

## Contents

### Special Issue: Transition Metal Mediated Metathesis

Preface ..... 5077

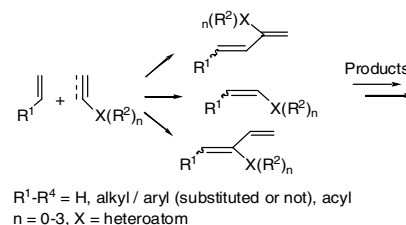
### Regular papers

**Pierre Van de Weghe, Philippe Bisseret,  
Nicolas Blanchard, Jacques Eustache**

*J. Organomet. Chem. 691 (2006) 5078*

Metathesis of heteroatom-substituted olefins  
and alkynes: Current scope and limitations

The use of vinyl- or alkynyl derivatives of the type  $C=C-X$  or  $C\equiv C-X$  (where X is an heteroatom) as substrates for metathesis increases further this reaction's versatility. Selected examples illustrating recent progress in this area of research are presented. Current scope and future potential developments are discussed.

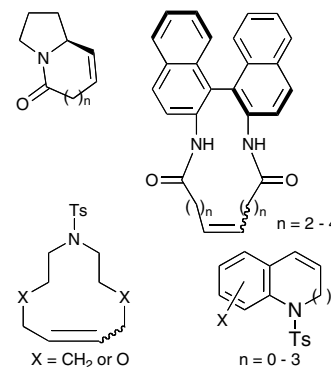


**Mitsuhiro Arisawa, Atsushi Nishida,  
Masako Nakagawa**

*J. Organomet. Chem. 691 (2006) 5109*

Preparation of nitrogen-containing hetero-  
cycles using ring-closing metathesis (RCM)  
and its application to natural product  
synthesis

Our synthetic study of nitrogen-containing  
heterocycles using ring-closing metathesis,  
such as chiral bicyclic lactams, azacyclounde-  
cenes, axially chiral macrolactams, 1,2-dihy-  
droquinolines, 2-quinolinones and indoles,  
including a development of silyl-enol ether ene  
metathesis and isomerization of terminal olef-  
ins, are described. Their applications to nat-  
ural product synthesis are also reported.

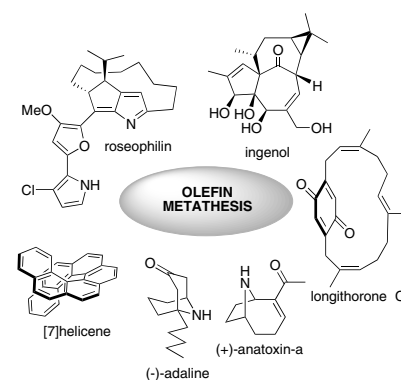


**Shawn K. Collins**

*J. Organomet. Chem. 691 (2006) 5122*

Preparation of cyclic molecules bearing  
“strained” olefins using olefin metathesis

Recent advancements in metathesis catalyst  
design have allowed chemists to re-examine  
olefin metathesis as a route to systems bearing  
strained olefins embedded in their skeletons.  
The variety of different catalysts that has been  
developed allows for the possibility to select a  
catalyst having the necessary level of reactivity  
to access a strained system but also to avoid  
catalysts which may be so reactive as to favour  
ring-opening of the desired ring system.

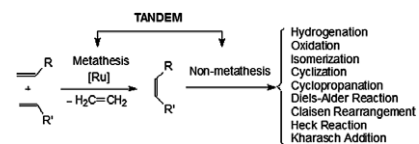


**Valerian Dragutan, Ileana Dragutan***J. Organomet. Chem.* 691 (2006) 5129

A resourceful new strategy in organic synthesis: Tandem and stepwise metathesis/non-metathesis catalytic processes

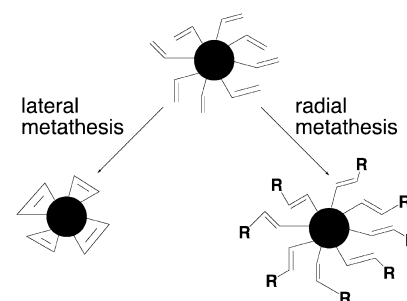
Highlighting the impressive potential of tandem and stepwise metathesis/non-metathesis reactions in synthesis, the present review extends the scope of the newly gained renown of metathesis as a progressive policy for advanced, elegant and

economical organic synthesis. Background is provided for the most encountered to date applications where fundamental non-metathetical synthetic transformations (hydrogenation, oxidation, isomerization, allylation, cyclopropanation, etc.) and a variety of name reactions (Diels-Alder, Claisen, Heck, Ugi, Pauson-Khand, Kharasch addition, etc.) are occurring in tandem, as concurrent or sequential processes, with every known type of metathetical reactions catalyzed by ruthenium or molybdenum complexes.

**Xiang Liu, Amit Basu***J. Organomet. Chem.* 691 (2006) 5148

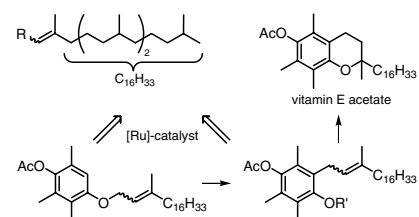
Olefin metathesis on nanostructures

Alkene metathesis processes on nanostructures can proceed via radial or lateral pathways. Radial metathesis installs new functionalities on the surface of a nanostructure through outward growth from its core. Lateral metathesis involves successive crosslinking of neighboring alkenes on the nanostructure and creates a polymer shell around the particle.

**Thomas Netscher***J. Organomet. Chem.* 691 (2006) 5155

Preparation of trialkyl-substituted olefins by ruthenium catalyzed cross-metathesis

The application of ruthenium catalyzed olefin cross-metathesis towards the synthesis of key-intermediates containing trialkyl-substituted olefinic double bonds on the way to tocopherols (vitamin E) is discussed. The results of a recent study presented may be of interest for the area of syntheses of isoprenoid natural products in general.

