**Inorganic Chemistry with Doc M.**
**Fall Semester, 2012**
**Day 23. Organotransition Metal Chemistry II: Reactions**

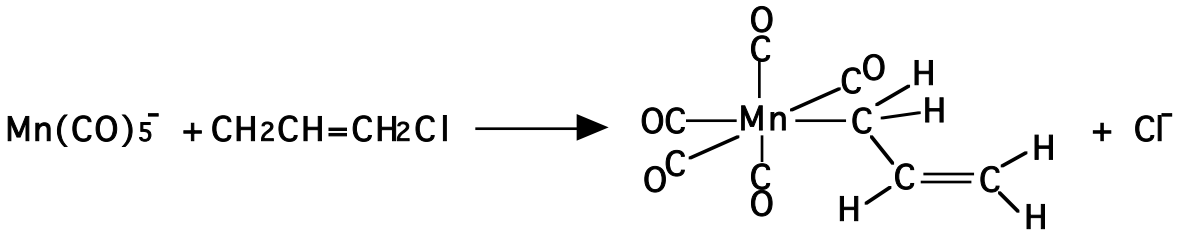
| Name(s): | Element: |
|---|---|
| | |

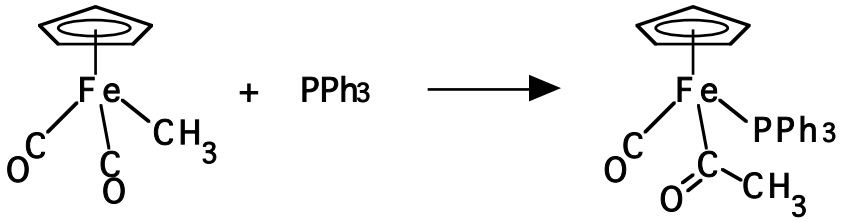
**Topics:**

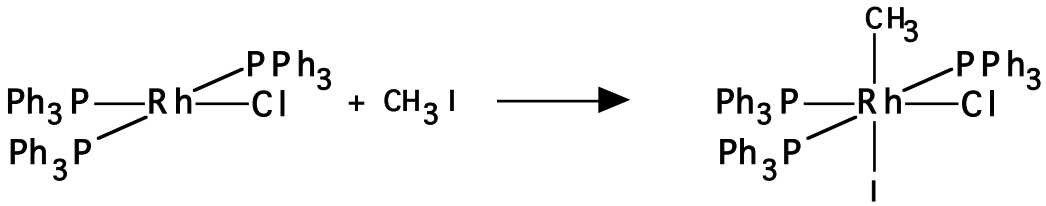
1. Organometallic reaction types
2. Catalytic cycles

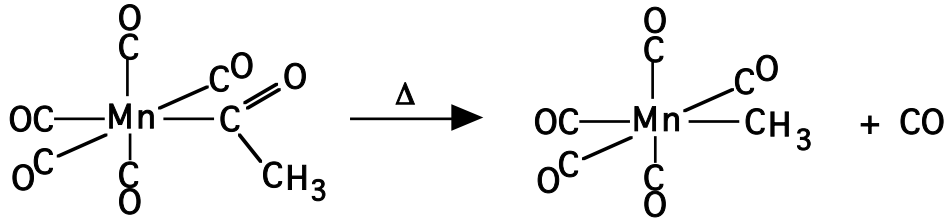
**1. Organometallic reaction types.** Classify the following reactions by their type. The choices are:

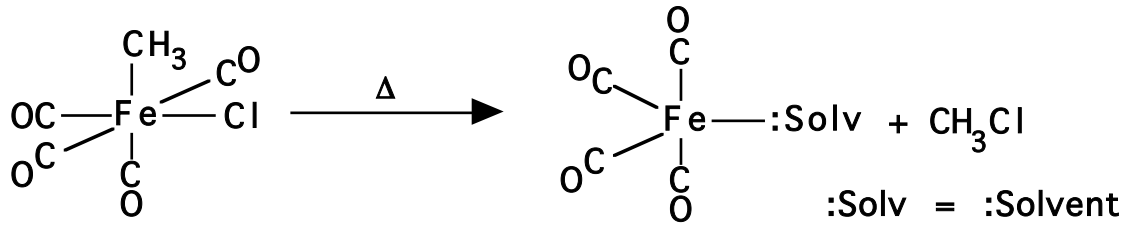
1. Ligand dissociation/substitution.
2. Oxidative addition
3. Reductive elimination (opposite of #2)
4. Nucleophilic displacement
5. Insertion (alkyl migration)
6. Retro-insertion (opposite of #5)

