] and that the tri(*tert*-butoxy)silanolate-supported tungsten benzylidyne complex [PhC≡W{OSi(O*t*Bu)$_3$}$_3$] (**2**) can metathesise conjugated diynes selectively.[2] Regarding these results the conclusion can be set, that the ligands in metal alkylidyne complexes have a relevant role in alkyne metathesis reactions. To observe different behaviors in catalytic reactions, the synthesis of different substituted tungsten alkylidyne complexes was achieved with a new reaction pathway based on the complex synthesis of tri(dimethylamido)tungsten nitrido by the researchgroup of Prof. Dr. L. McElwee-White.[3] The tri(dimethylamido)tungsten benzylidyne complex (**3**) is a good precursor for different substituted novel alkylidyne complexes that are hardly obtainable under conventional pathways. By adding dry alcohols step by step to a solution of the title compound, the substitution of the amido ligands can be achieved stoichiometrical (see Figure). A problem however is that the resulting free dimethylamine coordinates to the metal centre leading to no activity in alkyne metathesis reactions. Sometimes polymerisation of the used alkynes can be observed. This issue could be solved by removing the strong coordinated amine, which is currently under investigation.



*The well established alkylidyne complexes **1** and **2** in our workgroup and the versatility of the reaction of tri(dimethylamido)tungsten benzylidyne complex (**3**) with alcohols.*

References:

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Olefin-Metathesis Method: A Valuable Tool for the Investigation of Rubber-Metal Adhesion Interfaces

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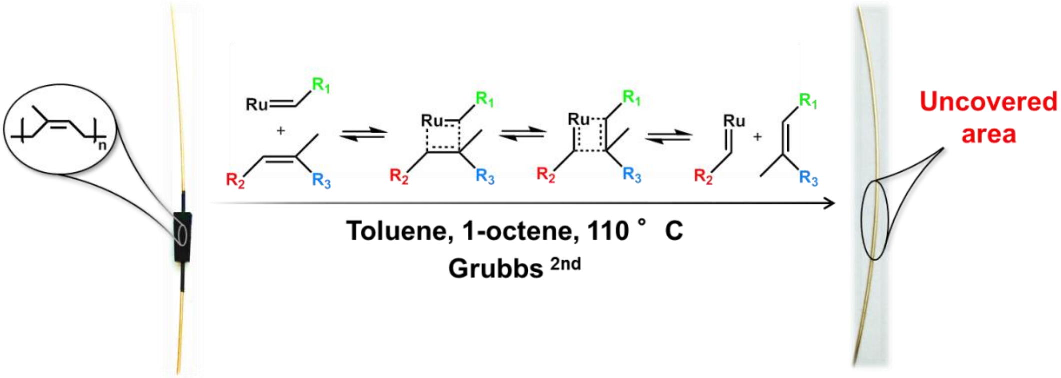
The incorporation of brass-coated steel wires in rubber products such as tires, hydraulic hoses and handrails is a widely used reinforcing method. To attain the highest standards of mechanical properties an outstanding adhesion between rubber and metal is required. This is accomplished by the formation of a Cu_xS-ZnS interface, created during the sulfur vulcanization of the rubber.[1] Thus, the cured rubber macromolecules are able to bind mainly mechanically on this interface, for which reason the adhesion properties are influenced by the rubber mixture as well as the brass surface.



Reaction scheme of the Olefin-Metathesis Method

Due to the strong adhesive strength of the rubber on the wire, it is difficult to uncover the brass-surface necessary to study the adhesion layer. In this contribution we use an olefin cross metathesis approach to degrade the crosslinked rubber network and to uncover the adhesion layer. For this, the coated wires were immersed into toluene solutions of a Grubbs 2nd generation catalyst. 1-Octene was used as co-reagent. By optimization the reaction conditions, the rubber-metal interface can be exposed for detailed investigations using e.g. optical microscopy, focus variation microscopy and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX).

References:
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Syntheses of Arylphosphonium Salts from Cyclotrimerization of Terminal Aryl Alknyes by a Ruthenium Pentadienyl Complex and Revisiting the Catalytic Dimerization

