

Ring-Closing Metathesis (RCM)

A Detailed Guide with Mechanism & Worked Example

1. What Is Olefin Metathesis?

Olefin metathesis is a powerful carbon–carbon bond-forming reaction in which two alkene (olefin) substrates exchange their alkylidene fragments in the presence of a transition-metal carbene catalyst. The word **metathesis** comes from the Greek *meta* (change) + *thesis* (position), literally meaning “**change of position.**” Yves Chauvin, Robert Grubbs, and Richard Schrock shared the 2005 Nobel Prize in Chemistry for their development of this reaction.

Key idea: In metathesis, C=C double bonds are broken and reformed. No net oxidation state change occurs at the metal center — the catalyst cycles through a series of [2+2] cycloadditions and retro-[2+2] steps.

Major Types of Olefin Metathesis

Type	Abbr.	Description
Ring-Closing Metathesis	RCM	Intramolecular reaction of a diene to form a cyclic alkene + ethylene ($\text{CH}_2=\text{CH}_2$)
Ring-Opening Metathesis Polymerization	ROMP	Strained cyclic olefin opens and polymerizes (you studied this with norbornene!)
Cross Metathesis	CM	Intermolecular exchange between two different acyclic alkenes
Acyclic Diene Metathesis Polymerization	ADMET	Diene polymerizes by repeated intramolecular metathesis

This guide focuses on **RCM** — the intramolecular variant where a diene substrate cyclizes to form a ring with loss of a small gaseous alkene (usually ethylene). Because ethylene escapes the reaction mixture, Le Châtelier’s principle drives the equilibrium toward the cyclic product.

2. Ring-Closing Metathesis — The Big Picture

In RCM, a **diene** (a molecule with two terminal C=C bonds connected by a tether) reacts with a metal–carbene catalyst. The two double bonds undergo intramolecular metathesis to close a ring, releasing ethylene ($\text{CH}_2=\text{CH}_2$) as a byproduct.

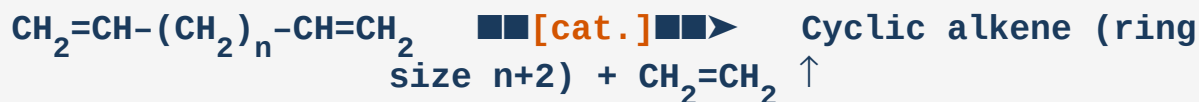


Figure 1. General RCM scheme: a diene closes to a cycloalkene with loss of ethylene.

Why Does RCM Work?

- **Thermodynamic driving force:** Ethylene is a gas and escapes the solution. By Le Châtelier's principle, removing a product shifts equilibrium toward the cyclic product. Reactions are often run under mild vacuum or with a N_2 purge to help remove ethylene.
- **Dilute conditions:** RCM is run at low concentration (typically 0.01–0.05 M) to favor *intramolecular* cyclization over *intermolecular* oligomerization (which would give ADMET polymers instead).
- **Ring size:** RCM works best for forming 5-, 6-, and 7-membered rings. Larger rings (macrocycles) require even higher dilution and longer reaction times.
- **Functional group tolerance:** Grubbs catalysts tolerate a wide range of functional groups (esters, amides, alcohols, ethers, protected amines), unlike many other organometallic reactions.

3. The Catalysts

The most commonly used catalysts for RCM are the **Grubbs catalysts**, which are ruthenium–carbene complexes. The key advantage of Ru-based catalysts over earlier Mo/W-based Schrock catalysts is their greater tolerance of air, moisture, and diverse functional groups.

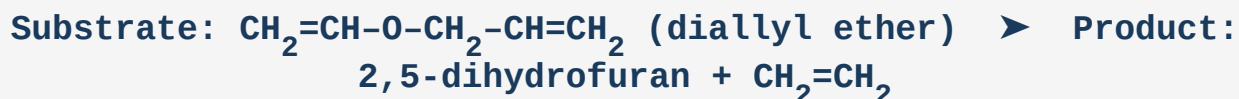
Catalyst	Key Features	Typical Use
Grubbs 1st Gen (G-I)	$\text{Ru}=\text{CHPh}$ with two PCy_3 ligands. Moderately active, good for simple RCM.	Simple 5- and 6-membered rings
Grubbs 2nd Gen (G-II)	One PCy_3 replaced by NHC (SIMes). More active, more thermally stable.	Challenging substrates, tri-substituted alkenes
Hoveyda–Grubbs 2nd Gen (HG-II)	Chelating isopropoxy-styrenyl ligand. Recyclable, very robust.	Industrial / large-scale, macrocyclization

Connection to ROMP: These are the *same* Grubbs catalysts you encountered with Ring-Opening Metathesis Polymerization! The difference is substrate and conditions: ROMP uses strained cyclic olefins (like norbornene) and concentrated conditions to polymerize, while RCM uses acyclic dienes and dilute conditions to cyclize.

4. Chauvin Mechanism of RCM (Step-by-Step)

The accepted mechanism for all olefin metathesis reactions is the **Chauvin mechanism**, which proceeds through a series of [2+2] cycloadditions and retro-[2+2] cycloreversions via metallocyclobutane intermediates.

