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# Ruthenium Chemistry

- ❖ Introduction
- ❖ Hydrogenation
- ❖ Oxidation
  - RuO<sub>4</sub>-Promoted Oxidation
  - Oxidation with Ru Complex Catalysts and Oxidants
- ❖ Nucleophilic Addition to C-C Multiple Bonds
- ❖ C- C Bond Formation
  - Ruthenacycle Intermediates
  - C-H Activation
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  - Diazo Compounds: Cyclopropanation
- ❖ Literature

# Ruthenium Chemistry

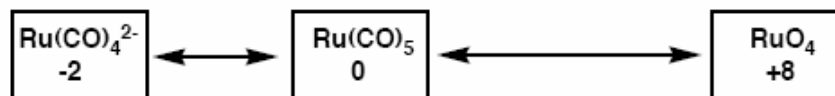
## Introduction

- **Name:** from the latin *Ruthenia* (Russia)
- **History:** ruthenium was discovered by Karl Karlovich Klaus, a Russian chemist, in 1844
- **Occurrence:** ruthenium is exceedingly rare and is the 74th most abundant metal on Earth. Found in platinum and other ores
- **Commercially,** it is obtained from *pentlandite* (a sulfide of iron and nickel) which contains small quantities of ruthenium. Ruthenium can also be extracted from spent nuclear fuel, however if obtained this way it will contain radioactive isotopes. It has to be stored safely for at least ten years until the radioactive isotopes have
- **Cost:** the metal is priced at about \$30/g
- **Uses:** used as a catalyst in many industrial processes and to increase the corrosion resistance of titanium
- **Isotopes:** Ruthenium has 26 isotopes whose half-lives are known, with mass numbers from 90 to 115. Of these 7 are stable:  $^{96}\text{Ru}$ ,  $^{98}\text{Ru}$ ,  $^{99}\text{Ru}$ ,  $^{100}\text{Ru}$ ,  $^{101}\text{Ru}$ ,  $^{102}\text{Ru}$ , and  $^{104}\text{Ru}$ . Naturally, the most common isotope is  $^{102}\text{Ru}$  with an abundance of 31.6%
- **Behavior:** ruthenium is a suspected carcinogen and its compounds strongly stain the skin. Ruthenium tetroxide ( $\text{RuO}_4$ ) is volatile, highly toxic and explosive

# Ruthenium Chemistry

## Introduction

- Ruthenium has **the widest range of oxidation states** of any element



- Ruthenium complexes can adopt **several coordination geometries**

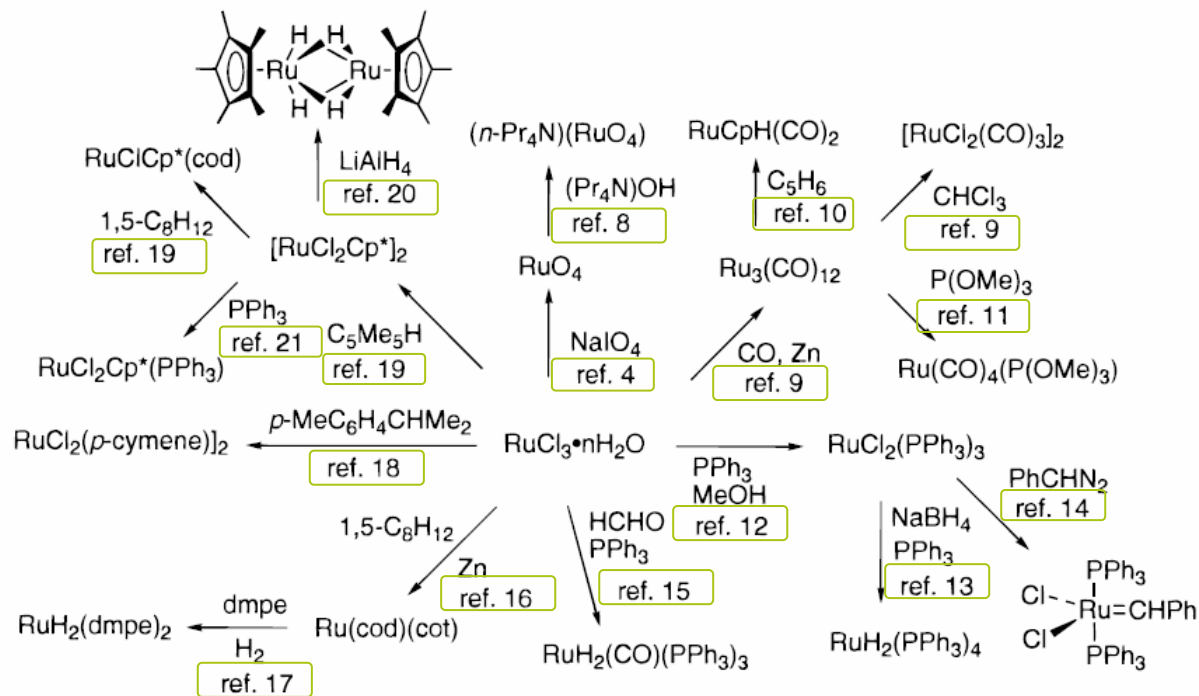
Oxidation State	Coordination number	Geometry	Example
Ru(0)	5	trig. bipy.	$\text{Ru(CO)}_5$
Ru(II)	5	trig. bipy.	$\text{RuHCl(PPh}_3)_3$
	6	octahedral	$\text{RuCl}_2\text{CO(PR}_3)_3$
Ru(III)	6	octahedral	$[\text{Ru(NH}_3)_5\text{Cl}]^{2+}$
Ru(VI)	4	tetrahedral	$\text{RuO}_4^{2-}$
Ru(VII)	4	tetrahedral	$\text{RuO}_4^-$
Ru(VIII)	4	tetrahedral	$\text{RuO}_4$

- **Range of reactivity** due to properties of Ru complexes:
1. High **electron transfer ability**
  2. High **Lewis acidity**
  3. **Low redox potentials**
  4. **Stabilities** of reactive metallic species such as oxometals, metallacycles, and metal carbene complexes

# Ruthenium Chemistry

## Introduction

- The ability of ruthenium to assume a wide range of oxidation states (from -2 to +8) and coordination geometries provides unique opportunities for **catalysis**
- As such, a wide range of mechanistically very different processes are catalyzed by ruthenium. These include reactions initiated by metallacycle formation, vinylidene formation, C-H activation, and activation of carbon-carbon multiple bonds by coordination
- The majority of the **ruthenium complexes** used are in the +2 to +4 oxidation state. These catalysts are generally the most versatile due to the facile redox chemistry between those oxidation states and therefore have the greatest ability to react in catalytic cycles

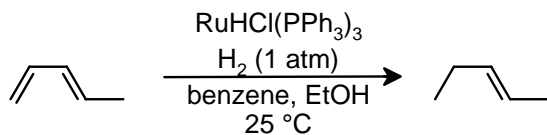


# Ruthenium Chemistry

## Hydrogenation

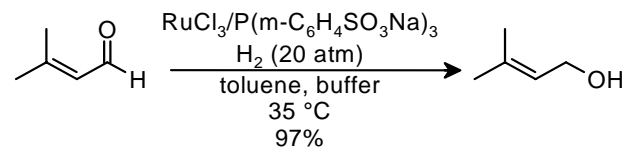
- Compared to other metal complexes of Rh, Ir, and Co, Ru complexes generally have less effective catalytic activities for hydrogenation of simple and functionalized alkenes. **Mild reactivities** of ruthenium complex are often used for **chemoselective hydrogenations**
- Great progress has been made on the **asymmetric hydrogenations** with homogeneous ruthenium complexes bearing chiral phosphine ligands

### chemoselective hydrogenations of polyolefins



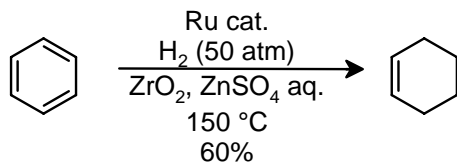
*J. Chem. Soc., Chem. Comm.* **1967**, 305

### chemoselective hydrogenations of aldehydes (COR)



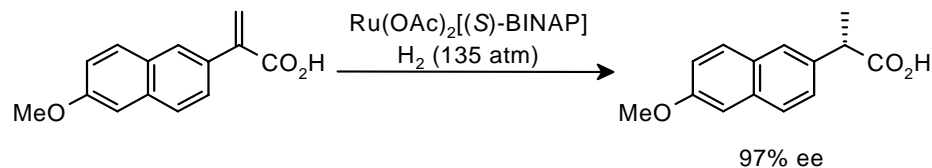
*Organometallics* **1991**, 10, 2126

### regioselective hydrogenation of aromatic hydrocarbons



*Rev. J. Surf. Sci. Technol. Avant-Garde* **1992**, 30, 951

### enantioselective hydrogenations



*J. Org. Chem.* **1987**, 52, 3174

**(S)-Naproxen**

# Ruthenium Chemistry

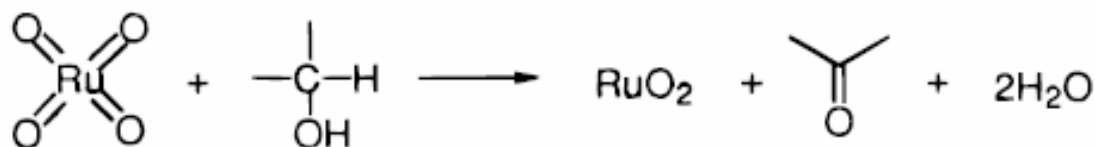
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# Ruthenium Chemistry

