Olefin-Metathese: Ruthenium-katalysierte C=C -Bindungsknüpfungen

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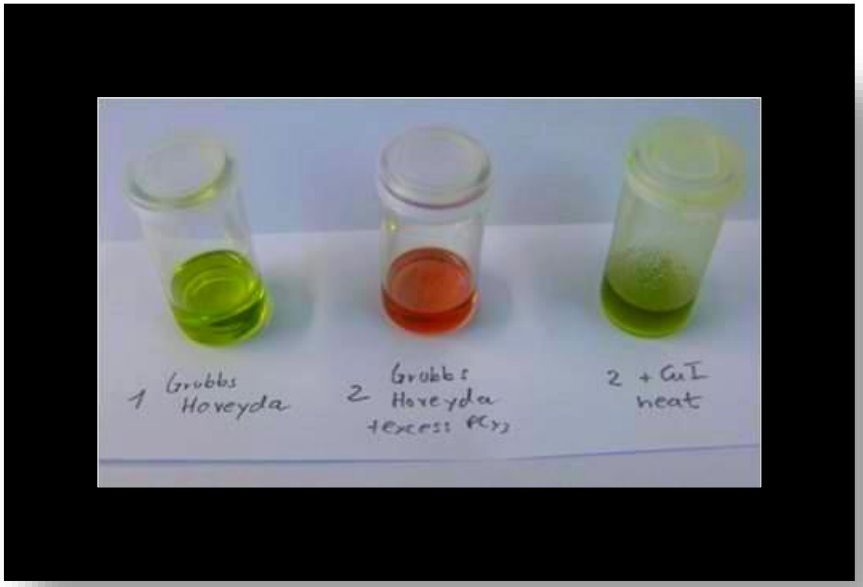

Prof. Dr. Herbert Plenio, Organometallic Chemistry, Petersenstr. 18, TU Darmstadt, 64287 Darmstadt, Germany, plenio@tu-darmstadt.de

A decade of Homogeneous Catalysis

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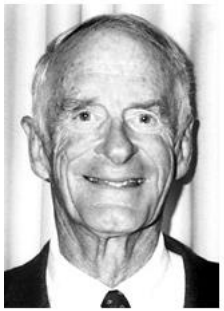
The Nobel Prize in Chemistry 2001
William S. Knowles, Ryoji Noyori, K. Barry Sharpless

- The Nobel Prize in Chemistry 2001
- Nobel Prize Award Ceremony
- William S. Knowles
- Ryoji Noyori
- K. Barry Sharpless


William S. Knowles


Ryoji Noyori


K. Barry Sharpless

The Nobel Prize in Chemistry 2001 was divided, one half jointly to William S. Knowles and Ryoji Noyori *"for their work on chirally catalysed hydrogenation reactions"* and the other half to K. Barry Sharpless *"for his work on chirally catalysed oxidation reactions"*.

The Nobel Prize in Chemistry 2010
Richard F. Heck, Ei-ichi Negishi, Akira Suzuki

- The Nobel Prize in Chemistry 2010
- Richard F. Heck
- Ei-ichi Negishi
- Akira Suzuki

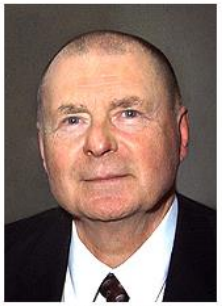


Photo: University of Delaware, USA
Richard F. Heck

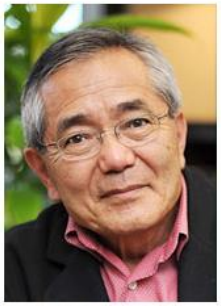


Photo: Purdue University, USA
Ei-ichi Negishi


Photo: Hokkaido University, Japan
Akira Suzuki

The Nobel Prize in Chemistry 2010 was awarded jointly to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki *"for palladium-catalyzed cross couplings in organic synthesis"*.

The Nobel Prize in Chemistry 2005
Yves Chauvin, Robert H. Grubbs, Richard R. Schrock

- The Nobel Prize in Chemistry 2005
- Nobel Prize Award Ceremony
- Yves Chauvin
- Robert H. Grubbs
- Richard R. Schrock


Photo: U. Montan
Yves Chauvin


Photo: R. Paz
Robert H. Grubbs


Photo: L.B. Hetherington
Richard R. Schrock

The Nobel Prize in Chemistry 2005 was awarded jointly to Yves Chauvin, Robert H. Grubbs and Richard R. Schrock *"for the development of the metathesis method in organic synthesis"*.

Olefin Metathesis (changing places)

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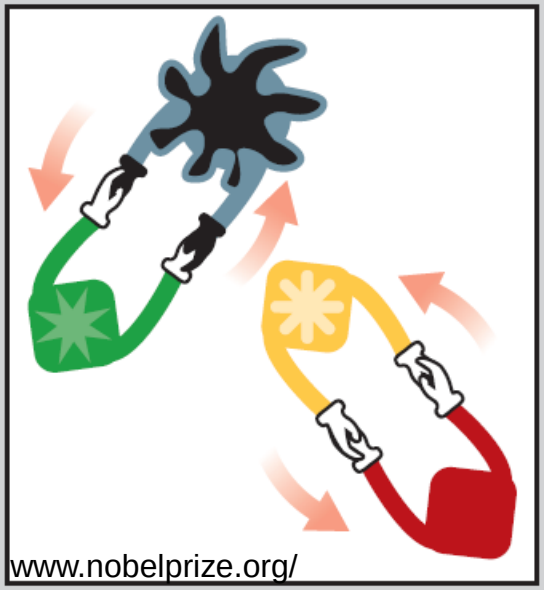
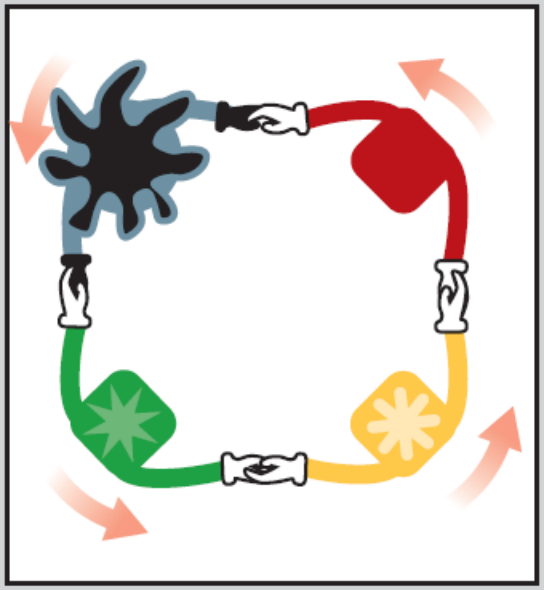
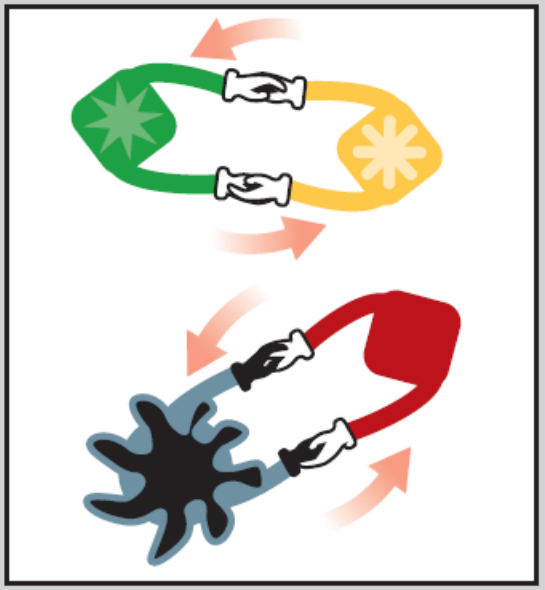
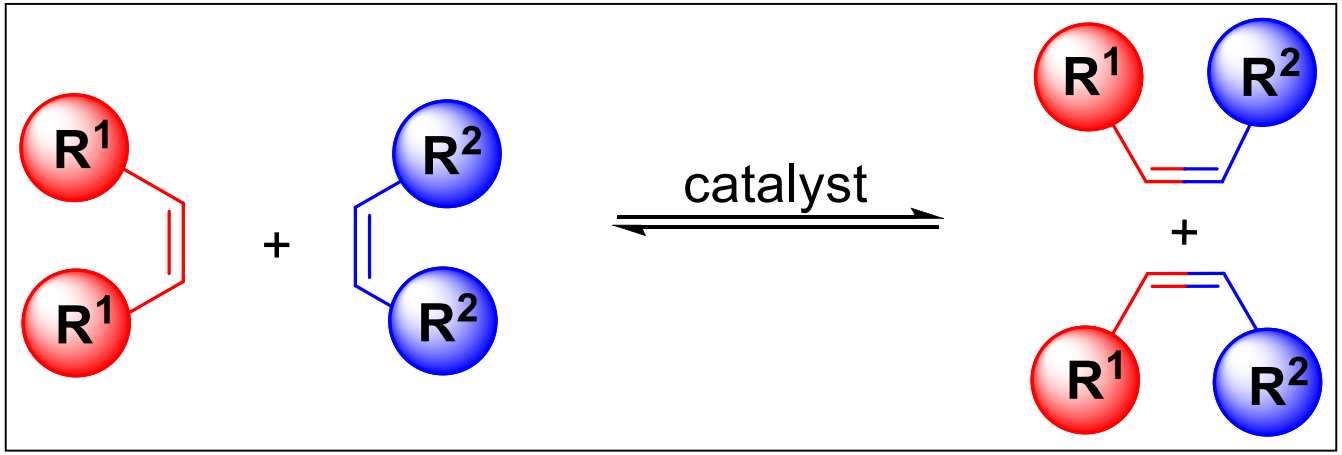




www.nobelprize.org/



H. S. Eleuterio - Du Pont 1957

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BUNDESREPUBLIK DEUTSCHLAND

KL. 39 c 25/01

INTERNAT. KL. C 08 f

DEUTSCHES PATENTAMT

AUSLEGESCHRIFT 1 072 811

P 20792 IVb/39 c

ANMELDETAG: 3. JUNI 1958

BEKANNTMACHUNG DER ANMELDUNG UND AUSGABE DER AUSLEGESCHRIFT: 7. JANUAR 1960

Verfahren zur Polymerisation cyclischer, insbesondere mono-, bi- oder tricyclischer Olefine

Anmelder:

E. I. du Pont de Nemours and Company, Wilmington, Del. (V. St. A.)

Vertreter: Dr.-Ing. W. Abitz, Patentanwalt, München 27, Gaußstr. 6

Beanspruchte Priorität:

V. St. v. Amerika vom 20. Juni 1957

Herbert Sousa Eleuterio, Wilmington, Del. (V. St. A.), ist als Erfinder genannt worden

