A Guided-Inquiry Approach to Building a Catalytic Cycle

A catalytic cycle is influenced by a number of factors that include selectivity, control of reaction conditions, and rate-determining step. However, it may be built on paper by assembling steps based on the type of fundamental organometallic reaction involved, and by focusing on how these steps complement each other.

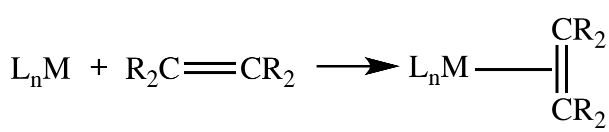
Note. Students need to be able to count electrons in an organometallic complex.

A1. Lesson

Below are examples of fundamental types of reactions that involve organometallic complexes.

1. Addition:

a. olefin



b. CO

$$L_nM + CO \longrightarrow L_nM\text{—}CO$$

c. phosphine

$$L_nM + PR_3 \longrightarrow L_nM\text{—}PR_3$$

2. Dissociation

a. CO

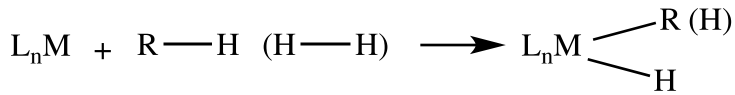
$$L_nM\text{—}CO \longrightarrow L_nM + CO$$

b. phosphine

$$L_nM\text{—}PR_3 \longrightarrow L_nM + PR_3$$

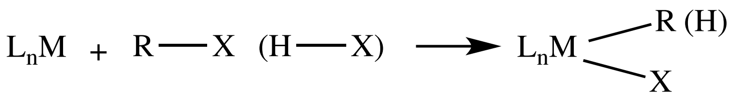
3. Oxidative Addition

a. RH (H_2)



- The addition product may be in *cis* or *trans* configuration, based on the mechanism involved (concerted or stepwise).

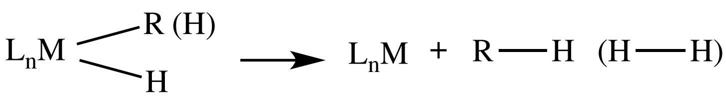
b. RX (HX)



- The addition product may be in *cis* or *trans* configuration, based on the mechanism involved (concerted or stepwise).

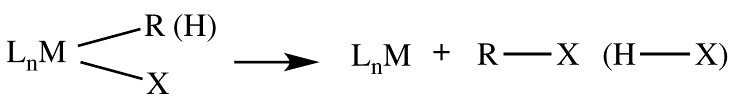
4. Reductive Elimination

a. RH (H_2)



- The ligands (-R, -H) may be in *cis* or *trans* configuration, based on the mechanism involved (concerted or stepwise).

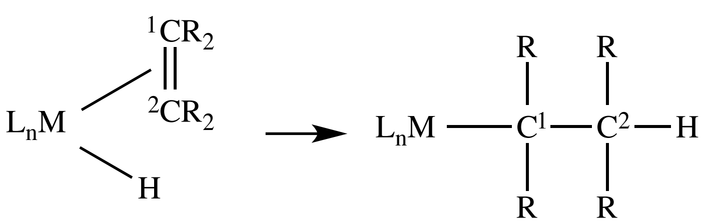
b. RX (HX)



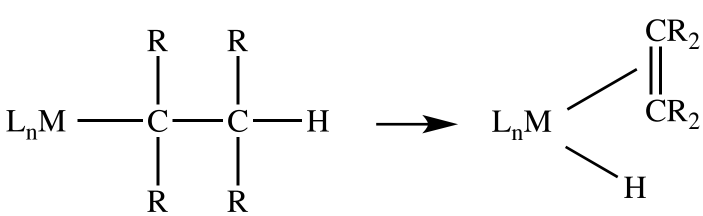
- The ligands (-R, -X) may be in *cis* or *trans* configuration, based on the mechanism involved (concerted or stepwise).

5. 1,2 Insertion

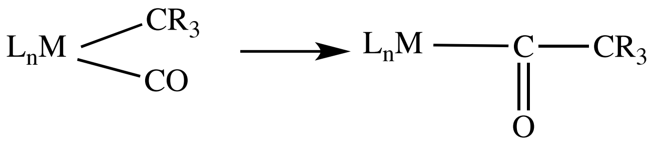
a. olefin



6. β-Elimination



7. Carbonyl Insertion (= Alkyl Migration)



- The ligands (CO and $-CR_3$) must be in *cis* configuration.

