6.6: Insertion at Coordinated Alkenes

Metal alkoxides can undergo 1,2-elimination (or beta-elimination) to give organic carbonyl compounds. This reaction is the reverse of a nucleophilic addition of a metal hydride to an organic carbonyl.

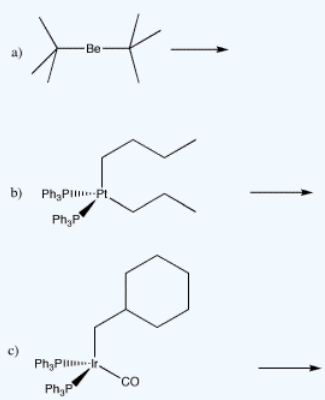
Metal alkyls can also undergo 1,2-elimination. In this case, an alkene is formed. Like the carbonyl compounds formed from 1,2-elimination, the alkene usually remains bound to the metal. It can dissociate to form the free alkene, though. For more information on alkene binding, take a look at this page.

These reactions are sometimes called "beta hydride eliminations", emphasizing that the hydrogen attached to the metal usually acts as a nucleophile. Thus, when the hydrogen transfers to the metal, it is forming a hydride.

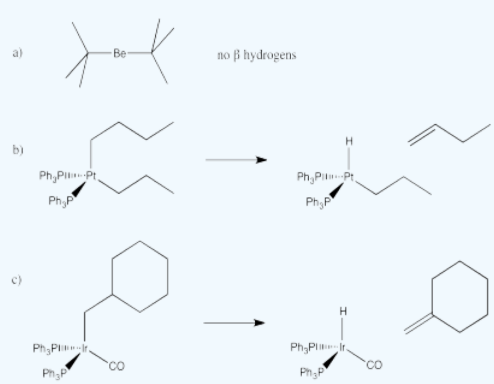
- Alkyl groups that are coordinated to metals can also undergo elimination.
- In order to undergo elimination, an alkyl group must have a hydrogen.
- When a metal alkyl undergoes elimination, it forms an alkene.

Exercise 6.6.1

Draw the elimination products in the following cases.

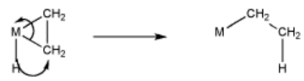


Answer

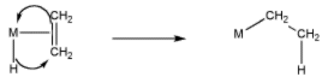


The reverse of a 1,2-elimination is a 1,2-insertion. Just like aldehydes and ketones, alkenes can undergo 1,2-insertions (also called beta hydride insertions). In terms of electrophiles and nucleophiles, this reaction is a little harder to imagine. However, we can still think of the hydride as a nucleophile. Maybe the alkene is an electrophile. Given that it is donating its pi electrons to the metal, we can think of it as "activated", a little bit like an activated carbonyl.

The formalisms of drawing a beta alkene insertion are tricky. If we use the metallacycle drawing of a bound alkene, it might look like this:



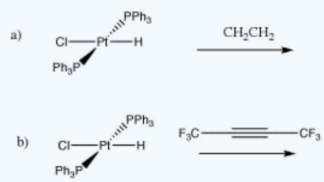
More often, bound alkenes are drawn as shown as in the picture below. In that case, we could try to show the pi bond forming a new carbon-metal bond. The bond between the metal and alkene on the picture to the left does not really stand for a separate pair of electrons in this case; it just stands for the pi bond donating to the metal.



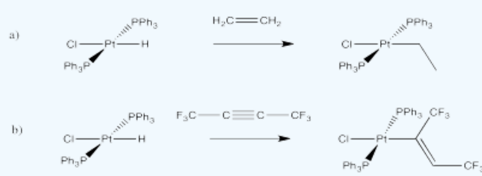
- The reverse of elimination is insertion.
- A coordinated alkene is sometimes considered electrophilic because it is giving electrons to the metal.
- A coordinated alkene is activated, like a coordinated carbonyl compound.

Exercise 6.6.2

Draw the insertion products in the following cases.