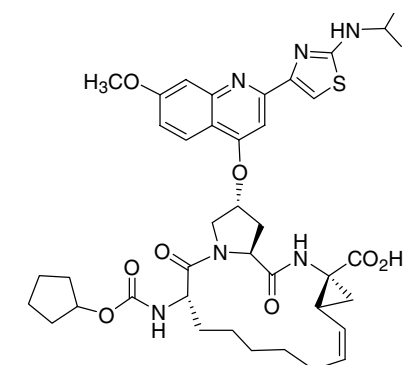


**Youla S. Tsantrizos, Jean-Marie Ferland, Andrew McClory, Martin Poirier, Vittorio Farina, Nathan K. Yee, Xiao-jun Wang, Nizar Haddad, Xudong Wei, Jinghua Xu, Li Zhang**

*J. Organomet. Chem.* 691 (2006) 5163

Olefin ring-closing metathesis as a powerful tool in drug discovery and development – potent macrocyclic inhibitors of the hepatitis C virus NS3 protease

Tripeptide dienes composed of three unnatural amino acid residues with numerous chiral centers were efficiently converted to macrocyclic peptides, in high diastereomeric purity, using ring-closing metathesis (RCM). These studies provided the first small molecule (BILN 2061) that was clinically validated for the treatment of hepatitis C infection in man and opened the door to a plethora of new pre-clinical pharmaceutical agents that can be made in multi kilogram quantities using RCM chemistry.

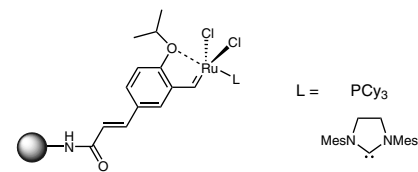


**Florian Michalek, Daniel Mäde, Jürgen Rühe, Willi Bannwarth**

*J. Organomet. Chem.* 691 (2006) 5172

The activity of covalently immobilized Grubbs–Hoveyda type catalyst is highly dependent on the nature of the support material

New solid supported Grubbs–Hoveyda olefin metathesis catalysts have been prepared on four different materials. We observed that the materials influenced strongly the activity of the reaction. Besides the ring closing metathesis, also cross metathesis and ring opening metathesis reactions were performed.

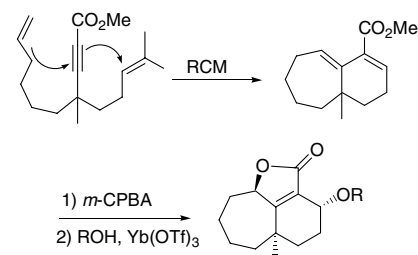


**François-Didier Boyer, Issam Hanna**

*J. Organomet. Chem.* 691 (2006) 5181

An efficient construction of bicyclic systems containing a seven-membered ring by tandem ring-closing metathesis reactions of dienyne

A series of (5–7) and (6–7) bicyclic dienes bearing quaternary methyl group and ester functionality have been synthesized from acyclic dienyne by tandem ring-closing metathesis (RCM) reaction. Epoxidation of these conjugated dienes followed by methanolysis of the resulting oxiranes led to highly oxygenated compounds.

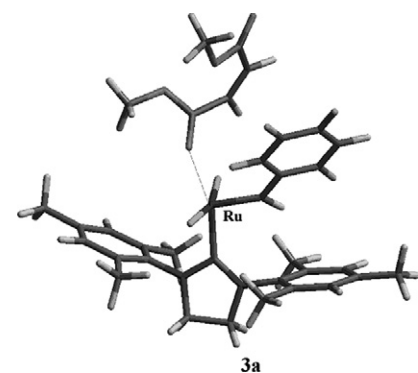


**Serguei Fomine, Mikhail A. Tlenkopatchev**

*J. Organomet. Chem.* 691 (2006) 5189

Cross-metathesis of dimethyl maleate and ethylene catalyzed by second generation ruthenium carbene complexes: B3LYP and MPW1K comparison study

The low reactivity of **2** in the metathesis reaction can be explained by the a non-productive complex formation **3a** between carbonyl oxygen and Ru center that impedes the metathesis.

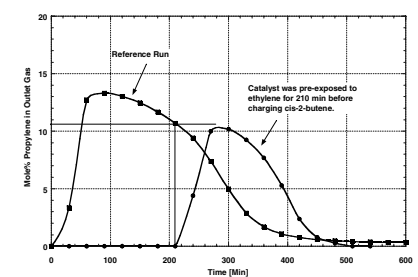


**Zenon Lysenko, Bob R. Maughon, Tezi Mokhtar-Zadeh, Michael L. Tulchinsky**

*J. Organomet. Chem.* 691 (2006) 5197

Stability of the first-generation Grubbs metathesis catalyst in a continuous flow reactor

Pretreatment of the  $(PCy_3)_2Cl_2Ru=CHPh$  catalyst with ethylene in the continuous flow reactor in pentadecane prior to charging *cis*-2-butene to initiate cross-metathesis with formation of propylene indicates that the active catalyst loss due to pre-exposure to ethylene occurs with the same rate as in the productive reaction environment with both ethylene and *cis*-2-butene initially present.

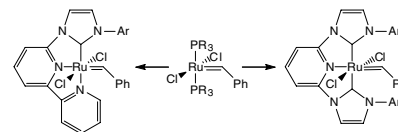


**Joseph A. Wright, Andreas A. Danopoulos,  
William B. Motherwell, Robert J. Carroll,  
Simon Ellwood**

*J. Organomet. Chem.* 691 (2006) 5204

'Pincer' pyridyl- and bipyridyl-*N*-heterocyclic carbene analogues of the Grubbs' metathesis catalyst

New analogues of the Grubbs' metathesis catalysts with 'pincer' *N*-heterocyclic carbene co-ligands are reported and assessed as catalysts.

