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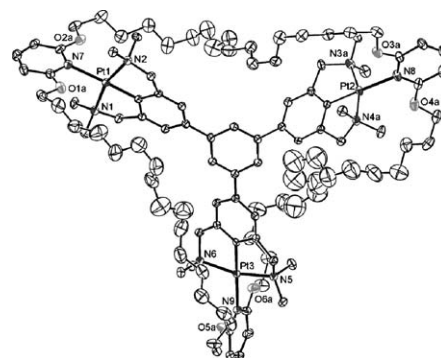
Articles

**Preston A. Chase, Martin Lutz,
Anthony L. Spek, Gerard P.M. van Klink,
Gerard van Koten**

*Journal of Molecular Catalysis A: Chemical 254
(2006) 2*

Ring closing metathesis employing organometallic
substrates and the templated synthesis of macrocycles

Olefin metathesis has been employed in the selective generation of a number of pyridine containing macroheterocycles using multi-meric rigid pincer platinum complexes as templates. The trispyridine cycles have been used in host–guest chemistry for the complexation of trimeric pincer species. As well, details of the utility and generality of olefin metathesis employing these organometallic substrates are explored.

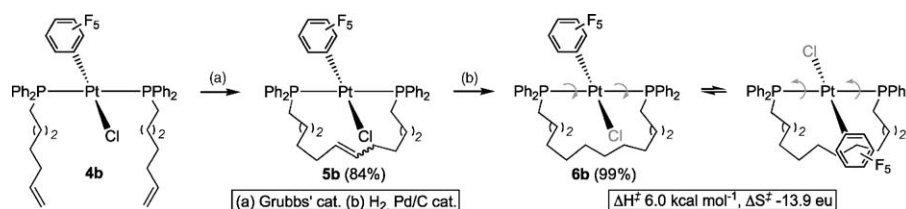


**Natascha Lewanzik, Thomas Oeser,
Janet Blümel, John A. Gladysz**

*Journal of Molecular Catalysis A: Chemical 254
(2006) 20*

Generation of *trans*-spanning diphosphine ligands
via alkene metathesis: Synthesis, structure, and
dynamic behavior of a missing link in a series of
square-planar platinum complexes

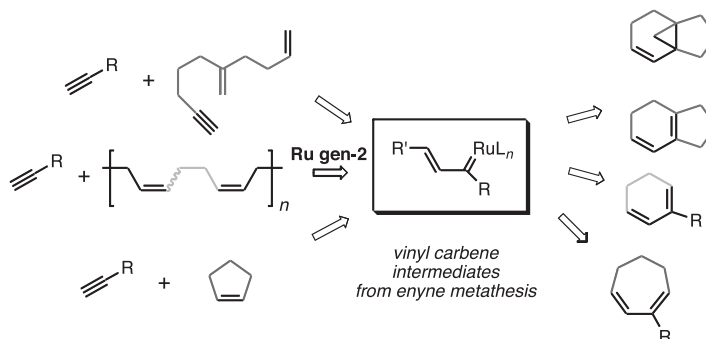
Complex **4b** undergoes ring-closing alkene metathesis to give the 15-membered macrocycle **5b**, the *Z* C=C isomer of which is crystallographically characterized; hydrogenation yields **6b**, for which NMR data show the chloride ligand can pass through the macrocycle ($\Delta H^\ddagger = 6.0 \pm 0.4 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -13.9 \pm 2.6 \text{ eu}$).