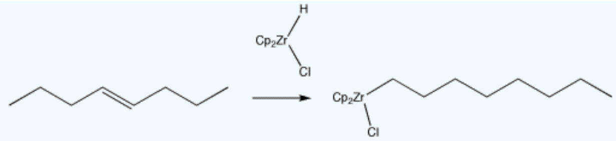


Answer

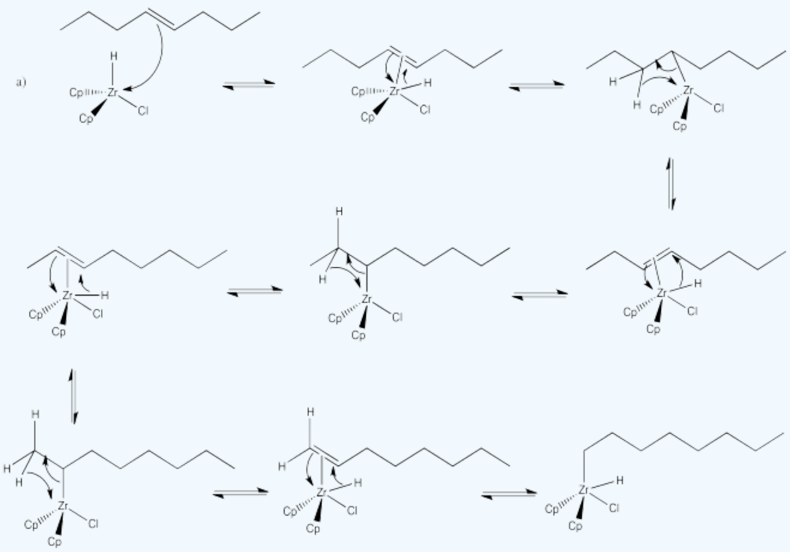


Exercise 6.6.3

Alkenes can be converted into other compounds through the use of organometallic reagents, such as "Schwartz's reagent" (below). In this case, the resulting alkyl compound can easily be converted into a long-chain alkyl halide or alcohol through the addition of appropriate reagents. Provide a mechanism for the reaction shown below.



Answer



? Exercise 6.6.4

1,2-alkyl insertions and -eliminations are also known in a few cases, although they are much slower than 1,2-hydride insertions and -eliminations. Show the 1,2-insertion products for the following cases.

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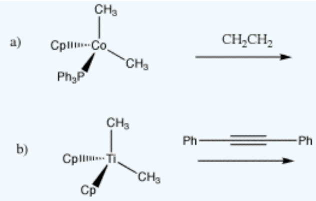
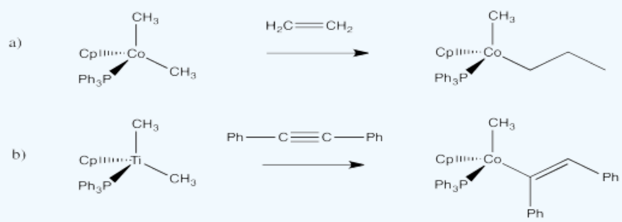
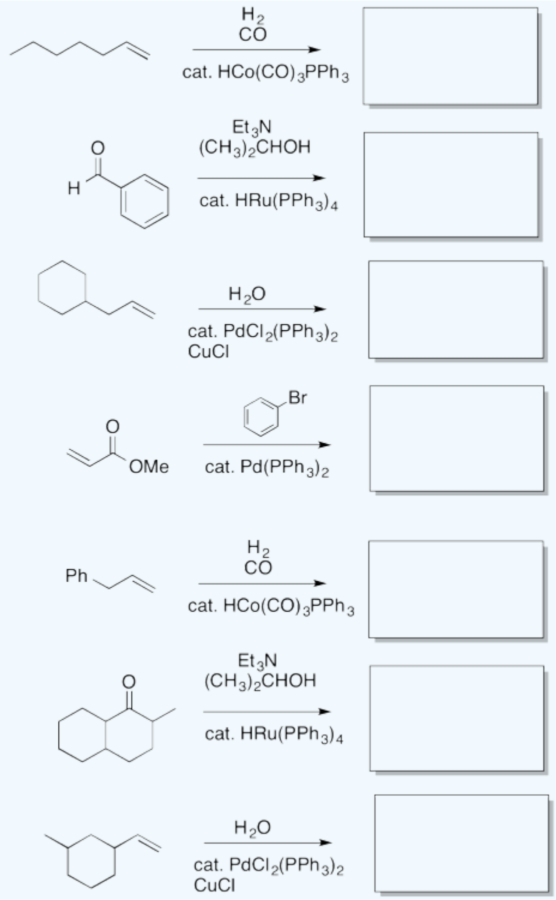


Answer

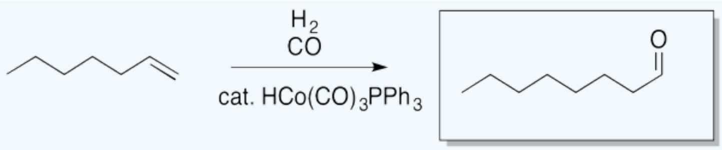


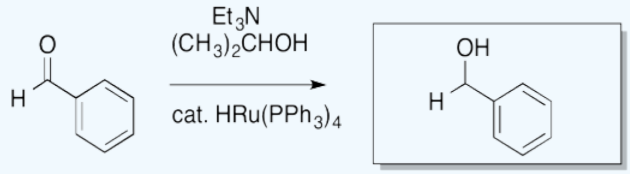
? Exercise 6.6.5

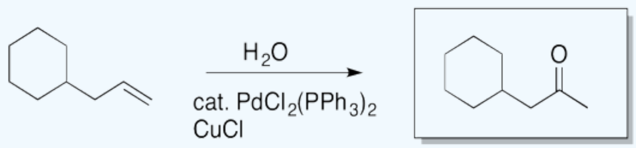
https://chem.libretexts.org/@go/page/189872