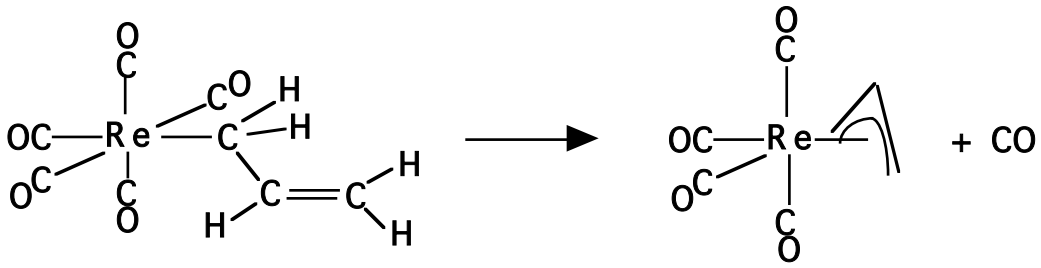











3. Predict the products of the following reactions. Start by sketching the reactants. Also sketch the products. In each case, state the reaction type that you are using (See list in previous problem.) Count electrons to justify your answer. Sketch structures as you go.

(a) trans-$Ir(CO)(Cl)(PPh_3)_2 + H_2 \longrightarrow$

(b) $(C_5H_5)Mn(CO)_3 + AsPh_3 \xrightarrow{\Delta} CO +$

(c) $(C_5H_5)Fe(CO)_2CH_2CH_3 \xrightarrow{\Delta} CH_2CH_2 +$

(d) $K[Mn(CO)_5] + (C_5H_5)Fe(CO)_2Br \longrightarrow$

(e) cis-$Re(CH_3)(PEt_3)(CO)_4 + {}^{13}CO \longrightarrow$

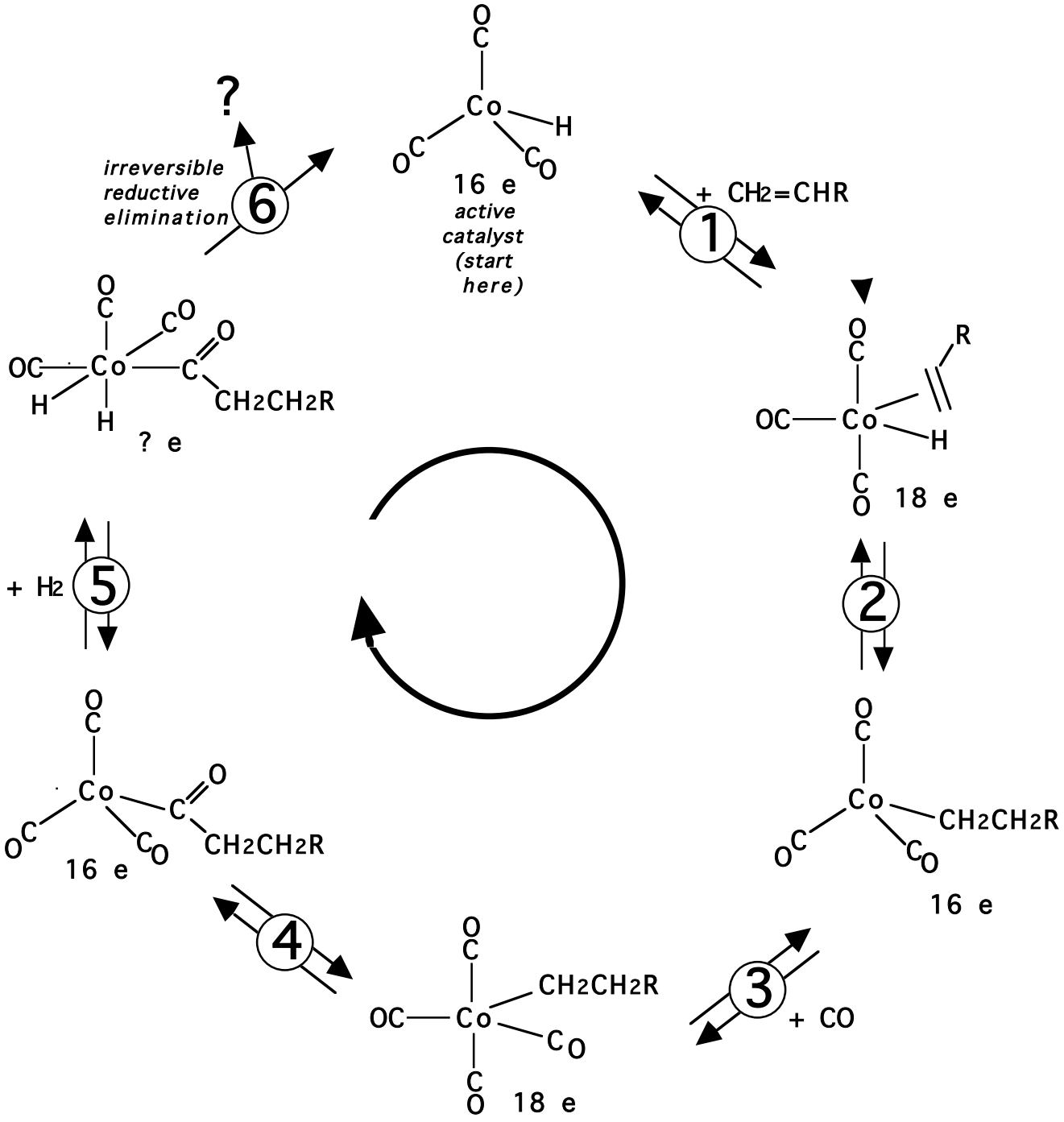
(f) $PhCH_2Mn(CO)_5 \xrightarrow{uv} CO +$