Steven T. Diver

*Journal of Molecular Catalysis A: Chemical 254
(2006) 29*

Metal carbenes in enyne metathesis: Synthetic and
mechanistic studies

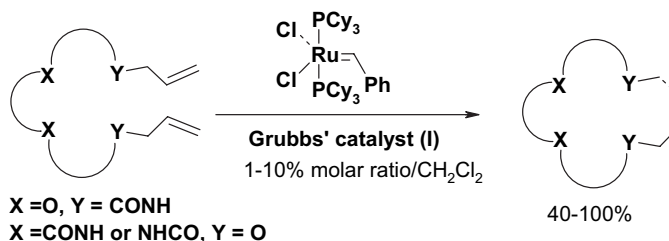


Ru gen-2 = Grubbs' second generation carbene complex,
(H₂I₂Me)(Cy₃P)Cl₂Ru=CHPh

Yehia A. Ibrahim

Journal of Molecular Catalysis A: Chemical 254 (2006) 43

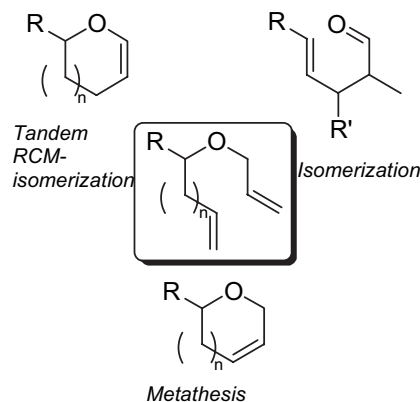
Application of ring closing metathesis in efficient synthesis of macrocyclic crown compounds



Bernd Schmidt

Journal of Molecular Catalysis A: Chemical 254 (2006) 53

Olefin metathesis and isomerization: From undesired side reactions to useful synthetic methodology

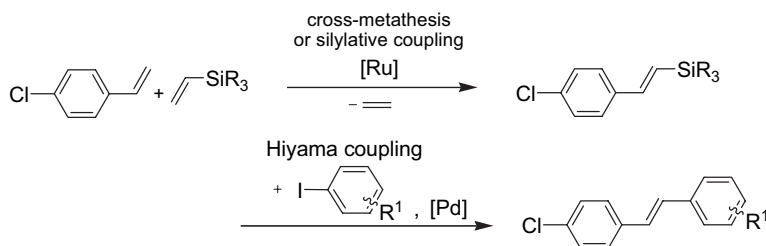


Wiesław Prukała, Mariusz Majchrzak, Cezary Pietraszuk, Bogdan Marciniak

Journal of Molecular Catalysis A: Chemical 254 (2006) 58

Highly stereoselective synthesis of *E*-4-chlorostilbene and its derivatives via tandem cross-metathesis (or silylative coupling) and Hiyama coupling

Highly effective new tandem reactions: cross-metathesis–Hiyama coupling (**CM–HC**) and silylative coupling–Hiyama coupling (**SC–HC**) lead to stereoselective synthesis of unsymmetrical stilbenoids.

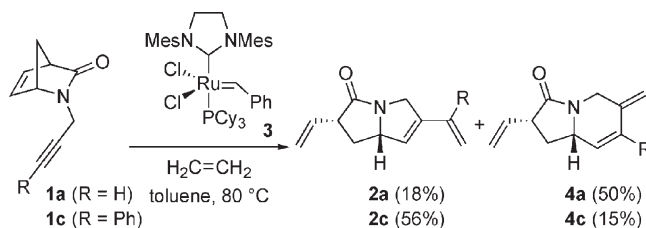


Miwako Mori, Hideaki Wakamatsu, Yoshihiro Sato, Reiko Fujita

Journal of Molecular Catalysis A: Chemical 254 (2006) 64

ROM–RCM of azabicycloheptene derivatives—Study of products distribution by the substituent on alkyne

When an azabicycloheptene derivative **1a** was exposed to a catalytic amount of a ruthenium carbene complex **3**, indolizidine derivative **2a** was obtained as a main product along with a fair amount of pyrrolizidine derivative **4a**. However, pyrrolizidine derivative **2c** was obtained as a major product, when the reaction of **1c** was carried out under the same reaction conditions.