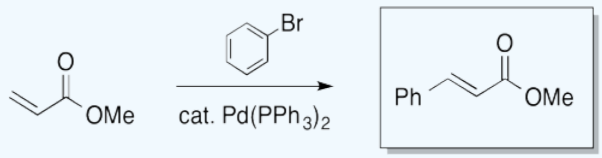

H2
CO
cat. HCo(CO)3PPh3
O
H
Et3N
(CH3)2CHOH
cat. HRu(PPh3)4
H2O
cat. PdCl2(PPh3)2
CuCl
O
OMe
Br
cat. Pd(PPh3)2
Ph
H2
CO
cat. HCo(CO)3PPh3
O
Et3N
(CH3)2CHOH
cat. HRu(PPh3)4
H2O
cat. PdCl2(PPh3)2
CuCl

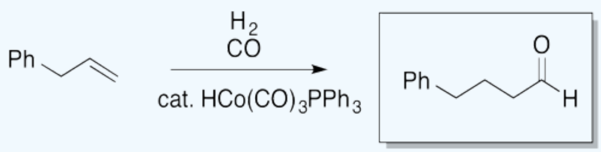
Answer

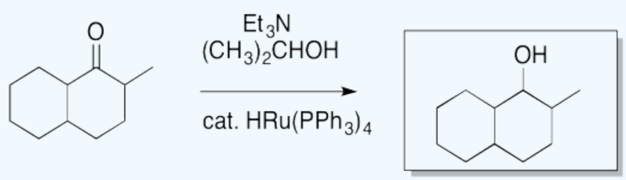


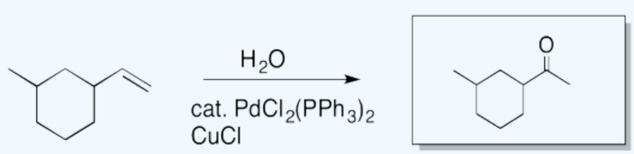






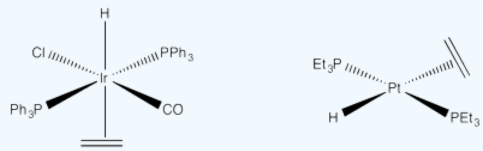






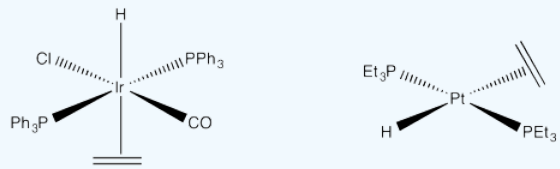
? Exercise 6.6.6

Why don't either of these complexes undergo hydride insertions at room temperature?



Answer

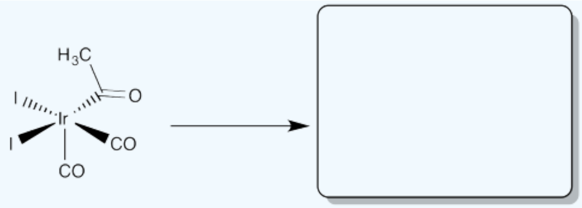
Why don't either of these complexes undergo hydride insertions at room temperature?

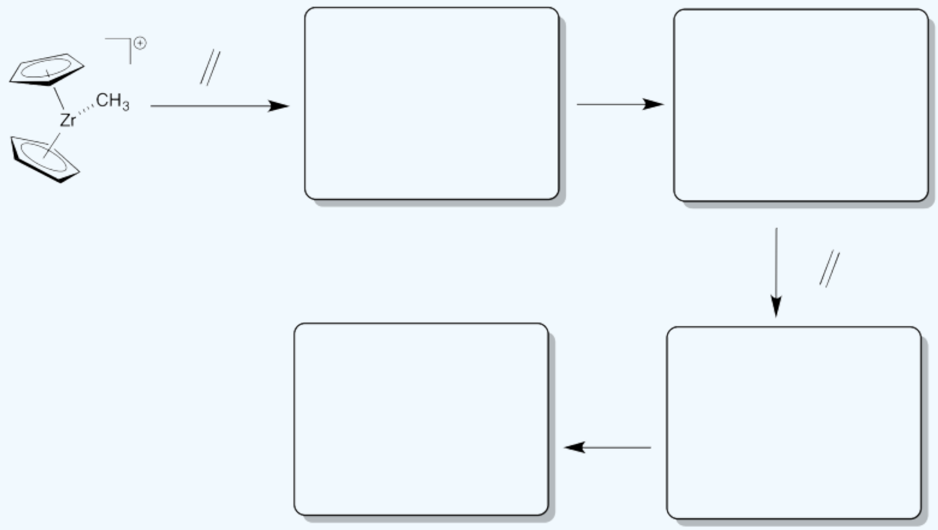


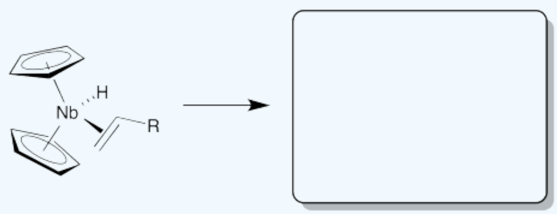
The hydride and the alkene group are trans to each other in this complex. In order for ar insertion reaction, the two ligands need to be closer.