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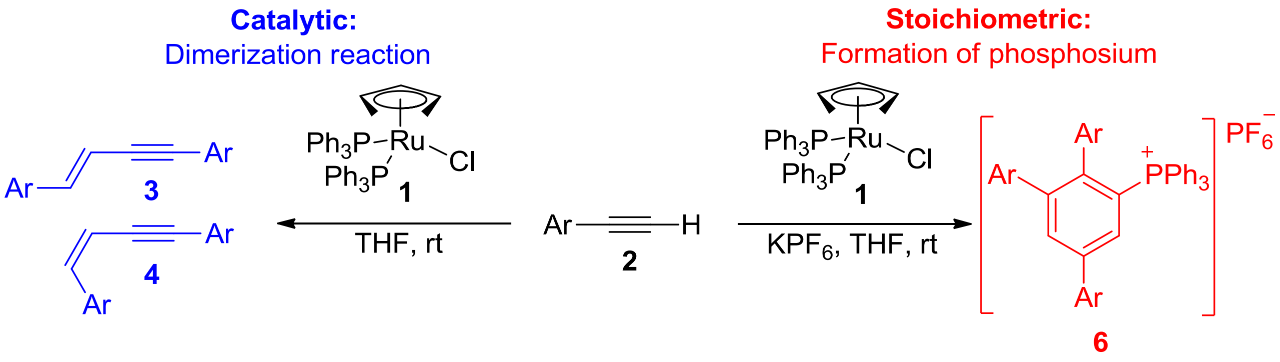
The catalytic dimerization of terminal alkynes represents an attractive route for the preparation of 1,4-disubstituted enynes, which are versatile building blocks in organic synthesis.[1] These C-4 unsaturated moieties are key units in naturally occurring compounds,[2] and in organic materials,[3] especially when derived from aromatic alkynes. Recently we found that (η^5-C_5H_7)(PPh_3)$_2$RuCl (**1**)[4] is an useful catalyst for the selective dimerization of phenylacetylene. A new method has been also found for the preparation of polyaryl phosphonium salts (APSs) from terminal arylalkynes and complex (**1**).



Treatment of an arylalkyne with **1** and KPF_6, both in stoichiometric quantities, gives an APS, whose structure has been confirmed. Complex **1** is also an efficient catalyst for the synthesis of 1,4-disubstituted butenynes in THF from the dimerization of aryl alkynes with a catalyst loading as low as 1−2 mol % under mild conditions, furnishing the (*Z*)-butenyne as the major product along with a small amount of the *E* isomer. The steric effect affects the yields of the desired enyne products more than the electronic effect of the substituents. A mechanism consisting of continuous insertion reactions of aryl alkynes into Ru−C bonds is proposed for the formations of enynes and APSs.

Acknowledgement: Financial support from the Ministry of Science and Technology of Taiwan, ROC, under grant no. NSC 100-2113-M-002-003-MY3 is appreciated.

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Long-chain Polyethers *via* $GaBr_3$-catalyzed Reduction of Fatty Acid Derived Carboxylic Acid Esters Obtained *via* Metathesis Reactions

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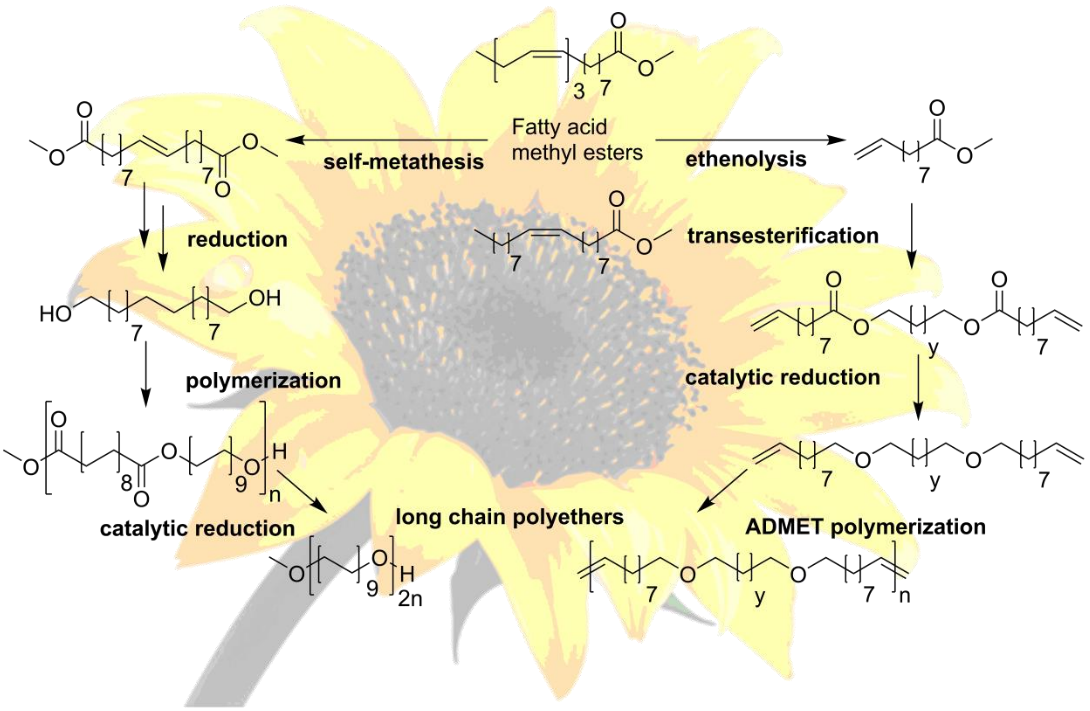
Recently, a $GaBr_3$/TMDS (1,1,3,3-tetramethyldisiloxane) system was introduced as an efficient method for the reduction of esters of long-chain fatty acids and polyols, such as triglycerides to the corresponding ethers.[1] While the reducing agent TMDS is used in stochiometric amounts, $GaBr_3$ can be used in catalytic amounts of 0.5-1 mol%. The reaction is carried out under mild conditions without solvent giving full conversion of the substrate.



