Heterogeneous catalysis (C9981)

Lecture 10

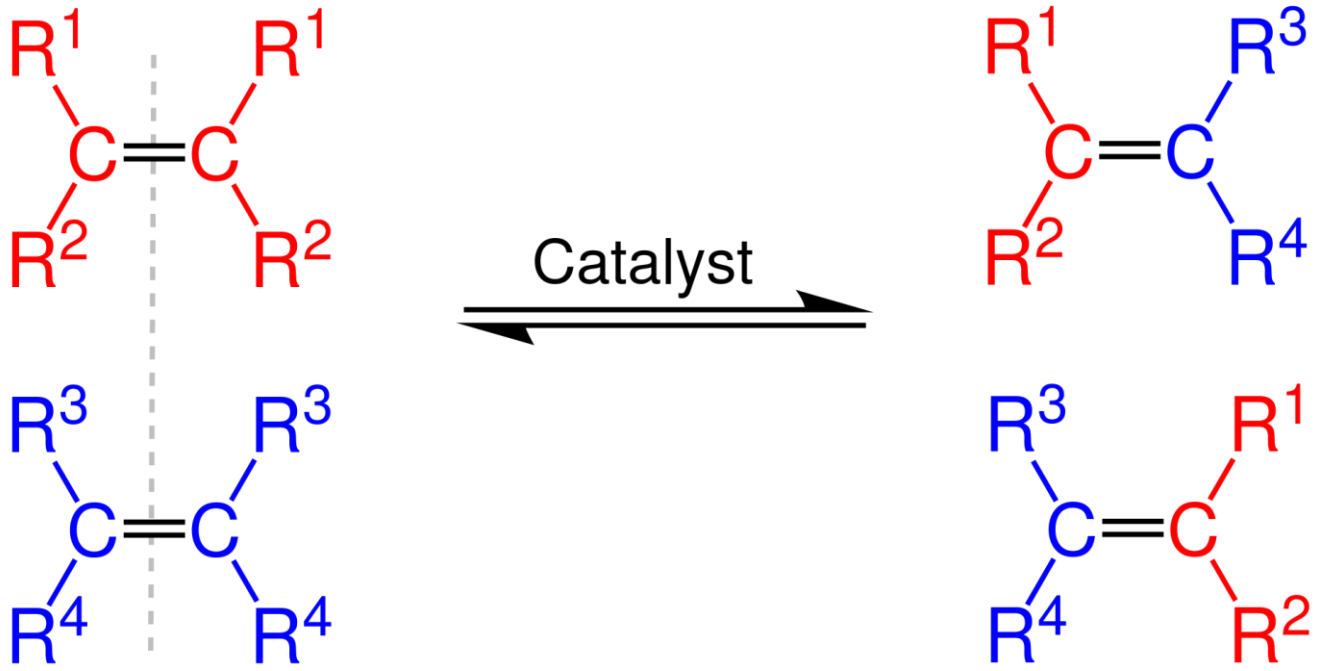
Olefin Metathesis

styskalik@chemi.muni.cz

styskalik.sci.muni.cz

Olefin metathesis

- “Two dancing couples exchange their partners”



$CH_2{=}\mathbf{CH_2} + \mathbf{CH_3{-}CH}{=}CH{-}CH_3 \rightleftharpoons \mathbf{CH_3{-}CH}{=}CH_2 + CH_3{-}CH{=}\mathbf{CH_2}$

Olefin metathesis

- 1931: Ethylene and 2-butenes found as products of propene heating at 852 °C
- 1956–1964: $W(CO)_6$ and $Mo(CO)_6$ supported on alumina for olefin metathesis
- 1964: First metal alkylidene complex; Cyclopentene polymerization
- Nobel prize in 2005

Yves Chauvin

1930 - 2015

Robert H. Grubbs

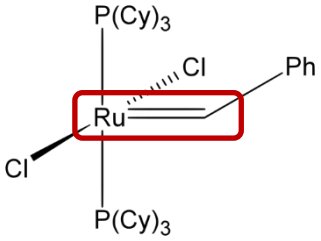
1942 - 2021

Richard R. Schrock

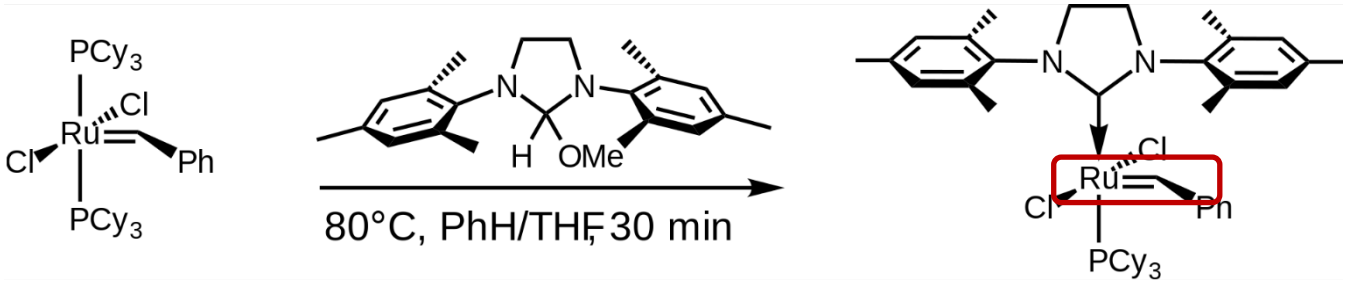
1945 -

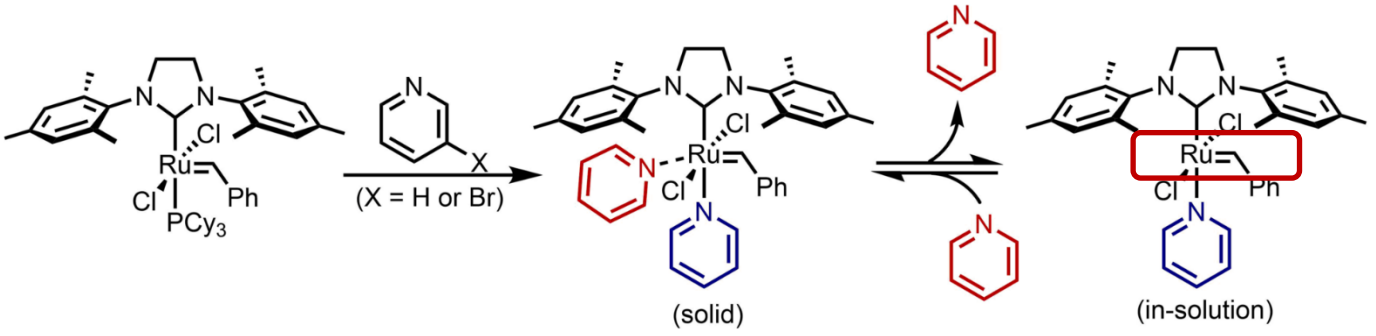
Olefin Metathesis

- Homogeneous catalysts = metal alkylidene complexes
- Grubbs catalysts: Ru based, 1st, 2nd, and 3rd generation