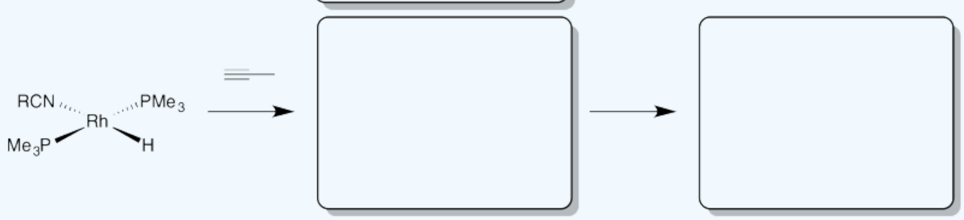
? Exercise 6.6.7

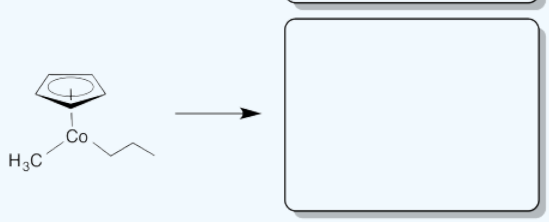
Fill in the missing insertion / elimination products.



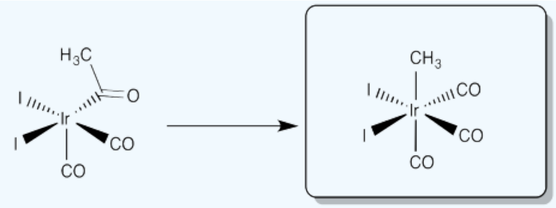


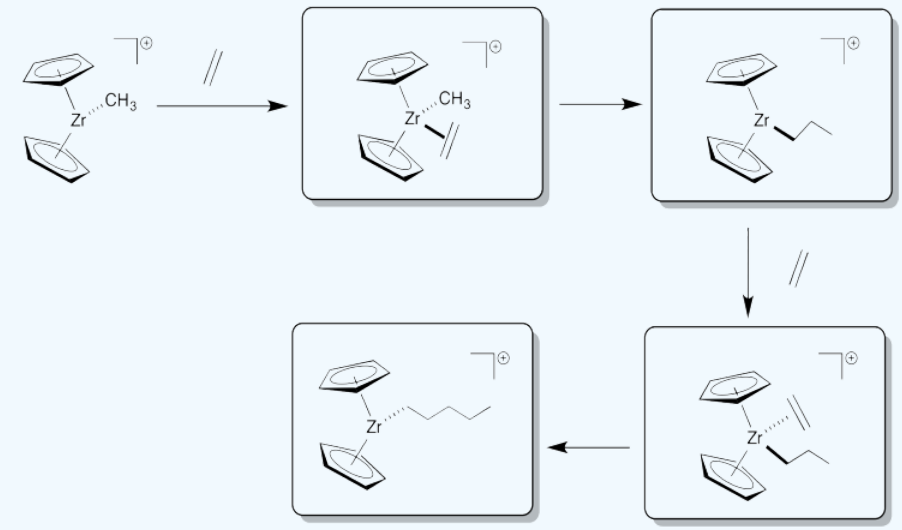


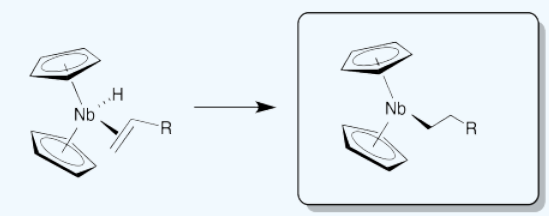


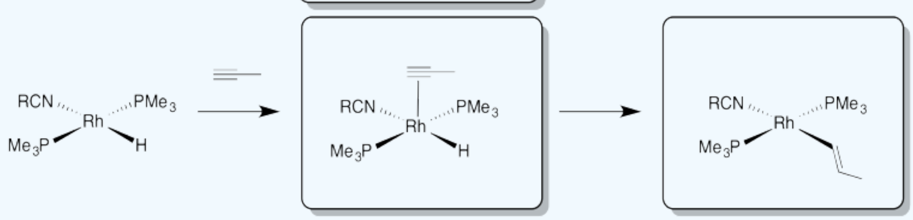


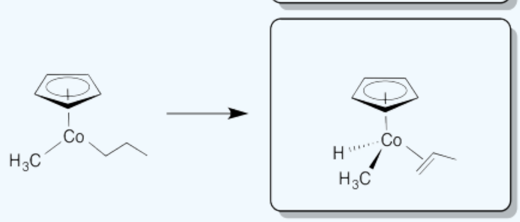
Answer









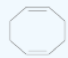


Exercise 6.6.8

The following multi-part problem is based on an article in the primary research literature.