Two synthesis routes to different long chain polyethers obtained from fatty acid methyl esters.

Here, the $GaBr_3$/TMDS system is applied to monomeric and polymeric plant oil derived carboxylic acid esters and in combination with self-metathesis, ethenolysis and ADMET polymerizations with the aim to obtain long-chain polyethers in a sustainable fashion (compare Scheme above).

References:

1 a) Biermann, U.; Metzger, J. O. *ChemSusChem*. **2014**, *7*, 644; b) Biermann, U.; Metzger, J. O. *Macromol. Eur. J. Lipid Sci. Technol.* **2014**, *116*, 74.

Defined Star Polymers *via* ADMET Polymerization of a Renewable Monomer and their Post-polymerization Functionalization

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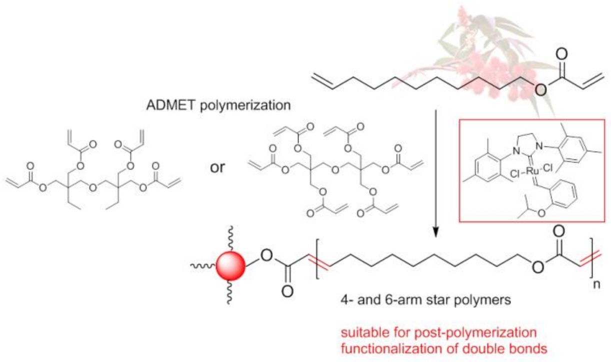
Olefin metathesis includes ring-opening metathesis (ROM), ring-closing metathesis (RCM), ring-opening metathesis polymerization (ROMP), acyclic diene metathesis (ADMET), cross-metathesis (CM), and self-metathesis (SM). First reported in 1991 by the Wagener group, ADMET polymerization is a step-growth polymerization of α,ω-dienes to obtain polyenes under the release of volatile ethylene gas. It can be used to design various polymeric architectures.[1] Here, the synthesis of star shaped polymers with 4 and 6 arms and ten or twenty repeating units per arm *via* ADMET polymerization is described. The core unit with acrylate endgroups is polymerized with fatty acid derived 10-undecenyl acrylate as unsymmetric α,ω-diene monomer catalyzed by the Hoveyda-Grubbs 2nd generation catalyst. Thereby, the cross-metathesis selectivity of terminal olefins and acrylates allows the buildup of defined polymer architectures.[2]



Synthesis of star shaped polymers via ADMET polymerization.

Subsequent modification of internal as well as external α,β-unsaturated esters was realized *via* base-catalyzed thia-Michael addition. Functionalization of only acrylate endgroups was performed by thio-bromo click chemistry of thioglycerol-functionalized 4-arm star polymer. Combination of esterification and thio-bromo click reaction provides star polymers bearing a dendritic corona with a variable quantity of hydroxyl groups on the surface.[3]

References:

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The Utilisation of Styrene in the Controlling of Gel Times in Polyesters

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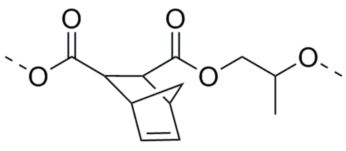
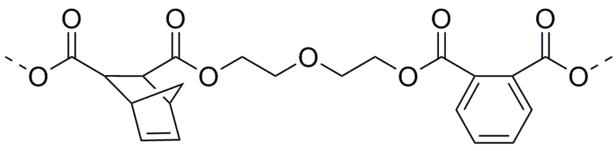
It has been shown that unsaturated polyesters with norbornene functionality can be synthesised and undergo Ring Opening Metathesis Polymerisation (ROMP)[1]. This specifies the fact that the polymers formed are ‘zero styrene’. The poster however, describes the utilisation of styrene in the ROMP of unsaturated polyesters and shows that gel time can be drastically altered using a low level of styrene. This could be preferable in situations which require a slower curing. Polyesters 1 and 2 (example structures shown) were dissolved in dichloromethane solution containing varying amounts (0 – 5 equivalents w.r.t. initiator) of styrene. This was then added to Grubbs’ 1st generation ruthenium catalyst. The gelation time was observed and a trend was seen between styrene level and gel point, showing that styrene can control the rate of gelation – *e.g.* for polyester 1 from 30.5 minutes to 44.0 minutes.