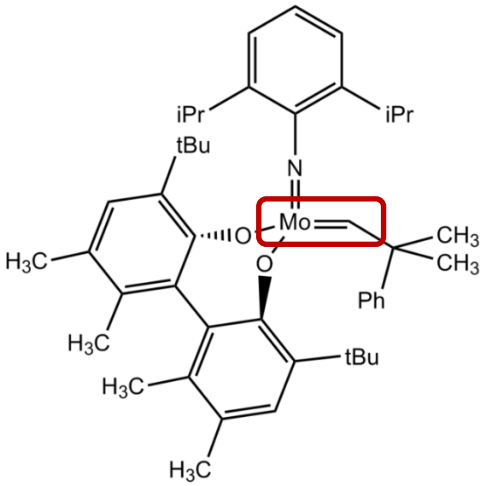
$P(Cy)_3$ = tricyclohexylphosphine

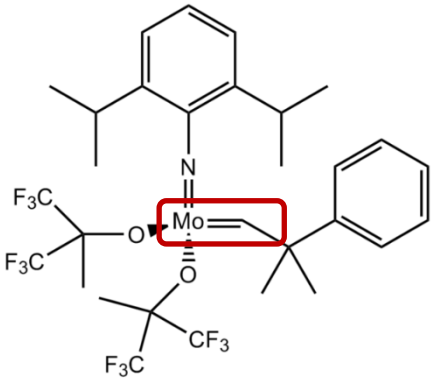


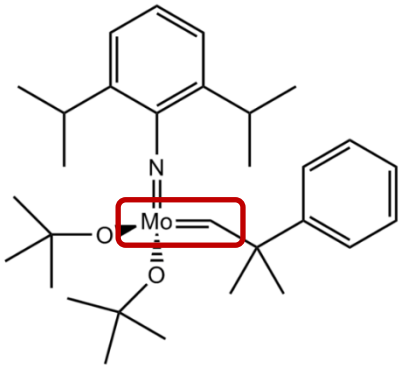


Olefin Metathesis

- Homogeneous catalysts = metal alkylidene complexes
- Schrock catalysts: Mo based

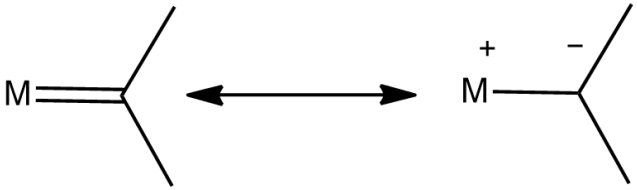




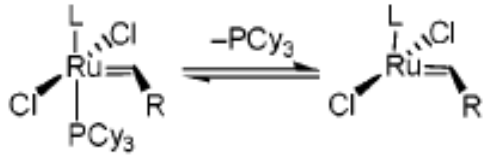


Olefin Metathesis

- Homogeneous catalysts: metal alkylidene complexes
  - Transition metals Ta, W, Mo, Ru
  - α-carbon in metal alkylidene complexes is nucleophilic



  - Bulky ligand (i.e., tricyclohexylphosphine) cannot bind strongly to the metal due to steric reasons
  - Bulky ligand easily leaves and active species is formed (14 e^-)



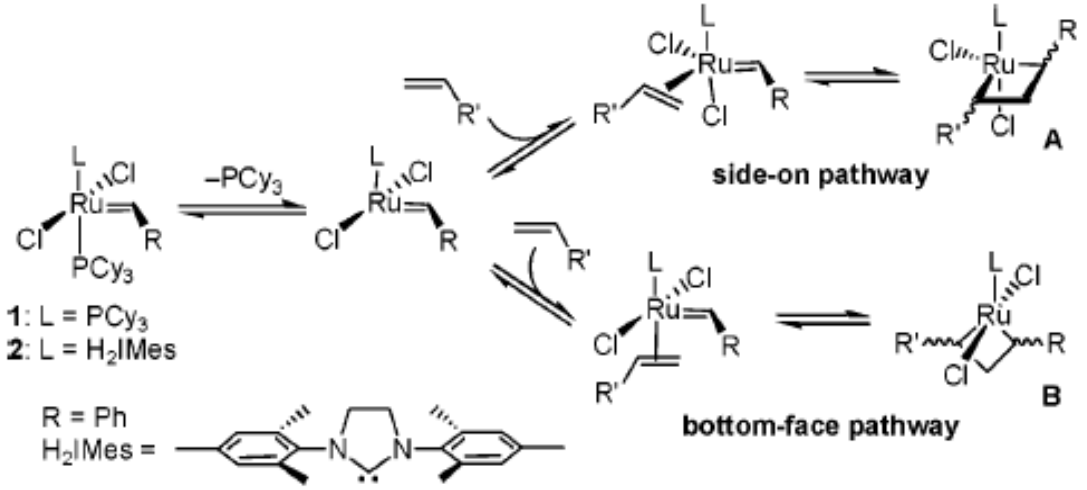
1: L = PCy_3
2: L = H_2IMes

J. AM. CHEM. SOC. 2006, 128, 16048-16049

Olefin Metathesis

- Homogeneous catalysts: metal alkylidene complexes form metallacycles (metallacyclobutane) upon reaction with alkene

