EXPERIMENT **3**

Grubbs' Inspired Ruthenium Catalysts for Olefin Metathesis-Nobel Prize Winning Chemistry

REFERENCES

a. Shaw, A. P.; Ryland, B. L.; Norton, J. R.; Buccella, D.; Moscatelli, A. *Inorg. Chem.* **2007**, *46*, 5805.
b. Trnka, T. M.; Grubbs, R. H. *Accounts of Chemical Research* **2001**, *34 (1)*, 18–29.
c. Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110 (3),* 1746–1787.
d. Jean-Louis H. P.; Chauvin, Y. *Die Makromolekulare Chemie* **1971**, *141 (1):* 161–176.

SAFETY RECOMMENDATIONS

Ruthenium(III) chloride hydrate ($RuCl_3*2H_2O$): Causes eye and skin burns. May be harmful if swallowed.

Triphenyl phosphine (PPh_3): May cause skin, eye and respiratory track irritation. Harmful if swallowed. May cause neurotoxic effects including paresthesia.

1,1-diphenylprop-2-yn-1-ol: May cause skin, eye and respiratory track irritation. Harmful if swallowed.

Tricyclohexylphosphine (PCy_3): Skin and eye irritation. Harmful if swallowed.

Diethyl diallylmalonate: Skin and serious eye irritation. May cause respiratory track irritation.

INTRODUCTION

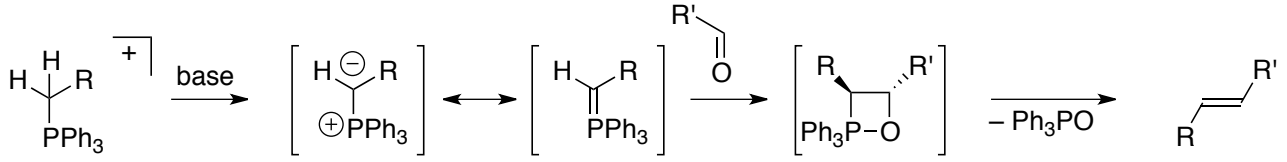
Materials that contain carbon-carbon multiple bonds have tremendous chemical value because multiple bonds are sites of reactivity for producing materials like polymers or fine chemicals. Table 1 shows values for bond dissociation energies (BDEs) for C–C bonds in ethane, ethylene, and acetylene. Naturally, the energies increase with bond order with the C=C bond in ethylene being almost twice as strong as the C–C bond in ethane.

Table 1. BDE values for carbon-carbon bonds.

Bond	BDE (kcal/mol)
CH_3–CH_3	90.4
CH_2=CH_2	174.1
HC≡CH	230.7

C–C multiple bonds are found in natural products and in petroleum feedstocks. There are many well-known methods for synthesizing them—a famous example being the Wittig olefination (Scheme 1). In this reaction, *E*-alkenes are produced from aldehydes and triphenylphospinium compounds that are typically prepared from triphenylphosphine and alkyl halides. For his pioneering contributions to the synthesis and reactivity of phosphorous ylides,

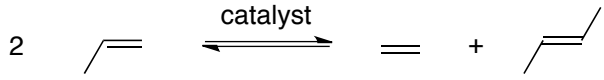
Scheme 1



Georg Wittig shared the 1979 Nobel Prize in Chemistry with Herbert C. Brown, who was recognized for developing the hydroboration reaction.

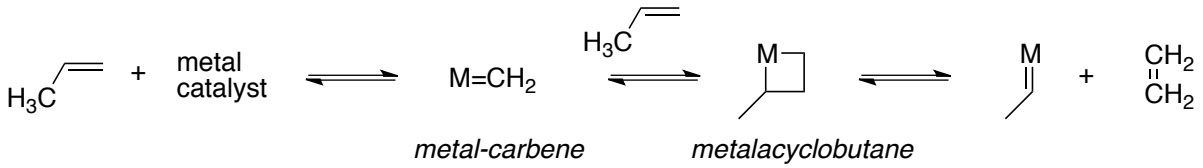
In the 1950s, Herbert Eleuterio, a chemist at DuPont who received his Ph.D. from MSU working with Professor Harold Hart, was studying catalysts for the polymerization of propylene to make polypropylene. While analyzing the polymers with IR spectroscopy, he saw absorptions that were characteristic of polyethylene in the materials he

Scheme 2



obtained. After excluding the possibility that his propylene was contaminated with ethylene, Eleuterio realized that the reaction in Scheme 2 was being catalyzed. In the overall reaction, the exchange, or metathesis, of the C=C bonds in propylene was occurring to produce ethylene and 2-butene.