Polyester 1



Polyester 2

References:

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Active Sites in Re-based Alkene Catalysts Supported on γ-Al_2O_3 : Structure and Density

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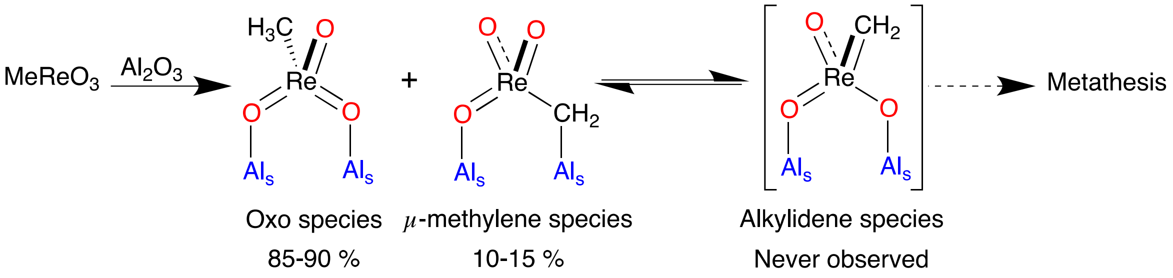
While Re_2O_7/γ-alumina is an active room temperature catalyst in alkene metathesis, the structure of the active sites is still unknown despite forty years of research.[1] Previous studies on the model system CH_3ReO_3/Al_2O_3 have revealed that the active site is based on μ-methylene species, Al-CH_2-ReO_3, which results from the activation of the C-H bond of CH_3ReO_3 on the defect sites of alumina, and which generates the catalytically active alkylidene in the presence of alkenes.[2]



Grafting of CH_3ReO_3 on Al_2O_3.

Here, we address the structure of active sites and reaction intermediates in alumina supported Re-based alkene metathesis, and also link the activity of the catalyst with the different sites of γ-alumina by a combined used of solid-state NMR spectroscopy and computational chemistry.

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Classification of Heteroaromatic Substituted Fischer-type Metal Carbenes: a QSAR Type Approach

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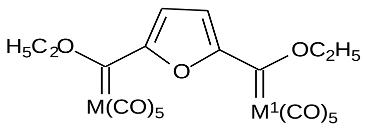
[b] *Department of Chemistry, University of Pretoria, Pretoria, South Africa*

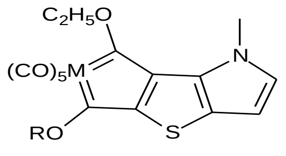
Fischer-type metal carbenes are used as catalysts in various organic synthesis reactions e.g. metathesis, cyclopropanation and benzannulation.[1] In previous studies in the Catalysis and Synthesis Group at North West University,[2] a modified molecular modelling method was developed to investigate the catalytic activity of metal carbenes for alkene metathesis.

In this study the focus was on the application of the modified molecular modelling method to classify various Fischer-type metal carbene complexes with heteroaromatic groups (furan, bithiophene, N-methyl-thieno[3,2-b]pyrrole, 2-(2'-thienyl)furan and N-methyl-2-(2'-thienyl)pyrrole). The above-mentioned complexes were synthesised by a research group at the University of Pretoria.[3]

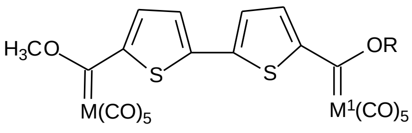
The following software packages were used for geometry optimization, orbital energy calculation and analysis of data: Material Studio 6.0 DMol[3], Gaussian09, NBO, Solid-G and Statistica version 12. It was concluded from this study that compounds **A3**, **B9** and **C15** are suitable candidates for nucleophilic attack reaction, while compounds **A4**, **C12**, **C13** and **D23** are suitable for benzannulation and metathesis reactions. Compound **B6** is suitable for both nucleophilic attack reactions and benzannulation.