Scheme 1. Initial Steps of the Olefin Metathesis Mechanism

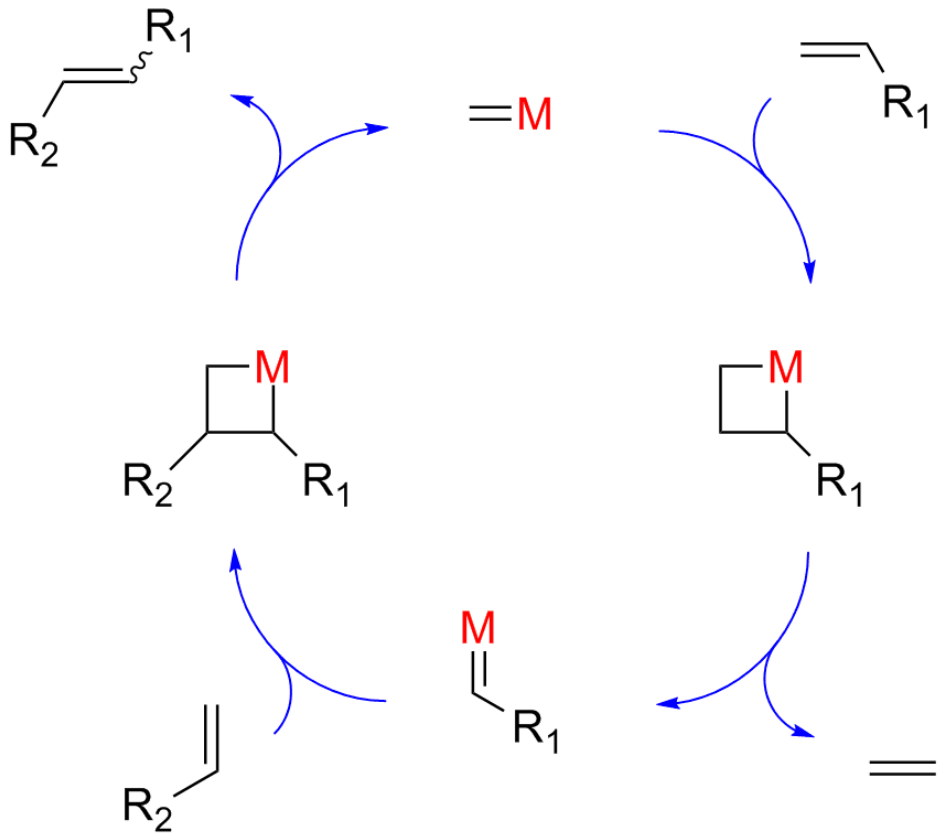


- Metallacyclobutanes isolated for the first time in 2005

J. AM. CHEM. SOC. 2006, 128, 16048-16049

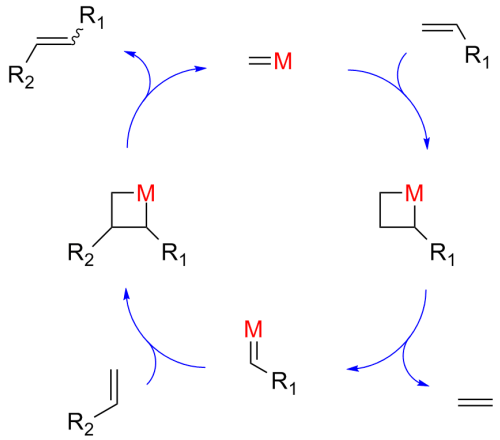
Olefin Metathesis

- Chauvin's mechanism:



Olefin Metathesis

- Chauvin's mechanism:

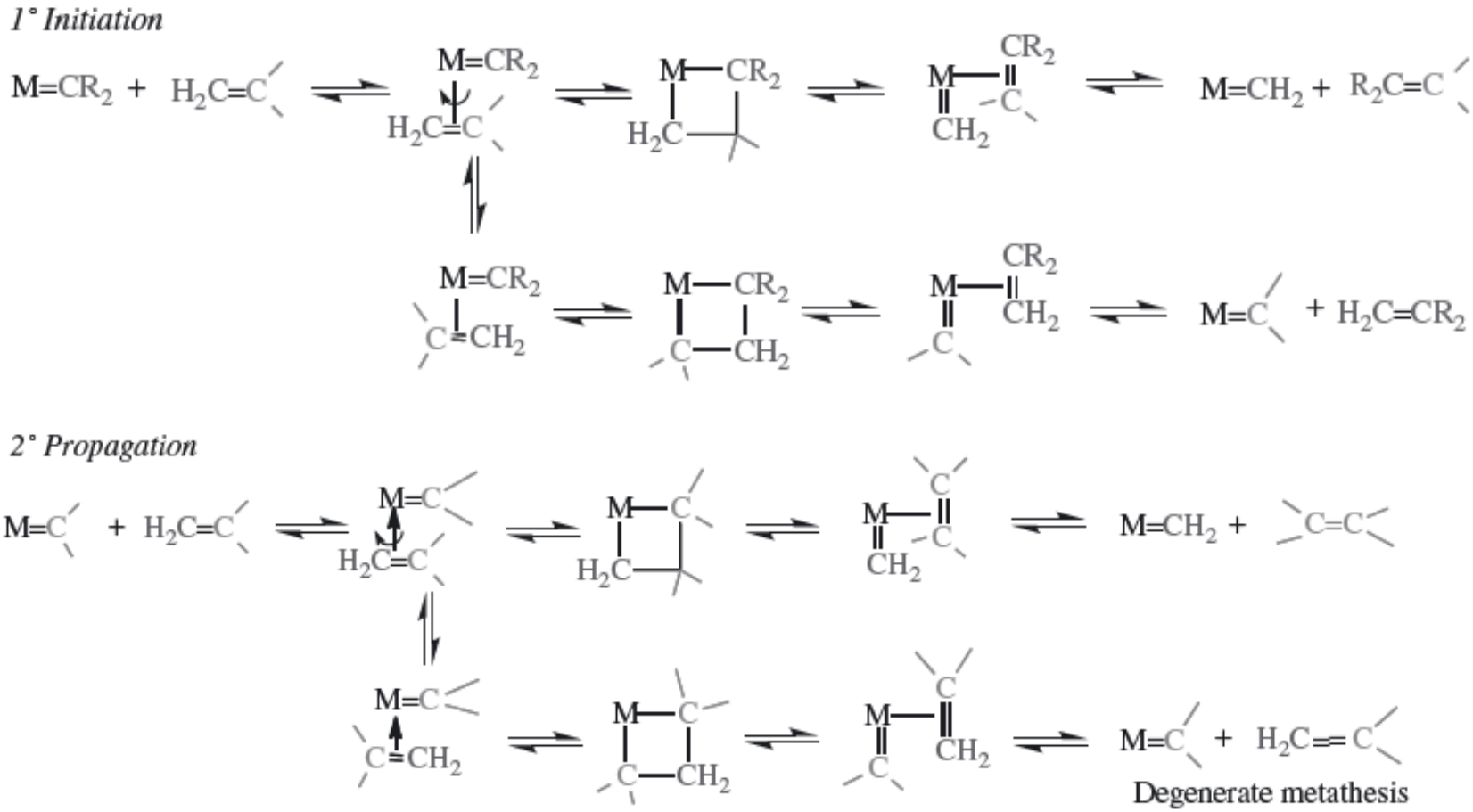


- "Two dancing couples exchanging their partners, but they need the master of ceremony (i.e., the catalyst) for the exchange…

When the Chemistry Nobel prize was announced on October 5, 2005, Chauvin's metathesis mechanism was compared in a video to a dance in which couples exchange partners, which represents the two carbene fragments of the olefin. The dancers cannot exchange their partner directly, but they have to do the exchange by coupling with a master of ceremony that is the metal center. The master of ceremony also has a partner and, with the entering couple they form a circle so that the master of ceremony can exchange partners within the circle by taking a new partner from the couple. Then with his new partner, he can go to another couple for another exchange, and so on (31).