Scheme 3

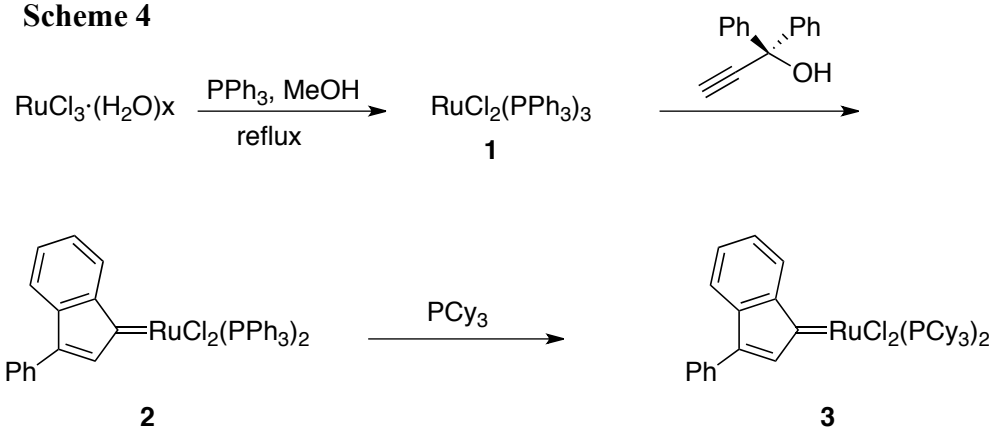


Several mechanisms were suggested for this reaction. Yves Chauvin proposed that a metal-carbene catalyzed the process (Scheme 3). The key step in the reaction is a 2+2 cycloaddition, a reaction that is "forbidden" for two ethylene molecules, occurs between the carbene and the alkene to produce a metallacyclobutane intermediate. The carbene and olefin can be regenerated by two similar pathways. The first is the simple reverse reaction to give the starting olefin and carbene. The second pathway generates a new C=C bond.

Chauvin's mechanism was confirmed by Robert Grubbs, who was a Professor in MSU's Chemistry Department at the time. Grubbs later moved to Caltech and developed ruthenium based catalysts that are widely used today. In 2005, Chauvin and Grubbs, were awarded the Nobel Prize in Chemistry for Olefin and Alkyne Metathesis, which they shared with Richard Schrock who developed alkyne and olefin metatheses (Figure 1). I

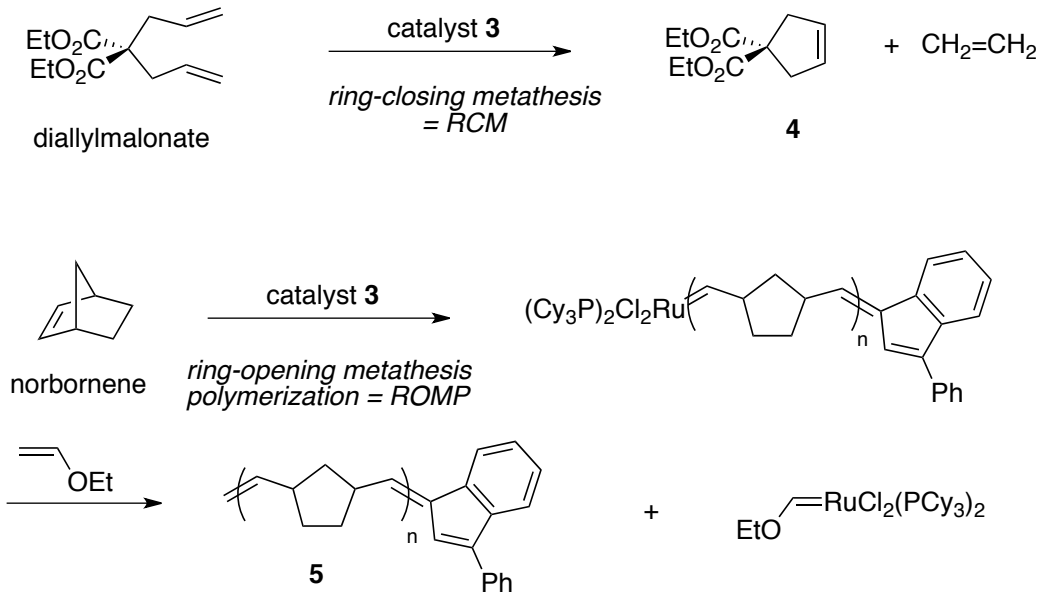
In this module you will begin with the most common ruthenium starting material, $RuCl_3 \cdot H_2O$. The first step involves a reaction with triphenylphosphine to prepare $RuCl_2(PPh_3)_3$ (**1**). You will then react **1** with 1,1-diphenyl-2-propyn-1-ol to produce carbene complex 2. To improve the reactivity, the triphenylphosphine ligands in **2** were replaced with tricyclohexylphosphines affording **3**, which has the trade name Neolyst M1™ (Scheme 4).

Scheme 4



You will use catalyst **3** to carry out the ring-closing metathesis (RCM) of diallylmalonate and ring-opening metathesis (ROMP) of norbornene to afford products **4** and **5**, respectively (Scheme 5). In both cases, olefin metathesis is highly selective for the products shown. The examples in Scheme 5 illustrate the versatility that olefin metathesis provides for the synthesis of fine chemicals and advanced materials.