## Oxidation

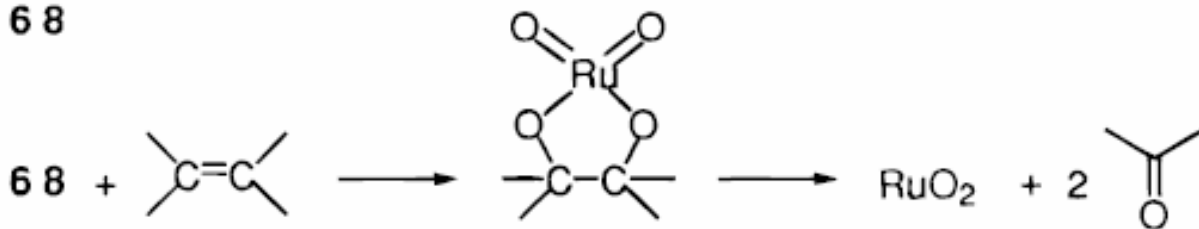
### ❖ RuO<sub>4</sub>-Promoted Oxidation

- RuO<sub>4</sub> has been widely used as a **powerful oxidant** for oxidative transformations of various organic compounds since the discovery by Djerassi in 1953
- RuO<sub>4</sub> shows specific power of **oxygenation** and **hydrogen abstraction** toward a variety of organic compounds
- Typical **reactivity** of RuO<sub>4</sub> is shown in the scheme:



6 8

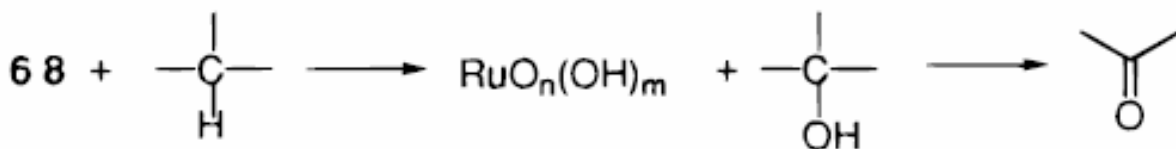
1. abstraction of activated α-H
2. electron transfer



6 8

oxidative cleavage of C-C bond

6 9



6 8

1. abstraction of inactivated H
2. oxidation



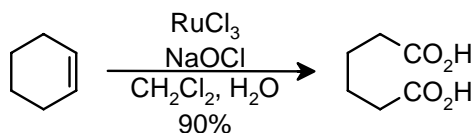
# Ruthenium Chemistry

## Oxidation

### ❖ RuO<sub>4</sub>-Promoted Oxidation

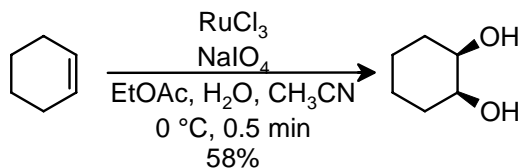
- Olefins undergo **oxidative cleavage** to afford the carbonyl compounds
- **cis-Dihydroxylation** occurs selectively when the reaction is carried out in a short time
- **Epoxidation** of olefins can be performed with RuO<sub>4</sub> modified by coordination of nitrogen ligands

oxidative cleavage of olefins



*J. Chem. Soc., Chem. Comm.* **1970**, 1420

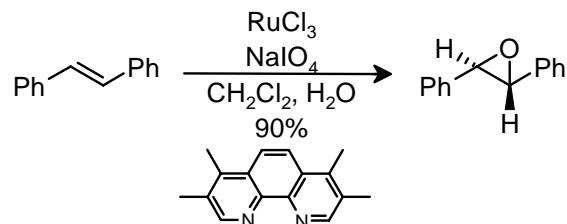
cis-dihydroxylation of olefins



*Angew. Chem., Int. Ed. Engl.* **1994**, 33, 2312

alternative to OsO<sub>4</sub>

epoxidation of olefins



*J. Chem. Soc., Chem. Commun.* **1985**, 1111

# Ruthenium Chemistry

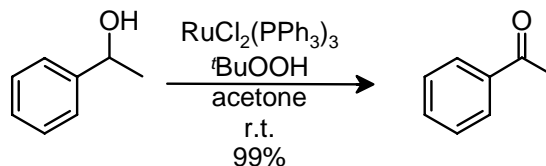
## Oxidation

### ❖ Oxidation with Ru Complex Catalysts and Oxidants

#### • Oxidation of Alcohols and Phenols

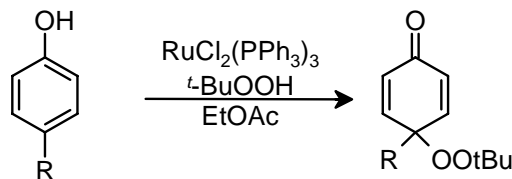
➤ **Low-valent ruthenium complexes** catalyze the oxidation of alcohols and the related hydroxy compounds in combination with various oxidants such as  $t\text{BuOOH}$ ,  $\text{AcOOH}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Me}_3\text{SiOOSiMe}_3$ ,  $\text{PhIO}$ ,  $N$ -methylmorpholine  $N$ -oxide and pyridine  $N$ -oxide

➤ **Secondary alcohols** are converted into the corresponding **ketones**; **primary alcohols** are normally oxidized to **carboxylic acids**



*Synthesis* **1993**, 433

➤ The **oxidation of phenols** generally lacks selectivity because the initially formed phenoxy radical intermediate causes various unpleasant coupling reactions. Thus, metal-catalyzed oxidation of phenols generally proceeds with nonselectivity, giving a variety of side products such as radical coupling products and over oxidation products

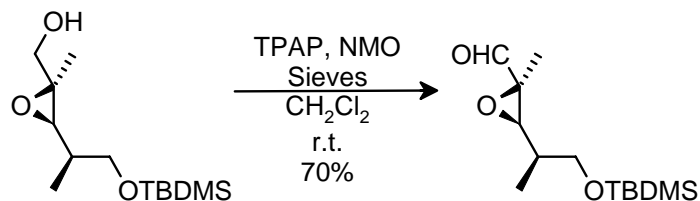


*J. Am. Chem. Soc.* **1996**, 118, 2509

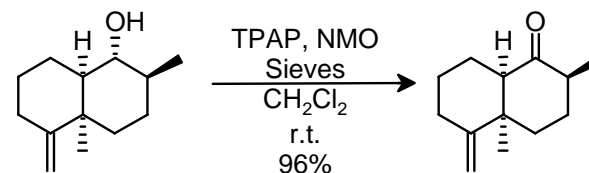
# Ruthenium Chemistry

## Oxidation

- The salts of perruthenium ion  $[\text{Ru}^{\text{IV}}\text{O}_4]^-$  with quaternary ammonium salts, show far milder oxidizing properties than  $\text{RuO}_4$ , and act as efficient catalysts for selective oxidation of primary alcohols with a combined use of stoichiometric amount of *N*-methylmorpholine *N*-oxide (NMO)
- $[\text{RuO}_4]^-$  is a **milder oxidant than  $\text{RuO}_4$** , can cleave some C=C bonds
- $[\text{RuO}_4]^-$  salts with large organic cations are soluble in organic solvents
- Water inhibits catalyst turnover; use **molecular sieves**
- Catalytic (5 mol%) with suitable co-oxidants; **NMO** most effective
- Most used: **tetrapropylammonium perruthenate (TPAP)**
- Wide tolerance of **functional groups**:
  - Double bonds, polyenes, enones, halides, cyclopropanes, epoxides, and acetals
  - Esters, amides, lactones, amines, peroxides, and catechols
  - Protecting groups: SEM, MOM, BOM, MEM, trityl, silyl, benzyl, PMB, THP, acetate, and benzoate
  - Piperidines, pyrroles, indoles, furans, thiophenes, and pyridines are unreactive