Scorpionate Ligands: A Ligand with a Greater Propensity to Sting?
Dyson, Zech, Rawe, Haddow, Hamilton and Owen, *Organometallics*, **2011**, *30*, 5844-5850.

1. A ligand that we have seen before, **COD**.

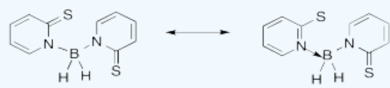


COD

a. What will the denticity of this ligand be? __________
b. Circle the sites that bind to the metal.

2. Show a molecular orbital cartoon showing how the orbitals of COD that bind to the M.

3. New Ligand, **Bmp**.
   a. Add formal charges to these two resonance structures.



When rhodium is complexed with Bmp and the COD, the following complex is formed.

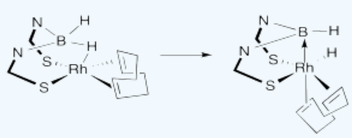
4. What is the geometry of the rhodium in this complex?

Geometry: __________________

5. What is the valence electron count on Rh in this complex?

Valence electrons on Metal:	_______
Charge on the ligands:	_______
Charge on the Metal:	_______
Revised Count on the Metal (accounting for charge):	_______
Number of electrons donated from the ligands:	_______
Total electrons in this complex:	_______

6. Upon formation, the hydride quickly moves to the metal.

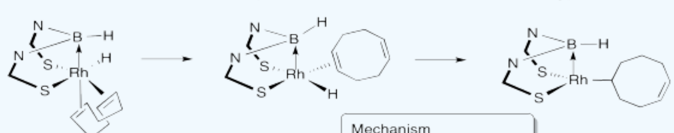


a. Why did this occur?

b. Why is there an arrow toward the B in the product?

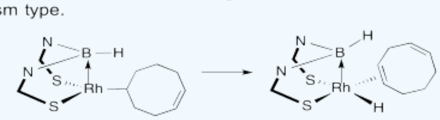
For the rhodium complex, a novel "chain-walking mechanism" is observed.

7. In this reaction, the COD partially dissociates and then the first step of the "chain-walking" occurs. Show the mechanism and provide a name for the mechanism type.



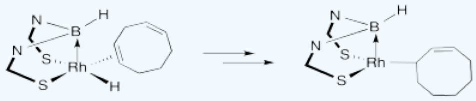
Mechanism Type:____________

8. The second step of the "chain-walking" occurs. Show the mechanism and provide a name fo the mechanism type.

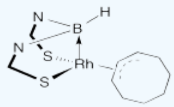


Mechanism Type:____________

9. Eventually the hydride "walks" to the final position. Show the rest of the mechanism.



10. The final product can also be represented in the following way. Show how this structure is equivalent to the one above.



11. Considering structure and thermodynamics, why is this the final product?

Answer

Scorpionate Ligands: A Ligand with a Greater Propensity to Sting?
Dyson, Zech, Rawe, Haddow, Hamilton and Owen, *Organometallics*, **2011**, *30*, 5844-5850.

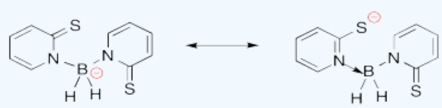
1. A ligand that we have seen before, **COD**.

 COD

a. What will the denticity of this ligand be? ____2______
b. Circle the sites that bind to the metal.

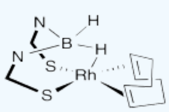
2. Show a molecular orbital cartoon showing how the orbitals of COD that bind to the M.

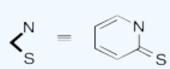
3. New Ligand, **Bmp**.
   a. Add formal charges to these two resonance structures.



When rhodium is complexed with Bmp and the COD, the following complex is formed.

4. What is the geometry of the rhodium in this complex?



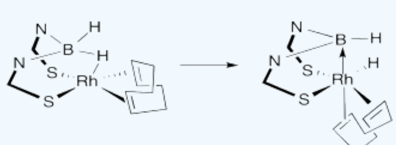


Geometry: distorted square pyramidal

5. What is the valence electron count on Rh in this complex?

Valence electrons on Metal:	____9____
Charge on the ligands:	____-1____
Charge on the Metal:	____+1____
Revised Count on the Metal (accounting for charge):	____8____
Number of electrons donated from the ligands:	____10____
Total electrons in this complex:	____18____

6. Upon formation, the hydride quickly moves to the metal.



a. Why did this occur?

b. Why is there an arrow toward the B in the product?