ıren zur Poly-

ı Metallen der
ems auf inerten
ı Behandeln mit
ıktive Katalysa-
olekularen festen
n. Die Aktivität
ıtz eines Hydri-
III des Periodi-
rhöht. Die Her-
ter anderem in
47, 2 726 231,
beschrieben.
ß die Aktivität
nerisation end-
fonomerer, wie

talysatoren aus
VI a auf einem
g durch Behan-
n Gas, bei Um-

Hüls-Vestenamer-Prozess

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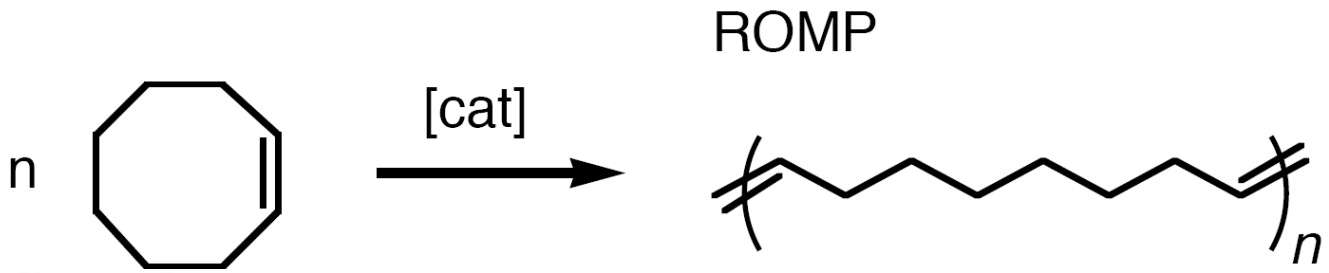
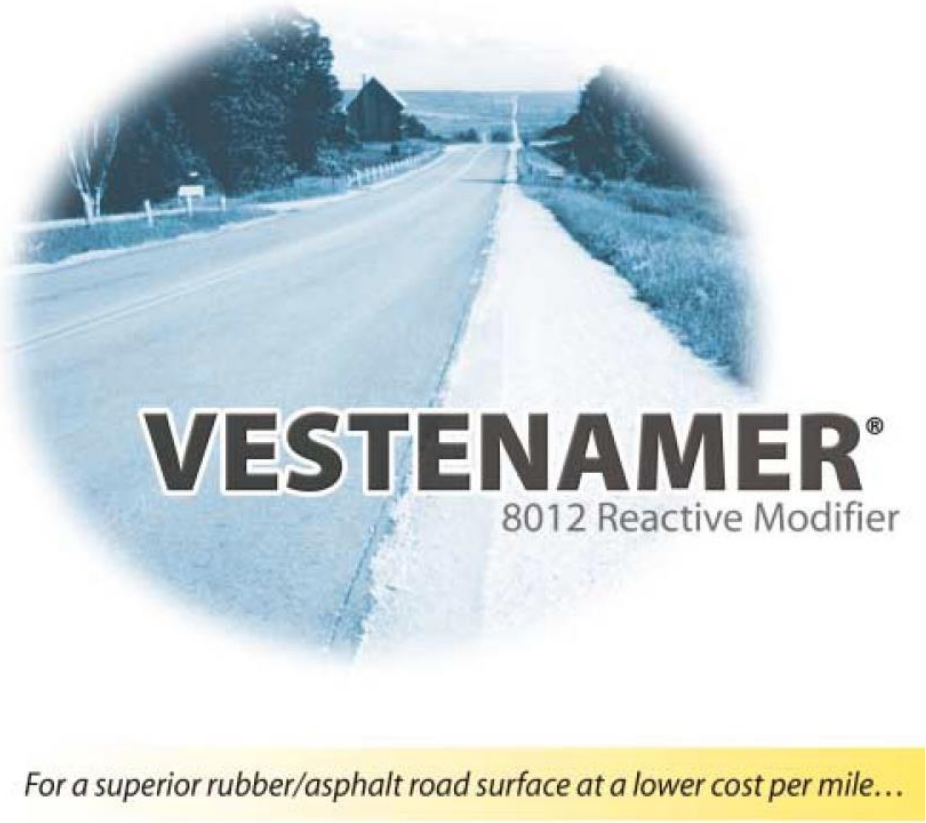
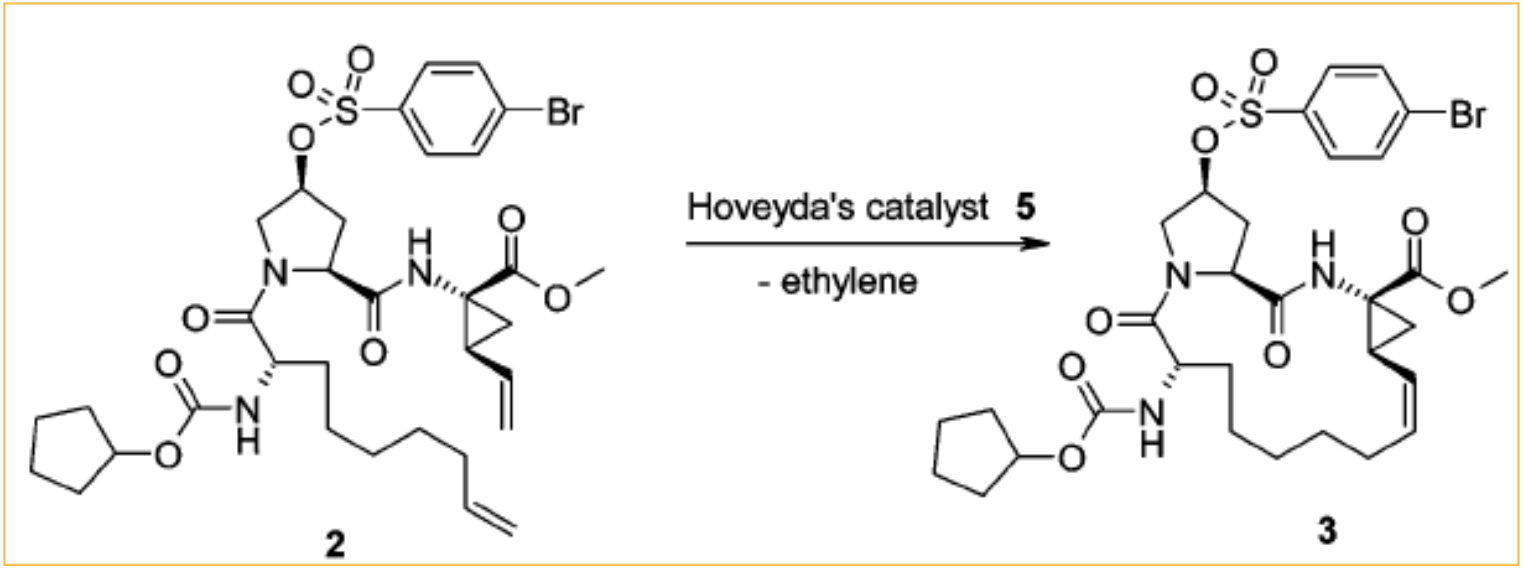




HCV Protease Inhibitor – BILN 2061

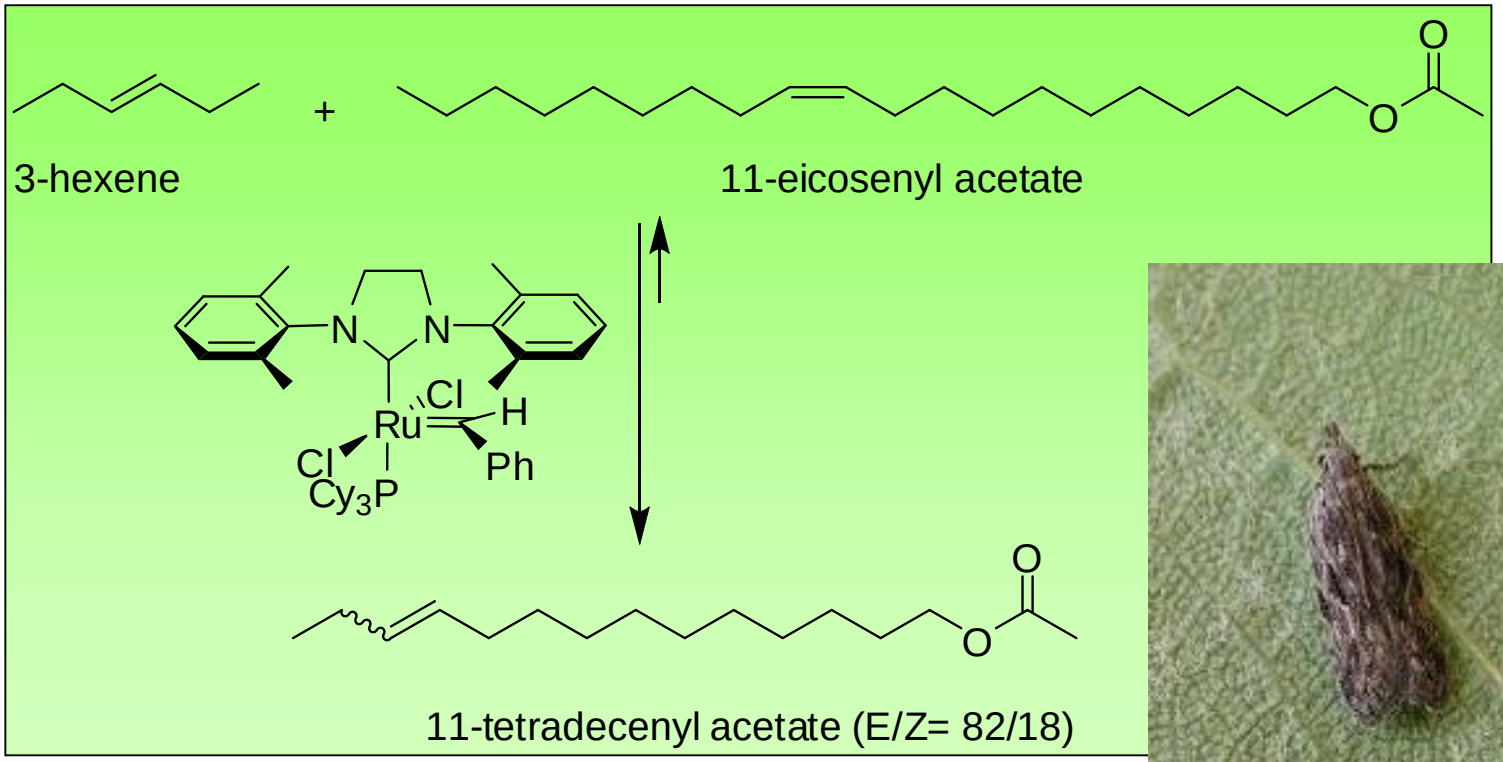


This first-generation RCM was scaled to produce >100 kg of the active pharmaceutical ingredient (API).