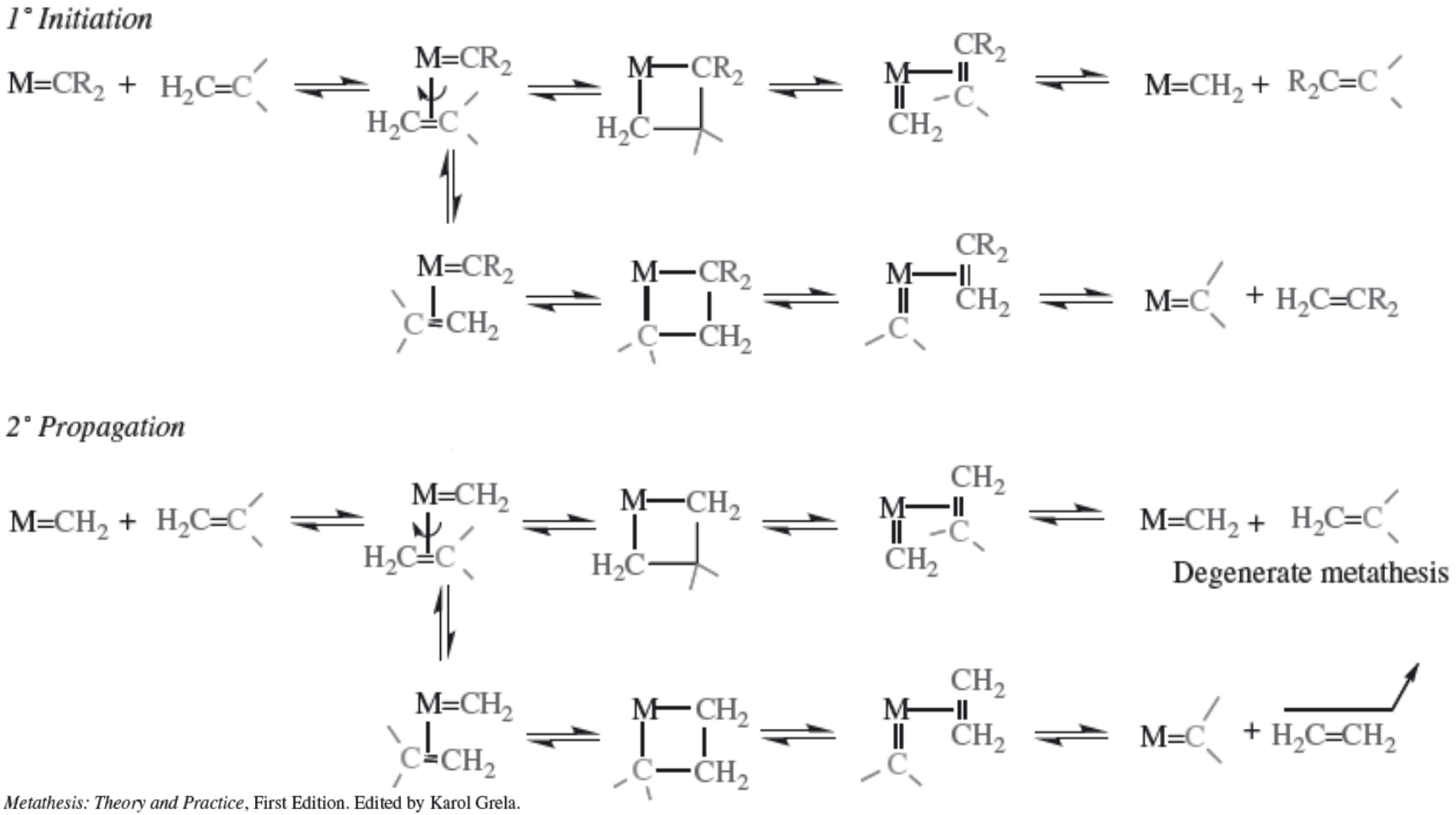
Olefin Metathesis

- Chauvin's mechanism:



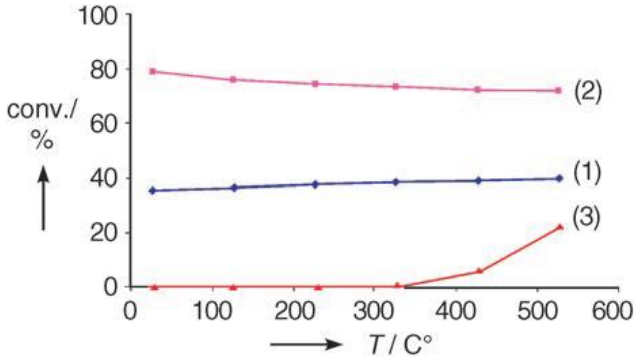
Olefin Metathesis

- Chauvin's mechanism:



Olefin Metathesis

- Reversible, equilibrium reaction
- “Thermoneutral”



1,2 = Metathesis reaction

3 = Alkane dehydrogenation

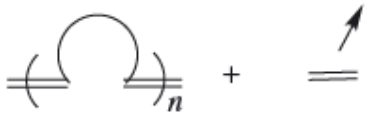
- We need something that will push the reaction towards desired products
  - Ethylene as a gaseous product released
  - Ring strain in cyclic olefins released (i.e., cyclopentene)
  - …

Olefin metathesis

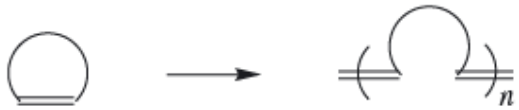
(a) Cross Metathesis (CM)

(b) Ring Closing Metathesis (RCM)

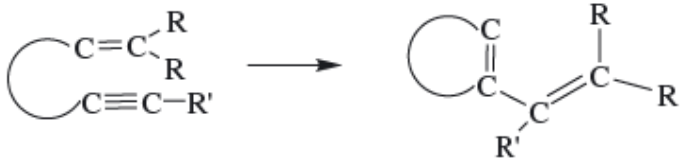
(c) Acyclic Diene Metathesis Polymerization (ADMEP)



(d) Ring Opening Metathesis Polymerization (ROMP)



(e) Enyne Metathesis (EYM)



(f) Ring-Opening Cross Metathesis (ROCM)

OM in industrial processes

- The Phillips triolefin process/Olefins conversion technology
- The Shell higher olefin process
- Ring opening metathesis polymerization: Polynorbornene

J.C. Mol / Journal of Molecular Catalysis A: Chemical 213 (2004) 39–45

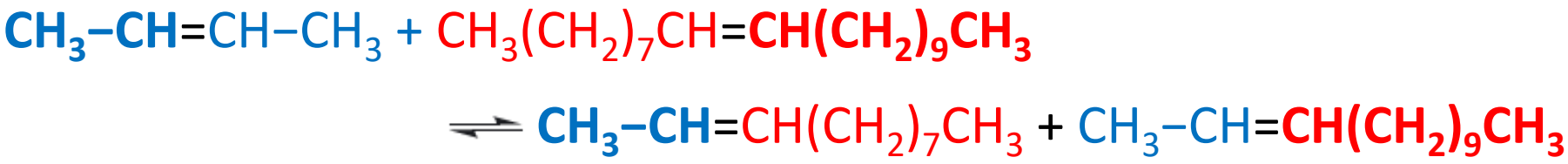
OM in industrial processes

- **The Phillips triolefin process/Olefins conversion technology (OCT)**

- WO_3/SiO_2 OM catalyst, >260 °C, 30–35 bar
- Feedstock = ethylene and butenes, MgO isomerization catalyst
- Ethylene can be used as a sole feedstock (first partial dimerization to butenes over Ni-based catalyst)
- Millions of tons per year