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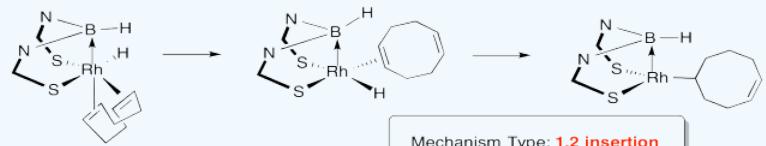
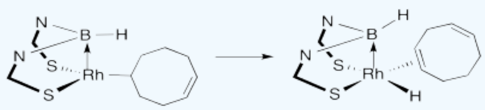
For the rhodium complex, a novel “chain-walking mechanism” is observed.

7. In this reaction, the COD partially dissociates and then the first step of the “chain-walking” occurs. Provide a name for the mechanism type.



Mechanism Type: **1,2 insertion**

8. The second step of the “chain-walking” occurs. Provide a name for the mechanism type.

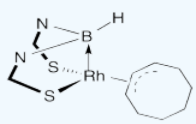


Mechanism Type: **beta elimination**

9. Eventually the hydride “walks” to the final position. Show the rest of the mechanism.

Chain walking is a series of 1,2 insertions and beta eliminations

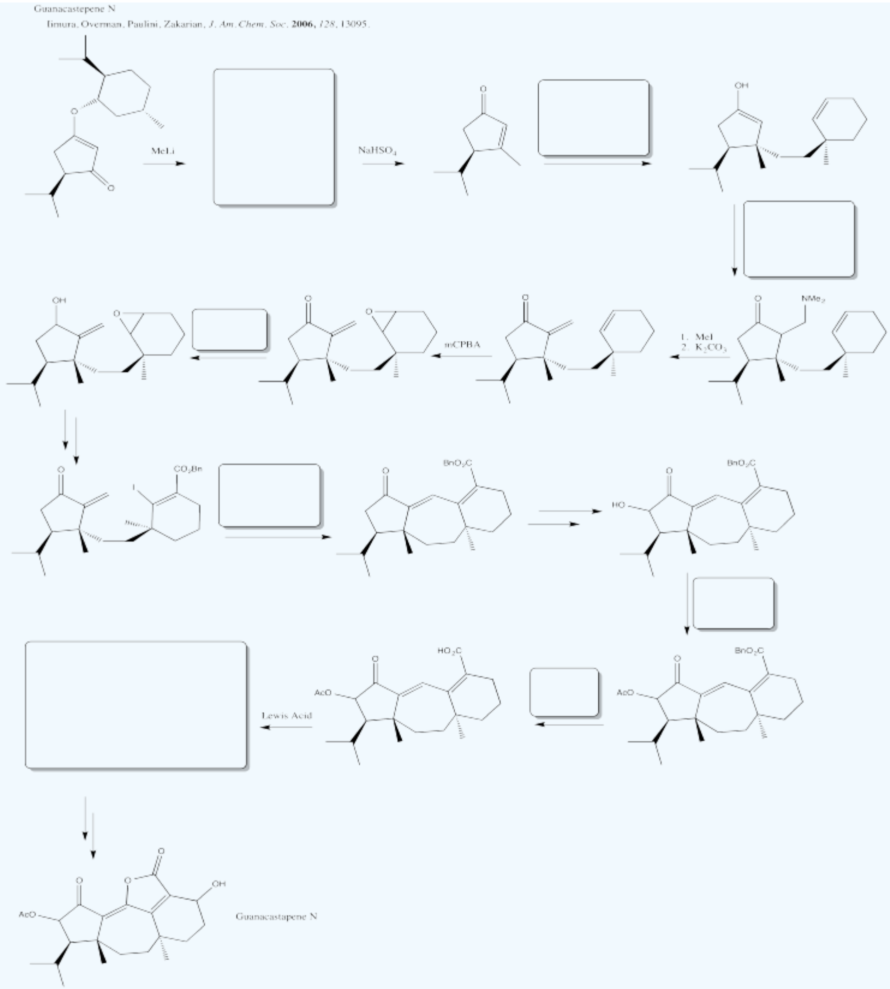
10. The final product can also be represented in the following way. Show how this structure is equivalent to the one above.