……optimization of the initial RCM, leading to a second-generation process, which dramatically improves throughput and reaction efficiency.

Second-Generation Process for the HCV Protease Inhibitor BILN 2061: A Greener Approach to Ru-Catalyzed Ring-Closing Metathesis, Boehringer Ingelheim, *Org. Process Res. Dev*. **2009**, *13*, 250.
The Growing Impact of Catalysis in the Pharmaceutical Industry, *Adv. Synth. Catal*. **2011**, *353*, 1825; C. H. Senanayakea et al. doi: 10.1002/adsc.201100488

Pheromones



omnivorous leafroller

Speciality Chemicals, Olefins, Oleochemicals from Palm Oil

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Elevance Renewable Sciences and Wilmar International Limited Begin Commercial Shipment of Specialty Chemicals from New World-Scale Biochemical Refinery in Asia

July 18, 2013 (Woodridge, IL)

Elevance-Wilmar Joint Venture Produces Renewable Performance Specialty Chemicals, Olefins and Oleochemicals

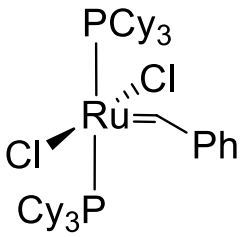
Woodridge, Ill., USA/Singapore (July 18, 2013) – Wilmar International Limited, Asia's leading agribusiness, and Elevance Renewable Sciences, Inc., a high-growth specialty chemicals company, announced today that they have begun shipping commercial products, including novel specialty chemicals, to customers from their first world-scale joint venture biorefinery, located in Gresik, Indonesia. The biorefinery is the first based on Elevance's proprietary metathesis technology.

production sites

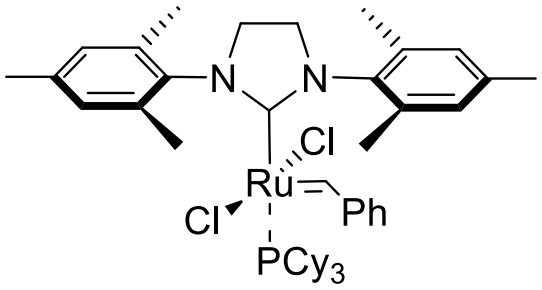
180.000 t/a Gresik, Indonesia 2013

+ Natchez, Mississippi 2016?

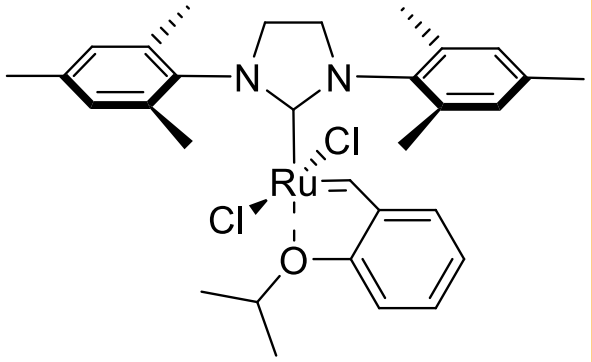
Olefin metathesis precatalysts



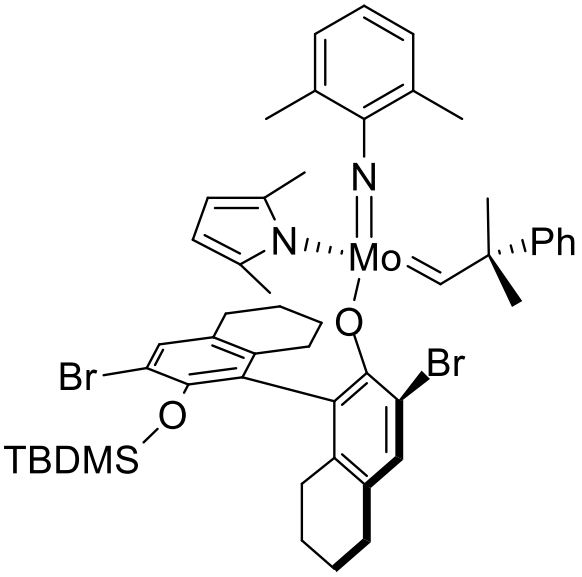
Grubbs I



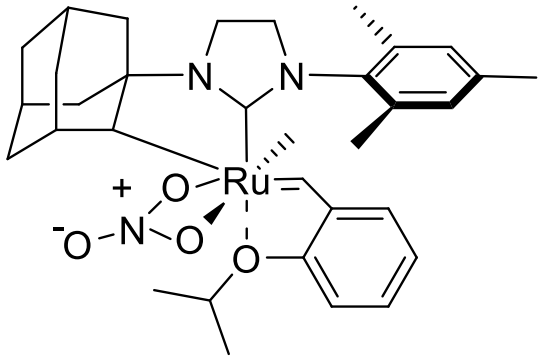
Grubbs II



Grubbs-Hoveyda



Hoveyda-Schrock



Grubbs

RingClosingMetathesis leading to sterically-demanding alkenes

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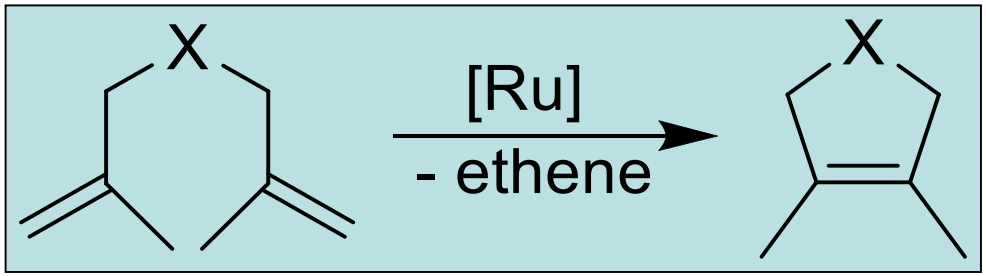
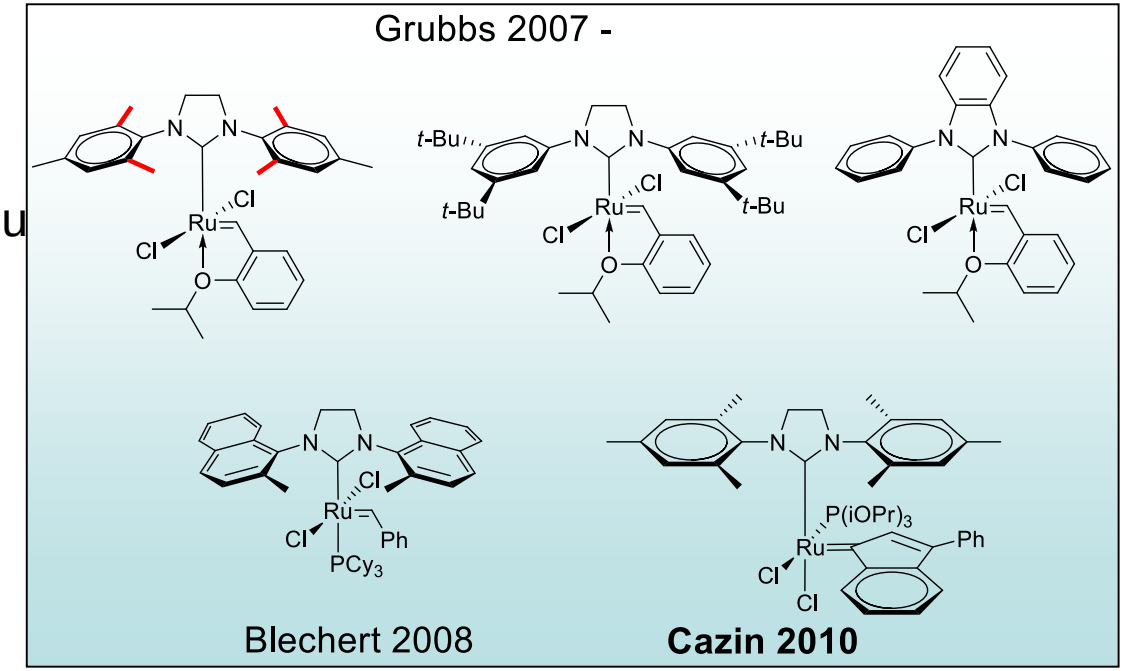


Problems: - excessive catalyst loading (5 - 10 mol%)
- modest product formation

How to solve the problem?

- decreased steric bulk around Ru
- Increased precatalyst stability



Weakly donating *N*-heterocyclic Carbenes

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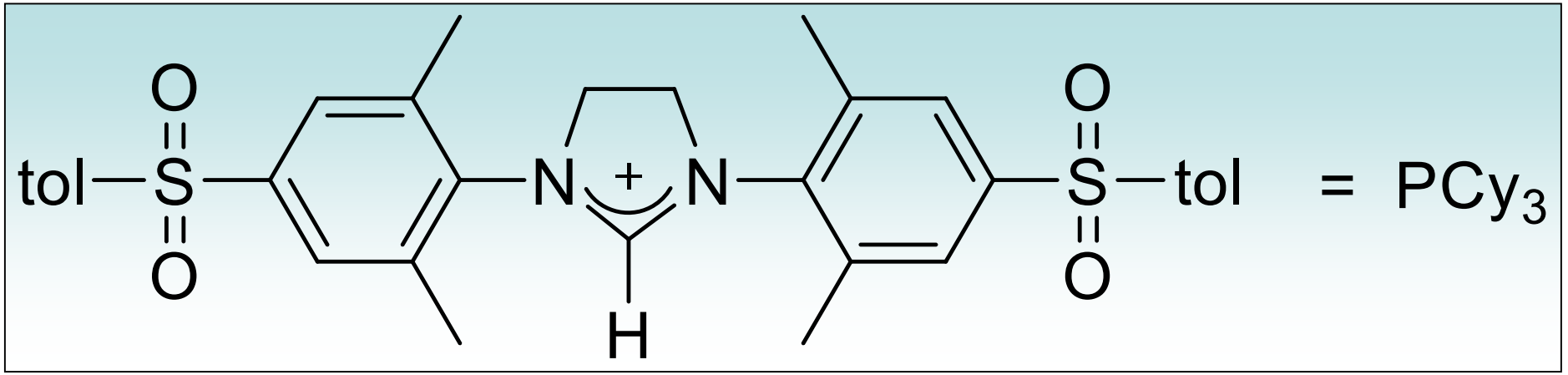
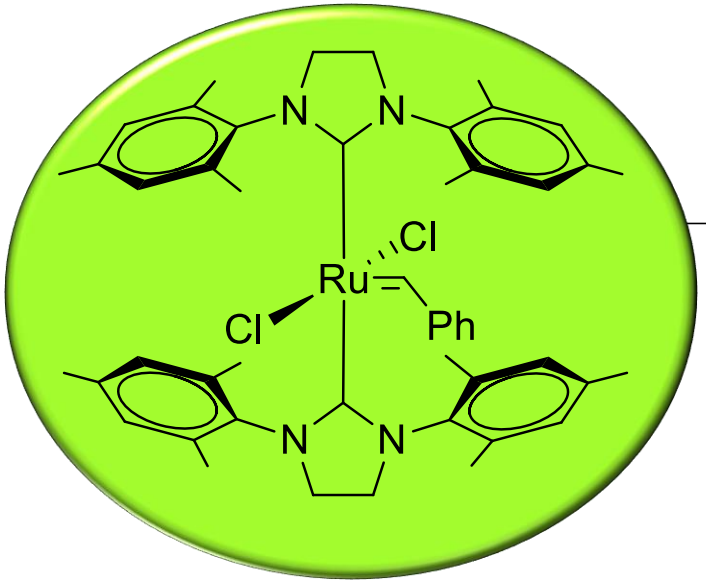
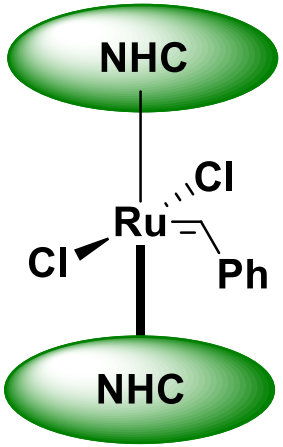