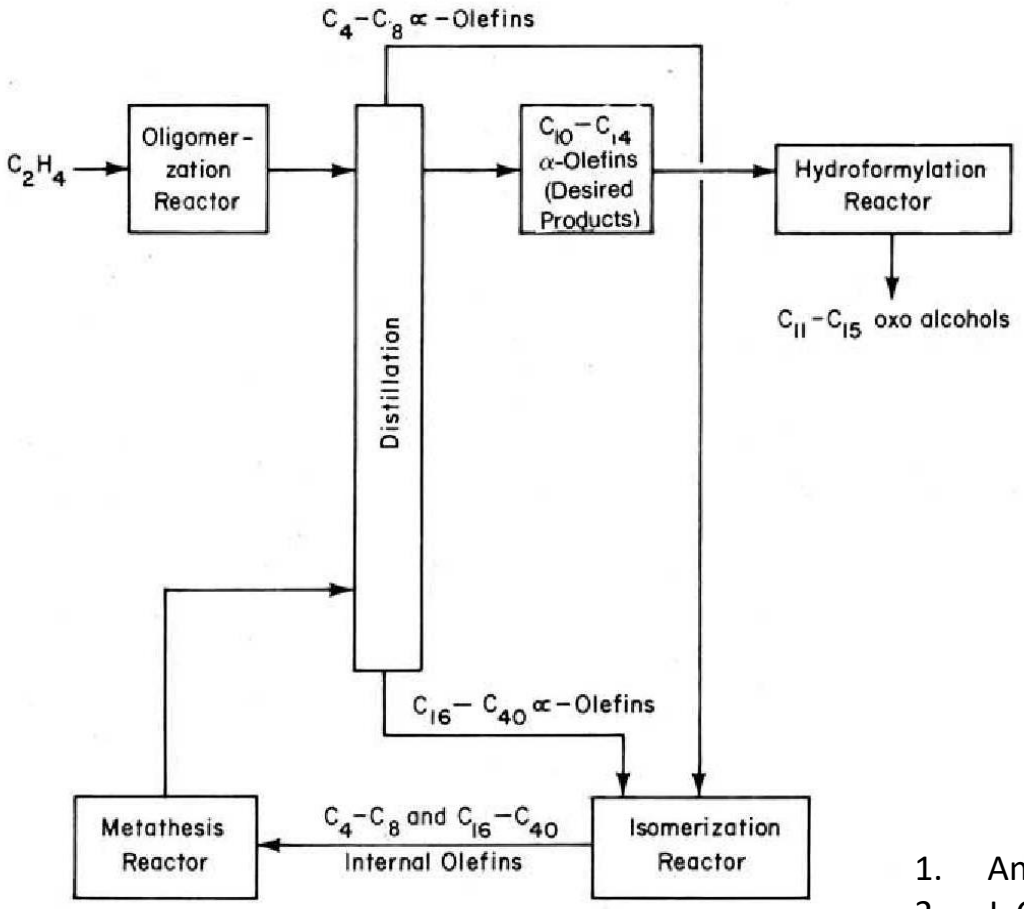
OM in industrial processes

- **The Shell higher olefin process (SHOP)**
- C11−C14 alkenes desired = detergent precursors
- Production of higher olefins from ethylene in three steps
  - Ethylene oligomerization over Ni-based catalyst (C4−C40, even-numbered 1-olefins) and distillation to three fractions: <C6; C6−C18; >C18
  - <C6 and >C18 fractions mixed and isomerized (1-olefins useless!)
  - MoO_3/Al_2O_3 OM, 100−125 °C, 10 bar = statistical distribution of alkenes (both odd and even-numbered), 10−15 % of desired fraction
  - 1 500 000 tons per year



OM in industrial processes

- **The Shell higher olefin process (SHOP)**

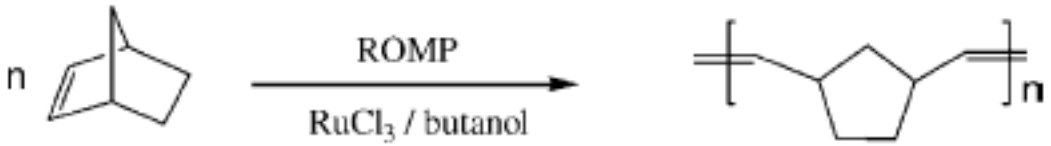


1. Oligomerization
2. Isomerization
3. Metathesis

1. Angew. Chem. Int. Ed. 2013, 52, 12492 – 12496
2. J. Chem. Ed., Volume 65 Number 7 July 1988

OM in industrial processes

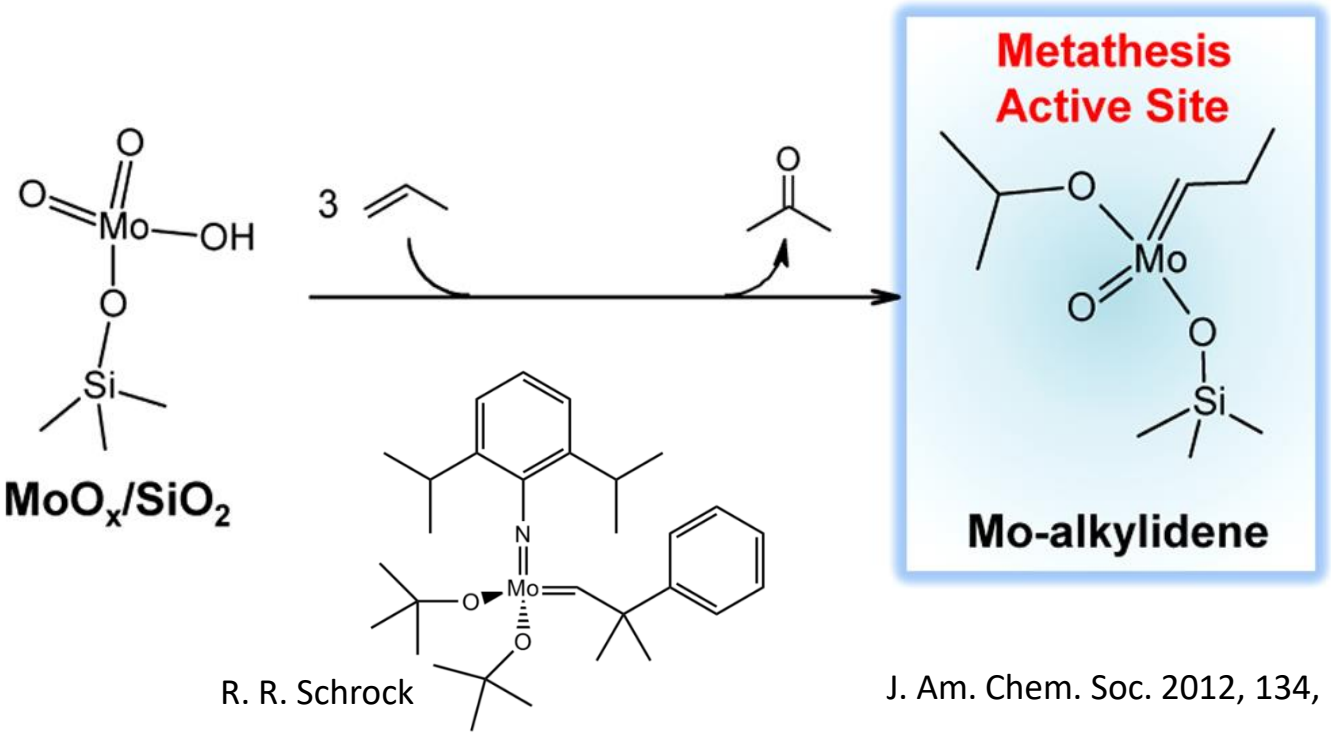
- **Ring opening metathesis polymerization: Polynorbornene**