A2. Questions

a. Which of the reactions above will keep the *oxidation state of the central metal* constant?
b. Which of the reactions above will show an increase in the *oxidation state of the central metal*? What will be the increase?
c. Which of the reactions above will show a decrease in the *oxidation state of the central metal*? What will be the decrease?
d. Which of the reactions above will keep the *total electron count of the organometallic complex* constant?
e. Which of the reactions above will show an increase in the *total electron count of the organometallic complex*? What will be the increase?
f. Which of the reactions above will show a decrease in *the total electron count of the organometallic complex*? What will be the decrease?
g. Which of the reactions above will keep the *coordination number around the central metal* constant?
h. Which of the reactions above will show an increase in the *coordination number around the central metal*? What will be the increase?
i. Which of the reactions above will show a decrease in the *coordination number around the central metal*? What will be the decrease?

B1. Lesson

Consider the following overall reaction for the catalyzed hydrogenation of an olefin.

$$CH_2{=}CH_2 + H_2 \xrightarrow{\text{catalyst}} CH_3{-}CH_3$$

Here the catalyst has the general formula $\mathbf{L_nMH}$, with a total electron count of 16 electrons and an oxidation state of (I) on the central metal

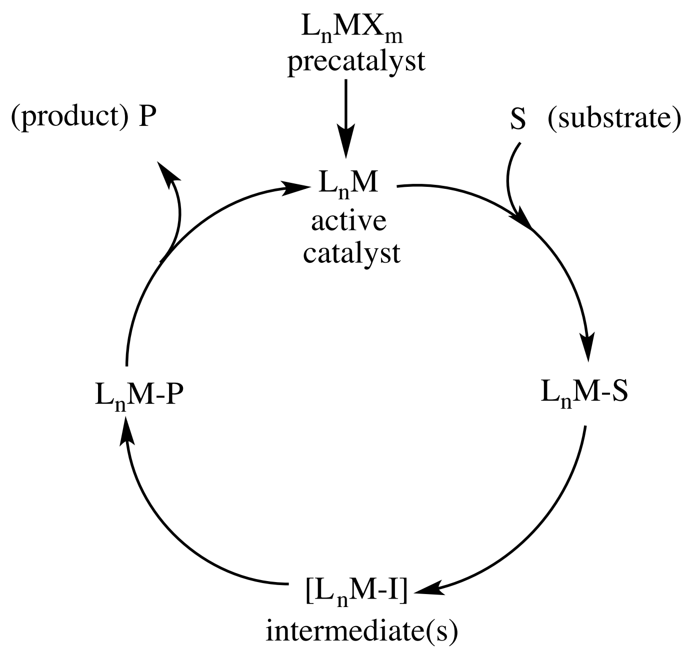
B2. Questions

a. Which of the reactions listed in A1 have the effect of creating a new C-H bond? How many new C-H bonds are created in this reaction?
b. Which other reactions listed in A1 will be needed to bring the reactants onto the organometallic complex that is the catalyst?
c. Determine the type and number of steps that will be needed to go from reactants to products with the help of an organometallic complex, by adding questions B2.a and B2.b (each reaction in B2.a. is involved here).
d. Determine the order in which these steps must take place (there is only one possibility).

- Determine which should be the last step (there the product is released from the organometallic complex).
- Consider how these reactions complement each other.
- Remember that (i) the total electron count must be 16 or 18 electrons, and (ii) the oxidation state of the central metal must be (I) or (III).

C1. Lesson

Below is a simplified version of a catalytic cycle.
(adapted from R.H. Crabtree *The Organometallic Chemistry of Transition Metals* and J.F. Hartwig *Organotransition Metal Chemistry*)



Here the *precatalyst complex* has the formula **$RhHCO(PPh_3)_3$**, while the *catalyst complex* has the formula **$RhHCO(PPh_3)_2$**.

C2. Questions

a. Build your own catalytic cycle for the hydrogenation reaction in B1 using the sequence of steps determined in B2. Also include the conversion from precatalyst to catalyst.

For each step, you must
-show the product(s)
-name the type of organometallic reaction
-give the total electron count for the organometallic complex
-give the oxidation state of the central metal

b. Why is **$RhHCO(PPh_3)_2$** considered to be the catalyst, and not **$RhHCO(PPh_3)_3$**?