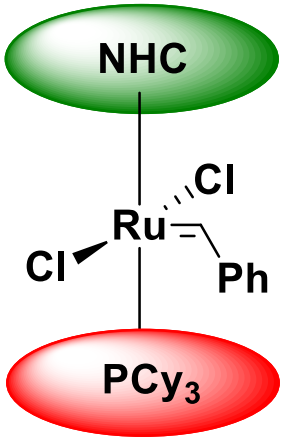
NHC_{ewg}

bisNHC complexes

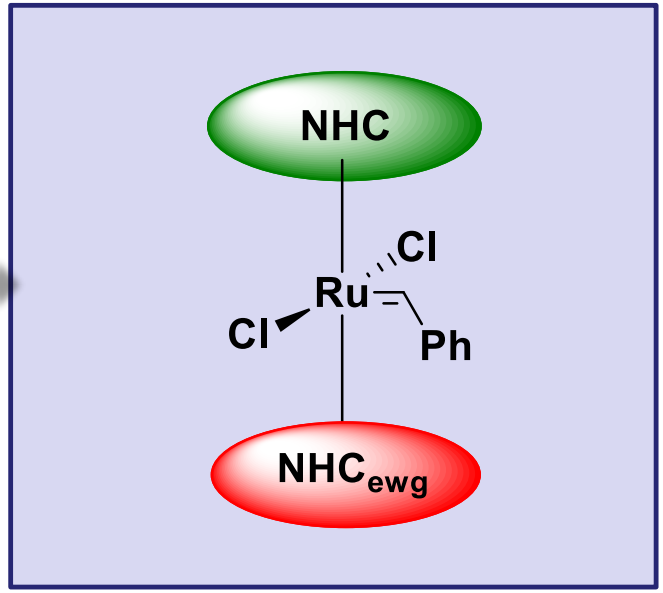


Herrmann, Grubbs 1999
modest activity





Grubbs II - Komplex



T. Vorfalt, S. Leuthäußer, H. Plenio, *Angew. Chem., Int. Ed.* **2009**, *48*, 5191

ABC

Synthesis of (NHC)(NHC$_{ewg}$)RuCl$_2$(CHPh)

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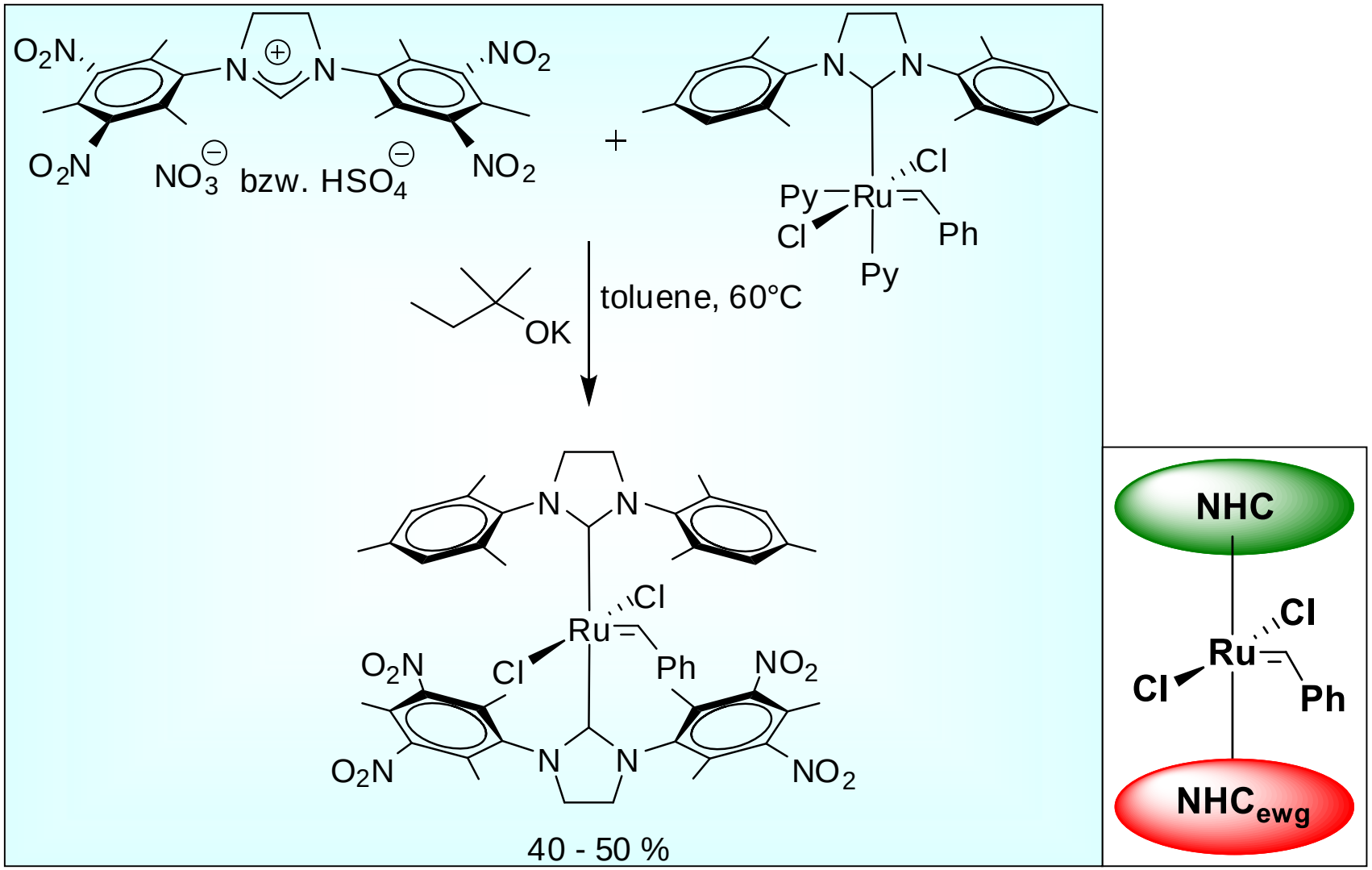

Test of Ring-closing Metathesis Activity

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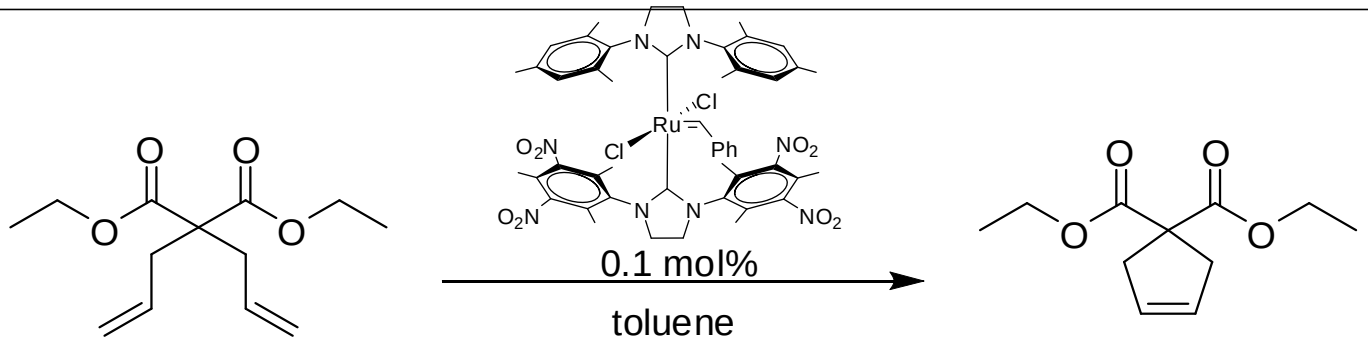