- First commercial metathesis polymer (1976)
- Performed in **air**
- Norsorex®
- Elastomer used in oil spill recovery, sound barrier,…

Induction period

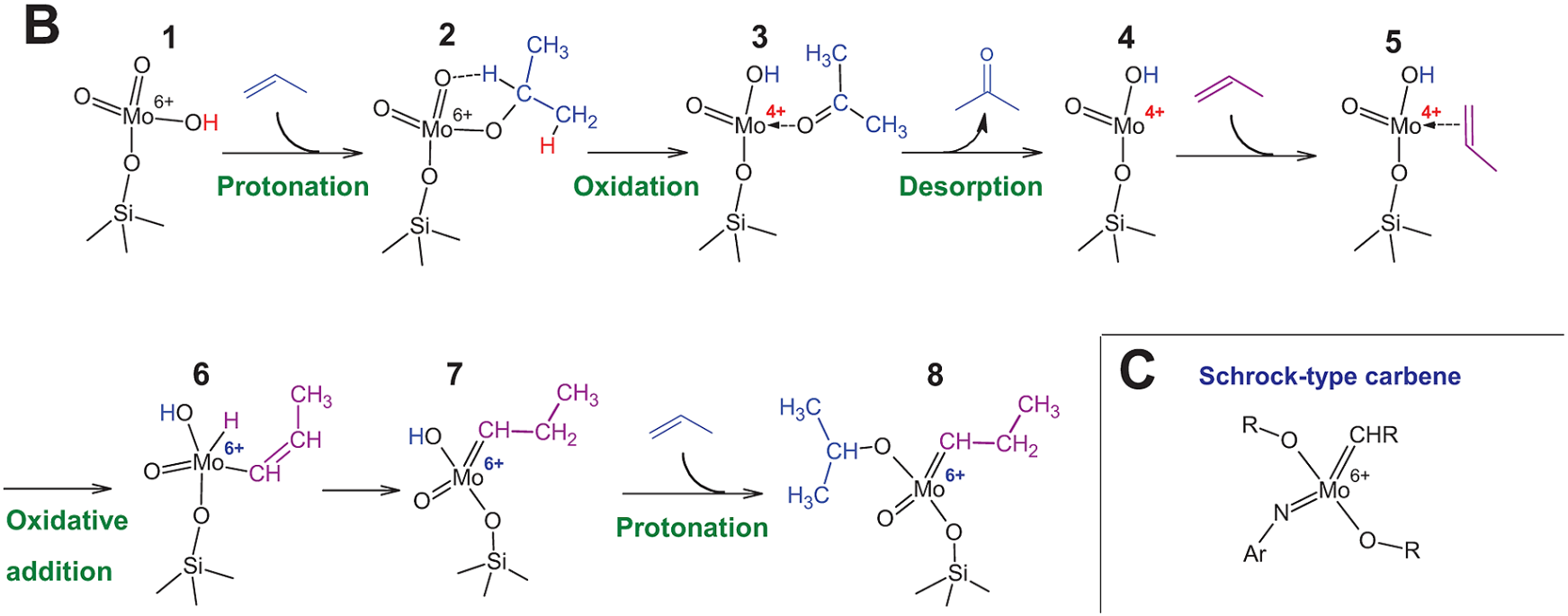
- Heterogeneous catalysts = metals (Mo, W) supported on silica, alumina, silica-alumina in their oxidized form
- Only **~1–2 %** of all Mo, W, Re atoms form active sites
- Metal alkylidene species have to be created first



J. Am. Chem. Soc. 2012, 134, 11462−11473

Induction period

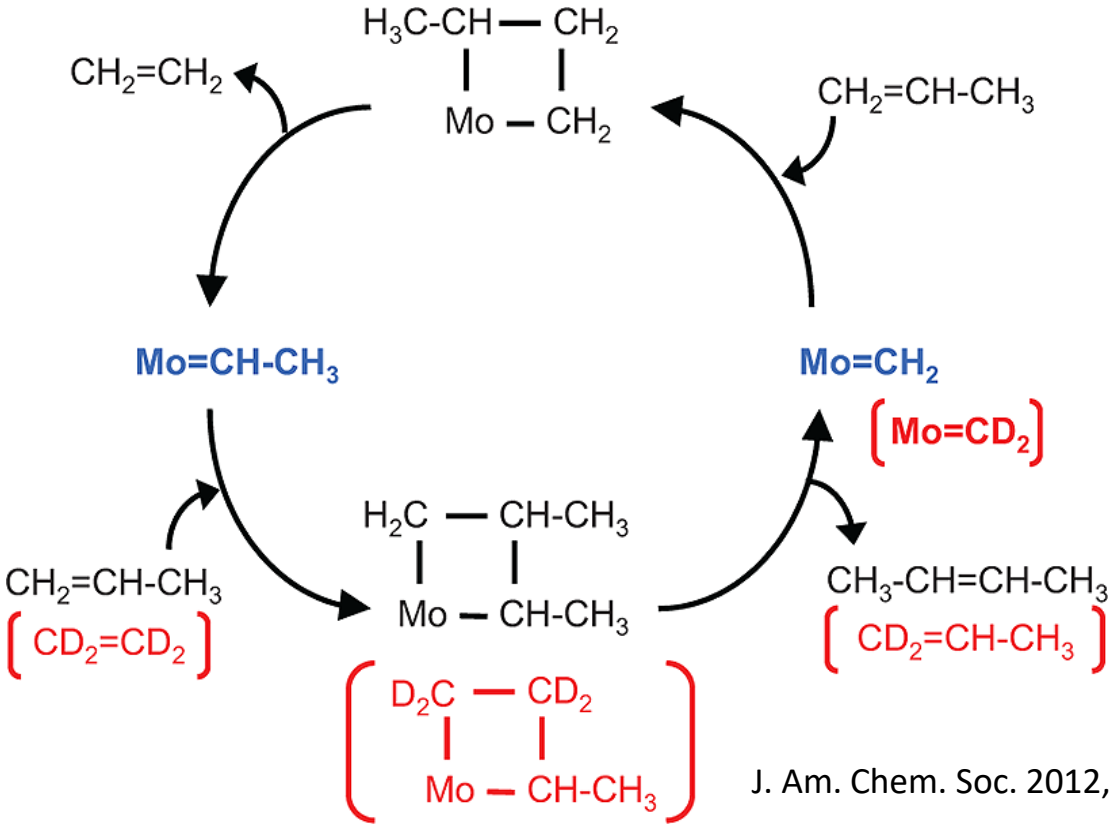
- Heterogeneous catalysts = metals (Mo, W) supported on silica, alumina, silica-alumina in their oxidized form
- Only **~1–2 %** of all Mo, W, Re atoms form active sites
- Metal alkylidene species have to be created first