*Synthesis* **1994**, 639



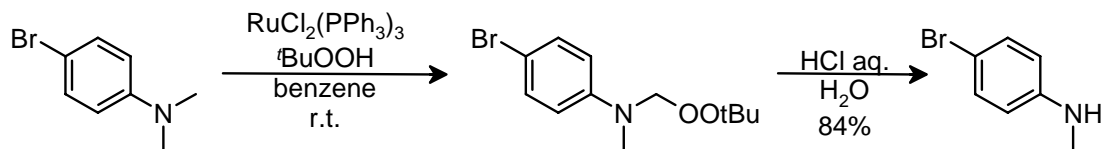
*Tetrahedron Lett.* **1991**, 32, 5219

# Ruthenium Chemistry

## Oxidation

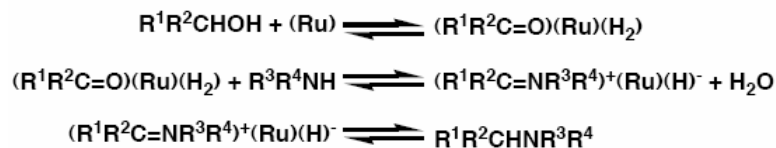
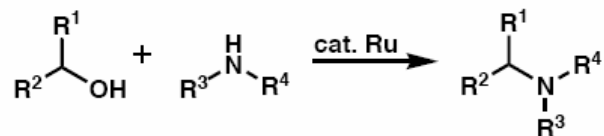
- ❖ Oxidation with Ru Complex Catalysts and Oxidants
- Oxidation of Amines and Amides

➤  $\alpha$ -Methoxylation of tertiary amines can be carried out with  $\text{H}_2\text{O}_2$  in the presence of  $\text{RuCl}_3$  catalyst in MeOH. In these reactions *N*-methyl groups are oxidized chemoselectively in the presence of other alkyl groups. Therefore, the reaction provides a practical synthetic method for **selective *N*-demethylation of tertiary methylamines** by the oxidation and the subsequent hydrolysis of the peroxide with an aqueous HCl solution:



*J. Am. Chem. Soc.* **1988**, *110*, 8256

➤ Alcohol oxidation-reductive amination:



*Tetrahedron Lett.* **1982**, 229

catalyst	amine	alcohol	product	% yield
$\text{RuH}_2(\text{PPh}_3)_4$	$\text{C}_8\text{H}_{17}\text{NH}_2$	$\text{C}_7\text{H}_{15}\text{OH}$	$\text{C}_7\text{H}_{15}\text{NHC}_8\text{H}_{17}$	92
$\text{RuCl}_2(\text{PPh}_3)_3$	$\text{PhNH}_2$	$\text{C}_3\text{H}_7\text{OH}$	$\text{Ph}(\text{C}_3\text{H}_7)_2$	88
$\text{RuCl}_3 \cdot n\text{H}_2\text{O} \cdot \text{P}(\text{OBu})_3$		$\text{CH}_3\text{OH}$		99
$\text{Ru}(\text{cod})(\text{cot})$		$\text{C}_2\text{H}_5\text{OH}$		85
$\text{RuCl}_2(\text{PPh}_3)_3$				100

# Ruthenium Chemistry

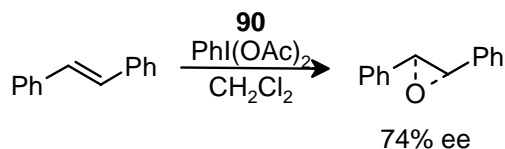
## Oxidation

### ❖ Oxidation with Ru Complex Catalysts and Oxidants

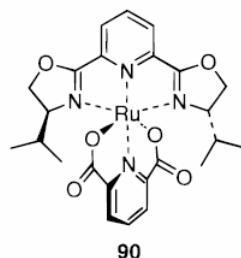
#### • Oxidation of Alkenes

➤ **Epoxidation of alkenes** using Ru complexes is one of the most important reactions. It's necessary the use of oxidants

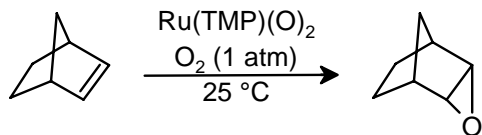
➤ The use of Ru complexes bearing optically active nitrogen ligands provides **enantioselective catalytic epoxidation of olefins**:



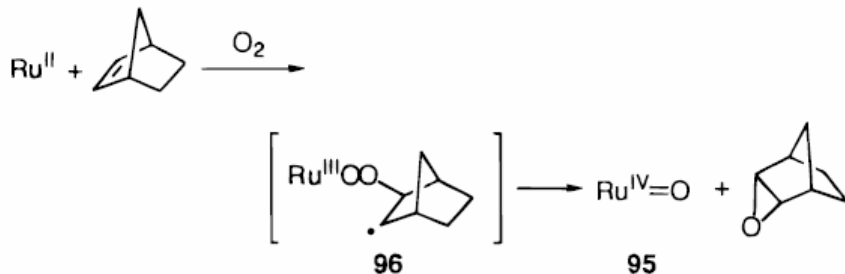
*J. Chem. Soc., Chem. Commun.* **1997**, 1863



➤ Direct **aerobic epoxidation of olefins**, which has never been reported using other transition metal catalysts, can be carried out at ambient pressure of O<sub>2</sub> using ruthenium porphyrin catalyst, such as Ru(TMP)(O)<sub>2</sub>, Ru(TMP)(OH)<sub>2</sub>. The applicable substrate is limited to reactive olefins such as norbornene:



*J. Am. Chem. Soc.* **1985**, 107, 5790



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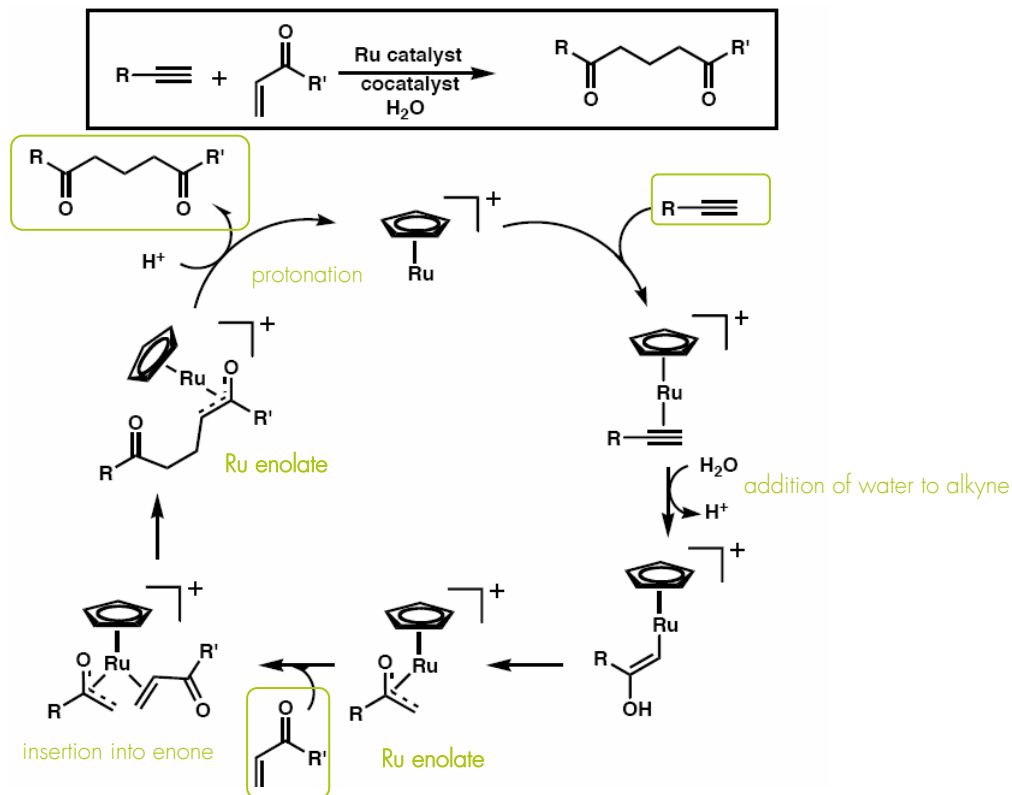
# Ruthenium Chemistry

## Nucleophilic Addition to C-C Multiple Bonds

### ❖ Nucleophilic Addition to Alkynes

- Addition of Water

➤ Ruthenium has been shown to catalyze the **addition of water to alkynes** followed by **trapping with enones** to generate **1,5-diketones**:



*J. Am. Chem. Soc.* 1997, 119, 836

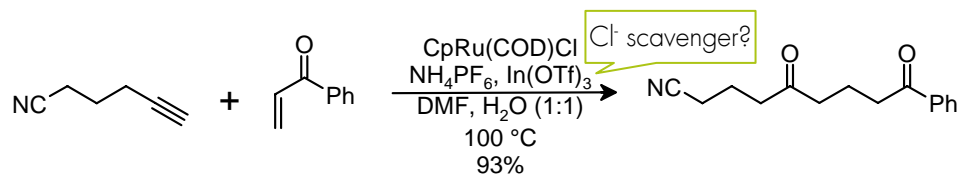
# Ruthenium Chemistry

## Nucleophilic Addition to C-C Multiple Bonds

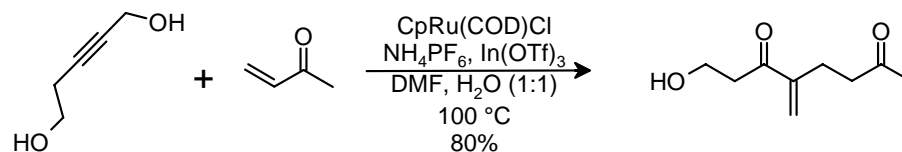
### ❖ Nucleophilic Addition to Alkynes

#### • Addition of Water

➤ The optimal conditions for the reaction involve the use of **5% CpRu(COD)Cl** and a mixture of ammonium hexafluorophosphate and indium triflate as cocatalysts in a DMF/water mixture

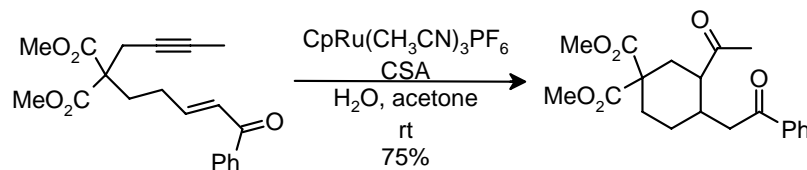


*J. Am. Chem. Soc.* **1997**, 119, 836



*J. Am. Chem. Soc.* **1997**, 119, 11319

➤ Intramolecular variant:



*J. Am. Chem. Soc.* **2000**, 122, 5877

alternative mechanism?



