Olefin Metathesis and Oligomerization

- Definitions
- Carbene Complexes
- Polymers by homogeneously catalyzed metathesis (ROMP)
  - Polyoctenamer Vestenamer®
  - Polynorbornene Norsorex®
  - Polydicyclopentadiene Telene®, Metton®
- Industrial reactions with olefin that involve metathesis:
  - The Phillips triolefin process / OCT process
  - Neohexene (and related) processes
  - The Shell Higher Olefin Process (SHOP)
  - Examples of industrial products

Sources:
Definitions:

– Metathesis ("olefin disproportionation"): 

\[
2 \quad \rightleftharpoons \quad \text{H}_2\text{C} = \text{C} \quad \text{H}_2\text{C} = \text{CH}_2 \quad + \quad \text{ }
\]

All metathetic reactions are thermoneutral \(\rightarrow\) equilibrium

However, the reaction can be driven to completion if one volatile component (e.g., ethene) is removed from equilibrium.

– Cross Metathesis:

\[
\text{H}_2\text{C} = \text{CH}_2 \quad + \quad \text{ }
\quad \rightleftharpoons \quad 2 \quad \text{ }
\]

– ROMP (Ring Opening Metathesis Polymerization):

\[
\text{n} \quad \rightleftharpoons \quad (\text{CH} - \text{(CH}_2)_6 \text{CH})_n
\]

– ADMET (Acyclic Diene METathesis Polymerization):

\[
\text{n} \quad \rightarrow \quad (\text{ })_n \quad + \quad (n - 1) \quad \text{C}_2\text{H}_4
\]
Historically, metal carbene complexes have been classified into two classes:

**Schrock "alkyldenenes"**

[MoCl₂(O)(CR₂)]:

![Schrock alkylidene structure](image)

The Schrock-type carbene complexes contain an early transition metal in a formal high oxidation state (often in the d⁰ electron configuration) stabilized by strong π-donor ligands.

Generally, the carbene ligand is not stabilized by the presence of heteroatoms and is regarded as negatively charged (alkylidene). Accordingly, most Schrock alkylidens are nucleophilic.

Most of these complexes have an electron count below 18 and are, thus, coordinatively unsaturated. Therefore, nucleophilic attack involving the metal is possible because of the electron deficiency.
Fischer "carbenes"

[Mo(=C(OMe)Ph)(CO)₅]:

The Fischer-type carbene complexes are low-valent complexes stabilized by strong π-accepting ligands (often CO).

One or two heteroatoms (O, N, or S) are bonded to the carbene carbon atom and stabilize it by delocalizing the positive formal charge. The carbene is formally regarded as a neutral ligand. Accordingly, Fischer carbenes are relatively inert, but tend to react as electrophiles.

In general, Fischer carbenes are 18 e⁻, coordinatively saturated complexes. Therefore, nucleophilic attack at the metal is not possible in general (unless ligand dissociation is induced thermally, photochemically, or chemically, see page 70).
π-Bonding in M=CR₂ Complexes

The effect of the decreasing energy of the $d$-orbitals on going from early to late $d$-metals:

The M=C bond is covalent (like in ethylene)

A C→M dative $\sigma$ bond and a M→C retrodative $\pi$ bond (like in carbonyl complexes)

The localization of the LUMO changes from left to right of the periodic table. Effect on the reactivity?
Electronic Structure and Reactivity

The reactions of π-bonded ligands (like those of C=C and C=O) are **frontier-orbital controlled** (NOT charge-controlled!):

- **A**
  - [MoCl₂(O)(CH₂)]
  - Schrock:
    - nucleophilic alkylidene ligand.
    - Early transition metal, coordinatively unsaturated complex: nucleophilic attack at the metal is possible

- **B**
  - [RuCl₂(=C(H)Ph)(PR₃)₂]
  - the carbene is neither a good electrophile nor a good nucleophile, apolar mechanisms are favored, like in metathesis, provided that the complex is coord. unsaturated

- **C**
  - Rh / Cu:
    - the carbene ligand is strongly electrophilic: it attacks olefins and gives insertion into C–H bonds
Carbene Complexes and Olefin Metathesis

In principle, 3 different reactions are possible:

(a) Olefin Metathesis / (b) Olefin Cyclopropanation / (c) Insertion into C–H-Bonds (or N–H, O–H)
A General Mechanism

attack at the metal (2+2)

\[ L_nM = CHR^1 \]

attack at the carbone (2+1)

\[ R^2 \]

\[ H \]

\[ M = CHR^1 \]

metallacyle

reductive elimination

\[ L_nM = CHR^2 \]

\[ R^2 \]

\[ H \]

\[ M = CHR^1 \]

\[ R^2 \]

\[ H \]

\[ ML_{n-1} \]

the carbene ligand is lost

\[ R_1H_2C \]

\[ R^2 \]

\[ C \]

\[ H \]

\[ C \]

\[ H \]

\[ R^2 \]

\[ R^2 \]
Reactivity

Originally, the Fischer / Schrock classification was based on reactivity, with the Schrock alkylidenes being nucleophilic and the Fischer carbenes being electrophilic. However, these differences are not very pronounced, because the carbene C atom bears a small charge both in Fischer- and in Schrock-type carbenes as discussed above. Therefore, the preference for attack at M or C is similar, and other effects play a role, too. In particular, the electron count at the metal influences the kind of reactivity observed.

As an example of the importance of the electron count, we mention here that Fischer-type carbene complexes do not normally initiate the chain metathesis of olefins, since they are both coordinatively and electronically saturated (18-electron complexes). However, they can sometimes be activated for metathesis by heating, or by reaction with a co-catalyst, or photochemically:

<table>
<thead>
<tr>
<th>Complex</th>
<th>Activator</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CO)$_2$Mo=C(OPh)NBu$_4^+$</td>
<td>MeAlCl$_2$</td>
<td>PrCH=CH$_2$</td>
</tr>
<tr>
<td>(CO)$_2$W=C(OEt)Et</td>
<td>Bu$_4$NCl</td>
<td>PrCH=CH$_2$</td>
</tr>
<tr>
<td>(CO)$_2$W=C(OEt)Bu</td>
<td>TiCl$_4$</td>
<td>Cyclopentene</td>
</tr>
<tr>
<td>(CO)$_2$W=CPh$_2^b$</td>
<td>Heat (38°C)</td>
<td>cis-Cycloalkenes</td>
</tr>
<tr>
<td>(CO)$_2$W=C(OMe)Ph</td>
<td>21-25°C</td>
<td>EtCH=CHMe</td>
</tr>
<tr>
<td></td>
<td>Heat (50°C)</td>
<td>Cyclobutene,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>norbornene</td>
</tr>
<tr>
<td></td>
<td>Heat (40°C)</td>
<td>RC=CR</td>
</tr>
<tr>
<td></td>
<td>PhC≡CH</td>
<td>Cyclopentene</td>
</tr>
<tr>
<td></td>
<td>$hv$</td>
<td>Cycloocta-1,5-diene</td>
</tr>
<tr>
<td></td>
<td>Halides</td>
<td>PrCH=CH$_2$</td>
</tr>
</tbody>
</table>


Eventually, with the development of different classes of carbene complexes, in particular Grubb's catalyst (see below) and the Arduengo / Herrmann carbene ligands (not discussed), the Fischer / Schrock distinction has lost some of its usefulness.
Grubbs’ Catalyst: \([\text{RuCl}_2(\equiv \text{CHR})(\text{PR’})_3]\)

Meets the conditions for metathesis: attack at the metal, no reductive elimination.

→ A significant part of the LUMO is localized on Ru (not Fischer, middle transition metal).

→ Neutral: C is less electrophilic than a rhodium or copper carbene complex.

→ Coordinatively unsaturated (16 electrons, but the active species has only 14 e. Formulation of the metallacycle is preferred over elimination, which would give a 12-e complex:

Grubbs’ complex gives metathesis because ruthenium needs at least 4 ligands (14 electron count).

Metathesis in Industry

General Considerations

– Discovered in the 1950's, taken up by many petrochemical companies as opportunity to manipulate their olefin streams arising from primary processes such as naphtha cracking and Fischer-Tropsch conversion of syngas.

– Numerous processes developed over the last 50 years, but few large-scale processes commercialized to date.

– Improvements in the technology and the targeting of smaller volume, higher value products have ensured the continuation of active metathesis research.

– Metathesis polymerization processes are unlikely ever to rival the massive polyethylene and polypropylene industries. However, smaller scale but higher value ROMP products find application in niche markets such as the motor and sporting goods industries due to their unique properties.