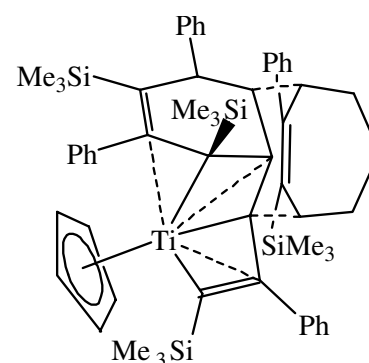


**Benjamin G. Harvey, Atta M. Arif,  
Richard D. Ernst**

*J. Organomet. Chem.* 691 (2006) 5211

Coupling reactions of alkynes with half-open titanocenes: Agostic (C–C) → Ti interactions in a tetra(alkyne) coupling product with the  $\text{Ti}(\text{C}_5\text{H}_5)(\text{c-C}_8\text{H}_{11})$  fragment

The reaction of four equivalents of  $\text{PhC}_2\text{SiMe}_3$  with the  $\text{Ti}(\text{C}_5\text{H}_5)(\text{c-C}_8\text{H}_{11})$  fragment leads to a complicated coupling reaction, through which a formal 14 electron complex is isolated. In addition to the allyl and cyclopentadienyl coordinations, one also observes a titanacyclobutene fragment. Structural and spectroscopic data indicate that there is an agostic interaction taking place between this fragment's C–C bond and the metal center.

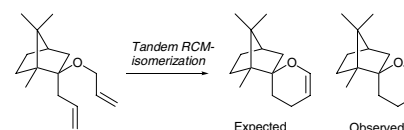


**Bernd Schmidt, Lucia Staude**

*J. Organomet. Chem.* 691 (2006) 5218

Unexpected transfer hydrogenation of C–C double bonds during Tandem-RCM-isomerization reactions

Unexpected hydrogen transfer from 2-propanol to C–C double bonds has been observed in the course of a Tandem RCM-isomerization reaction leading to sterically congested spirocycles.

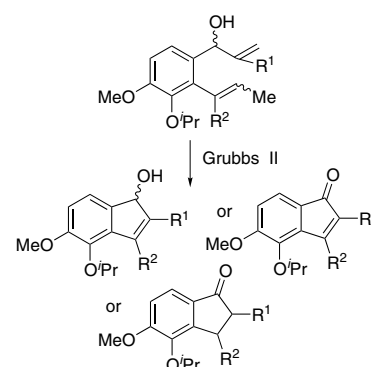


**E. Mabel Coyanis, Jenny-Lee Panayides,  
Manuel A. Fernandes, Charles B. de Koning,  
Willem A.L. van Otterlo**

*J. Organomet. Chem.* 691 (2006) 5222

Ring-closing metathesis for the synthesis of substituted indenols, indenones, indanones and indenes: Tandem RCM-dehydrogenative oxidation and RCM-formal redox isomerization

Grubbs second generation catalyst converts substituted 1-(2-propenylphenyl)prop-2-en-1-ols into substituted indenols, indenones or indanones depending on the reaction conditions employed. The formation of the indenones represents one of the first examples of a tandem ruthenium-mediated ring-closing metathesis (RCM)-dehydrogenative oxidation whilst the formation of the indanones is proposed to be by way of a RCM-formal redox isomerization sequence.

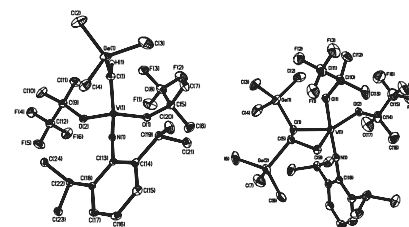


**Leonid N. Bochkarev, Yulia E. Begantsova, Andrey L. Bochkarev, Natalia E. Stolyarova, Irina K. Grigorieva, Irina P. Malysheva, Galina V. Basova, Elena O. Platonova, Georgii K. Fukin, Evgenii V. Baranov, Yurii A. Kurskii, Gleb A. Abakumov**

*J. Organomet. Chem.* 691 (2006) 5240

Synthesis, structures and catalytic properties of germanium-containing tungsten alkylidene complex  $\text{Me}_3\text{Ge}-\text{CH}=\text{W}(\text{NAr})(\text{OR})_2$  and metallacycle  $[\text{CH}(\text{GeMe}_3)\text{CH}(\text{GeMe}_3)\text{CH}_2]\text{W}(\text{NAr})(\text{OR})_2$

Tungsten alkylidene complex  $\text{Me}_3\text{Ge}-\text{CH}=\text{W}(\text{NAr})(\text{OCMe}_2\text{CF}_3)_2$  (**1**) ( $\text{Ar} = 2, 6\text{-Pr}_2\text{C}_6\text{H}_3$ ) and metallocycle  $[\text{CH}(\text{GeMe}_3)\text{CH}(\text{GeMe}_3)\text{CH}_2]\text{W}(\text{NAr})(\text{OR})_2$  (**2**) were synthesized and structurally characterized. The both compounds **1** and **2** were found to have low activity in metathesis of 1-hexene and high activity in ROMP of cyclooctene and norbornene.

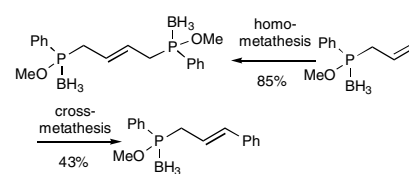


**Katherine S. Dunne, Sarah E. Lee, Véronique Gouverneur**

*J. Organomet. Chem.* 691 (2006) 5246

Homometathesis and cross-metathesis coupling of phosphine-borane templates with electron-rich and electron-poor olefins

The scope and limitation of intermolecular metathesis reactions of borane-protected phosphines have been investigated and it is revealed that allyl-substituted P-templates underwent both homocoupling and cross-coupling in good yields and high levels of *E*-selectivity. Reactions of vinyl-substituted phosphine boranes underwent cross-metathesis with diverse olefinic partners with exclusive *E*-selectivity but were not suitable for homodimerisation when using a Ru catalyst featuring a imidazol-2-ylidene ligand.

