Student Corner

# Metathesis and Polymerization of Olefins

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Metathesis of simple salts is a double replacement reaction as shown below.

$$AX + BY \rightarrow AY + BX$$

In Greek, "Metathesis" is known as the change of position or transposition. **Olefin metathesis** (OM) is the catalytic **scission** and **regeneration** of C=C bonds as shown in Figure 1. This is a **reversible** process and the reverse reaction is called "**cross metathesis**" of olefins.

$$2 \begin{array}{c} CH_2 \\ \parallel \\ CHR^1 \end{array} \longleftrightarrow \begin{bmatrix} H_2C - CH_2 \\ R^1HC - CHR^1 \end{bmatrix} \rightleftharpoons \begin{array}{c} H_2C = CH_2 \\ + \\ R^1CH = CHR^1 \end{array}$$



Ethene is a volatile molecule, thus, metathesis of a

terminal olefin  $R^1CH=CH_2$  produces a quantitative amount of  $R^1CH=CHR^1$ . Using this procedure tetrasubstituted alkenes such as  $R_2C=CR_2$  are obtained in good yields.



Figure 2: Synthesis of tetra-substituted alkenes

#### Catalysts for olefin metathesis

Olefin metathesis is normally catalyzed by homogeneous catalysts. Homogeneous catalysis refers to reactions

where the catalyst and the reactants are present in the same phase. Metal carbene or alkylidene complexes with the M=CR<sub>2</sub> moiety are used as catalysts.

The well-known metathesis catalysts are  $[{Me(CF_3)_2CO}_2Mo=CHCMe_2Ph)(=NAr)]$  (1) (Schrock),  $[(PCY_3)_2Cl_2Ru(=CHCH=CPh_2)]$  (2) (Grubbs),  $[(PCY_3)_2Cl_2Ru(=CHPh)]$  (3) (Grubbs-1),  $[(PCY_3)(L)Cl_2Ru(=CHPh)]$  (4) (Grubbs-2), (L = NitrogenHeteroCarbene). Richard R. Schrock, Robert H. Grubbs and Yves Chauvin shared the Nobel Prize in 2005 for their extensive work on olefin metathesis and polymerization.



 $(\text{Mes} = \text{mesityl} = -C_6H_2 - 2,4,6-Me_3)$ 

Schrock catalyst (1) has shown high efficiency towards OM but it is extremely unstable in air or in water. The efficiency of Grubbs-1 catalyst (3) is low but it is stable in air and in aqueous media. The Grubbs-2 catalyst (4) has shown increased reactivity, recyclability and stereospecificity. Grubbs catalysts tolerate a wide variety of functional groups.

## Synthesis of Grubbs catalysts

The syntheses of Grubbs catalysts are quite easy from  $[RuCl_2(PPh_3)_4]$  (5) as shown in scheme 1.



Scheme 1: Syntheses of Grubbs catalysts

## Mechanism for cross metathesis

OM was discovered by Robert L. Banks in 1964. He reported the disproportionation of propylene to ethylene and butenes using  $[Mo(CO)_6]$  supported on alumina. It is an interesting process because there is no equivalent reaction in traditional organic chemistry. The mechanism for the following cross metathesis reaction using the Grubbs catalyst (3) is given in scheme 2.

## $R^{1}CH=CH_{2} + R^{2}CH=CH_{2} \longrightarrow R^{1}CH=CHR^{2} + CH_{2}=CH_{2}$

The complex  $[(PCY_3)_2Cl_2Ru(=CHPh)]$  (3) is an 16e-complex, it loses one PCY\_3 ligand to give the reactive intermediate with 14e. One of the olefins joins on to this 14e-complex forming a "ruthenocyclobutane ring" which can generate Ru=CH<sub>2</sub> or Ru=CHR<sup>1</sup> or Ru=CHR<sup>2</sup> moieties as shown in scheme 2. Other ligands on Ru are not drawn for clarity.



Scheme 2: Mechanism for cross metathesis

The steps (**a**) and (**c**) involve the formation of the "metallocyclobutane" between  $\text{Ru}=\text{CH}_2 \otimes \text{R}^1\text{CH}=\text{CH}_2$ and  $\text{Ru}=\text{CHR}^1 \otimes \text{R}^2\text{CH}=\text{CH}_2$ , respectively. In step (**b**), ethene is released giving  $\text{Ru}=\text{CHR}^1$ . The step (**d**) produces  $\text{R}^1\text{CH}=\text{CHR}^2$  while generating the active catalyst  $\text{Ru}=\text{CH}_2$ . This is a random process and this mechanism is known as "**Chauvin Mechanism**".