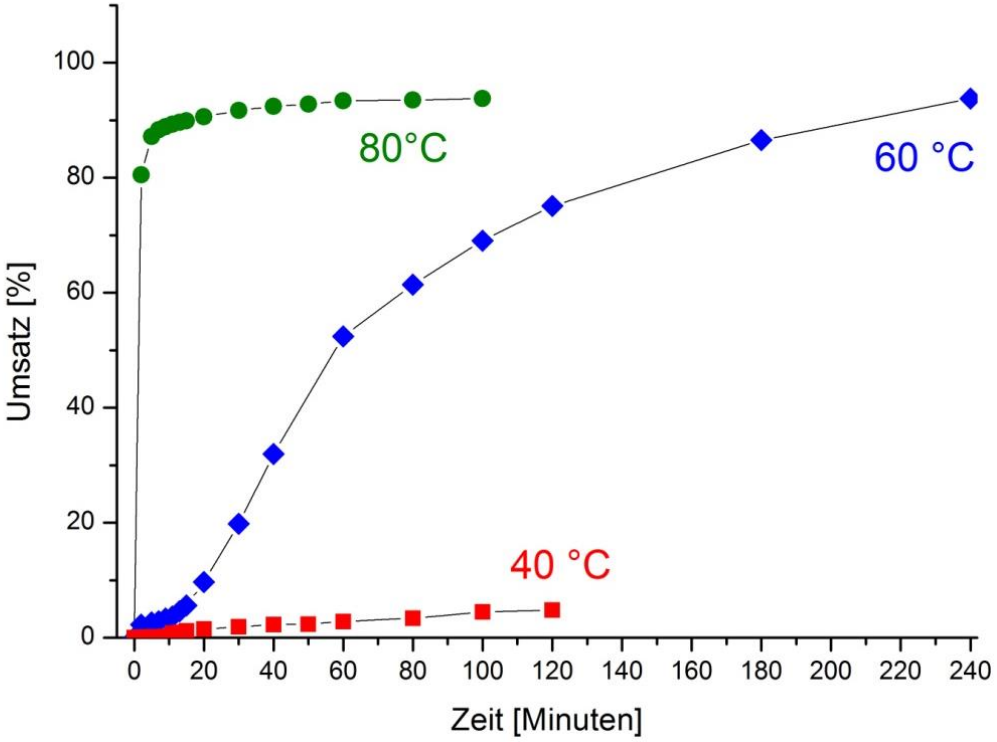

Selected examples for sterically demanding substrates

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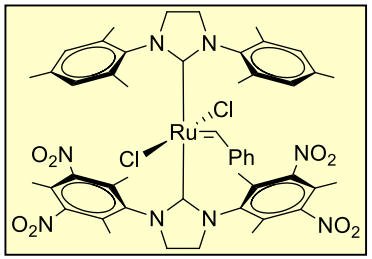
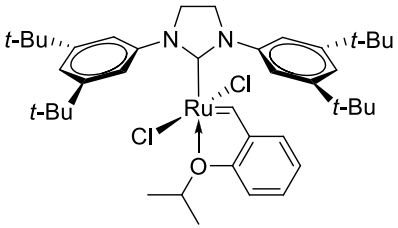
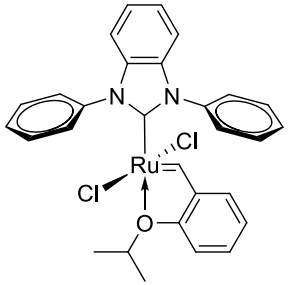
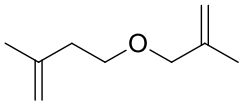
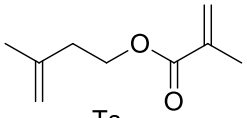
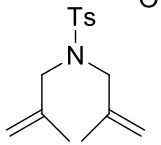
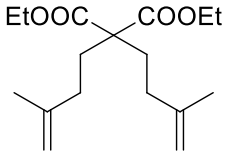
	80°C Toluol **- 0.5 mol%**	60°C C_6D_6 **- 5 mol%**	
	Vorfalt 2009 		 **Grubbs 2007**
	98%	78%	< 1%
	26%	< 1%	< 1%
	98%	> 95%	> 95%
	60% 87% (1 mol%)	51%	36 %

T. Vorfalt, S. Leuthäußer, H. Plenio, *Angew. Chem., Int. Ed.* **2009**, *48*, 5191.

Optimized (NHC)(NHC$_{ewg}$)RuCl$_2$(CHPh)

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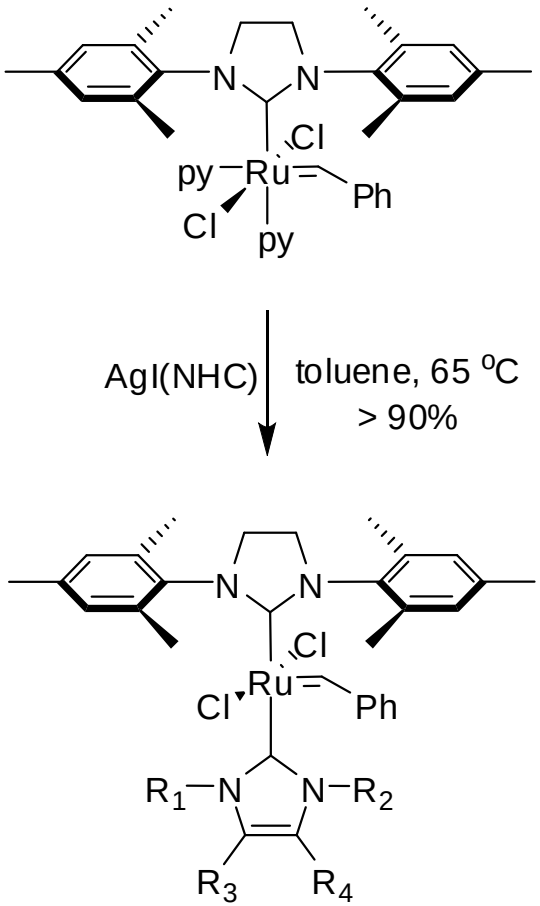
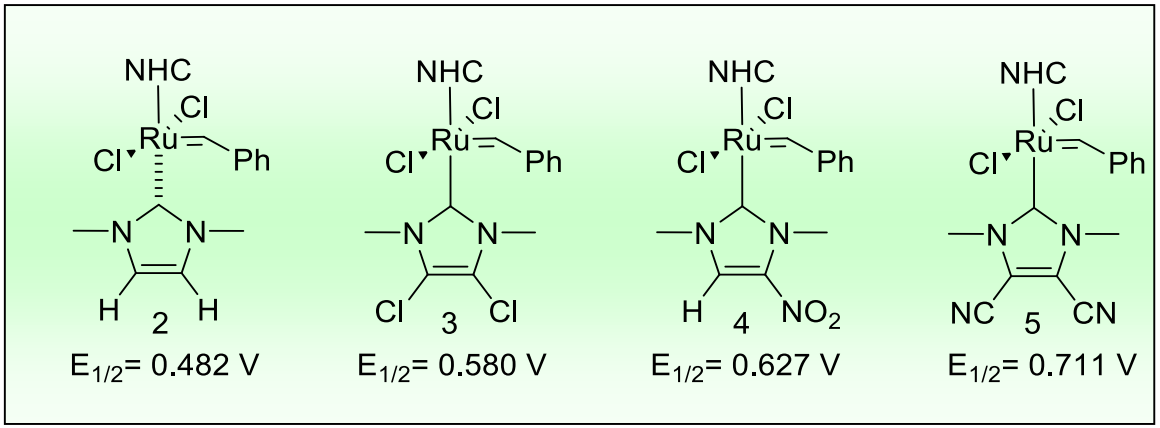
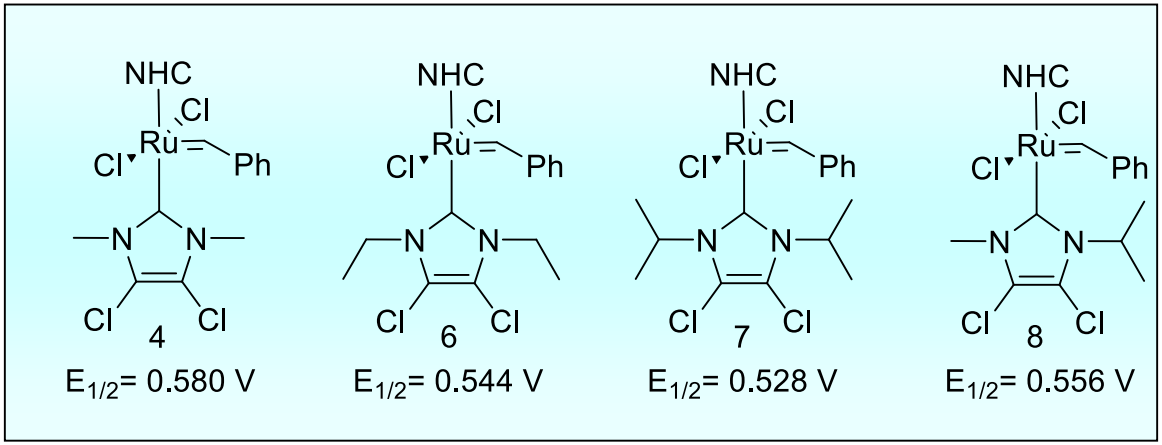


electronic series





steric series

catalytic activity
…ca. three times higher activity……

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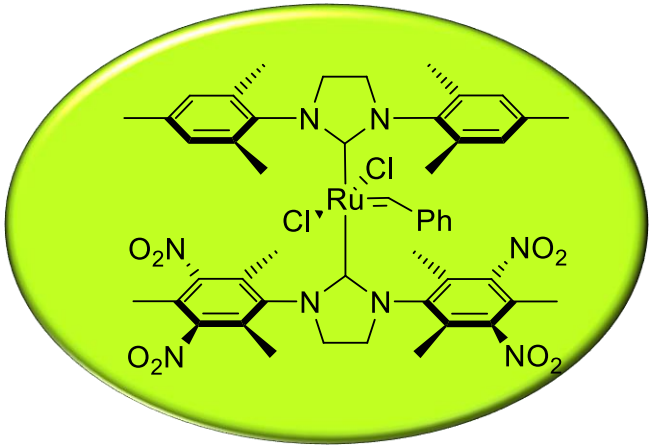

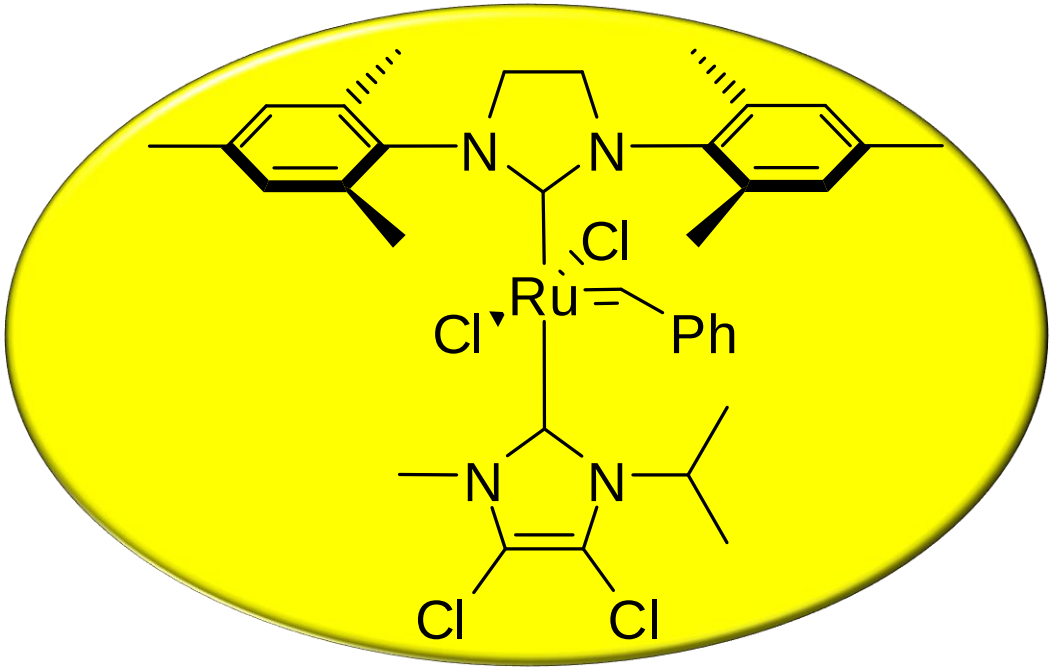

V. Sashuk, L. H. Peeck, H. Plenio, *Chem. Eur. J.* **2010**, *16*, 3983-3993
L. H. Peeck, H. Plenio, *Organometallics* **2010**, *29*, 2761-2768
S. Wolf, H. Plenio, *J. Organomet. Chem.* **2010**, *695*, 2418-2422.