Worked Example: RCM of diallyl ether to form 2,5-dihydrofuran



Step 1: Catalyst Initiation

The Grubbs catalyst $[\text{Ru}]=\text{CHPh}$ first loses one phosphine ligand (PCy_3) to generate a 14-electron active species with a vacant coordination site. This is the **rate-determining step** for Grubbs 1st generation catalysts.



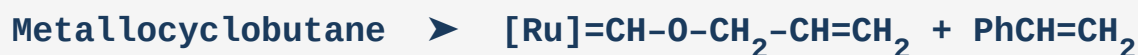
Step 2: First [2+2] Cycloaddition

The active $\text{Ru}=\text{CHPh}$ coordinates to **one** of the two terminal alkenes of diallyl ether. The metal carbene and the alkene undergo a [2+2] cycloaddition to form a **metallocyclobutane** intermediate — a strained 4-membered ring containing Ru.



Step 3: First Retro-[2+2] (Productive Cleavage)

The metallocyclobutane can break in **two ways**. The productive pathway cleaves the bond opposite to where it formed, releasing **stilbene** ($\text{PhCH}=\text{CH}_2$) and generating a new Ru–carbene now tethered to the substrate: $[\text{Ru}]=\text{CH}-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2$.



Step 4: Intramolecular [2+2] (Ring Closure!)

This is the **key step**. The Ru–carbene is now tethered to the substrate, and the *other* terminal alkene of the same molecule is nearby. An **intramolecular** [2+2] cycloaddition occurs between $[\text{Ru}]=\text{CH}-$ and the pendant $-\text{CH}=\text{CH}_2$, forming a **second metallocyclobutane** — this time as part of a bicyclic system incorporating the growing ring.



Step 5: Second Retro-[2+2] (Product Release)

The second metallocyclobutane undergoes retro-[2+2] to release the cyclic product **2,5-dihydrofuran** and regenerate the active catalyst as $[\text{Ru}]=\text{CH}_2$ (a methyldiene species). Ethylene ($\text{CH}_2=\text{CH}_2$) is released when this methyldiene reacts with the next substrate molecule.

Bicyclic intermediate ➤ 2,5-Dihydrofuran + $[\text{Ru}]=\text{CH}_2$

Catalyst turnover: The $[\text{Ru}]=\text{CH}_2$ generated in Step 5 re-enters the catalytic cycle at Step 2, reacting with a new substrate molecule. Each catalyst molecule can perform hundreds to thousands of turnovers.

5. Putting It All Together

Catalytic Cycle Summary

The entire RCM catalytic cycle can be summarized in five words: **coordinate** → **[2+2]** → **retro-[2+2]** → **intramolecular [2+2]** → **retro-[2+2]**. The catalyst shuttles between $\text{Ru}=\text{CR}_2$ (carbene) and $\text{Ru}-\text{C}_4$ ring (metallocyclobutane) states throughout.

Feature	Detail
Substrate	Diene with two terminal alkenes connected by a tether
Catalyst	Grubbs 1st/2nd gen or Hoveyda–Grubbs ($\text{Ru}=\text{CHR}$)
Mechanism	Chauvin: alternating [2+2] / retro-[2+2] via metallocyclobutanes
Byproduct	Ethylene ($\text{CH}_2=\text{CH}_2$) — gas, drives equilibrium forward
Best ring sizes	5, 6, 7 (larger rings need higher dilution)
Conditions	Dilute (0.01–0.05 M), DCM or toluene, RT–40 °C, N_2 atm
Key advantage	Exceptional functional group tolerance

6. RCM vs. ROMP — Same Catalyst, Different Reactions

Since you've already studied ROMP in CH410, here's a side-by-side comparison to solidify the distinction:

	RCM	ROMP
Direction	Closes a ring	Opens a ring (then polymerizes)
Substrate	Acyclic diene	Strained cyclic olefin (e.g., norbornene)
Product	Cyclic alkene (small molecule)	Polymer with $\text{C}=\text{C}$ in backbone
Driving force	Entropy (ethylene loss)	Ring strain release ($\Delta G < 0$)
Concentration	Dilute (~0.01 M)	Concentrated
Catalyst	Grubbs I / II	Grubbs I / II / III

7. Practice Problem

Predict the product of the following RCM reaction:

$\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}=\text{CH}_2$ + Grubbs II catalyst, DCM, RT ➤
???

Answer: The two terminal alkenes close to form **2,5-dihydro-1H-pyrrole** (a 5-membered nitrogen heterocycle) + ethylene. The N–H bond and the internal C=C are both preserved. This is a classic example of RCM being used to build **nitrogen heterocycles** — incredibly useful in pharmaceutical synthesis!

Prepared for CH410 Organic Chemistry review. Key references: Grubbs, R. H. (Ed.), Handbook of Metathesis (2003); Chauvin, Y., Angew. Chem. Int. Ed. (2006) 45, 3740–3747.