Scheme 5



Objectives

1. Using the attached procedures prepare the complexes **1**, **2**, and **3**.
2. Carry out an RCM reaction of 0.50 g diethyl diallyl malonate using a 5 mol% loading of **3**.
3. Perform a ROMP of norbornene.

PROCEDURE

1st Lab Period: Synthesis of $RuCl_2(PPh_3)_3$ (1)

$RuCl_3$*$3H_2O$ (300 mg, 1.1 mmol) was refluxed with PPh_3 (1.8 g, 7 mmol) in 50 mL of deoxygenated anhydrous methanol for 1 h (or until you get dark brown

precipitate). Filter your reaction, collect the brown solid, wash it with ether (3 X 10 mL) and dry under vacuum.

Record the yield and obtain ^{1}H and ^{31}P NMR spectra (in $CDCl_3$) for **1**. Save the complex for the next part of this module.

2nd Lab Period: Synthesis of $RuCl_2(PPh_3)_2$(3-phenylinden-1-ylidene) (2)

Under a N_2 atmosphere, add 25 mL dry THF to a dry 100 mL round-bottom Schlenk flask containing a stir bar and 500 mg (0.521 mmol) $RuCl_2(PPh_3)_3$. Add 1.5 equivalents of 1,1-diphenyl-2-propyn-1-ol in one portion to the solution and then connect a reflux condenser and gas flow adapter to the flask. Connect the gas flow adapter to a glass T that is also connected to N_2 and a mineral oil bubbler. Close the stopcock on the Schlenk flask so that the only N_2 source is the gas inlet adapter. Heat the stirring solution to reflux in a silicon oil bath for 2 h. Cool the solution completely and transfer to a 50 mL one neck round-bottom flask so the solvent can be removed by rotary evaporation. Dissolve the residue in 4-5 mL CH_2Cl_2 and slowly add 25 mL hexanes to precipitate the complex. Further precipitation can be induced by rotovapping a small portion of the solvent. Filter the solid and wash with hexanes (3 x 5 mL). Record yield and ^{1}H and ^{31}P NMR spectra (in $CDCl_3$) for **2**. Save the complex for the next part of this module.

3rd Lab Period: Synthesis of $Cl_2(PCy_3)_2$Ru-(3-phenylinden-1-ylidene) (3)

Under an N_2 atmosphere, add 25 mL dry CH_2Cl_2 to a dry 100 mL round-bottom Schlenk flask containing a stir bar and 300 mg (0.338 mmol) **2**. To this solution add 313 mg (1.115 mmol) PCy_3 and then add a stopper the flask. Stir the solution at room temperature for 1.5 h to 2 h. Transfer the solution to a 50 mL one neck round-bottom flask so the solvent can be removed by rotary evaporation. Suspend the residue in ~20 mL hexanes and stir at room temperature for 30 min. Filter and wash the solid with hexanes (3 x 5 mL). Record the yield and obtain ^{1}H and ^{31}P NMR spectra (in $CDCl_3$) for **3**. NOTE: The ^{31}P NMR spectra should be taken immediately after dissolving the complex in $CDCl_3$ to avoid increased conversion to impurities. Save the complex for a later part of this module.

4th Lab Period: Ring-closing metathesis of diethyl diallylmalonate

Under a N_2 atmosphere, add 6 mL dry CH_2Cl_2 to a dry 25 mL round-bottom flask containing a stir bar and 9.2 mg (0.010 mmol) **3**. Add 0.1 mL (0.44 mmol) diethyl diallylmalonate to the flask and stir at room temperature for 1 h. After stirring, remove the solvent by rotary evaporation and determine the conversion to the ring-closed product **4** by ^{1}H NMR in $CDCl_3$.

Ring-opening metathesis of norbornene

Under a N_2 atmosphere, add 6 mL dry CH_2Cl_2 to a dry 25 mL round-bottom flask containing a stir bar and 9.2 mg (0.010 mmol) **3**. Add 100 equivalents of norbornene to the flask and stir for 1 h. Quench the reaction by adding vinyl ether (0.5 ml) and rotovap to remove volatile materials. Characterize polymer **5** by ^{1}H NMR and propose and average molecular weight.

In your report, address the following points:

1. Write balanced reactions for all of the reactions you perform.
2. Propose structures and mechanisms of formation for compounds **1**-**3**.
3. Discuss the differences between the room temperature ^{31}P spectrum of **1** and the low temperature spectrum that we will provide.
4. Assign your NMR spectra and discuss any relevant trends in chemical shifts for **1**, **2**, and **3**.
5. Assign the spectra for **4** from the RCM reaction and **5** from the ROMP. For **5**, calculate the molecular weight using end group analysis. Propose mechanisms for these reactions and explain why ring closure is favored in one instance and ring opening occurs in the other.