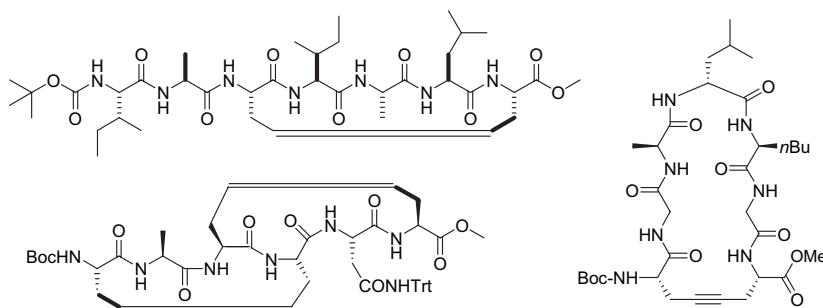


**Nourdin Ghalit, Dirk T.S. Rijkers,
Rob M.J. Liskamp**

Journal of Molecular Catalysis A: Chemical 254
(2006) 68

Alkene- and alkyne-bridged mimics of nisin as potential peptide-based antibiotics

Here we highlight our recent results of the application of ring-closing metathesis and ring-closing alkyne metathesis in biologically relevant biomolecules in order to introduce alkene- and/or alkyne bridges as novel covalent constraints for stabilizing their bioactive conformation and increasing their metabolic stability.

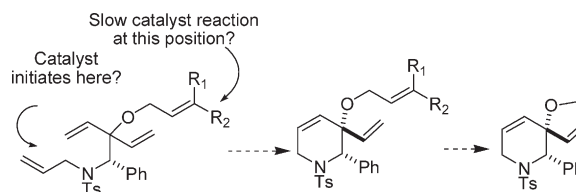


Debra J. Wallace

Journal of Molecular Catalysis A: Chemical 254
(2006) 78

Exploiting catalyst characteristics: A protocol for increasing diastereoselectivity in a double ring-closing metathesis reaction

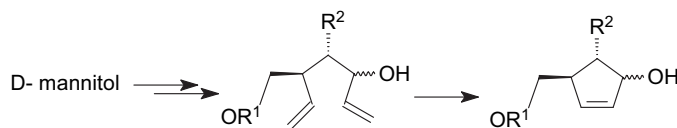
A procedure for obtaining increased selectivity in a diastereoselective double ring-closing metathesis reaction is presented. The key to success was design of a substrate, which directed the reaction mechanism through a selective pathway and use of a suitable catalyst combination to achieve the desired balance between reactivity and selectivity.



**Shyamapada Banerjee, Abhijit Nayek,
Saikat Sinha, Tanurima Bhaumik,
Subrata Ghosh**

Journal of Molecular Catalysis A: Chemical 254
(2006) 85

Alkoxy group facilitated ring closing metathesis (RCM) of acyclic 1,6-dienes. Facile synthesis of non-racemic highly substituted Cyclopentenols

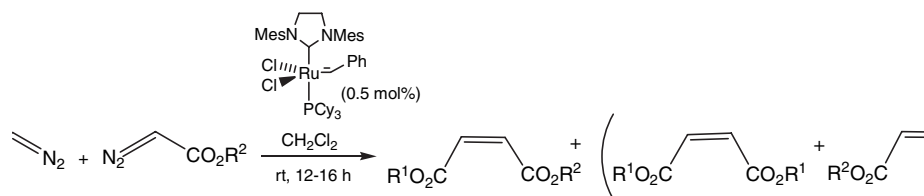


David M. Hodgson, Deepshikha Angrish

Journal of Molecular Catalysis A: Chemical 254
(2006) 93

Unsymmetrical maleates from stereoselective decomposition of diazoacetates using Grubbs' 2nd-generation Ru carbene catalyst