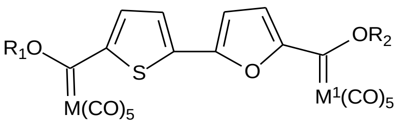
A3: M = M^1 = W
A4: M = Cr, M^1 = W



B6: M = Cr, R = CH_3
B9: M = W, R = C_2H_5



C12: M = M^1 = Cr, R = CH_3
C13: M = M^1 = Cr, R = $C_4H_8OCH_3$
C15: M = M^1 = W, R = CH_3



D23: M = W, M^1 = Cr, R_1 = R_2 = CH_3

References:

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Characterization of Pyridinyl Alcoholato Grubbs-type Pre-catalysts with NMR and Mass Spectrometry

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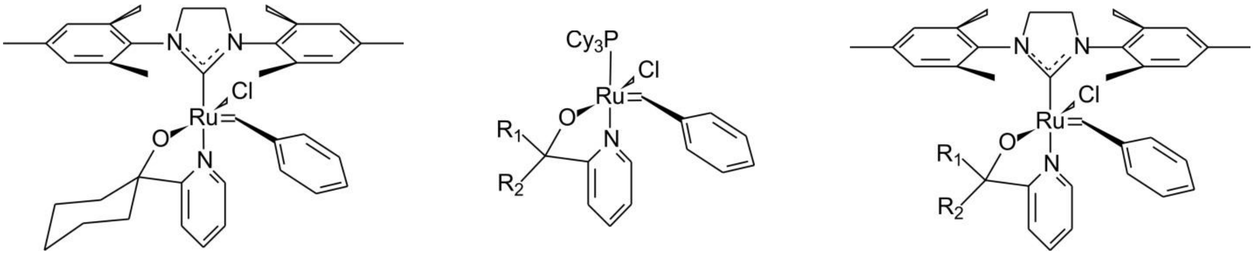
New Grubbs-type pre-catalysts are continuously being developed for various metathesis reactions since the advent of the first generation of these pre-catalysts. In the process different analytical techniques were used for the characterization of these pre-catalysts. Although the standard ^{1}H NMR pulse programs are to some extent sufficient for the characterization of the pre-catalysts shown in the figure,[1-3] it however becomes problematic when the progress of the metathesis reaction is investigated, *inter alia* due to overlapping signals to mention but one example.[4]



1

2a $R_1 = R_2 = Ph$

2b $R_1 = Ph, R_2 = Tol$

3a $R_1 = R_2 = Ph$

3b $R_1 = Ph, R_2 = Tol$

Grubbs-type pre-catalysts used during this study

In an attempt to shed some light on the operation of the metathesis reaction in the presence of these pre-catalysts the results obtained from NMR and different MS ionization methods will be presented.

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Application of Pyridinyl-alcoholato Ligand Containing Grubbs 2-type Pre-catalysts in Alkene Metathesis Reactions

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Olefin metathesis is increasingly used as a general tool in synthesis. Since the development of the Grubbs[1,2] pre-catalysts numerous Grubbs-type pre-catalysts have been produced for alkene metathesis. Although these showed remarkable resilience to a variety of functional groups these catalysts have relatively short lifetimes. The Grubbs-type pre-catalysts are of great interest in alkene metathesis due to their high activity and stability.[3] Jordaan and Vosloo[4] showed that the reactivity, lifetime and stability of the Grubbs 1 and 2 pre-catalysts can be increased through the replacement of the phosphine ligand by a bidentate ligand with a rigid backbone. These bidentate ligands have the ability to place two or more donor atoms with different electronic properties close to the metal atom. The concept of hemilability of bidentate ligands increase the stability and lifetime by releasing a free coordination site on demand and preventing decomposition.[4] In this project with the intention to increase the stability of Grubbs pre-catalysts, several Grubbs 2-type ruthenium complexes were synthesized by introducing bidentate hemilabile pyridinyl-alcoholato ligands that have shown enhanced catalyst lifetime compared to Grubbs pre-catalysts. The synthesized Grubbs 2-type pre-catalysts were tested for activity in the various alkene metathesis reactions.

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Naphthalimide-functionalized Polymers via Ring-opening Metathesis Polymerisation

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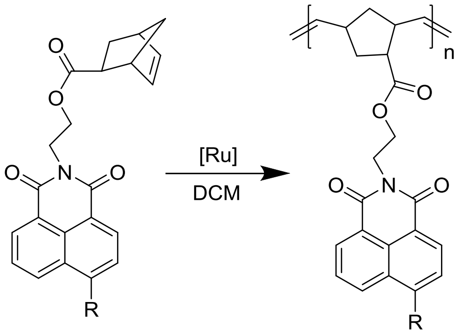
1,8-Naphthalimide derivatives are highly fluorescent and photostableand thus precursors for different applications e.g. in fluorescent synthetic polymers and textiles and fluorescent down shift materials, as electro-optically sensitive materials, in laser technology, as liquid–crystal additives and as fluorescent markers in medicine and biology. In this work the defined naphthalimide-functionalized polymers are prepared using ring opening metathesis polymerization (ROMP). The influence of substituents at position 4 on the spectroscopic properties has been studied in norbornene monomers as well as in the corresponding polymers.