In recent years, the development of highly selective homogeneous catalysts has prompted extensive studies towards fine chemicals and pharmaceutical manufacture.
### Heterogeneously Catalyzed Metathesis

<table>
<thead>
<tr>
<th>Process</th>
<th>feeds</th>
<th>products</th>
<th>catalyst / cond.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phillips Triolefin Process (1966-1972)</td>
<td>propene</td>
<td>ethene (15 kt/a) + 2-butene (30 kt/a)</td>
<td>WO₃/SiO₂, 400 °C</td>
</tr>
<tr>
<td>OCT (ethene + 2-butene) (since 1985)</td>
<td>ethene + 2-butene</td>
<td>propene (ca. 800 kt/a)</td>
<td>WO₃/SiO₂, 350 – 400 °C, 20 bar</td>
</tr>
<tr>
<td>Phillips Neohexene Process (since 1980)</td>
<td>diisobutene + ethene</td>
<td>neohexene (1.4 kt/a) (isobutene recycled)</td>
<td>WO₃ / MgO / SiO₂, 370 °C, 30 bar</td>
</tr>
</tbody>
</table>
Heterogeneous Catalysts for Olefin Metathesis:
The Production of Light Olefins
One of the more difficult type of metathesis: No driving force (such as release of ring strain), equilibrium, difficult to control the selectivity in acyclic olefins. First industrial metathesis process was:

Phillips Triolefin Process
The process was operated at Phillips Petroleum Co. from 1966 to 1972 near Montreal, Canada for the conversion of propene into ethane and 2-butene:

$$2 \text{CH}_3\text{-CH=CH}_2 \underset{\text{CH}_2\text{-CH}_2}{\text{\rightarrow}} \text{CH}_2\text{=CH}_2 + \text{CH}_3\text{-CH=CH-CH}_3$$

Propene is produced from naphtha steam crackers (about 65 %) as a co-product with ethene and as a co-product in refineries for gasoline-making.

Production of ca 15 kt/a ethylene and 30 kt/a butene from 50 kt/a propylene was achieved over a WO$_3$/SiO$_2$ catalyst (doped with Na to decrease surface acidity and prevent double bond shift reactions) at temperature of around 400°C. However, the demand for propene (60 % is used for polypropene) has increased dramatically since then. Small amounts are obtained from propane dehydrogenation and by coal gasification via Fischer-Tropsch chemistry.
Olefin Conversion Technology (OCT)

An alternative route to propene is the metathesis of ethane and 2-butene, that is, the inverse Phillips process: All metathesis reactions are thermoneutral $\rightarrow$ \textit{equilibrium}:

$$\text{CH}_2=\text{CH}_2 + \text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 \quad \leftrightarrow \quad 2\text{CH}_3-\text{CH}=\text{CH}_2$$


The plant can be fed by an ethane cracker that produces ethene. Butene is generally obtained from the dimerization of ethene with a homogeneous Ni-catalyst (see SHOP below).

The heterogeneous catalyst is either either is [WO$_3$] / SiO$_2$ or [WO$_3$] / MgO and operates at temperatures $> 260^\circ$C and 30–35 bar. Pressure is not necessary for the reaction, but both the ethane cracker and the downstream processes require high pressures.

1-Butene in the feedstock is isomerized to 2-butene by the acid heterogeneous catalyst

New OCT plants:  BASF FINA (300 kt/a)
        Mitsui Chemical (140 kt/a)
        Korea Petrochemical Industry (110 kt/a)  … more being planned
Neohexene Process

Neohexene (3,3-dimethyl-1-butene) is an intermediate in the synthesis of Tonalide® (perfume) and Terbinafine® (antifungal). Operated since 1980. Production: 1.4 kt/a.

The process is based on the dimer of isobutene, which consists of a mixture of 2,4,4-trimethyl-2-pentene and 2,4,4-trimethyl-1-pentene.

Cross-metathesis of the former with ethene gives neohexene:

\[
\text{CH}_2=\text{CH}_2 + \text{CH}_3-\text{C}-\text{CH}==\text{C}-\text{CH}_3 \xrightarrow{\text{metathesis catalyst}} \text{CH}_3-\text{C}-\text{CH}==\text{CH}_2 + \text{C}==\text{CH}_2
\]

2,4,4-Trimethyl-1-pentene is isomerized by using a dual catalyst, a 1:3 mixture of WO_3 / SiO_2 and MgO. The catalyst operates at 370°C and 30 bar and gives an average conversion of diisobutene of 65–70% and a selectivity to neohexene of ca. 85%.
## Homogeneous ROMP Processes