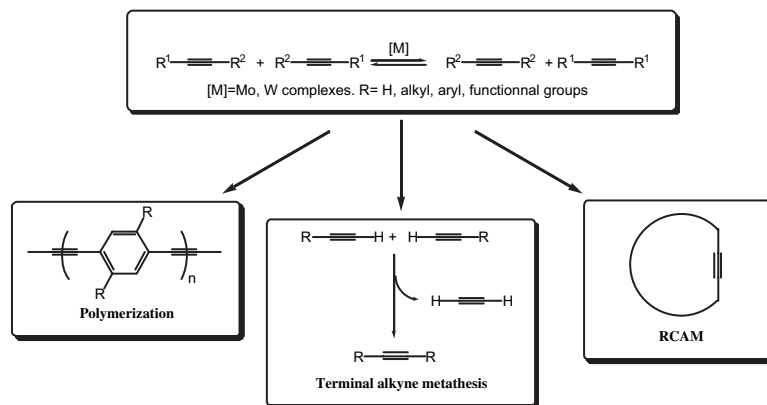
Grubbs' 2nd-generation ruthenium carbene catalyst heterocouples diazoacetates with high stereo selectivity to give unsymmetrical maleates.



André Mortreux, Olivier Coutelier

Journal of Molecular Catalysis A: Chemical 254 (2006) 96

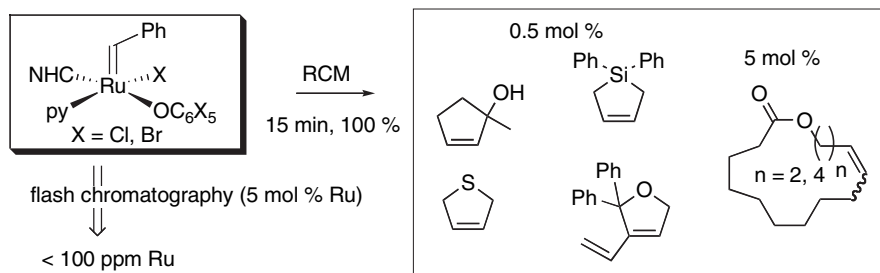
Alkyne metathesis catalysts: Scope and future


J.C. Conrad, J.L. Snelgrove, M.D. Eelman, S. Hall, D.E. Fogg

Journal of Molecular Catalysis A: Chemical 254 (2006) 105

Ruthenium aryloxide catalysts: Synthesis and applications in ring-closing metathesis

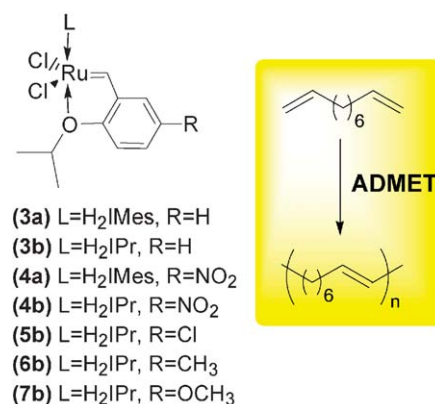
Advances in design of ruthenium catalysts for olefin metathesis are described. Catalyst decomposition via formation of chloride-bridged species is addressed by use of aryloxides as 'pseudohalide' ligands. The high performance of the new catalysts in ring-closing metathesis is discussed, as well as unexpected advantages associated with removal of spent catalyst following reaction.


Florence C. Courchay, John C. Sworen, Armando Coronado, Kenneth B. Wagener

Journal of Molecular Catalysis A: Chemical 254 (2006) 111

The utility of Hoveyda-type catalysts in ADMET chemistry: Sterics versus electronics

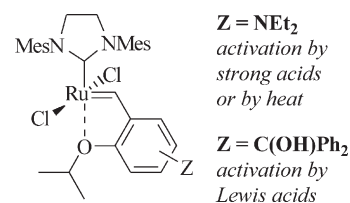
Exploration of the kinetic behavior of electronically modified Hoveyda-type catalysts in ADMET polymerization at various temperatures. Not only complexes bearing larger NHC ligands consistently afford higher degrees of polymerization, but the electronically modified catalysts tested exhibit the fastest initial rates ever witnessed in ADMET chemistry.