J. Am. Chem. Soc. 2012, 134, 11462−11473

Induction period

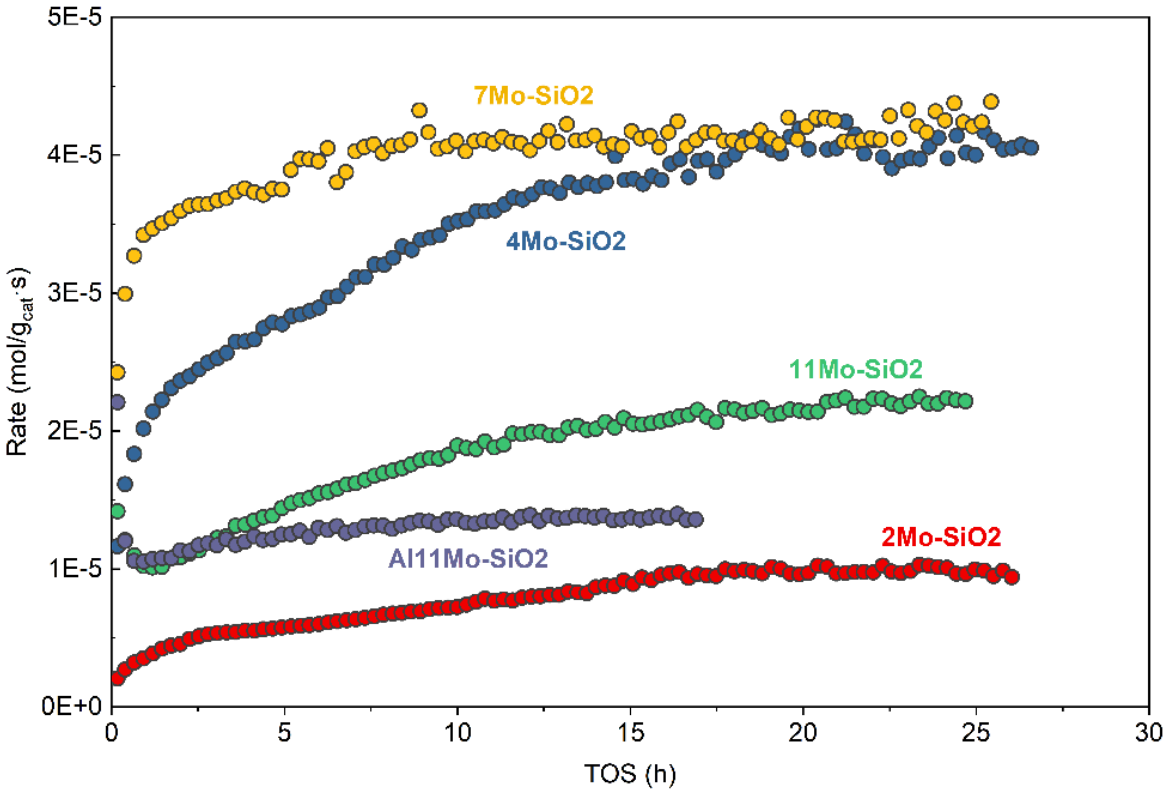
- Heterogeneous catalysts = metals (Mo, W) supported on silica, alumina, silica-alumina in their oxidized form
- Only **~1–2 %** of all Mo, W, Re atoms form active sites