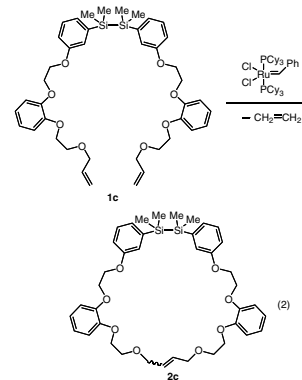


**Takeshi Umemiya, Daisuke Takeuchi, Kohtaro Osakada**

*J. Organomet. Chem.* 691 (2006) 5260

Synthesis of macrocyclic polyethers via Ru complex-catalyzed metathesis cyclization and their use as the ring component of rotaxanes

Ring closing metathesis of the vinyl group-terminated oligoethers catalyzed by  $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$  yielded macrocyclic polyethers containing vinylene group. The obtained 23-membered cyclic ether reacted with benzyl-(anthrylmethyl)ammonium hexafluorophosphate to produce the pseudo-rotaxane as colorless crystals. X-ray crystallography revealed  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds and stacking of the aromatic planes between the host and guest molecules, which stabilized the rotaxane structure in the solid state.

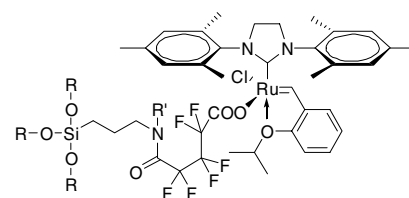


**Kati Vehlow, Simon Maechling, Katrin Köhler, Siegfried Blechert**

*J. Organomet. Chem.* 691 (2006) 5267

Versatile Ru-based metathesis catalysts designed for both homogeneous and heterogeneous processes

The selective exchange of one or both chloride ligands in the Hoveyda-Grubbs first and second generation catalysts with partially fluorinated trialkoxysilyl-containing silver(I) carboxylates has been achieved. This gives access to ruthenium catalysts which can be used both homogeneously or immobilized on silica. The synthesis and reactivity of these complexes are described including the mono-carboxylate ruthenium catalysts  $[\text{RuCl}((\text{RO})_3\text{Si}-\text{C}_3\text{H}_6-\text{N}(\text{R}')-\text{CO}-\text{C}_3\text{F}_6-\text{COO})(=\text{CH}-o\text{-O}-i\text{Pr}-\text{C}_6\text{H}_4)(\text{SIMes})]$  ( $\text{R} = \text{Et}$ ,  $\text{R}' = \text{H}$  and  $\text{R} = \text{R}' = \text{Me}$ ).

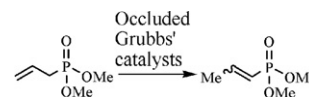


**M. Brett Runge, Martin T. Mwangi,  
Ned B. Bowden**

*J. Organomet. Chem. 691 (2006) 5278*

New selectivities from old catalysts. Occlusion of Grubbs' catalysts in PDMS to change their reactions

We describe how Grubbs' catalysts occluded in mm-slabs of polydimethylsiloxane are active isomerization catalysts for a variety of substrates that undergo metathesis with these catalysts in methylene chloride. This selectivity allows one to choose whether to react by metathesis or isomerization for a wide range of substrates.

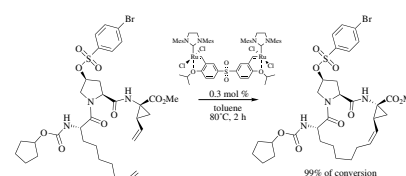


**Michał Bieniek, Robert Bujok,  
Halszka Stepowska, Albrecht Jacobi,  
Robert Hagenkötter, Dieter Arlt,  
Katarzyna Jarzemska, Anna Makal,  
Krzysztof Woźniak, Karol Grela**

*J. Organomet. Chem. 691 (2006) 5289*

New air-stable ruthenium olefin metathesis precatalysts derived from bisphenol S

Synthesis and screening of catalytic activity of two novel mono- and diruthenium carbene complexes **7a** and **7b** prepared from inexpensive Bisphenol S is described. These catalysts constitute an excellent tool for ring-closing metathesis by combining high stability with increased catalytic activity.

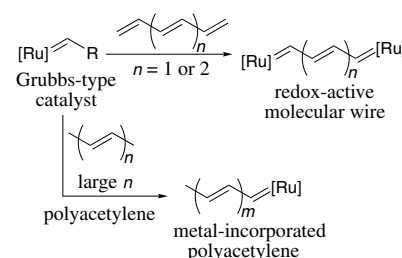


**Sarah L. Bolton, Danielle E. Schuehler,  
Xiang Niu, Lakshmi Gopal,  
Michael B. Sponsler**

*J. Organomet. Chem. 691 (2006) 5298*

Olefin metathesis for metal incorporation: preparation of conjugated ruthenium-containing complexes and polymers

Olefin Metathesis for Metal Incorporation (OMMI) was used for the stoichiometric attachment of ruthenium to both small and large polyenes. The complexes obtained through OMMI exhibit interesting structural, electronic, and reaction properties.

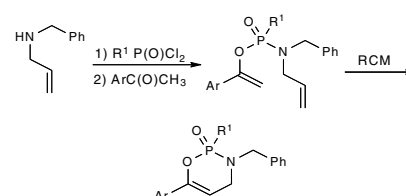


**Stephen R. Sieck, Matthew D. McReynolds,  
Chad E. Schroeder, Paul R. Hanson**

*J. Organomet. Chem. 691 (2006) 5307*

Metathesis studies to cyclic enol phosphonamidates

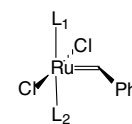
The development of cyclic, six membered enol phosphonamidates utilizing the ring-closing metathesis (RCM) reaction is discussed. Phosphonamidic monochloridates are generated and further functionalized to an array of acyclic, enol phosphonamidates. Subsequent metathesis studies aimed at optimizing desired RCM product over the corresponding cross metathesis (CM) dimer is discussed.



**Werner Janse van Rensburg,  
Petrus J. Steynberg, Megan M. Kirk,  
Wolfgang H. Meyer, Grant S. Forman**  
*J. Organomet. Chem.* 691 (2006) 5312

Mechanistic comparison of ruthenium olefin metathesis catalysts: DFT insight into relative reactivity and decomposition behavior

Gibbs free energy surfaces are calculated from DFT for the olefin metathesis mechanism catalyzed by three ruthenium catalysts, viz (PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>Ru=CHPh, (IMes)(PCy<sub>3</sub>)Cl<sub>2</sub>Ru=CHPh and (Phoban-Cy)<sub>2</sub>Cl<sub>2</sub>Ru=CHPh. A substrate-induced decomposition mechanism for all three catalysts is also investigated and compared. Relative calculated reactivity trends are correlated to available experimental data.