<table>
<thead>
<tr>
<th>Process / Product</th>
<th>feeds</th>
<th>production</th>
<th>catalyst / conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polycyclooctene</strong> (Vestenamer®) cyclooctene</td>
<td>12 kt/a</td>
<td>WCl₆ / 25 – 100 °C / hexane</td>
<td></td>
</tr>
<tr>
<td>Degussa – Hüls, since 1980</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polynorbornene (Norsorex®) norbornene</th>
<th>RuCl₃ / HCl / BuOH / 25 – 100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdF / Atofina, since 1976</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polydicyclopentadiene dicyclopentadiene</th>
<th>[R₃NH]₂ₓ₋₆ₓMoₓMoₓOᵧ /</th>
</tr>
</thead>
<tbody>
<tr>
<td>Telene® (Goodrich)</td>
<td>Et₂AlCl / ROH / 25 – 100 °C</td>
</tr>
<tr>
<td>Pentem® (Nippon Zeon)</td>
<td>Metton® (Hercules Inc.)</td>
</tr>
<tr>
<td>Materia, Hitachi</td>
<td>Materia, Hitachi</td>
</tr>
<tr>
<td>&gt; 136. kt/a</td>
<td>WCl₆/WOCl₄/Et₂AlCl/ROH/25–100°C</td>
</tr>
<tr>
<td>ruthenium-based catalysts / 25–100°C</td>
<td></td>
</tr>
</tbody>
</table>
The Vestenamer® Process

Since 1980, Degussa-Hüls has been producing the metathetical polymer of cyclooctene under the commercial name of Vestenamer® 8012, also known as TOR (trans-polyoctenamer). Vestenamer is used as a blending material to impart greater elasticity and durability to other rubbers (see http://www.degussa-hpp.com/ger/produkte/kautschuk/index.shtml).

The catalyst is WCl₆-based in hexane as solvent

Two polymer fractions:  
- high-molecular weight fraction (> 10⁵ Da), true polymer
- low-molecular weight fraction (25 %), different cyclic oligomers

Explanation:  
Competition between *propagation* and *intramolecular backbiting metathesis*:

Different commercial products depending on the *trans* isomer content (controlled by polymerization conditions):  
Vestenamer 8012 → 80% *trans*, high crystallinity, rigid  
Vestenamer 6013 → 60% *trans*, lower crystallinity, softer, suitable for lower temperature applications.
Polynorbornene

Polynorbornene is produced by ROMP of 2-norbornene:

\[
\text{Polynorbornene} \xrightarrow{\text{ROMP}} \begin{array}{c} n \end{array} \begin{array}{c} \text{RuCl}_3 / \text{butanol} \end{array} \begin{array}{c} \text{polymer} \end{array}
\]

The catalyst is based on RuCl$_3$ / HCl in butanol and operates in air.

Norsorex® is commercial name of the 90% trans polymer of norbornene with very high molecular weight (> $3 \times 10^6$ g/mol). It is the first commercial metathesis polymer (1976, CdF-Chimie, France), now produced by Elf Atochem.

It is sold as a molding powder and the final vulcanized product is used in various vehicle fittings such as bumpers, arm-rests and engine mounting.

Other uses: oil spill recovery (see http://www.freepatentsonline.com/y2007/0137528.html):

Several grades from Norsorex are available (Norsorex NS or Norsorex APX1 for instance). The behavior in oil may vary from simple gelling effect without expansion to gelling and expansion. Norsorex® is a white polymer powder, it is hydrophobic and oleophilic and has a low density (0.96 g/cm$^3$). It is insoluble and inert in water. It has been developed by ATOFINA to absorb high quantities of various hydrocarbons including for instance naphtenic oil, kerosene aromatic oil.
Polydicyclopentadiene

*endo*-Dicyclopentadiene (DCPD) is a by-product from naphtha-crackers (cheap). The product is a tough, rigid, thermoset polymer of excellent impact strength. Commercial products are: Telene® (Mo-based catalyst) and Metton® (WCl₆ / WOCl₄ catalyst). Polymers of DCPD are suitable for injection molding. Uses include bodies of lorries and ATM's (http://www.metton.com/apps.html), as well as archery and baseball products.