11. Considering structure and thermodynamics, why is this the final product?

resonance stabilized

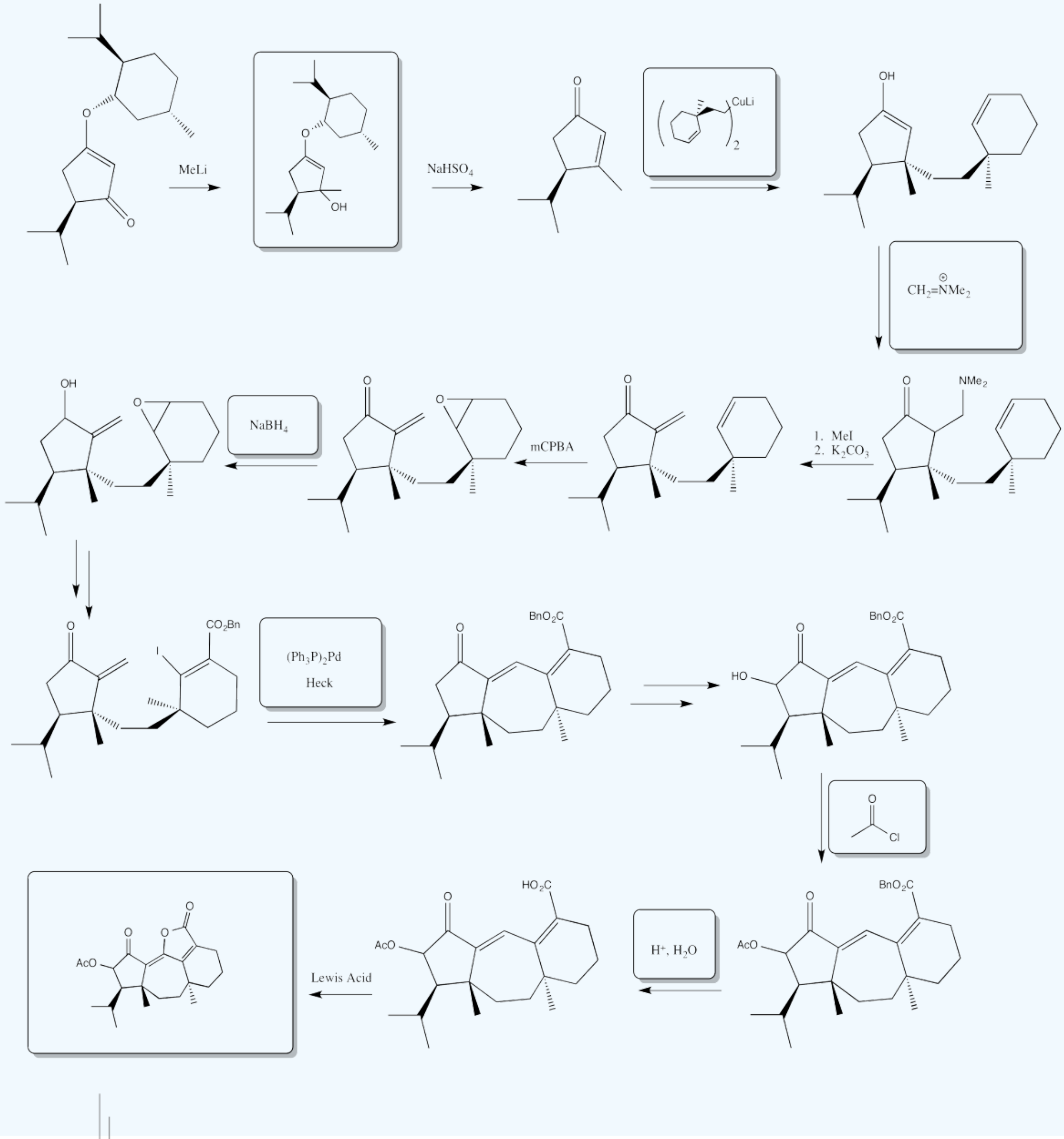
? Exercise 6.6.9


Guanacastepene N
Iimura, Overman, Paulini, Zakarian, J. Am. Chem. Soc. 2006, 128, 13095.
MeLi
NaHSO4
mCPBA
1. MeI
2. K2CO3
Lewis Acid
Guanacastepene N

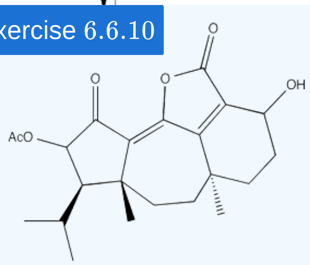
Answer

Guanacastepene N

Iimura, Overman, Paulini, Zakarian, *J. Am. Chem. Soc.* **2006,** *128*, 13095.