Łukasz Gułajski, Anna Michrowska, Robert Bujok, Karol Grela

Journal of Molecular Catalysis A: Chemical 254 (2006) 118

New tunable catalysts for olefin metathesis: Controlling the initiation through electronic factors

Synthesis and screening of catalytic activity of two novel ruthenium carbene complexes bearing substituents in 2-isopropoxybenzylidene ligand is described. These catalysts constitute excellent tools for RCM and enyne metathesis by combining high stability with a possibility of their on-demand activation by heat and Brønsted or Lewis acids.

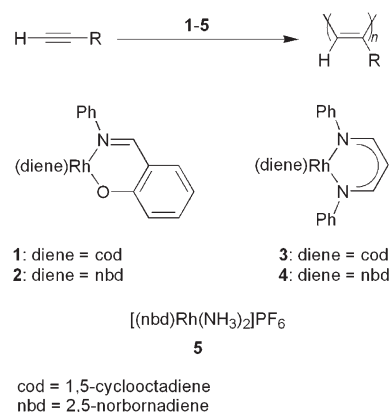


Irfan Saeed, Masashi Shiotsuki, Toshio Masuda

Journal of Molecular Catalysis A: Chemical 254 (2006) 124

Nitrogen ligand-containing Rh catalysts for the polymerization of substituted acetylenes

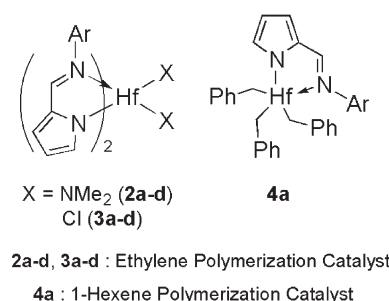
Rh complexes possessing a phenoxy-imine ligand (**1** and **2**), a β -diimine ligand (**3** and **4**), and ammonia ligands (**5**) were used as catalysts in the polymerization of monosubstituted acetylenes ($R-C\equiv CH$; **6a**: $R = Ph$, **6b**: $R = C_6H_4-m-NH_2$, **6c**: $R = C_6H_4-p-NH_2$, **6d**: $R = C_6H_4-p-SiMe_3$, **6e**: $R = CH_2CONH-n-C_5H_{11}$, **6f**: $R = COO-n-C_6H_{11}$, **6g**: $R = n-C_4H_9$, **6h**: $R = SiMe_3$). All the catalysts (**1**–**5**) were effective without any cocatalyst for the polymerization of monosubstituted acetylenes (**6a**–**e**) and afforded polymers with high molecular weights ($M_n = 15,000$ – $93,000$) in moderate to high yields.

**Hayato Tsurugi, Yutaka Matsuo, Kazushi Mashima**

Journal of Molecular Catalysis A: Chemical 254 (2006) 131

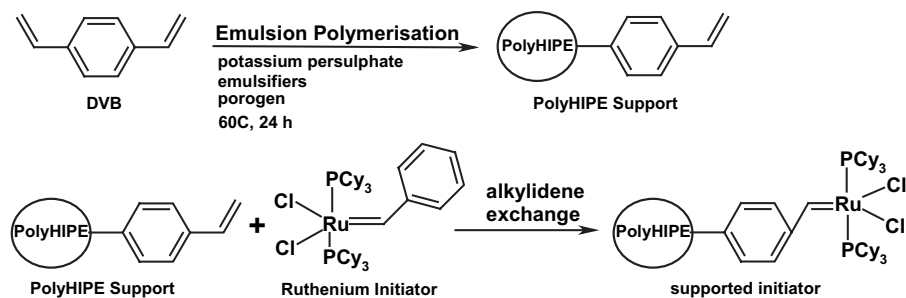
Preparation and characterization of iminopyrrolyl hafnium complexes as catalyst precursors for α -olefin polymerization