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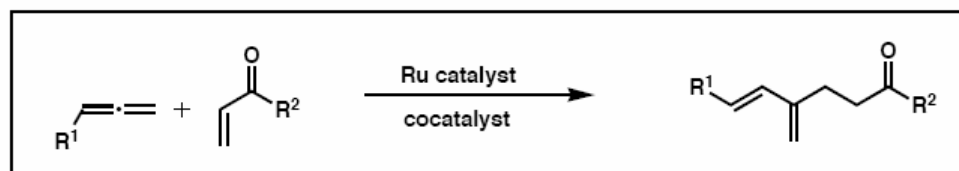
# Ruthenium Chemistry

## C-C Bond Formation

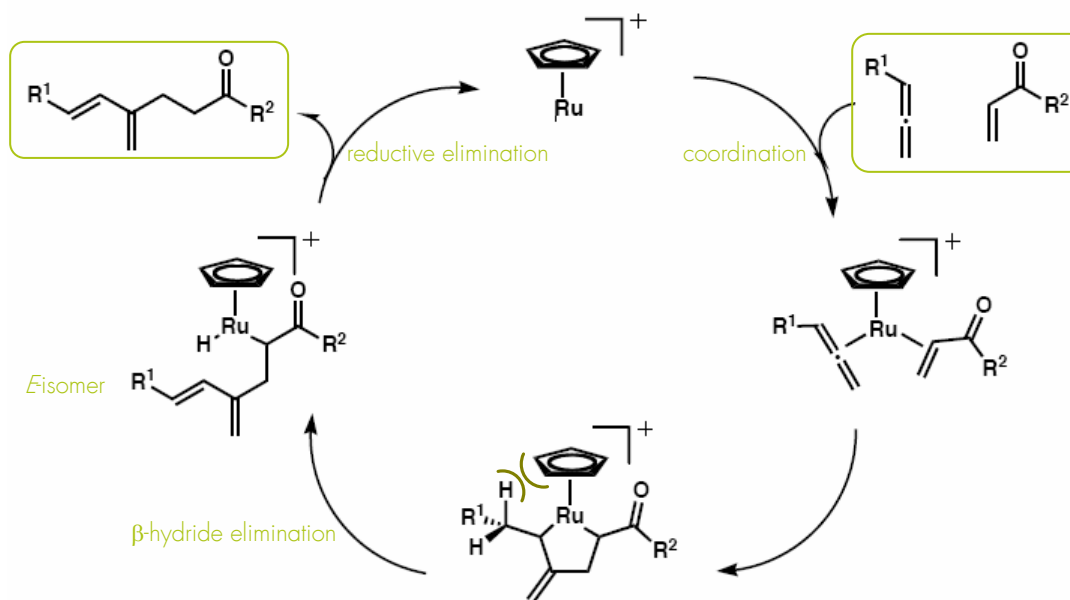
### ❖ Ruthenacycle Intermediates

- Ruthenacyclopentane

➤ **Ruthenacyclopentanes** have been proposed as intermediates in the **coupling of allenes and vinyl ketones** to form **1,3-dienes**. The proposed **reaction mechanism** is detailed in the scheme:



*E*-isomer



*J. Am. Chem. Soc.* 1999, 121, 4068

# Ruthenium Chemistry

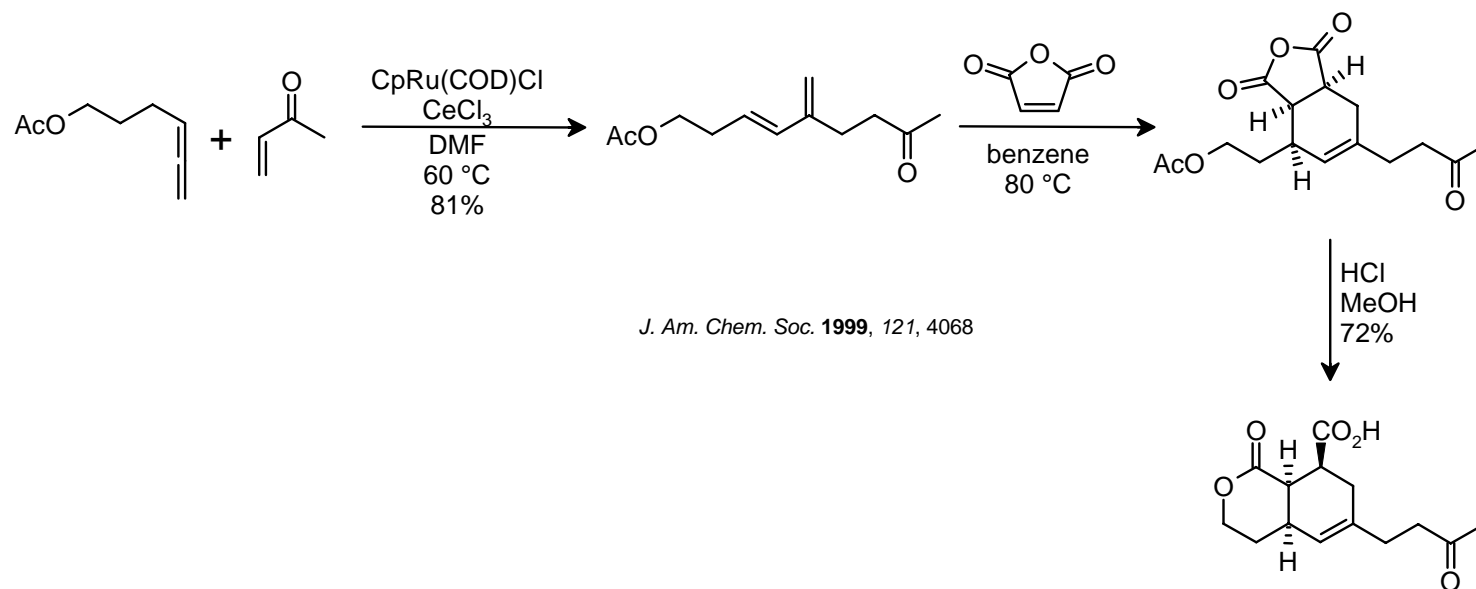
## C-C Bond Formation

### ❖ Ruthenacycle Intermediates

- Ruthenacyclopentane

➤ The reaction is catalyzed by 10%  $\text{CpRu}(\text{COD})\text{Cl}$  and 15% of  $\text{CeCl}_3$  as a cocatalyst. The role of the cocatalyst remains to be established in these reactions, but one possibility includes enone activation

➤ Under these conditions, a variety of allenes are coupled to methyl vinyl ketone or phenyl vinyl ketone to provide 1,3-dienes in good yields (53-81%). The 1,3-dienes thus obtained serve as valuable intermediates