**I:** L<sub>1</sub>, L<sub>2</sub> = PCy<sub>3</sub>

**II:** L<sub>1</sub> = IMes, L<sub>2</sub> = PCy<sub>3</sub>

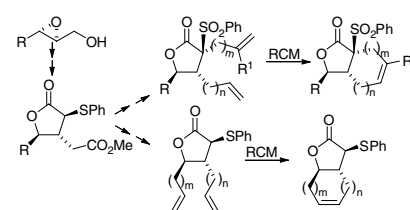
**III:** L<sub>1</sub>, L<sub>2</sub> =

**José Luis Ravelo, Carmen M<sup>a</sup> Rodríguez,  
Víctor S. Martín**

*J. Organomet. Chem.* 691 (2006) 5326

γ-Lactones as templates in ring-closing metathesis: Enantioselective synthesis of medium sized carbocycles fused to butyrolactones

A methodology for accessing enantiomerically enriched carbocyclic systems fused to γ-lactones is described. Key steps are the stereoselective synthesis of highly substituted γ-lactones and ring-closing metathesis of the suitable ramifications. The process permits the choice of stereochemistry, regioselectivity and ring size of the fused compounds.

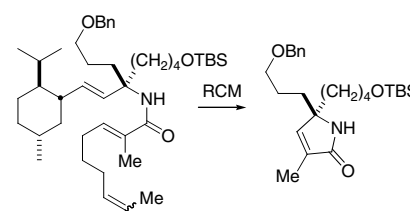


**Claude Spino, Luc Boisvert, Jasmin Douville,  
Stéphanie Roy, Sophie Lauzon,  
Joannie Minville, David Gagnon,  
Francis Beaumier, Christine Chabot**

*J. Organomet. Chem.* 691 (2006) 5336

Cleavage of a chiral auxiliary using RCM on an especially sterically crowded alkene: Syntheses of chiral carbo- and heterocycles

RCM is used to cleave a chiral auxiliary and generate carbo- and heterocycles directly. The alkene bearing the auxiliary has an uncommon steric demand challenging the limits of the catalysts.

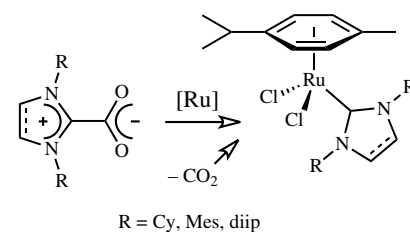


**Adriana Tudose, Albert Démonceau,  
Lionel Delaude**

*J. Organomet. Chem.* 691 (2006) 5356

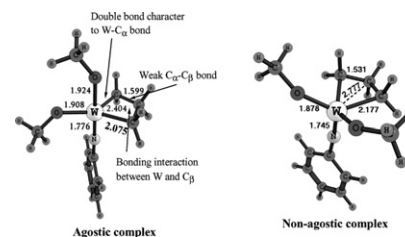
Imidazol(in)ium-2-carboxylates as N-heterocyclic carbene precursors in ruthenium-arene catalysts for olefin metathesis and cyclopropanation

Five imidazol(in)ium-2-carboxylates bearing alkyl or aryl substituents on their nitrogen atoms were prepared from the corresponding NHCs by reaction with CO<sub>2</sub>. They were characterized by IR, NMR, and TGA. Their ability to act as NHC precursors for in situ catalytic applications was probed in ruthenium-promoted olefin metathesis and cyclopropanation reactions.



**Cherumuttathu H. Suresh***J. Organomet. Chem.* 691 (2006) 5366Nature of  $\alpha,\beta$ -CCC agostic bonding in metallacyclobutanes

The  $\alpha,\beta$ -CCC agostic bonding in six metalla-cyclobutane complexes is examined on the basis of structural, bonding, energetics, and electron density features. This bonding stabilizes the system and at the same time considerably weakens the  $C_\alpha$ - $C_\beta$  bond and therefore it would play an important catalytic role in C-C bond metathesis reactions.

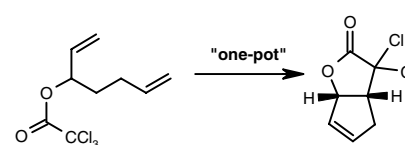


**Chris D. Edlin, James Faulkner, David Fengas, Madeleine Helliwell, Christopher K. Knight, David House, Jeremy Parker, Ian Preece, Peter Quayle, James Raftery, Stuart N. Richards**

*J. Organomet. Chem.* 691 (2006) 5375

Toward catalyst economy: A programmed approach to the synthesis of bicyclic lactones and lactams

The experiments leading to the development of tandem metathesis-ATRC sequences are presented. Deuterium labelling studies indicate that these sequences may involve competing elimination-intermolecular Kharasch addition reactions.

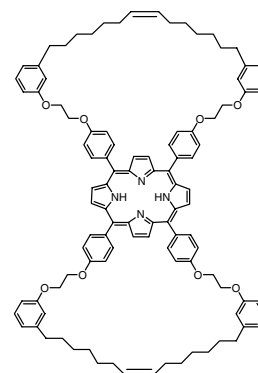


**Ying-Cen Guo, Giuseppe Mele, Francesca Martina, Eleonora Margapoti, Giuseppe Vasapollo, Wen-Jing Xiao**

*J. Organomet. Chem.* 691 (2006) 5383

An efficient route to biscardanol derivatives and cardanol-based porphyrins via olefin metathesis

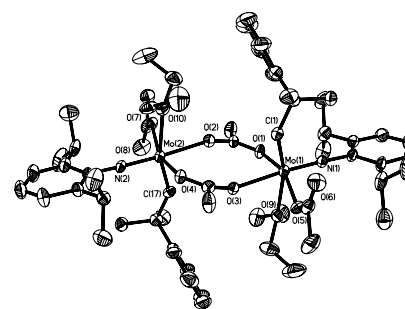
Ru-catalyzed olefin metathesis has been successfully applied to the synthesis of biscardanol derivatives and cardanol-based porphyrins. Using Hoveyda-Grubbs catalyst (**C627**), the reactions were performed with various cardanol derivatives (**2**, **5**, **7**, and **9**) to make novel biscardanol derivatives. With the use of the second-generation Grubbs catalyst (**C848**) and  $Ti(O^iPr)_4$ , the ring-closing metathesis of cardanol-based porphyrin **11** was carried out to afford cyclic cardanol-based porphyrin derivative **12**.