We prepared amido, chloro, and benzyl hafnium complexes bearing 2-(*N*-aryliminomethyl)pyrrolyl ligands. The diamido and dichloro bis(iminopyrrolyl)hafnium complexes were found to become active ethylene polymerization catalysts, when combined with MMAO. The mono(iminopyrrolyl)hafnium tribenzyl complex, which was prepared by the reaction of $Hf(CH_2Ph)_4$ with 1 equiv. of sterically demanding iminopyrrolyl ligand, became a highly active catalyst for 1-hexene polymerization, upon activation with $[Ph_3C][B(C_6F_5)_4]$.

**Sevil Cetinkaya, Ezat Khosravi, Richard Thompson**

Journal of Molecular Catalysis A: Chemical 254 (2006) 138

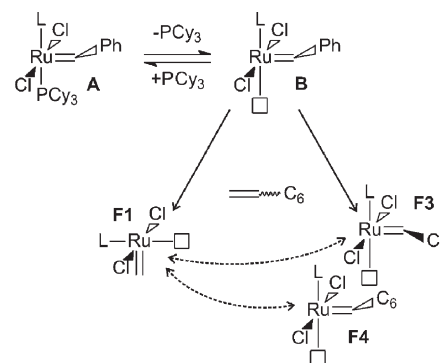
Supporting ruthenium initiator on PolyHIPE

**M. Jordaán, P. van Helden, C.G.C.E. van Sittert, H.C.M. Vosloo**

Journal of Molecular Catalysis A: Chemical 254 (2006) 145

Experimental and DFT investigation of the 1-octene metathesis reaction mechanism with the Grubbs 1 precatalyst

Using density functional theory (Accelrys DMol³ GGA-PW91/DNP) and experimental techniques (NMR and GC/MSD) the metathesis of 1-octene in the presence of Grubbs 1 [$RuCl_2(PCy_3)_2(=CHPh)$] is investigated. Grubbs 1 is an active metathesis precatalyst yielding the kinetically favoured *trans*-7-tetradecene as the major product. The rapid formation of the kinetically and thermodynamically favoured heptylidene species is observed by NMR. The dissociative metal carbene mechanism is supported.

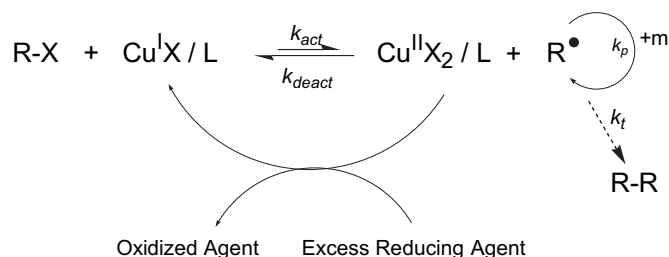


Wade A. Braunecker, Krzysztof Matyjaszewski

Journal of Molecular Catalysis A: Chemical 254 (2006) 155

Recent mechanistic developments in atom transfer radical polymerization

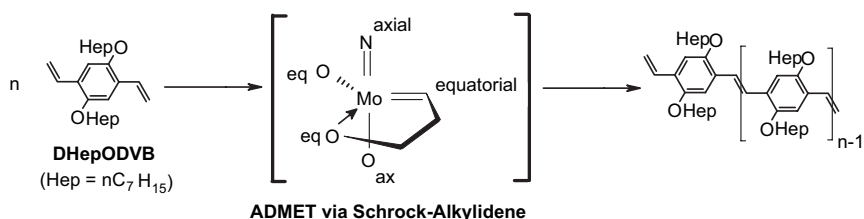
Recent mechanistic innovations concerning catalyst development in ATRP are discussed and include the finer components of the ATRP equilibrium, concurrent reactions that may occur during ATRP and will affect its efficiency, and novel methods for fine tuning catalyst systems to alleviate handling problems and enhance efficiency.