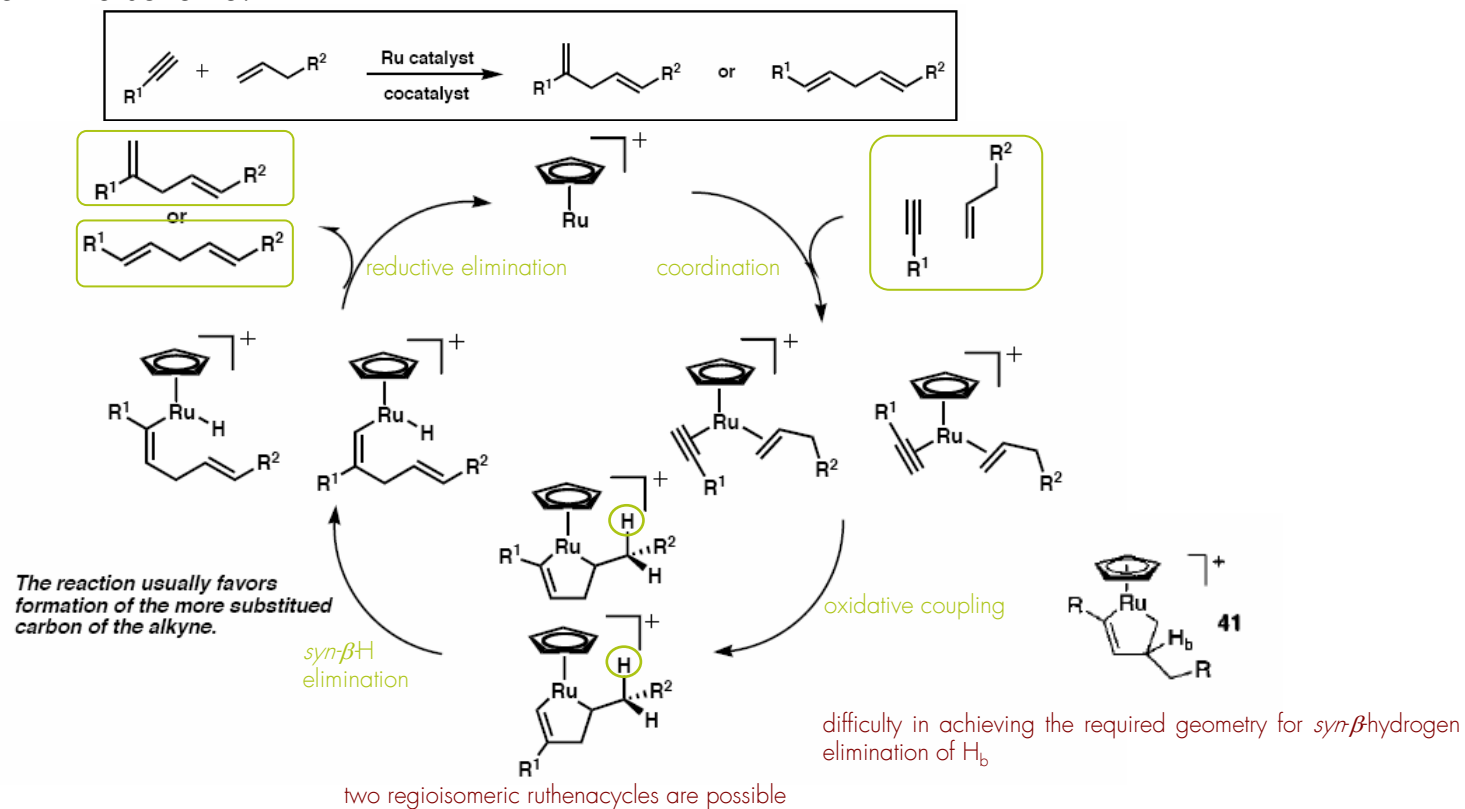


# Ruthenium Chemistry

## C-C Bond Formation

- ❖ Ruthenacycle Intermediates
- Ruthenacyclopentene

➤ Cationic Ru(+2) complexes catalyze the **coupling of alkynes and alkenes** (an **Alder-ene type reaction**). It is now generally believed that the reaction proceeds via a **ruthenacyclopentene**. The proposed **reaction mechanism** is detailed in the scheme:



*J. Am. Chem. Soc.* 1993, 115, 4361; *J. Am. Chem. Soc.* 1995, 117, 615

# Ruthenium Chemistry

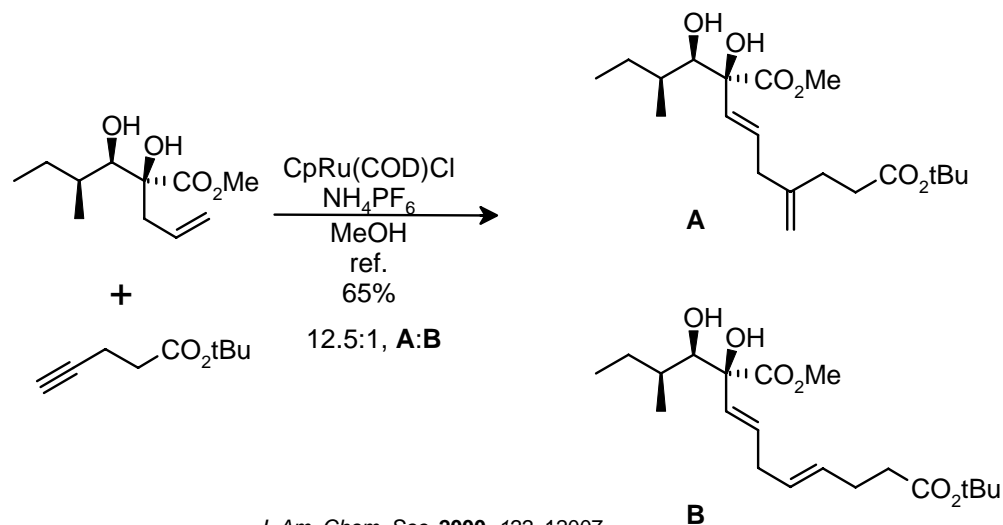
## C-C Bond Formation

### ❖ Ruthenacycle Intermediates

- Ruthenacyclopentene

➤ The reaction generally favors C-C bond formation at the more substituted carbon of the alkyne (**the branched product**) although several factors can reverse this trend

➤ The **Alder-ene reaction** of the example is catalyzed by 10% CpRu(COD)Cl and 20% ammonium hexafluorophosphate (NH<sub>4</sub>PF<sub>6</sub>) to afford a 12.5:1 mixture of isomeric 1,4-dienes **A** and **B**



*J. Am. Chem. Soc.* **2000**, 122, 12007

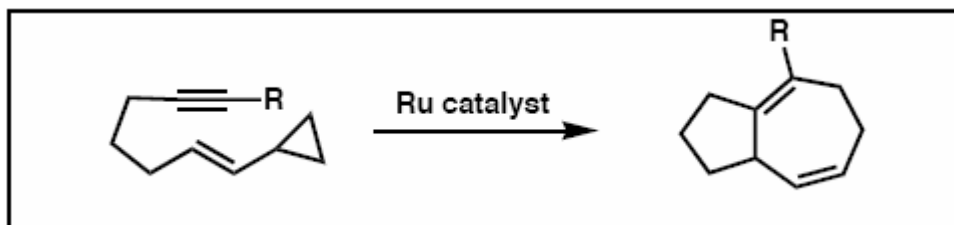
# Ruthenium Chemistry

## C-C Bond Formation

### ❖ Ruthenacycle Intermediates

#### • Ruthenacyclopentene

➤ **Intramolecular [5+2] cycloaddition:** intramolecular [5+2]-cycloaddition of an alkyne and vinylcyclopropane

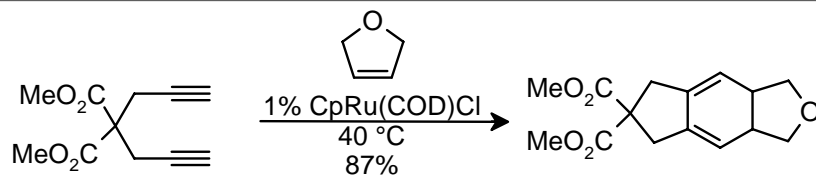
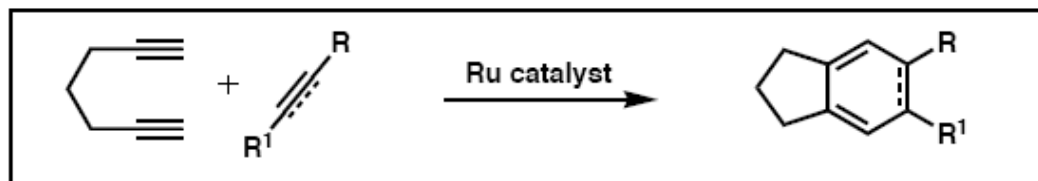


- Ru catalyst: 10 mol %  $\text{CpRu}(\text{CH}_3\text{CN})_3\text{PF}_6$
- Solvent: DMF or acetone
- Mild conditions: conducted at rt
- Bi- and Tricyclic cycloheptadienes formed in good yields (73-92%)

### ❖ Ruthenacycle Intermediates

#### • Ruthenacyclopentadiene

➤ **[2+2+2] cycloaddition:** ruthenacyclopentadienes have been postulated as intermediates in Ru-catalyzed reaction of 1,6-diynes in the presence of an alkene or an alkyne