(a) The highly strained norbornene ring is preferentially opened.
(b) also the cyclopentene ring can undergo metathesis to give cross-linking:
General Considerations on Homogeneous ROMP

Although ROMP is generally extremely rapid and high yielding due to the release of ring strain, the chemistry of ROMP is not trivial. Catalysts have extremely high productivity, as the rate of chain propagation far exceeds that of any decomposition reactions that might occur. However, due to the presence of repeating olefin units in the polymer product, it is also important to ensure that propagation is more rapid than:

i) intermolecular chain transfer (leading to break up of existing polymer chains):

\[
\begin{align*}
\text{Initiation} & \quad \xrightarrow{\text{Chain Propagation}} \quad \text{Termination} \\
\text{Chain 1} & \quad \xrightarrow{\text{Chain 2}} \quad \text{Chain 3} + \text{CH}_2
\end{align*}
\]

ii) intramolecular chain transfer (leading to macrocyclic products):

\[
\begin{align*}
\text{Initiation} & \quad \xrightarrow{\text{Chain Propagation}} \quad \text{Termination} \\
\text{Chain 1} & \quad \xrightarrow{\text{Chain 2}} \quad \text{Chain 3} + \text{M}
\end{align*}
\]

The intrinsic reactivity of strained cycloalkanes (norbornene, cyclobutene) ensures that they react as desired, and simple homogeneous metal halide catalysts are often effective for this transformation. What about less strained cyclic substrates?
Tayloring of the Catalyst

Less strained cyclic olefins require the manipulation of the catalyst activity and selectivity by means of modifying ligands. In such cases, well-defined alkylidene/carbene complexes as pioneered by Schrock and Grubbs are required. As example, the binuclear complex 1 readily catalyzes the ROMP of norbornene, but is not active enough for ROMP of functionalized norbornene derivatives.

In contrast, complexes 2 and 3 are active for the functionalized substrates, but suffer from the inter- and intramolecular and chain transfer reactions shown in the former slide when norbornene is the substrate.

Additionally, the catalyst influences the cis / trans stereochemistry of the double bond in the polymer. in turn, this dramatically affects the mechanical properties of the polymer.

In the case of prostereogenic monomers, the catalyst also influences the tacticity of the polymer. This issue will be discussed in detail in the case of propene polymerization in a later chapter.
Fine Chemicals

Recently, the use of homogeneous catalysis in fine chemicals manufacture has grown dramatically, due to the better selectivities that can be attained and to the robustness, particularly of the ruthenium-based catalysts, towards the range of functional groups commonly found in such molecules.

Agrochemicals

Pheromones can be used as biopesticides as they disrupt the breeding cycles of various crop pests in an environmentally friendly manner. A range of pheromones is accessible via cross metathesis with ruthenium-based Grubbs catalysts.

5-Decenyl acetate, the major component of the peach twig borer (*Anarsia lineatella*) pheromone, is produced from 5-decene and 1,10-diacetoxy-5-decene:

\[
\begin{align*}
    \text{AcO} &+ \text{AcO} \rightarrow 2 \text{OAc}
\end{align*}
\]

In order to maintain high selectivities, the reaction is carried out at low temperature (5 °C). The unreacted feed materials are separated out by distillation and recycled, leading to high process efficiencies and minimal waste.
Pharmaceuticals

Pharmaceuticals applications of metathesis are widespread in the patent literature. Cross Metathesis (CM) and Ring Opening Metathesis (ROM) are applicable in some syntheses, but it is Ring Closing Metathesis that predominates, as there are few reactions that are as effective for the synthesis of highly functionalized, medium ring compounds. Such macrolides are key components of a vast range of medicinally active compounds that can combat bacterial and viral infections as well as cancers, bone and neurological diseases. Epothilones are examples of a family of naturally occurring macrocyclic anti-cancer agents that can be prepared by RCM as a key step.

Pharmaceuticals are generally very high value products. Therefore, the catalyst cost is less critical for an economical process. However, pharmaceutical applications have much higher selectivity requirements, as the testing of materials for human consumption is a rigorous one. For pharmaceutical and fragrances, the separation of the homogeneous catalyst and ligands from the product is critical to meet law standards. Apart from its toxicity, residual metal may also lead to gradual degradation of the product. Published procedures for the removal of metal and ligands involve the use of a complexing or oxidizing agent, such as the water-soluble tris(hydroxymethyl)phosphine (Grubbs), DMSO or Ph₃PO (Georg) and lead tetraacetate (Paquette). However, a further reagent may introduce additional sources of contamination. Alternative strategies are heterogenizing the catalyst (problem: leaching of the catalyst). Such work is in its infancy and further development is required before these techniques become commercially viable.
An example of RCM

Other Processes