**Ralf M. Peetz, Volker Sinnwell, Emma Thorn-Csányi**

Journal of Molecular Catalysis A: Chemical 254 (2006) 165

In situ NMR investigations into the ADMET-reaction of 1,4-diheptyloxy-2,5-divinylbenzene via a Schrock-type molybdenum alkylidene complex

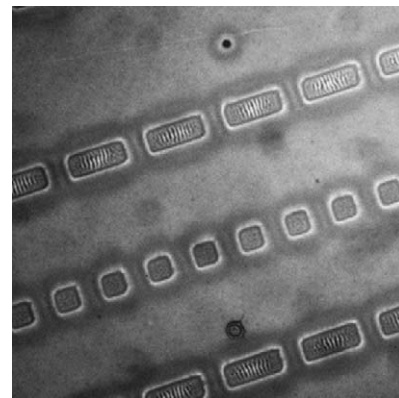
The acyclic diene metathesis (ADMET) polycondensation of 1,4-diheptyloxy-2,5-divinylbenzene (DHepODVB) with the Schrock-type alkylidene complex $\text{Mo}(\text{NAr}^{\text{Me}_2})_2(\text{CHCMe}_2\text{Ph})(\text{OCMe}(\text{CF}_3)_2)_2$ was investigated by means of in situ $^1\text{H}/^{13}\text{C}$ NMR spectroscopy. At least four novel alkylidene species were detected of which three species could be assigned to structures. These three structures show a Mo-coordination from the oxygen of a heptyloxy side chain from the substrate resulting in stabilized intermediates.

**Alexandra Lex, Gregor Trimmel, Wolfgang Kern, Franz Stelzer**

Journal of Molecular Catalysis A: Chemical 254 (2006) 174

Photosensitive polynorbornene containing the benzyl thiocyanate group—Synthesis and patterning

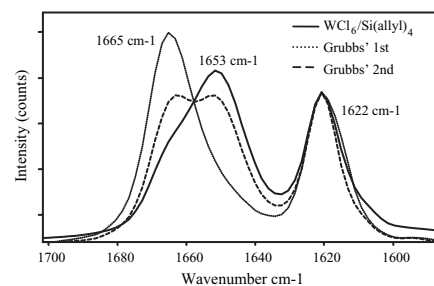
A new photosensitive polynorbornene containing the benzyl thiocyanate group was synthesised by ring opening metathesis polymerisation. Upon illumination with UV-light, the benzyl thiocyanate group undergoes a photoisomerisation to the benzyl isothiocyanate group that can selectively bind amines to form thiourea compounds. In combination with lithographic techniques, this process was used to obtain patterned polymer films.

**David Schaubroeck, Steven Brughmans, Carl Vercaemst, Joseph Schaubroeck, Francis Verpoort**

Journal of Molecular Catalysis A: Chemical 254 (2006) 180

Qualitative FT-Raman investigation of the ring opening metathesis polymerization of dicyclopentadiene

The qualitative analysis of the catalytic ring opening metathesis polymerization reaction of dicyclopentadiene (DCPD) and its resulting polymers by means of FT-Raman spectroscopy is described. The polymerization was conducted using $\text{WCl}_6/\text{Si}(\text{allyl})_4$ (**1**), Grubbs' first (**2**) and second (**3**) generation catalysts. It was found that **1** has a prevailing *cis* selectivity while **2** has a predominant *trans*-selectivity. Catalyst **3** exhibits a poor stereoselectivity.