# Types of olefin metathesis reactions

Olefin metathesis can be categorized as (i) **cross** (ii) **ring opening**, and (iii) **ring closing** metathesis reactions. All these reactions proceed *via* a **metallacyclobutane** intermediate.

## **Cross metathesis reactions**

We have already looked at cross metathesis reactions involving terminal olefins. Metathesis of two symmetrical olefins, R<sup>1</sup>CH=CHR<sup>1</sup> and R<sup>2</sup>CH=CHR<sup>2</sup> gives a single product R<sup>1</sup>CH=CHR<sup>2</sup> and vice versa. Metathesis of R<sup>1</sup>R<sup>2</sup>C=CR<sup>1</sup>R<sup>2</sup> with CH<sub>2</sub>=CH<sub>2</sub> gives a single product R<sup>1</sup>R<sup>2</sup>C=CH<sub>2</sub>. Internal olefins (R<sup>1</sup>CH=CHR<sup>2</sup>) appear to undergo metathesis much faster than terminal ones (R<sup>1</sup>CH=CH<sub>2</sub>).

#### Ring opening metathesis (ROM) reaction

In this case, a cyclic olefin is opened up in the presence of a carbene catalyst to form a polymer, which is called ring opening metathesis polymerization (ROMP).



Scheme 3: ROMP of cyclopentene

The mechanism of the above reaction is shown in scheme 4. During step (**a**), the metallacyclobutane ring is formed. During step (**b**), the ring is opened up to give a metal carbene with a terminal olefin group. The resulting metal carbene continues to react with cyclopentene molecules leading to a polymer.



**Scheme 4:** Mechanism for ROMP, coligands on the metal M are not drawn for clarity

Poly(norbornene) is produced by ROMP of norbornene (scheme 5).



Scheme 5: ROMP of norbornene

#### **Ring closing metathesis reactions**

In a ring closing metathesis (RCM) reaction, a **terminal diene** is converted into a carbocycle and an ethylene molecule is formed as a byproduct (scheme 6).

$$(CH_2)_n \xrightarrow{L_nM=CH_2} (CH_2)_n + CH_2=CH_2$$

Scheme 6: Carbocycles from diolefins

Some examples of RCM are shown in scheme 7.



Scheme 7: Examples for RCM

#### Olefin polymerization with other catalysts

Polyethylene (PE) and polypropylene (PP) are usually prepared using other catalysts. The Ziegler-Natta

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catalytic system {TiCl<sub>3</sub> or TiCl<sub>4</sub> with methylaluminoxane (MeAlO)<sub>n</sub>, AlEt<sub>3</sub> or AlEt<sub>2</sub>Cl} was discovered in late 1950s and it operates under mild conditions (at 25 °C and ethene pressure of 1 atm). Ziegler and Natta won the Nobel Prize in 1963 for the discovery of this catalytic system. The active catalyst is formed *in situ* and it could be an intermediate [L<sub>n</sub>Ti=CH<sub>2</sub>], [L<sub>n</sub>Ti=CHR] or [L<sub>n</sub>TiR]<sup>+</sup> as shown below.

$$L_n TiX_2 \xrightarrow{AlMe_3} L_n Ti \xrightarrow{Me} \xrightarrow{-CH_4} L_n Ti=CH_2$$
  
Me  $\alpha$ -H abstraction

**Scheme 8:** Formation of [L<sub>n</sub>Ti=CH<sub>2</sub>] from [L<sub>n</sub>TiMe<sub>2</sub>]

In the presence of  $(MeAlO)_n$ , metallocene dihalides  $(e.g., Cp_2MCl_2, M = Ti, Zr \text{ or } Hf)$  generate highly active homogenous catalysts for the polymerization of simple olefins. They are much better catalysts than Ziegler–Natta catalysts. The active catalyst is believed to be the cationic intermediate  $[Cp_2MR]^+$  with one alkyl group and a vacant site. Coordination of ethene followed by migration of the R group on to ethene (1,2-insertion) generates  $[Cp_2MCH_2CH_2R]^+$  ion. Propagation and polymerization steps are shown in scheme 9.



**Scheme 9:** Polymerization of ethene using the active catalyst [Cp<sub>2</sub>MR]<sup>+</sup>

The step (**a**) refers to coordination of ethene to the vacant site and the step (**b**) refers to 1,2-insertion of ethene into M-alkyl bond.

## Problems





2. What is the major product/s formed due to metathesis of

3. Write the mechanism for the polymerization of prop-1-ene using Cp<sub>2</sub>ZrCl<sub>2</sub> and (MeAlO)<sub>n</sub>.