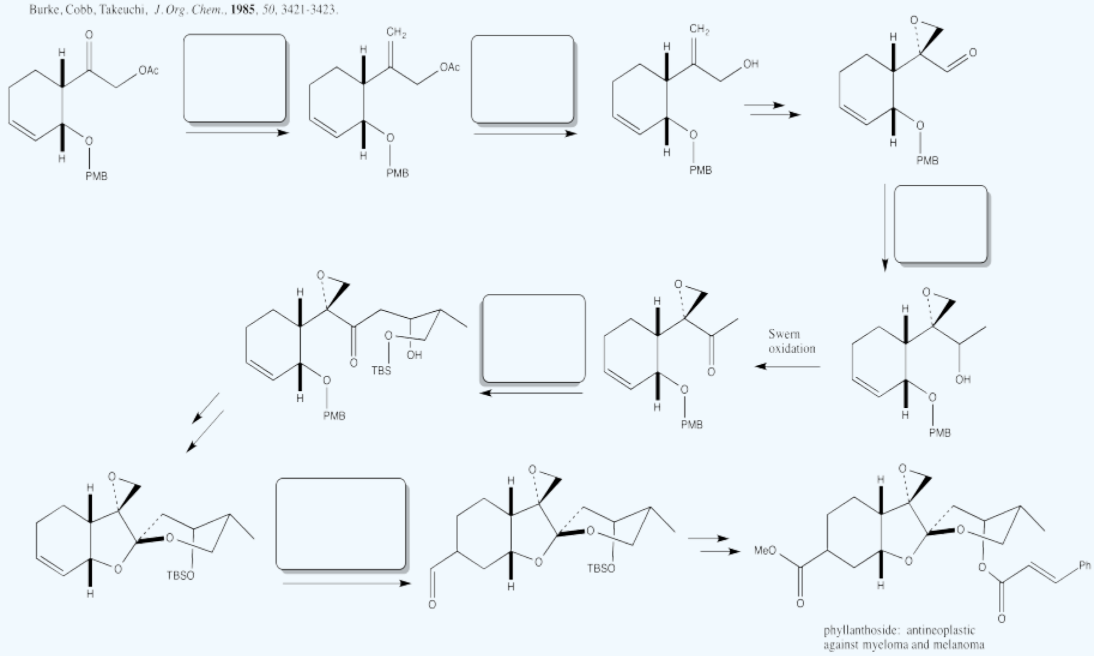
? Exercise 6.6.10



Guanacastapene N

Phyllanthocin

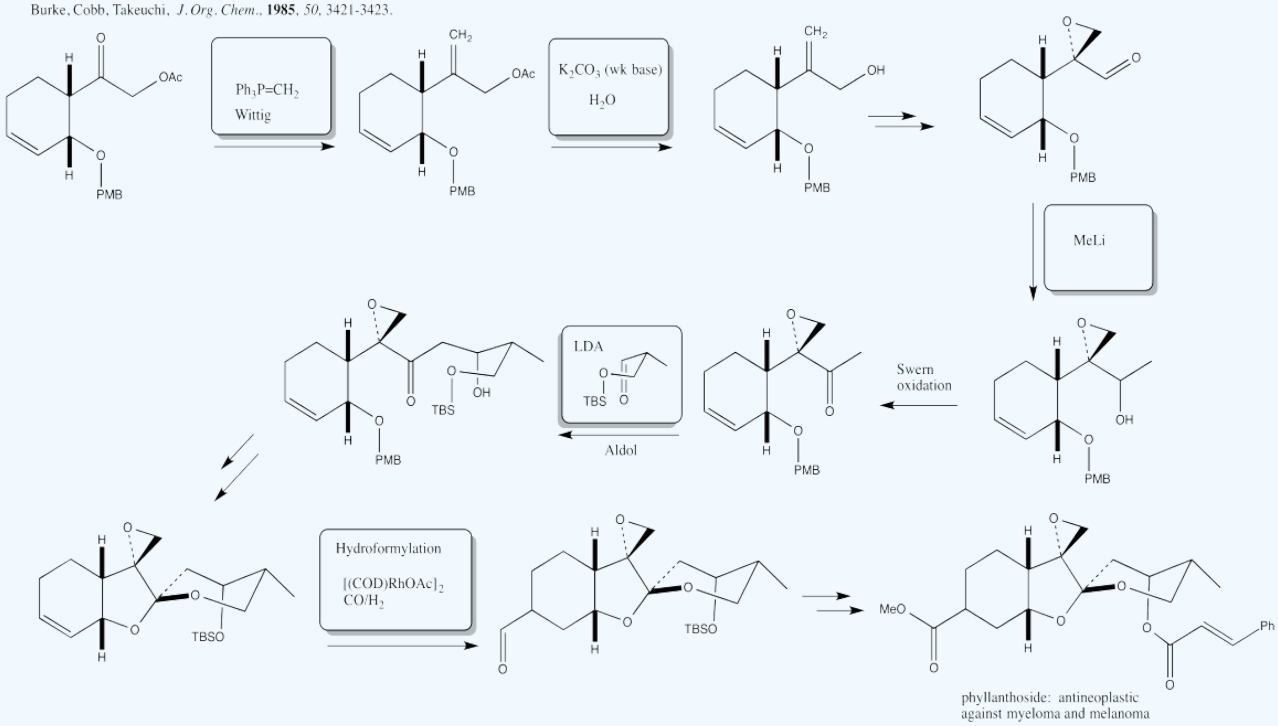
Burke, Cobb, Takeuchi, *J. Org. Chem.*, **1985**, *50*, 3421-3423.



Answer

Phyllanthocin

Burke, Cobb, Takeuchi, *J. Org. Chem.*, **1985**, *50*, 3421-3423.



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