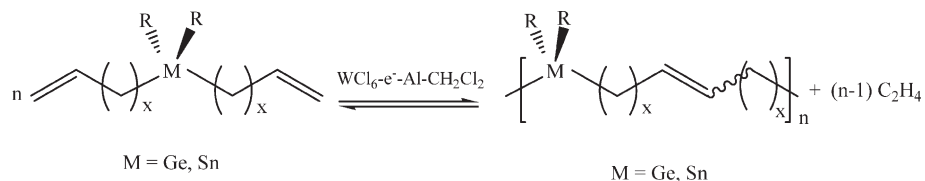


**Karabulut Solmaz, Aydogdu Cemil,
Düz Bülent, Yavuz İmamoglu**

Journal of Molecular Catalysis A: Chemical 254
(2006) 186

Synthesis and characterization of Ge- and Sn-containing ADMET polymers

The catalytic activity of the electrochemically generated tungsten-based catalyst was tested in the acyclic diene metathesis (ADMET) polymerization of Ge- and Sn-containing monomers. The $WCl_6 \cdot e^- - Al-CH_2Cl_2$ catalyst system produced various unsaturated polymers containing Ge and Sn with high *trans* content, exhibiting similar stereochemical characteristics seen in the previous ADMET systems.



**D. Jamanek, K. Niciński, R. Kazimierczuk,
T. Woźniewski, Z. Wiczorek, W. Skupiński**

Journal of Molecular Catalysis A: Chemical 254
(2006) 192

Effect of phenoxy ligands on catalytic properties of titanium half-sandwich complexes/MAO systems

Auxiliary phenoxy ligands of donor character in the titanium half-sandwich complex/MAO systems, can act as additional donor ligands in titanium active catalytic centers resulting in increasing the rate of termination step in olefin and styrene polymerization. Auxiliary phenoxy ligands of acceptor character in the titanium half-sandwich complex/MAO systems, enhances the rate of propagation steps in olefin and styrene polymerization processes resulting in high molecular weight ethylene and propylene polymers and enable ethylene–high olefin and ethylene–styrene copolymers formation. Ethylene polymerization in the presence of the

$CpTiCl_2(OC_6H_4X-p)/MAO$ catalytic system, where $X = NO_2, Cl, H, CH_3, t-C_4H_9, OCH_3$ under atmospheric pressure.

X	Yield g	m.p. °C	$M_w/10^4$ g/mol
NO_2	0.10	136	18.1
Cl	0.10	137	14.1
H	0.14	130	13.8
CH_3	0.11	132	6.6
$t-C_4H_9$	0.09	127	9.2
OCH_3	0.10	131	7.3

Kotohiro Nomura, Aki Tanaka, Shohei Katao

Journal of Molecular Catalysis A: Chemical 254
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Effect of aryloxy ligand in 1-hexene, styrene polymerization catalyzed by nonbridged half-titanocenes of the type, $Cp^*TiCl_2(OAr)$ ($Cp^* = C_5Me_5, ^tBuC_5H_4$). Structural analyses for $Cp^*TiCl_2(O-2,6-^tBu_2C_6H_3)$ and $Cp^*TiCl_2(O-2,6-^iPr_2-4-^tBuC_6H_2)$

Various half-titanocenes of the type, $Cp^*TiCl_2(OAr)$ ($Cp^* = C_5Me_5, ^tBuC_5H_4$; $Ar = 2,6-Me_2C_6H_3, 2,4,6-Me_3C_6H_2, 2,6-^iPr_2C_6H_3, 2,6-^iPr_2-4-^tBuC_6H_2, 2,6-^tBu_2C_6H_3, 2,6-^tBu_2-4-MeC_6H_2$), were prepared, and structures for $Cp^*TiCl_2(O-2,6-^iPr_2-4-^tBuC_6H_2)$ (4), $Cp^*TiCl_2(O-2,6-^tBu_2C_6H_3)$ (5) were determined. $Cp^*TiCl_2(2,6-^iPr_2C_6H_3)$ (3) and 4 possessed unique Ti–O–C bond angles (173.0–174.6°), and exhibited notable catalytic activities for 1-hexene polymerization. The aryloxy ligand affected the activity for syndiospecific styrene polymerization; (tBuC_5H_4) $TiCl_2(O-2,6-^iPr_2-4-^tBuC_6H_2)$ showed the highest activity.