Due to the living polymerisation character and high functional group tolerance ROMP is suitable for the synthesis of defined (block) copolymers. Optical characterisations using absorption and emission spectroscopy show that monomers as well as the polymers have similar properties which mean that the covalent bonding to the polymer does not influence the characteristic properties of naphthalimide derivatives.



Ring opening metathesis polymerization of napththalimide monomers
(R = Br, OCH_3, $N(CH_2CH_3)_2$, $N(CH_2CH_2)_2NH$, $N(CH_2CH_2)_2NCH_3$

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Perylene Functionalized Polymers via Ring-opening Metathesis Polymerisation with a High Dye Content

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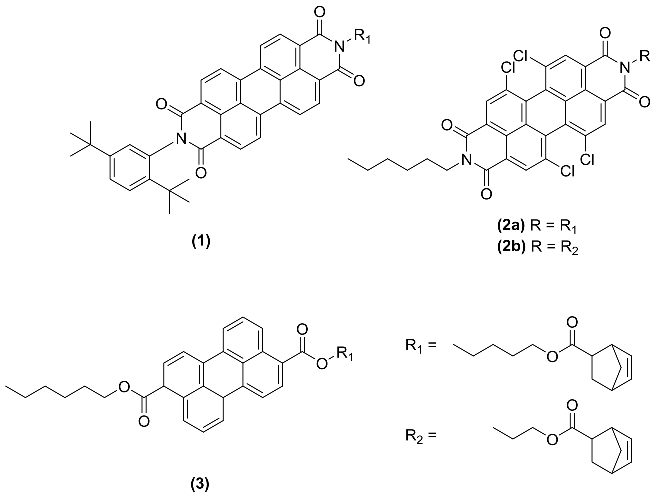
Perylenes are used as dyes and pigments since the 1910ies. Additionally, their specific properties such as near-unity fluorescence, high photo stability and at strong electron-accepting character make them qualified for different more advanced optical and electrochemical applications.

Examples are chromophores in light conversion layers and sensors, in which the perylene dyes often have to be embedded into a polymer matrix. However, in many cases the solubility of the chromophores, phase separation and aggregation are limiting for homogeneous and stable layers which can be circumvented by covalently bonding the dye molecules onto the polymeric structure.

In this work, four different polymerizable, fluorescent perylene derivatives with a norbornene ester side chains were synthesised and statistically copolymerized with various monomers via ring-opening metathesis polymerisation (ROMP) to give defined and highly fluorescent polymers. Using this approach, a high content of dyes can be introduced into the polymer matrix. However, due to the tendency to aggregate, aggregation cannot be fully prevented above dye contents of approximately 3%.



(1)

(2a) R = R_1
(2b) R = R_2

(3)

Overview of perylene derivatives

The polymers were investigated in respect to their physical (molar mass, thermal properties) and spectroscopic properties (absorption, photoluminescence).

This project "PoTTA" is funded by the Austrian "Klima und Energiefonds" within the program Energy Emission Austria.

A Nitrate Derivative of a Second Generation *cis*-Dichloro Ruthenium Benzylidene: Mechanistic Implications for Olefin Metathesis Reactions