Catalyst Availability
scale-up from 100 mg to 100 g

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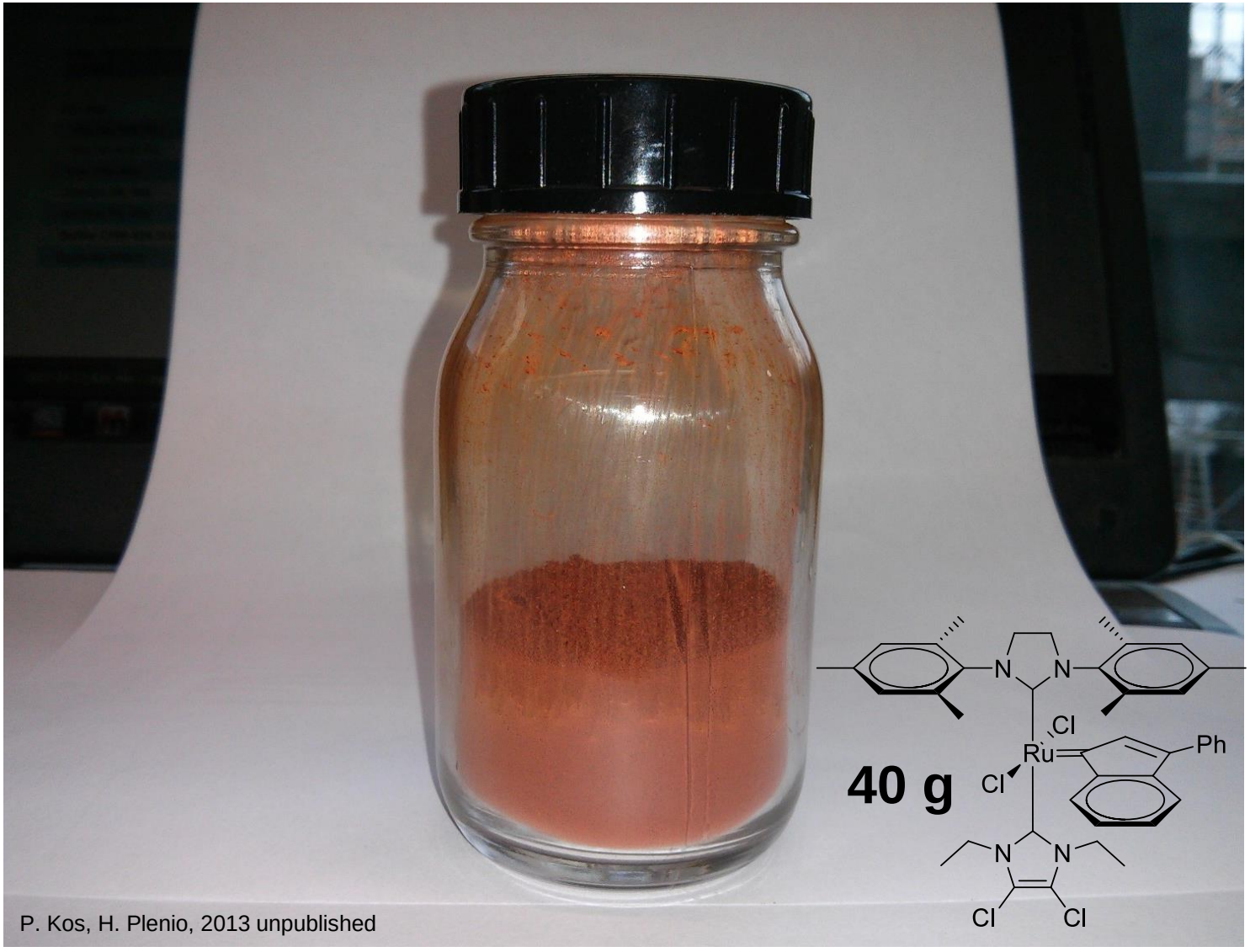
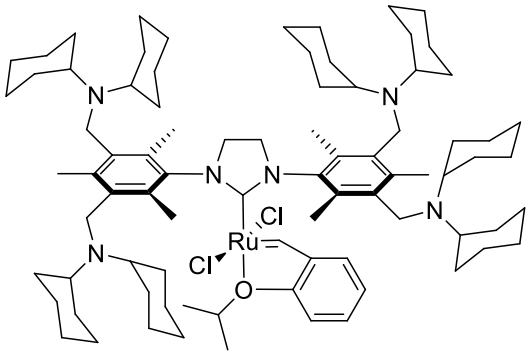
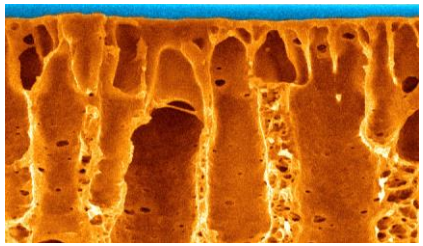
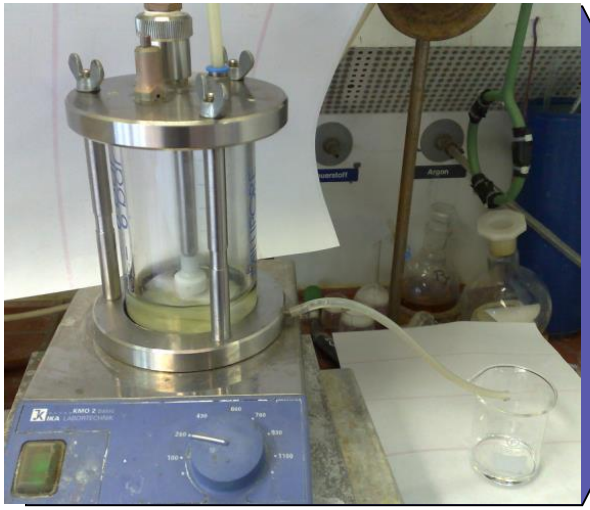


P. Kos, H. Plenio, 2013 unpublished

Catalyst Separation
Solvent resistant Nanofiltration







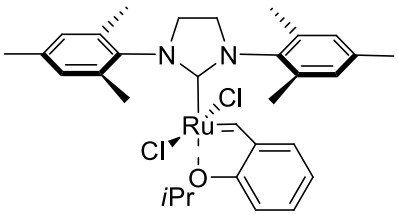
Δp = 5 bar

1.4 mL/min

- 99.9% retention of catalyst
- < 4 ppm Ru content

Batchwise and continuous organophilic Nanofiltration of Grubbs type Olefin Metathesis Catalysts.
D. Schoeps, K. Buhr, K. Ebert, H. Plenio, *Chem. Eur. J.* **2009**, *15*, 2960.
A. Datta, K. Ebert, H. Plenio, *Organometallics* **2003**, 22, *4685 for Palladium.*

fast RCM catalysis



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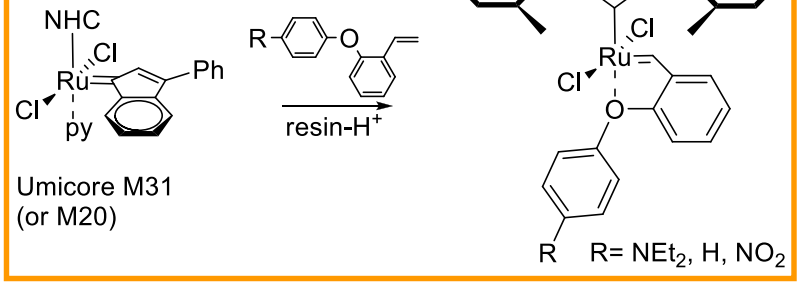