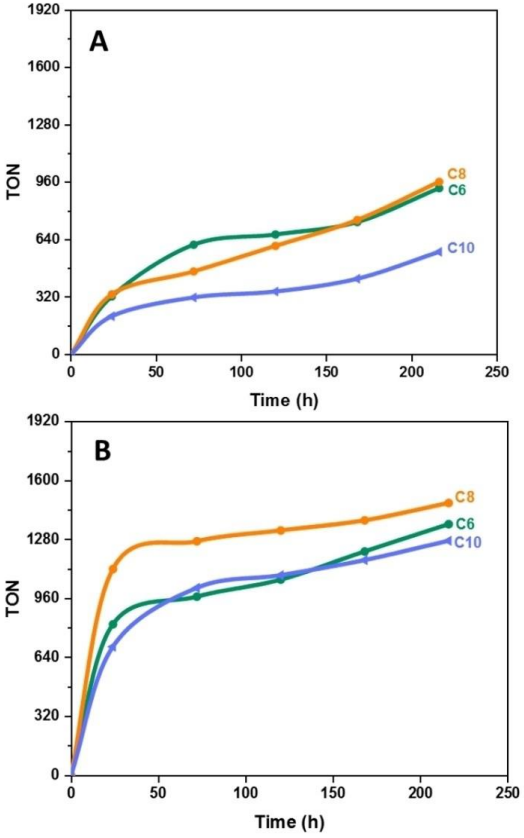


J. Am. Chem. Soc. 2012, 134, 11462−11473

Induction period

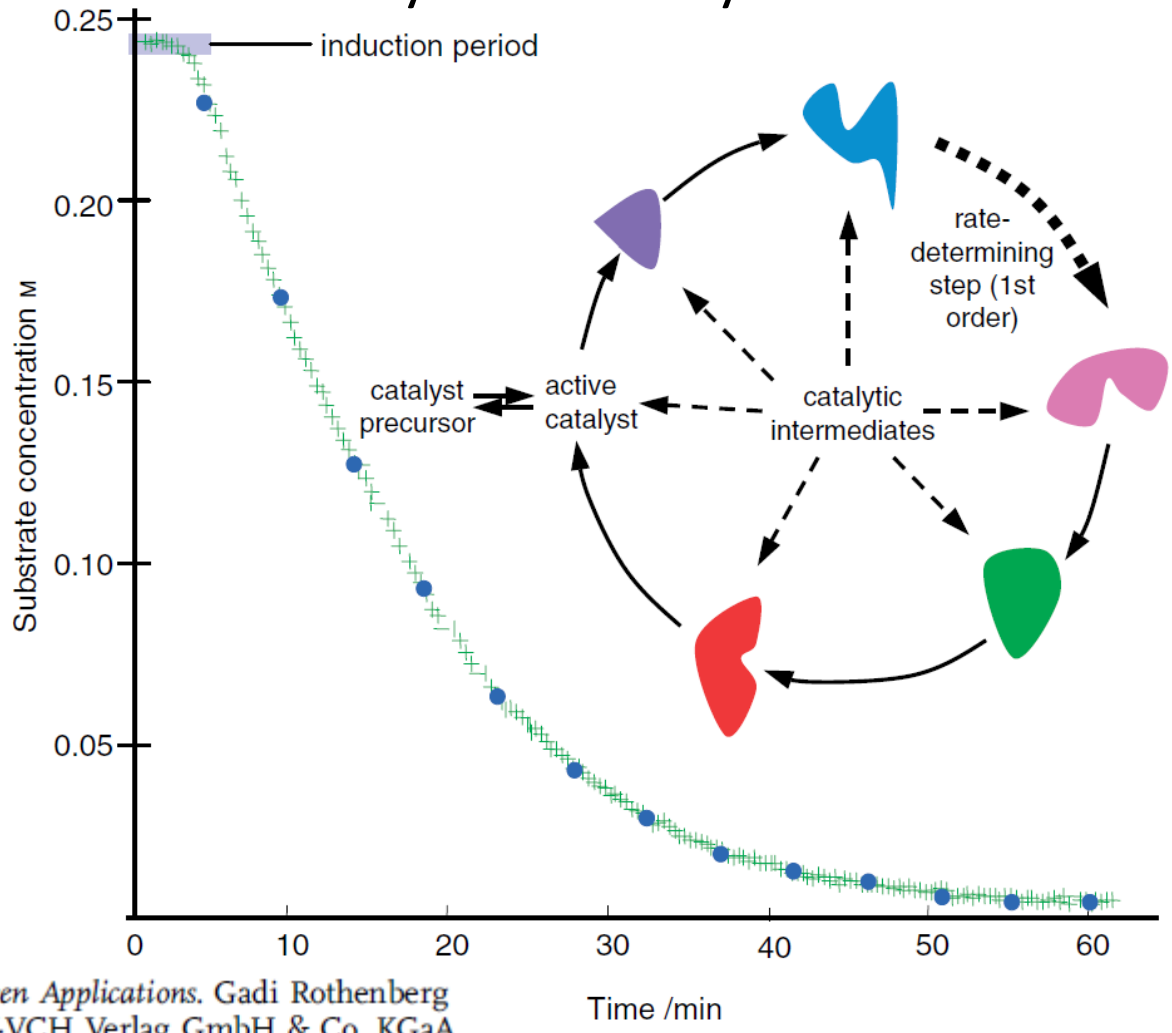
- Heterogeneous catalysts = metals (Mo, W) supported on silica, alumina, silica-alumina in their oxidized form
- Metal alkylidene species have to be created first





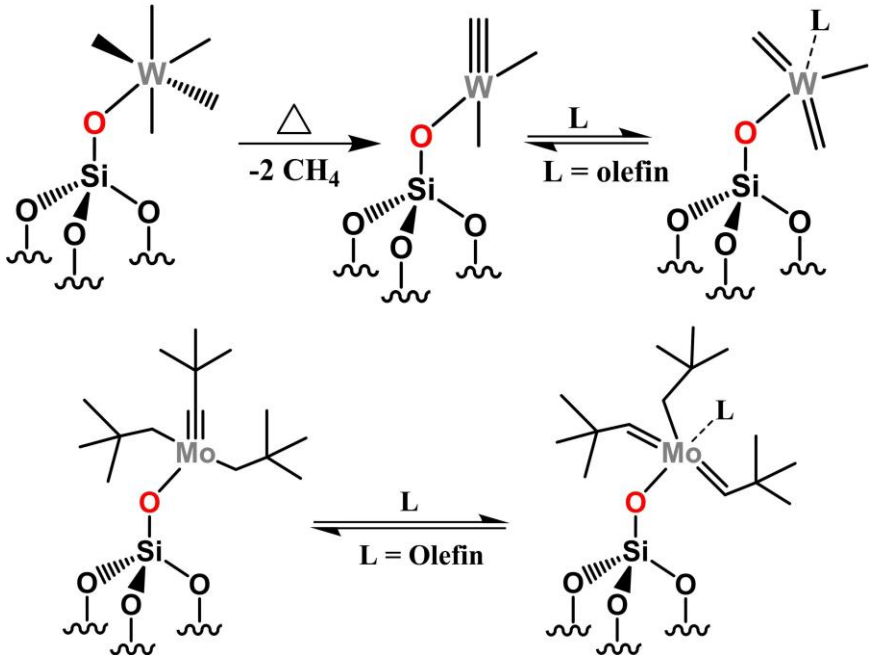
Active sites@Lecture 1

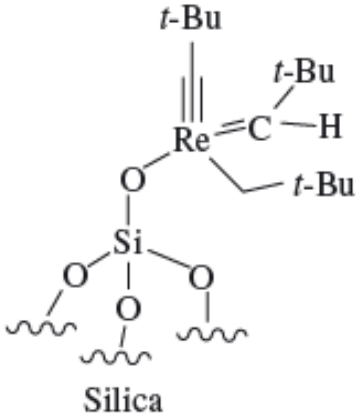
- Active sites are often dynamic: They has to be created first!



Supported metal alkylidene species

- Heterogeneous catalysts = metals (Mo, W) supported on silica, alumina, silica-alumina in their oxidized form
- Metal alkylidene species have to be created first OR
- **Metal alkylidene single site catalysts**

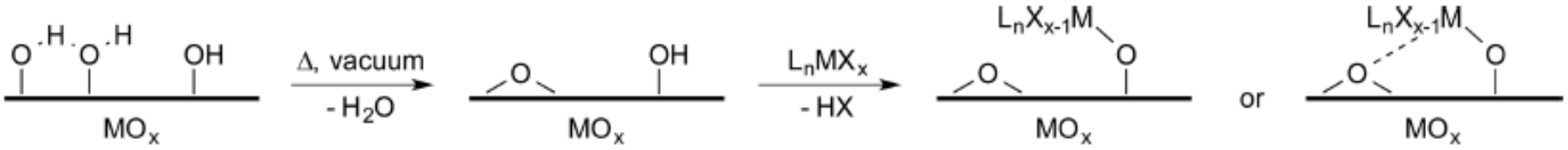




Basset, Copéret@Lecture 4: Single site catalysts
1. Angew. Chem. Int. Ed. 2006, 45, 6082 – 6085
2. ChemCatChem 2020, *12*, 6067–6075

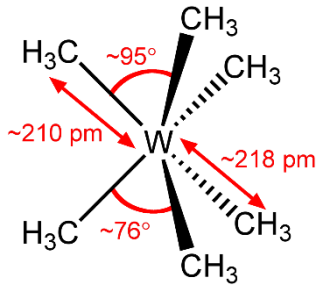
Single site catalyst@Lecture 4

- Grafting on silica



  - Detailed knowledge of surface (number of OH groups per nm^2)
  - Rigorous water- and oxygen-free environment

L_nMX_x =



DOI: 10.1021/acs.chemrev.5b00373
Chem. Rev. 2016, 116, 323–421