*J. Org. Chem.* **1998**, *63*, 9610

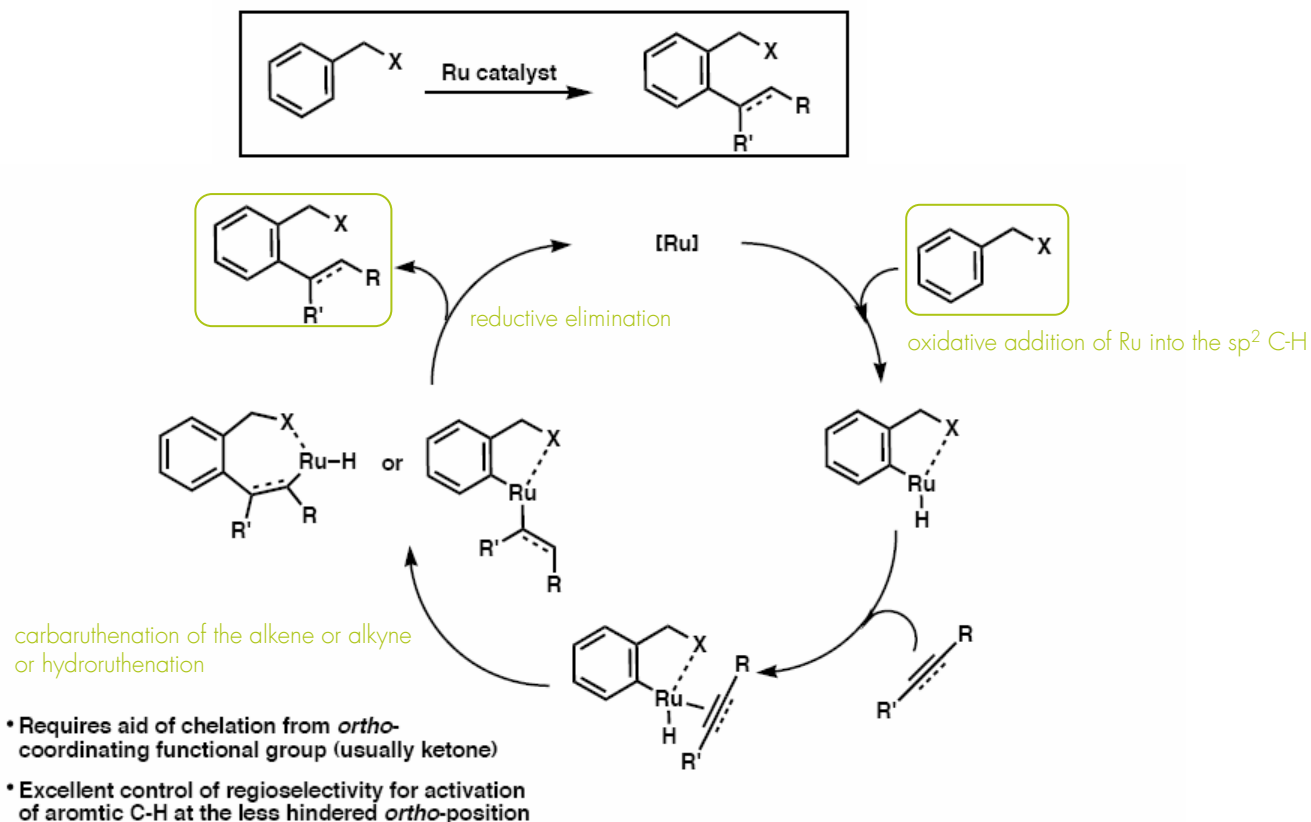
# Ruthenium Chemistry

## C-C Bond Formation

### ❖ C-H Activation

#### • Aromatic C-H Bond Activation

➤ Regio- and chemoselective addition of alkenes and alkynes to aromatic compounds can be accomplished by Ru-catalyzed aromatic C-H bond activation. The proposed reaction mechanism is detailed in the scheme:



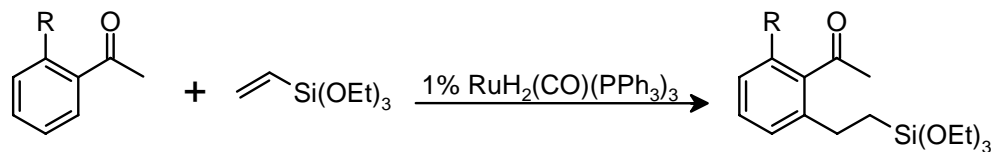
*Pure Appl. Chem.* 1997, 589

# Ruthenium Chemistry

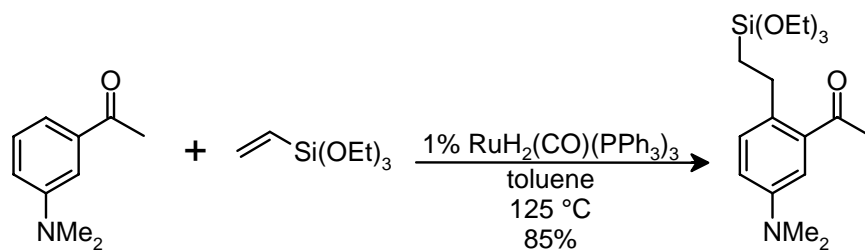
## C-C Bond Formation

### ❖ C-H Activation

- Aromatic C-H Bond Activation



*Pure Appl. Chem.* **1997**, 589



*Pure Appl. Chem.* **1997**, 589

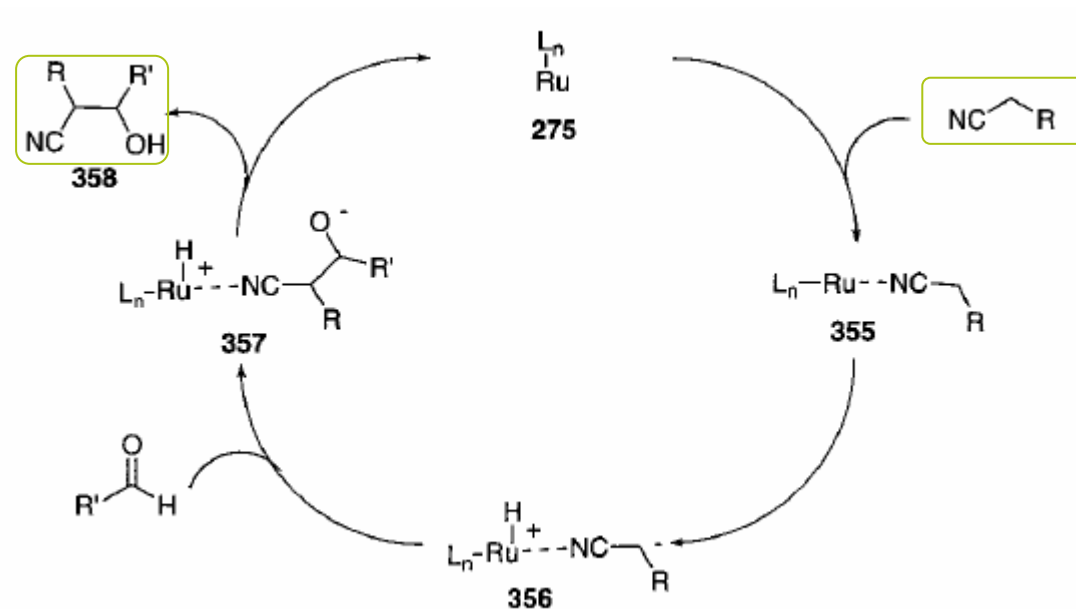
# Ruthenium Chemistry

## C-C Bond Formation

### ❖ C-H Activation

- $sp^3$ -CH Bond Activation

➤ Ru complexes can also activate the C-H bond of  $sp^3$ -carbons adjacent to an activating group. The most common activating group is a **nitrile**



# Ruthenium Chemistry

- ❖ Introduction
- ❖ Hydrogenation
- ❖ Oxidation
  - RuO<sub>4</sub>-Promoted Oxidation
  - Oxidation with Ru Complex Catalysts and Oxidants
- ❖ Nucleophilic Addition to C-C Multiple Bonds
- ❖ C- C Bond Formation
  - Ruthenacycle Intermediates
  - C-H Activation
  - C-C Bond Formation Initiated by Ru Carbene Complexes
  - Diazo Compounds: Cyclopropanation
- ❖ Literature

# Ruthenium Chemistry

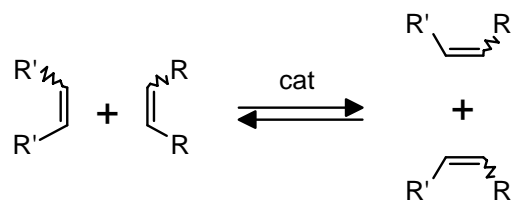
## C-C Bond Formation

### ❖ C-C Bond Formation Initiated by Ru Carbene Complexes

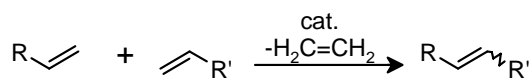
#### • Olefin Metathesis

➤ The olefin metathesis, the metal-catalyzed exchange of the alkylidene groups of two olefins, are representative catalytic reactions initiated by **metal carbene intermediates**

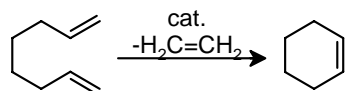
➤ **Olefin Metathesis** allows the exchange of substituents between different olefins - a **transalkyldination**



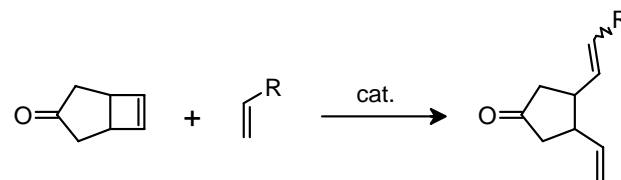
➤ Synthetically useful, high-yield procedures for lab use include **ring closure** between terminal vinyl groups, **cross metathesis** - the intermolecular reaction of terminal vinyl groups - and **ring opening** of strained alkenes. When molecules with terminal vinyl groups are used, the equilibrium can be driven by the ready removal of the product ethene from the reaction mixture. **Ring opening metathesis** can employ an excess of a second alkene, but can also be conducted as a homo- or co-polymerization reaction. The driving force in this case is the loss of ring strain.