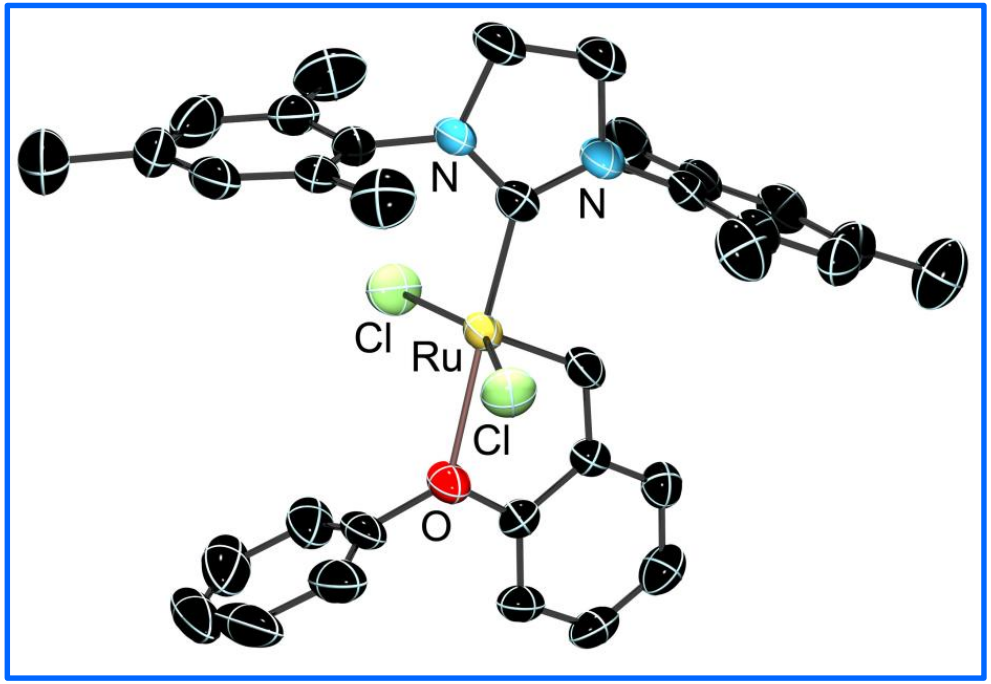

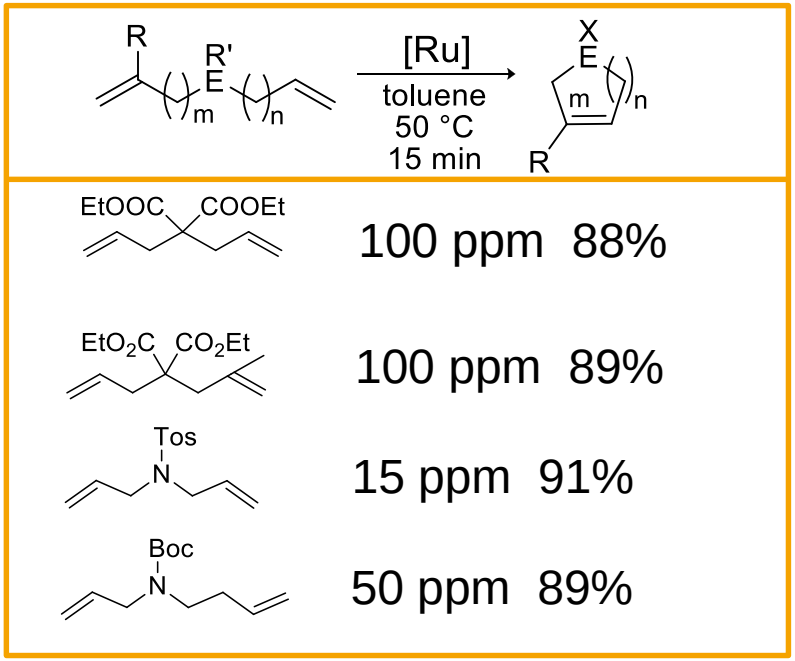

P. Kos, R. Savka, H. Plenio, *Adv. Synth. Catal.* **2013**, *355*, 439.

Industrial Olefin Cross Metathesis

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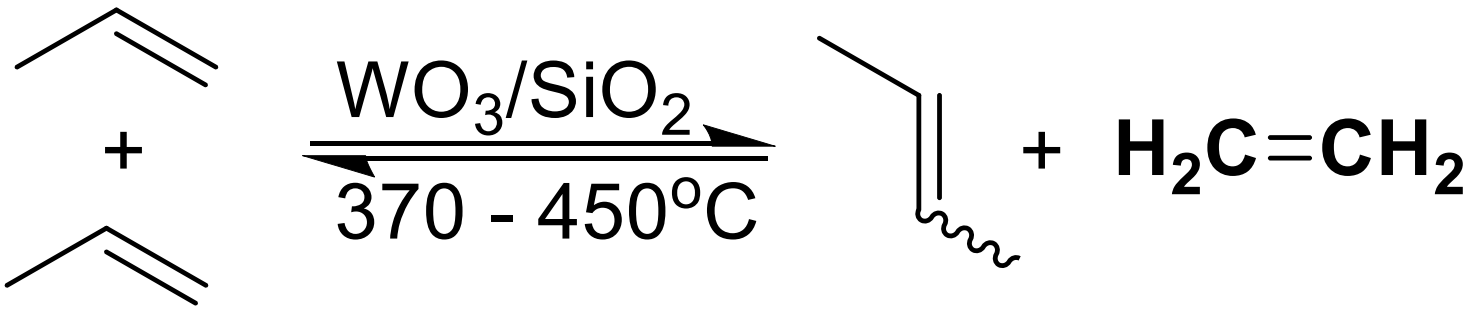
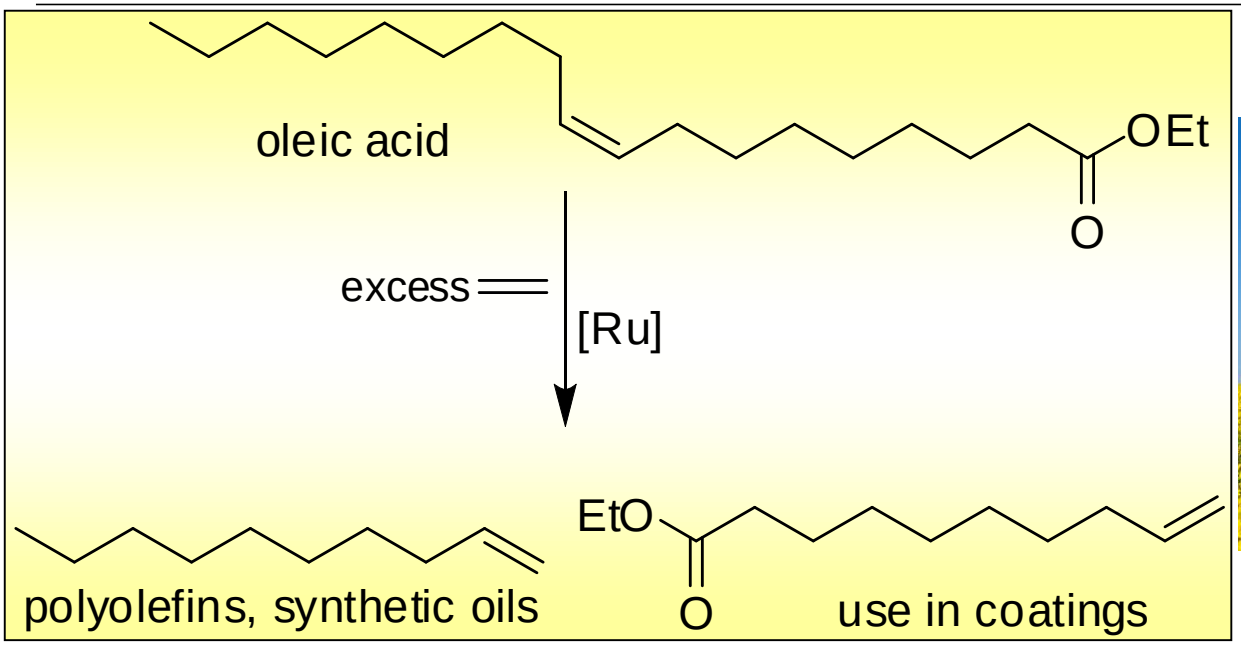
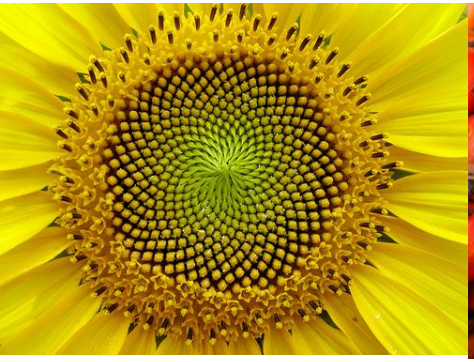
Phillips-Triolefin Process, -1972



Olefin-Conversion Technology, BASF-FINA

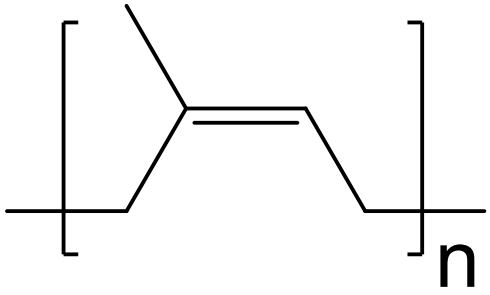
Plant oils for ethenolysis





U. Biermann, U. Bornscheuer, M. A. Meier, J. O. Metzger, H. J. Schäfer, *Angew. Chem. Int. Ed.* **2011**, *50*, 3854-3871

Natural Rubber



cis-Polyisoprene
Hevea brasiliensis

Annual production ca. $10 \cdot 10^6$ t/a
Philippines, Thailand, Malaysia
1.5 – 3 US$ /kg (2009/2010)

Squalene – a simple model for Natural Rubber

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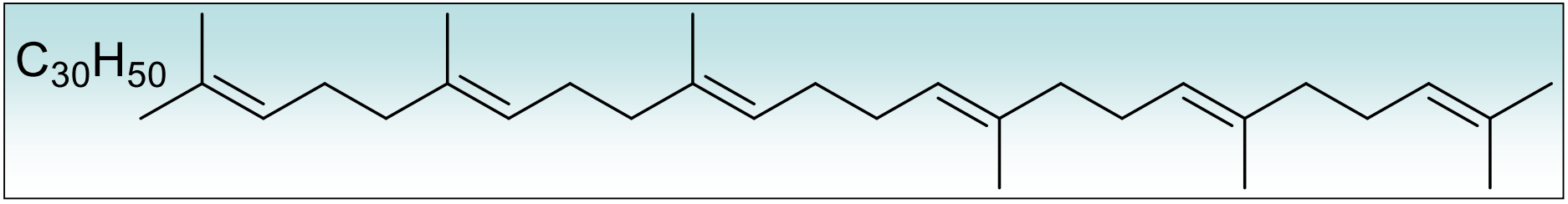

Squalene Ethenolysis (cross metathesis with ethene)