**Michael R. Buchmeiser, Dongren Wang, Sergej Naumov, Klaus Wurst**

*J. Organomet. Chem.* 691 (2006) 5391Synthesis, X-ray structure and reactivity of  $\mu$ -( $CF_3COO$ )<sub>2</sub>[Mo(N-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(CHCMe<sub>2</sub>Ph)(OOCF<sub>3</sub>)(Et<sub>2</sub>O)]<sub>2</sub>, the first Bis(trifluoroacetate) derivative of a Schrock catalyst

Reaction of  $Mo(N-2,6-*i*-Pr_2-C_6H_3)(CHCMe_2-C_6H_5)(OSO_2CF_3)(DME)$  (DME = 1,2-dimethoxyethane) with 2 equiv. of  $CF_3COOK$  yields  $\mu$ -( $CF_3COO$ )<sub>2</sub>[Mo(N-2,6-*i*-Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)(CHCMe<sub>2</sub>Ph)(OOCF<sub>3</sub>)(Et<sub>2</sub>O)]<sub>2</sub> (**1**). Addition of quinuclidine results in the in situ formation of **1a** ( $Mo(N-2,6-*i*-Pr_2-C_6H_3)(CHCMe_2C_6H_5)(OOCF_3)_2$ (quinuclidine)) which displays moderate activity in ROMP, cyclopolymerization and RCM. Theoretical investigations carried out on the B3LYP/LACVP\* level provide substantial explanation for these findings.



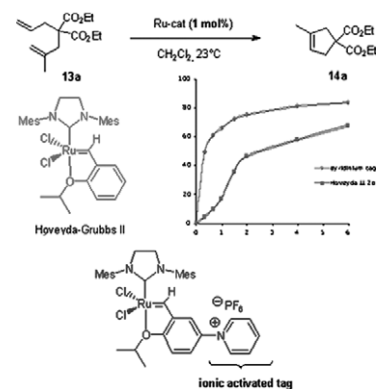


**Diane Rix, Hervé Clavier, Yann Coutard,  
Lukasz Gulajski, Karol Grela, Marc Mauduit**

*J. Organomet. Chem.* 691 (2006) 5397

Activated pyridinium-tagged ruthenium complexes as efficient catalysts for ring-closing metathesis

New pyridinium-tagged ruthenium catalysts have been synthesised to perform olefin metathesis in several media including both organic and aqueous solvents and room temperature ionic liquids (RTILs). High activity was obtained in the ring-closing metathesis (RCM) of a variety of di- or tri-substituted and/or oxygen-containing dienes. However, only fair levels of recyclability combined with low to moderate residual ruthenium levels (25–173 ppm) have been observed showing clearly the difficulty of associating high activity and recyclability.

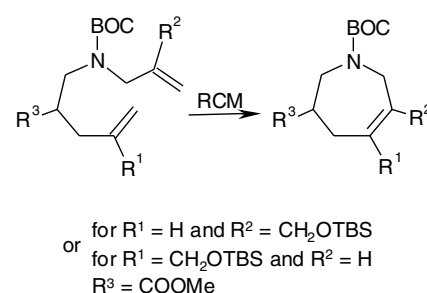


**Sascha Brass, Nan-Si Chan, Christof Gerlach,  
Torsten Luksch, Jark Böttcher,  
Wibke E. Diederich**

*J. Organomet. Chem.* 691 (2006) 5406

Synthesis of 2,3,4,7-tetrahydro-1*H*-azepines as privileged ligand scaffolds for the design of aspartic protease inhibitors via a ring-closing metathesis approach

A short and highly efficient synthesis of 3,5- and 3,6-disubstituted 2,3,4,7-tetrahydro-1*H*-azepines via a ring-closing metathesis approach utilizing inexpensive and readily available starting material is described. These azepines have been proven to be suitable core structures for the further design and synthesis of aspartic protease inhibitors.

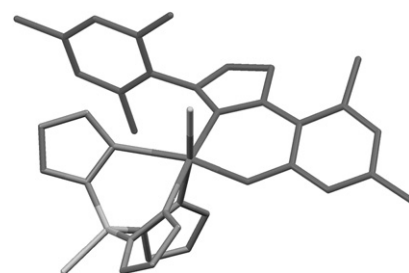


**Daniel Burtscher, Bernhard Perner,  
Kurt Mereiter, Christian Slugovc**

*J. Organomet. Chem.* 691 (2006) 5423

Peculiarities of the reaction of (*SPY*-5-34)-dichloro-( $\kappa^2$ (*C,O*)-2-formylbenzylidene)(1,3-bis-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene)ruthenium with potassium hydridotris-(pyrazolyl)borate

This report describes two unprecedented reaction-pathways which occurred during the reaction of (*SPY*-5-34)-dichloro-( $\kappa^2$ (*C,O*)-2-formylbenzylidene)( $\text{H}_2\text{IMes}$ )ruthenium with  $\text{KTP}$ . The first is the formation of chlorotris(pyrazolyl)borate from hydridotris(pyrazolyl)borate. The second is a formal double hydrogen transfer from a methyl group of the  $\text{H}_2\text{IMes}$  ligand to a carbene carbon, transforming the  $\text{H}_2\text{IMes}$  into a chelating biscarbene ligand.