**Cross Metathesis**



**Ring-Closing Metathesis (RCM)**



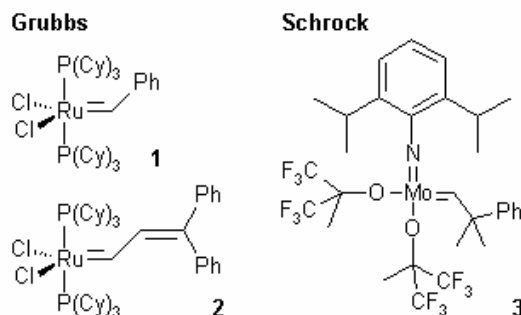
**Ring Opening Metathesis (Polymerization) [ROM (P)]**

# Ruthenium Chemistry

## C-C Bond Formation

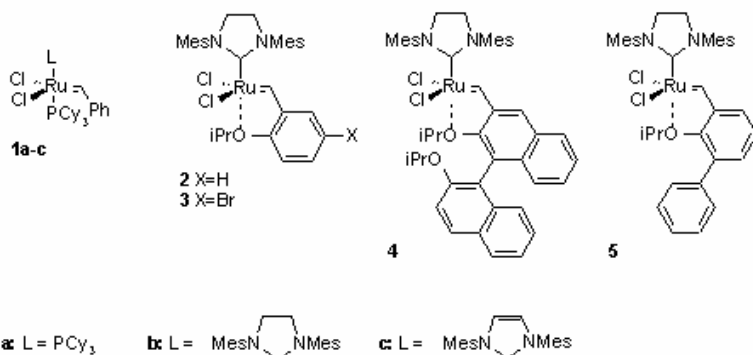
- Olefin Metathesis: catalysts

➤ All of these applications have been made possible by the development of new homogeneous catalysts. Shown below are some of these catalysts, which tolerate more functional groups and are more stable and easy to handle. The **Schrock catalysts** are more active and are useful in the conversion of sterically demanding substrates, while the **Grubbs catalysts** tolerate a wide variety of functional groups.



➤ The **second generation Grubbs catalysts** are even more stable and more active than the original versions. Some of these are depicted:

Activity: 2 < **1b** < 4 < 5



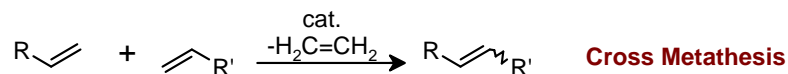
*Angew. Chem. Int. Ed.* 2002, 114, 4038

# Ruthenium Chemistry

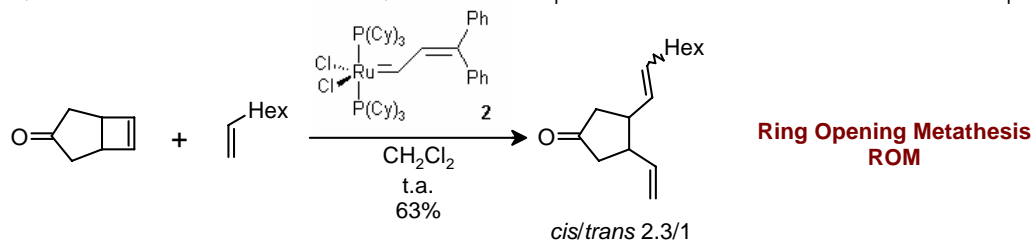
## C-C Bond Formation

- Olefin Metathesis

➤ **Cross Metathesis:** the transalkyldation of two terminal alkenes under release of ethene, catalyzed by ruthenium carbenoids (**Grubbs Catalyst**). Statistically, the reaction can lead to three possible pairs of geometric isomers, i.e. *E/Z* pairs for two homocouplings and the cross-coupling (R-CH=CH-R, R'-CH=CH-R', and R-CH=CH-R') - a total of 6 products. The selectivity of this reaction is currently undergoing further study, but various examples exist in which two alkenes with different reactivity give the cross-coupled product with excellent yields and excellent selectivity

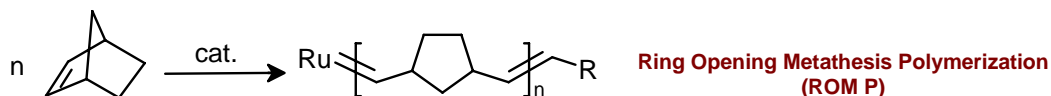


➤ **Ring Opening Metathesis (Polymerization) - ROM(P):** strained rings may be opened by a Ru carbene-catalyzed reaction with a second alkene. **The driving force is the relief of ring strain.** As the products contain terminal vinyl groups, further reactions of the Cross Metathesis variety may occur. Therefore, the reaction conditions (time, concentrations,...) must be optimized to favor the desired product



*J. Am. Chem. Soc.* **1995**, *117*, 9610

➤ In absence of excess of a second reaction partner, **polymerization** occurs (**ROMP**):



# Ruthenium Chemistry

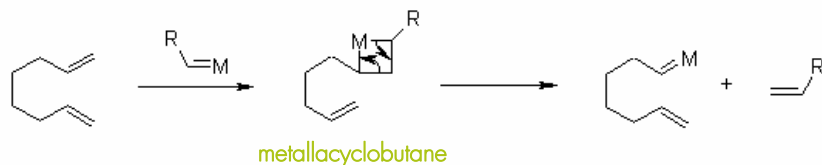
## C-C Bond Formation

- Olefin Metathesis

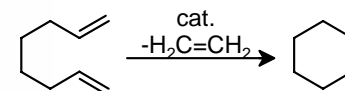
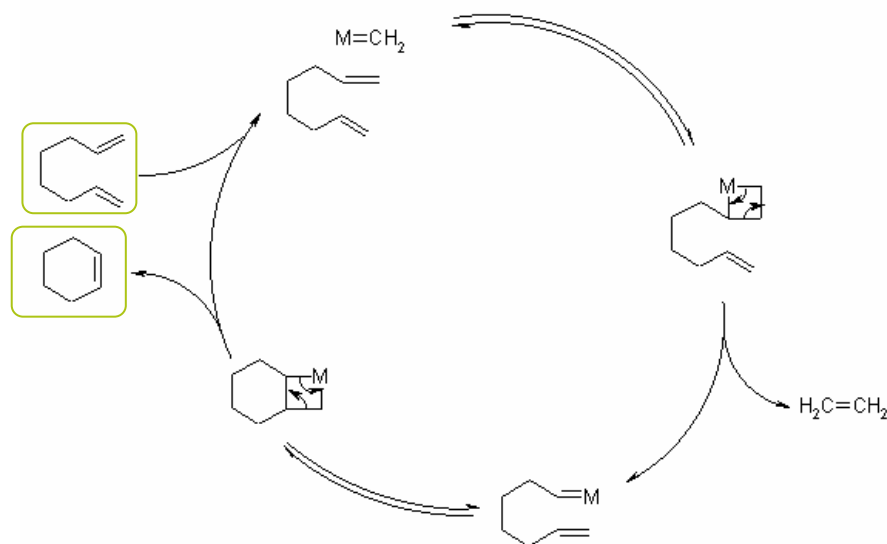
➤ **Ring-Closing Metathesis (RCM):** The Ring-Closing Metathesis (RCM) allows synthesis of 5- up to 30-membered cyclic alkenes. The *E/Z*-selectivity depends on the ring strain. The Ru-catalysts used tolerate a variety of functional groups, but normally the molecule must have polar side chains that are able to build a template for the catalyst. The modern Second Generation Grubb's Catalysts are more versatile

➤ **Mechanism:** The key intermediate is a **metallacyclobutane**, which can undergo cycloreversion either towards products or back to starting materials. When the olefins of the substrate are terminal, the driving force for **RCM** is the removal of ethene from the reaction mixture

Initiation:



Catalytic cycle:



**Ring-Closing Metathesis (RCM)**

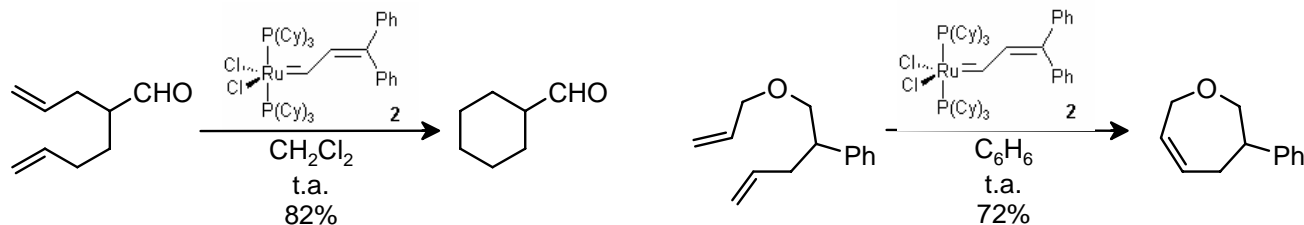
Chauvin's Mechanism

# Ruthenium Chemistry

## C-C Bond Formation

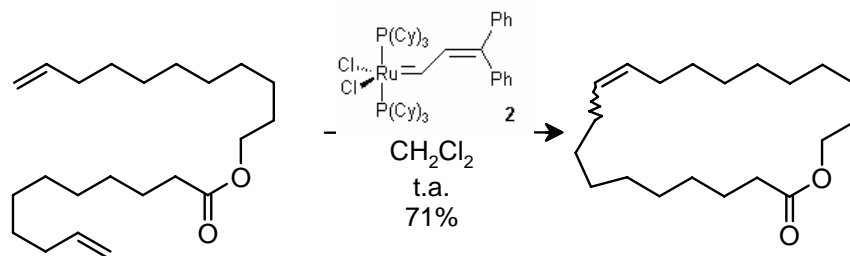
- Olefin Metathesis

➤ **Ring-Closing Metathesis (RCM)**: Ru-carbene complex-catalyzed reactions of various functionalized 1,6-, 1,7-, and 1,8-dienes give the corresponding five-, six-, and seven-membered **cyclic olefins**. Various amines, amides, ureas, ethers and siloxanes can be cyclized



*J. Am. Chem. Soc.* **1993**, 115, 9856  
*J. Org. Chem.* **1997**, 62, 7310.

➤ **Macrocyclic compounds** such as eight-membered cyclic amino compounds and even 38-membered macrocyclic peptides, 21-membered macrolides, crown ethers, and bridged calixarenes can be prepared directly from the corresponding dienes without a high-dilution technique (*Chem. Rev.* **1998**, 98, 2599-2660; *Chem. Rev.* **2009**, 109, 3743-3782):



*Synthesis* **1997**, 792

# Ruthenium Chemistry

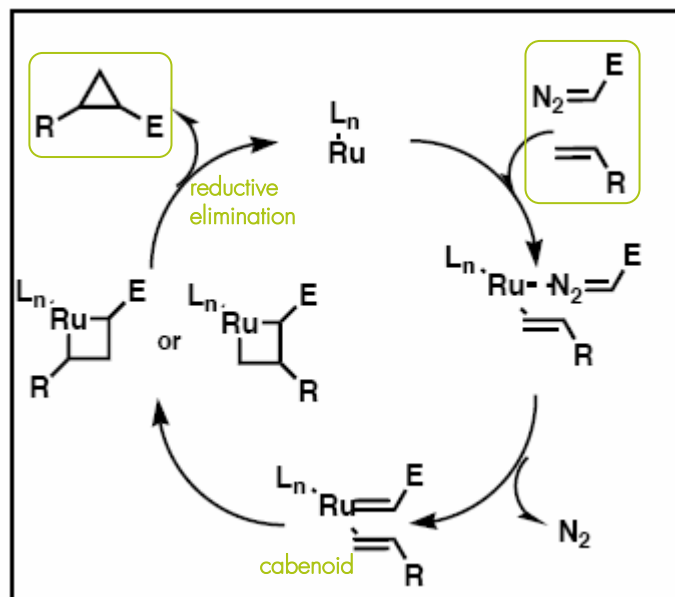
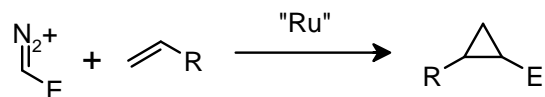
- ❖ Introduction
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# Ruthenium Chemistry

## C-C Bond Formation

### ❖ Diazo Compounds: Cyclopropanation

➤ The **mechanism** proposed for the **Ru-catalyzed cyclopropanation of olefins** involves coordination of the diazo compound and the olefin prior to formation of the **carbenoid**



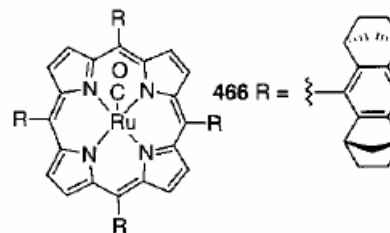
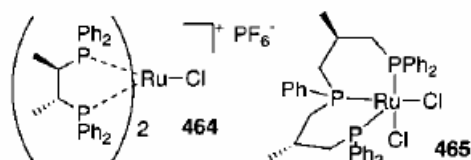
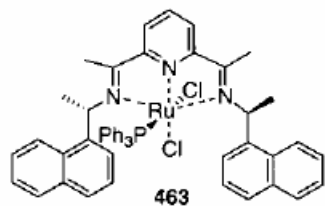
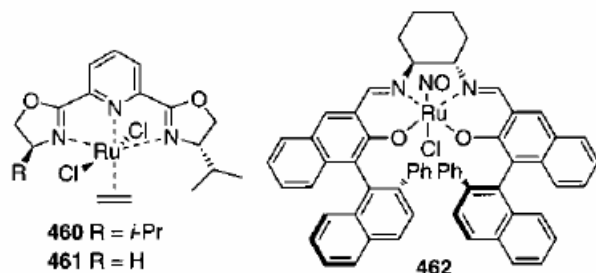
➤ A variety of Ru catalysts have been developed. Various **chiral ruthenium catalysts** have been employed in the **asymmetric cyclopropanation of olefins**

# Ruthenium Chemistry

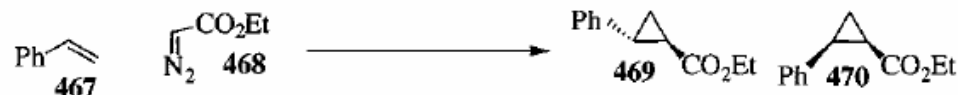
## C-C Bond Formation

### ❖ Diazo Compounds: Cyclopropanation

#### ➤ Ruthenium catalysts:



**Table 6. Ruthenium-Catalyzed Asymmetric Cyclopropanation of Styrene**



entry	catalyst	yield (%)	469 (%ee):470 (%ee)	ref
1	5% <b>460</b>	73	91 (89):8 (78)	132c
2	5% <b>461</b>	93	89 (90):11 (66)	132a
3	5% <b>462</b>	45	7 (15):93 (97)	138a
4	5% <b>463</b>	65	86 (-):14 (76)	137
5	1% <b>464</b>	29	58 (25):42 (14)	133a
6	2% <b>465</b>	84	59 (17):41 (40)	133b
7	0.15% <b>466</b>	100	95 (91):5 (27)	133d

*Chem. Rev.* 2001, 2067-2096 and ref. therein

# Ruthenium Chemistry

## Literature

*Ruthenium-Catalyzed Reactions for Organic Synthesis.* Takeshi Naota; Hikaru Takaya; Shun-Ichi Murahashi. *Chem. Rev.* 1998, 98, 2599

*Non-Metathesis Ruthenium-Catalyzed C-C Bond Formation.* Barry M. Trost; F. Dean Toste; Anthony B. Pinkerton. *Chem. Rev.* 2001, 101, 2067-2096

*Metathesis in the Synthesis of Aromatic Compounds.* Willem A. L. van Otterlo; Charles B. de Koning. *Chem. Rev.* 2009, 109, 3743–3782

*Some Aspects of the Coordination and Catalytic Chemistry of Ruthenium.* Jack Halpern. *Pure & Appl. Chem.*, 1987, 59(2), 173–180

Preparation of Ruthenium Catalysts:

4. *Encyclopedia Reagents Org. Syn.* 1996, Vol. 6, 4415

8. *Synthesis* 1994, 639; *Aldrichimica Acta* 1990, 23, 13

9. *J. Organomet. Chem.* 1981, 214, 391

10. *J.C.S., Dalton Trans.* 1975, 1710

11. *J. Organomet. Chem.* 1980, 195, 77

12. *Inorg. Synth.* 1970, 12, 237

13. *JACS* 1968, 90, 1089.

14. *ACIEE* 1995, 4, 2039; *JACS* 1996, 118, 100.

15. *Inorg. Synth.* 1974, 15, 45.

16. *JCS Dalton Trans.* 1980, 1961

17. *JCS Chem. Comm.* 1982, 1388

18. *JCS Dalton Trans.* 1974, 233

19. *Chem. Lett.* 1984, 1161

20. *Organometallics* 1988, 7, 2243

21. *J. Organomet. Chem.* 1986, 314, C46





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