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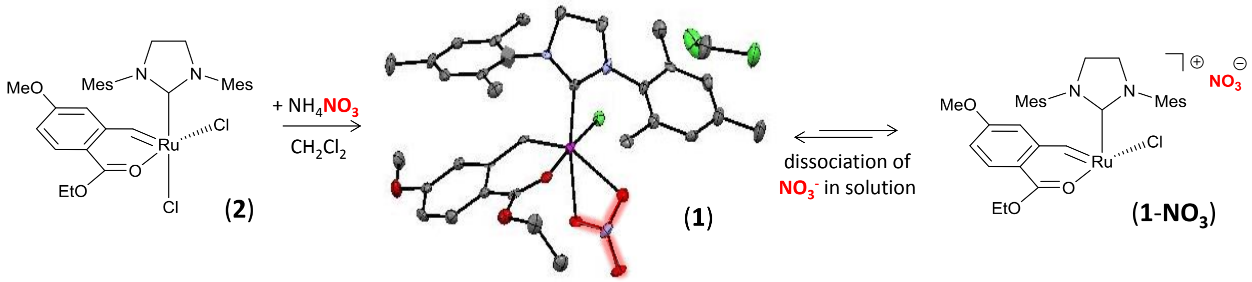
A novel second generation ruthenium benzylidene complex, in which one chloride was exchanged by a nitrate ligand leading to [RuCl(NO_3)(1,3-dimesitylimidayolin-2-ylidene)(2-ethlyester-5-methoxybenzylidene)] (**1**), was obtained from the reaction of its *cis*-dichloro ruthenium derivative (**2**) with NH_4NO_3. The selective exchange of the chloride *trans* to the NHC-ligand underlines (again[1]) the high lability of anionic ligands in this particular position. A coordinatively saturated 18e ruthenium(II) complex (**1**) is obtained as revealed by single crystal X-ray diffraction, whereas it is believed that in solution the nitrate dissociates forming a cationic 14e species (**1-NO$_3$**),[2] which is detrimental for catalyzing olefin metathesis.[3] Typical Ring-opening Metathesis Polymerization (ROMP) experiments using **1** and **2** (with and without additional Cl^- and NO_3^-) as the initiators reveal insights into the activation/deactivation mechanism of typical *cis*-dihalo ruthenium benzylidenes in olefin metathesis reactions.



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Porous poly(Dicyclopentadiene) Monoliths: Combining High Internal Phase Templating and Aerogel Recipes

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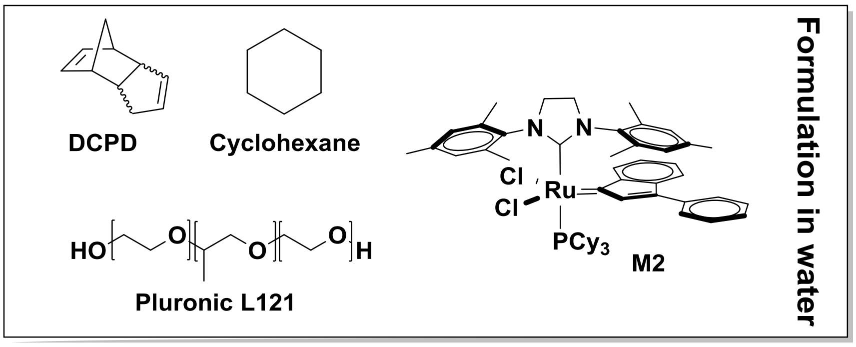
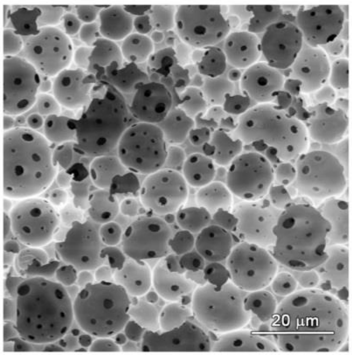
Dicyclopentadiene (DCPD), as a byproduct of oil cracking, is an easily accessible and cheap monomer. Ring-opening Metathesis Polymerization (ROMP) of this monomer results in a thermosetting polymer featuring favorable properties.[1]
In our group surfactant stabilized water in DCPD high internal phase emulsions have been used for the preparation of macroporous pDCPD since 2010,[2] leading to mechanically very robust specimen in the form of monoliths[3] or membranes.[4]
Another class of porous pDCPD is aerogels, which combine low density and low thermal conductivity with a porosity in the meso-scale and high surface area.[5]
Herein we wish to present our research on high internal phase templating of DCPD/solvent mixtures towards obtaining hierarchically porous pDCPD.





left: typical formulation used in this study; right: exemplary morphology of the obtained foams

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Sterically Hindered Cross Metathesis - Routes to Alkaloid Natural Products