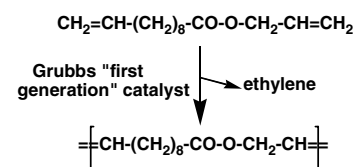


**Andrew J. Hall, Philip Hodge,  
Stephen D. Kamau, Abderrakak Ben-Haida**

*J. Organomet. Chem.* 691 (2006) 5431

Acyclic diene metathesis (ADMET) polymerization of allyl undec-10-enoate and some related esters

Allyl undec-10-enoate undergoes ADMET to give a polymer: typical DPs in the range 41–87. This is a rare example of an allyl ester polymerizing. Substituted allyl ester groups in a polymer and in macrocycles also undergo olefin metathesis. It is suggested that allyl undec-10-enoate may polymerize via ring-closing metathesis and entropically driven ring-opening polymerization.

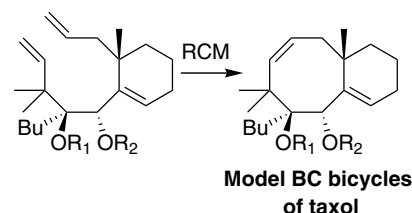


**Stéphanie Schiltz, Cong Ma, Louis Ricard, Joëlle Prunet**

*J. Organomet. Chem.* 691 (2006) 5438

Synthesis of model BC bicycles of taxol using C10–C11 ring-closing metathesis strategy

Model BC ring-systems of taxol have been synthesized by ring-closing metathesis (RCM). The influence of the stereochemistry and the protecting groups of the diol moiety on the formation of the eight-membered ring has been studied. Comparison with the RCM used on similar substrates in a previous route is presented.

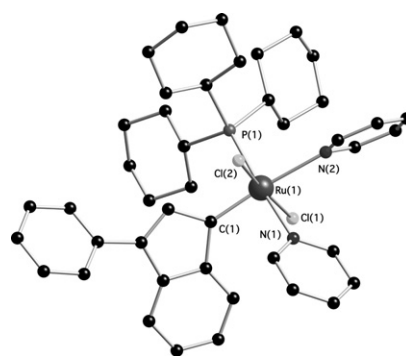


**Hervé Clavier, Jeffrey L. Petersen, Steven P. Nolan**

*J. Organomet. Chem.* 691 (2006) 5444

A pyridine-containing ruthenium–indenylidene complex: Synthesis and activity in ring-closing metathesis

Phosphine displacement in  $\text{Cl}_2\text{Ru}(\text{PCy}_3)_2$ -(3-phenylindenylidene) by two pyridines leads to  $\text{Cl}_2\text{Ru}(\text{PCy}_3)(\text{Py})_2$ -(3-phenylindenylidene) in good yield. After full characterization, the activity of this novel ruthenium–ruthenium based complex has been investigated for ring-closing metathesis. Kinetic studies have shown a moderate reactivity due to a rapid degradation of active species in spite of the robustness of the Ru–indenylidene moiety.

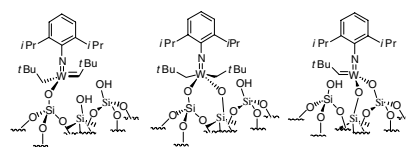


**Bouchra Rhers, Elsje Alessandra Quadrelli, Anne Baudouin, Mostafa Taoufik, Christophe Copéret, Frédéric Lefebvre, Jean-Marie Basset, Bernard Fenet, Amritanshu Sinha, Richard R. Schrock**

*J. Organomet. Chem.* 691 (2006) 5448

Understanding the reactivity of  $[\text{W}=\text{NAr}(\text{CH}_2t\text{Bu})_2(=\text{CH}t\text{Bu})]$  ( $\text{Ar} = 2,6\text{-}i\text{PrC}_6\text{H}_3$ ) with silica partially dehydroxylated at low temperatures through a combined use of molecular and surface organometallic chemistry

Reaction of  $[\text{W}=\text{NAr}(\text{CH}_2t\text{Bu})_2(=\text{CH}t\text{Bu})]$  ( $\text{Ar} = 2,6\text{-}i\text{PrC}_6\text{H}_3$ ) with silica dehydroxylated at 200 °C does not lead only to the expected digrafted carbene species but also to the monografted carbene complex and to a bis-neopentyl surface species.

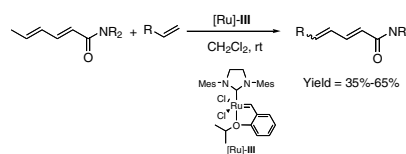


**Laurent Ferrié, Dominique Amans, Sébastien Reymond, Véronique Bellosta, Patrice Capdevielle, Janine Cossy**

*J. Organomet. Chem.* 691 (2006) 5456

Chemoselective cross-metathesis reaction between electron-deficient 1,3-dienes and olefins

Chemoselective cross-metathesis reactions between methyl sorbate or 1,3-dienic amides and various olefins in the presence of the Grubbs-Hoveyda catalyst have been investigated. Cross-metathesis reactions turned out to be more chemoselective with 1,3-dienic amides than with 1,3-dienic esters.

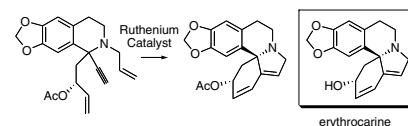


**Kazuya Shimizu, Masanori Takimoto,  
Yoshihiro Sato, Miwako Mori**

*J. Organomet. Chem.* 691 (2006) 5466

Total synthesis of ( $\pm$ )-erythrocarine using dienyne metathesis

Total Synthesis of ( $\pm$ )-erythrocarine was achieved using ruthenium-catalyzed dienyne metathesis as a key step.