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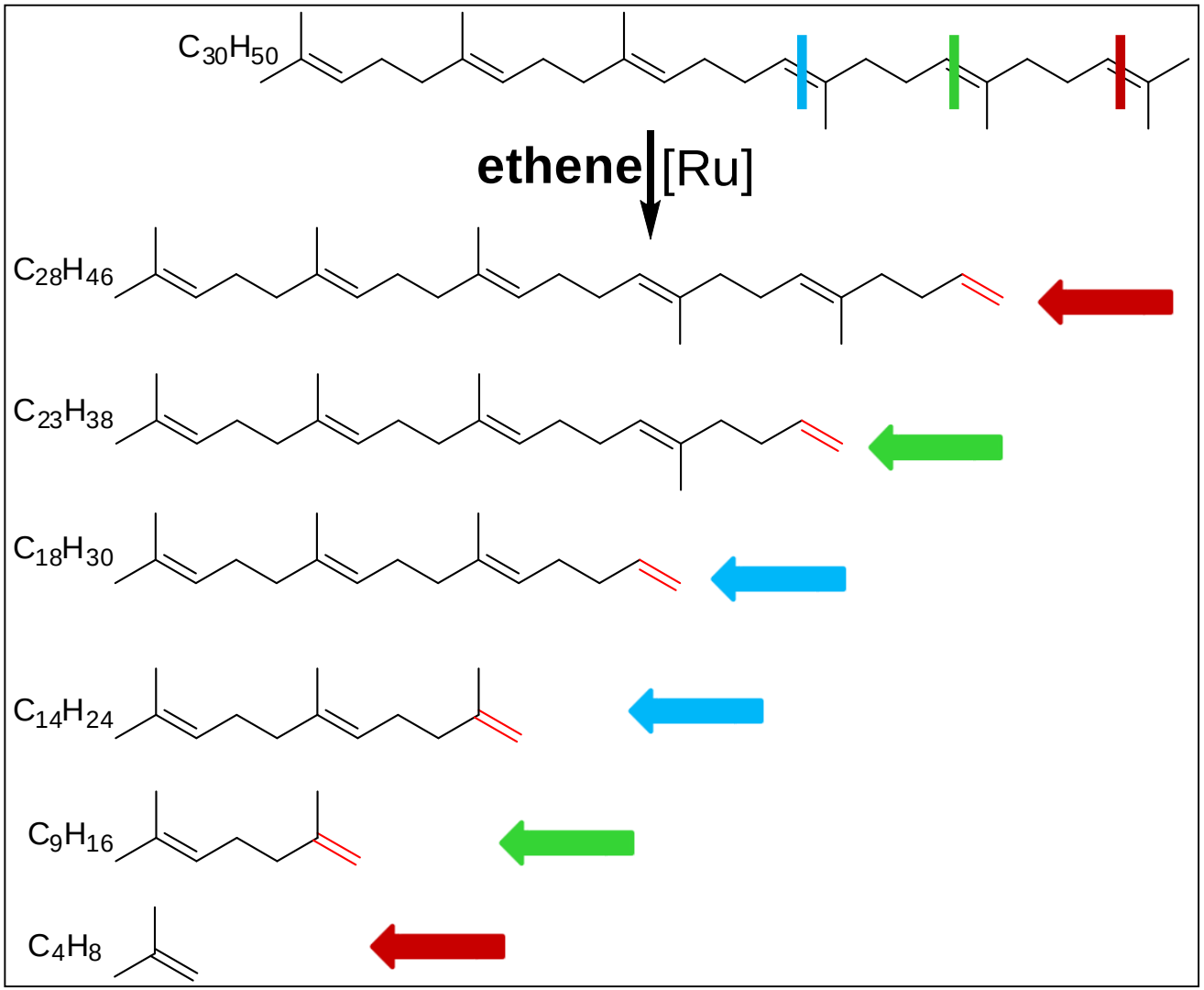

Ethenolysis of natural rubber

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Ethenolysis of Natural Rubber and Polyisoprene

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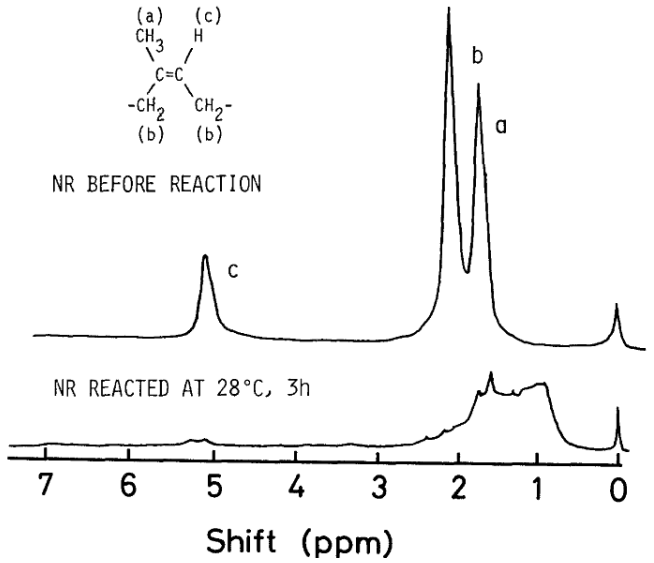
malaysian natural rubber
Catalyst: $WCl_6/SnMe_4$

A. **Alimuniar**, M. A. Yarmo, M. Z. A. Rahman, S. Kohjiya, Y. Ikeda, S. Yamashita, *Polymer Bull.*, **1990**, *23*, 119



"A significant decrease in the polymer's molecular weight is observed"

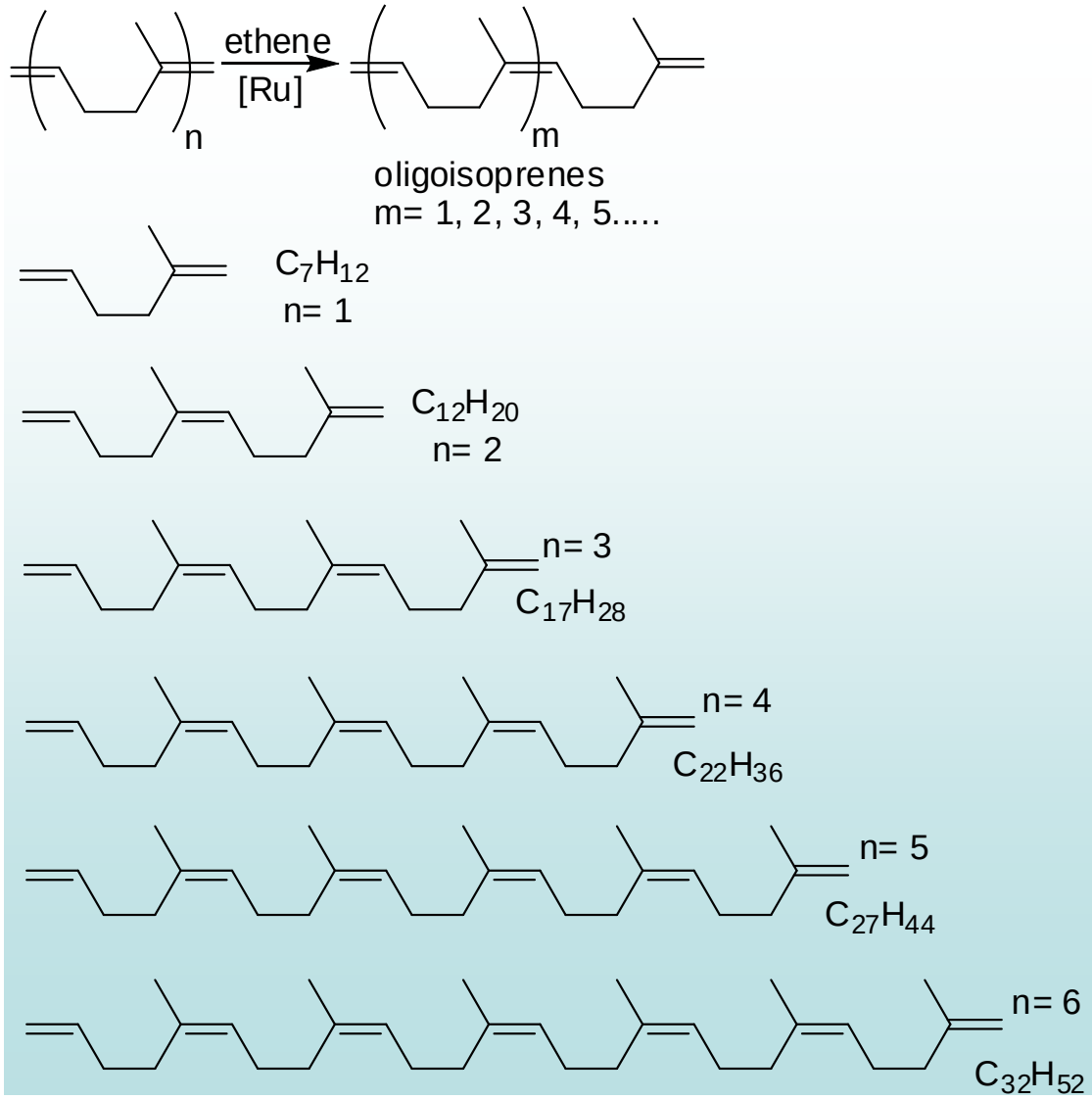
Poly-trans-isoprene
Catalyst $[(CF_3)_2CH_3CO)(NAr)W{=}CHt\text{Bu}]$
2.33 mol% per double bond

Tab. 1. Depolymerization results

Polymer	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Method	MW of products	Detected monomer
Polyoctenamer	108 000 [a]	(1,9)	A	1 000 [c]	1,9-Decadiene [f]
Polybutadiene	200 000 [b]	(2,1)	B, C	2 000 [d]	1,5-Hexadiene [f, g]
	200 000 [b]	(2,1)	C(THF)	1 000 [e]	1,5-Hexadiene [f, g]
Polyisoprene	$2{,}5 \cdot 10^5$ [b]	(1,0)	C	1 000 [e]	2-Methyl--1,5-hexadiene [f, g]

K. B. **Wagener**, R. D. Puts, D. K. Smith, *Makromol. Chem., Rapid Commun.* **1991**, *12*, 419

Depolymerization of Natural Rubber



S. Wolf, H. Plenio, *Green Chem*. **2011**, 13, 2008

global annual output: 1.500.000.000 units end-of-life tires (ELT)

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end-of-life tire rubber granulate

end-of-life tire rubber granulate

organic solubles obtained after ethenolysis of ELT powder

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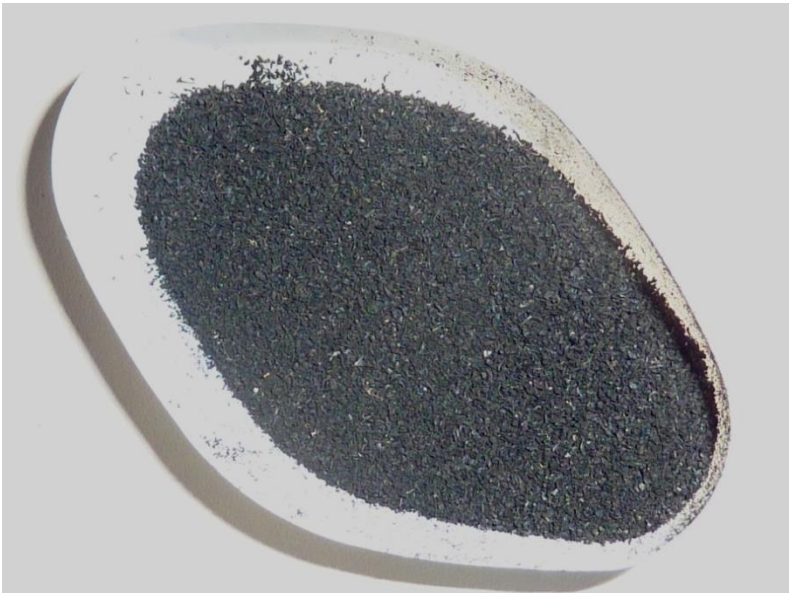

[Ru]
80 °C
7 bar
ethene
toluene

10 g of ELT yield up to 5 g of organic solubles

10 g of ELT require 0.04 g of ruthenium complex

Thank You!

TECHNISCHE UNIVERSITÄT DARMSTADT

Volodia Sashuk
Lars Peeck
Steffi Wolf
Roman Savka
Pavlo Kos
Tim Vorfalt

Dr. Ebert/GKSS

Deutsche Forschungsgemeinschaft
DFG