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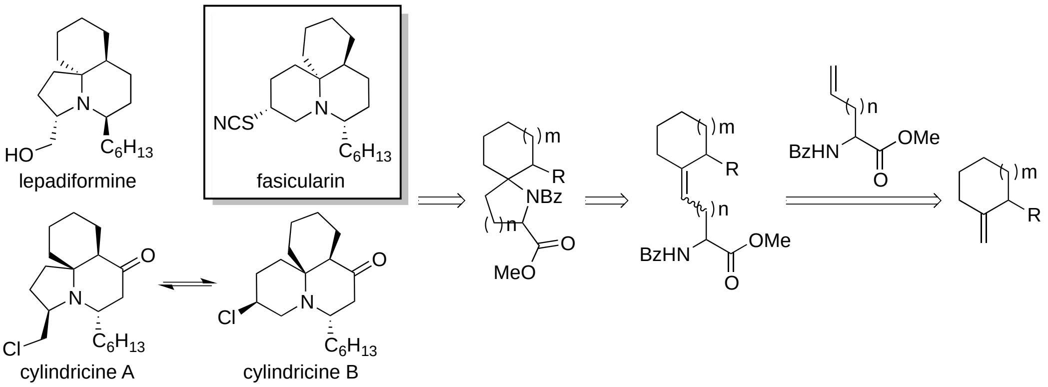
In the 1990s, a fellow Australian, Adrian Blackman from the University of Tasmania, isolated a family of tricyclic marine alkaloids from the marine ascidian *Clavelina cylindrica.*[1] The structures of the cylindricines were determined by spectral analysis in conjunction with X-ray crystallography and found to possess pyrrolo[2,1-*j*]quinoline and pyrido[2,1-*j*]quinoline frameworks. Later in the same decade, a related alkaloid fasicularin was isolated by the SmithKline Beecham group from *Neptheis fasicularis.*[2] Many research groups have since tackled the total synthesis of these complex marine natural products.[3]



In this paper a metathesis-driven approach to (-)-fasicularin will be presented. This work presents our efforts to overcome olefin isomerization,[4] chalconic effects, an inability to perform cross metathesis on highly hindered olefinic substrates,[5] catalyst poisoning by coordinating functional groups,[6] and unreliable literature reactions.[3] The 1-azaspirane core is generated *via* alkene cross metathesis (CM) and subsequent Brønsted acid-induced cyclisation. The resulting spiropyrrolidine analogue is then ring expanded *via* an aziridinium intermediate to generate the required spiropiperidine motif. Completion of the tricyclic core ultimately required the use of an α-substituted methylenecyclohexene and development of new methodology to facilitate efficient CM of sterically encumbered olefins.

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Transformations of Norbornene-functionalised Cellulose

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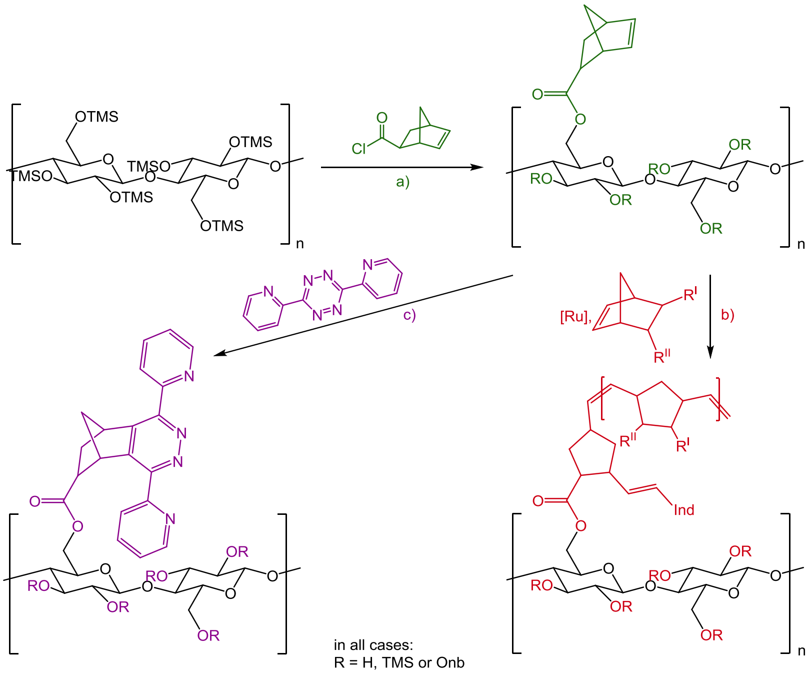
Cellulose is the most abundant natural polymer. Thus, there has been an increasing interest in the modification and application of cellulose derivatives over the last decades. In this contribution, we present two approaches yielding unconventional cellulose products taking advantage of our expertise in the fields of click chemistry and olefin metathesis.

Grafting of cellulose fibres using various living polymerisation reactions like ATRP, ROP, ROMP have been reported yielding products with tailor-made surfaces.[1] In contrast to this, we are aiming organosoluble grafts with controlled chain length derived via ROMP starting from commercially available trimethylsilylcellulose. (Scheme 1, a, b).



Scheme 1: Modification of cellulose starting from trimethylsilylcellulose.

Further, a copper free click reaction, the inverse electron demand Diels-Alder reaction (iEDDA), has been applied introducing pyridazines. Therefore, tetrazines have been reacted with the norbornene double bonds (Scheme 1, c).[2] These products might be a reasonable alternative in the biomedical applications to products derived via copper mediated click reactions since copper causes side reactions the human body and rigorous purification is required.

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