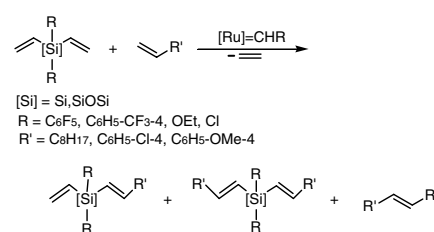


**Cezary Pietraszuk, Szymon Rogalski,  
Mariusz Majchrzak, Bogdan Marciniec**

*J. Organomet. Chem.* 691 (2006) 5476

Cross-metathesis of divinylsubstituted silanes and disiloxanes in the presence of Grubbs catalysts

Efficient cross-metathesis of divinylsilanes and divinylsilyloxanes, carrying different electron-withdrawing substituents at silicon, with selected olefins in the presence of the first and second generation Grubbs catalyst and Hoveyda-Grubbs catalyst is described.

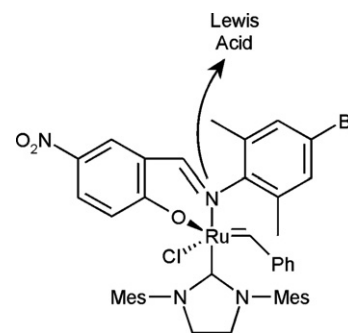


**Nele Ledoux, Bart Allaert, David Schaubroeck,  
Stijn Monsaert, Renata Drozdak,  
Pascal Van Der Voort, Francis Verpoort**

*J. Organomet. Chem.* 691 (2006) 5482

In situ generation of highly active olefin metathesis initiators

A ruthenium based benzylidene complex bearing an *O,N*-bidentate Schiff base ligand generates a highly active olefin metathesis catalyst when treated with acidic cocatalysts.

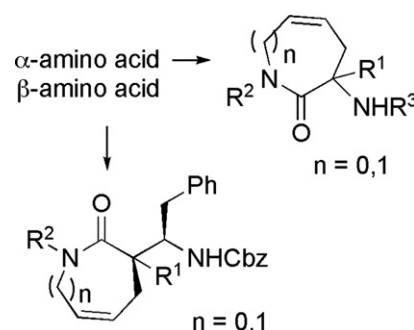


**James Gardiner, Steven G. Aitken,  
Stephen B. McNabb, Shazia Zaman,  
Andrew D. Abell**

*J. Organomet. Chem.* 691 (2006) 5487

Ring closing metathesis of  $\alpha$ - and  $\beta$ -amino acid derived dienes

Three new classes of conformationally constrained ( $C_{\alpha}$ - $N'$ ,  $C_{\beta 2}$ - $N'$ , and  $N$ - $C_{\beta 2}$  cyclisation) peptidomimetics have been prepared by ring closing metathesis (RCM). The key C-centred olefin of the precursor diene was introduced by stereoselective  $\alpha$ -allylation of an  $\alpha$ - or  $\beta$ -amino acid. The normal favourable influence of a tertiary amide linker in the diene towards RCM is negated by significant steric congestion, and the combination of a secondary amide linker and  $\alpha,\alpha$ -disubstitution promotes ring contraction on RCM.

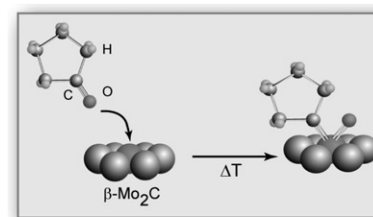


**Mohamed Sijaj, Israel Temprano,  
Nathalie Dubuc, Peter H. McBreen**

*J. Organomet. Chem. 691 (2006) 5497*

Preparation and olefin-metathesis activity of cyclopentylidene-oxo initiator sites on a molybdenum carbide surface

Olefin-metathesis initiating sites can be prepared on the surface of  $\beta\text{-Mo}_2\text{C}$  through the carbonyl bond scission dissociative chemisorption of cyclopentanone. The functionalized carbide provides a surface science analogue of organometallic oxo-alkylidene complexes.

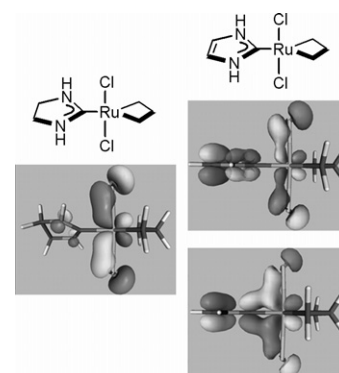


**Richard L. Lord, Huijun Wang,  
Mario Vieweger, Mu-Hyun Baik**

*J. Organomet. Chem. 691 (2006) 5505*

What difference one double bond makes: Electronic structure of saturated and unsaturated *n*-heterocyclic carbene ligands in Grubbs 2nd generation-type catalysts

We explore the impact of the N-heterocyclic carbene (NHC) ligand on the electronic structure of the Ruthenium center in Grubbs olefin metathesis catalyst. Electronic and steric effects were decoupled through simplified model carbenes and the electronic difference between saturated and unsaturated NHC ligands was highlighted.



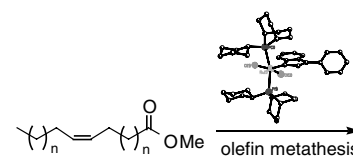
## Notes

**Grant S. Forman, Ronan M. Bellabarba,  
Robert P. Tooze, Alexandra M.Z. Slawin,  
Ralf Karch, Roland Winde**

*J. Organomet. Chem. 691 (2006) 5513*

Metathesis of renewable unsaturated fatty acid esters catalysed by a phoban-indenylidene ruthenium catalyst

The phoban-indenylidene complex is a robust catalyst for self-metathesis and ethenolysis reactions of methyl oleate. The phoban-indenylidene catalyst was characterized by X-ray analysis, NMR and microanalysis and was used in various self-metathesis and ethenolysis of methyl oleate, giving rise to significantly higher end of run conversions compared to Grubbs 1st generation catalyst.



**Simon M.E. Simpkins, Benson M. Kariuki,  
Liam R. Cox**

*J. Organomet. Chem. 691 (2006) 5517*

Towards the synthesis of insulated oligoynes: A ring-closing-metathesis approach to molecular encapsulation

Masked hexayne **18** was prepared in 11 steps from commercially available reagents. Attempted molecular encapsulation of the  $\pi$ -conjugated framework using a double ring-closing-metathesis operation generated **19**, where the desired macrocycle crowns, rather than encapsulates, the unsaturated framework.