(g) $V(CO)_6 + NO \longrightarrow CO +$

(h) cis-$Ru(SiMe_3)(H)(CO)_4 \xrightarrow{\Delta}$

(i) $2\ K[(C_5H_5)Mo(CO)_3]^{+} SnCl_2Ph_2 \longrightarrow 2KCl +$

**2. Catalytic cycles.** $Co_2(CO)_8$ is used to form a 16-e catalyst $HCo(CO)_3$ that can convert alkenes ($CH_2CHR$) plus CO and $H_2$ into aldehydes. Study the catalytic cycle below which proceeds by some of the simple reaction types that we have studied. Answer the questions that follow.




(I) The reaction in Step #2 would be described as:

A. Ligand dissociation/substitution
B. Oxidative addition
C. Reductive elimination
D. Nucleophilic Displacement
E. Insertion (alkyl migration)
F. Retro-insertion

(II) The REVERSE reaction in Step #4 would be described as:

A. Ligand dissociation/substitution
B. Oxidative addition
C. Reductive elimination
D. Nucleophilic Displacement
E. Insertion (alkyl migration)
F. Retro-insertion

(III) The reaction Step #5 would be described as:

A. Ligand dissociation/substitution
B. Oxidative addition
C. Reductive elimination
D. Nucleophilic Displacement
E. Insertion (alkyl migration)
F. Retro-insertion

(IV) What is the organic product produced in Step #6?

A. $CH_3CHRCHO$
B. $RCH_2CH_2CHO$
C. $H_2$
D. $RCH_2CH_2CH_2OH$
E. $RCH_2CH_2C(O)C(O)CH_2CH_2R$
F. HCHO

(V) Assume R = H for this question. Suppose a competing reaction also takes place in Step 3 in which $H_2$ is oxidatively added to $Co(CO)_3CH_2CH_2R$ instead of CO addition as shown in the figure. We would expect to see traces of:

A. methane
B. methanol
C. methanal
D. ethane
E. ethanol
F. ethanal

(VI) If we wanted to use this process to make n-heptanal, we should use:

A. n-hexane
B. 1-hexene
C. 2-hexene
D. n-heptane
E. 1-heptene
F. 2-heptene

(VII) Assume R = H for this question. Use a series of simple steps to show how traces of butane and pentanal are also possible from this catalytic cycle.

## Review for the ACS Standardized Final Exam

1. Which of these involves reductive elimination

(a) $Rh(Cl)(PPh_3)_3 + CH_3I \rightarrow$ *trans*-$Rh(Cl)(PPh_3)_3(CH_3)(I)$

(b) $NH_4[Re(CO)_5] + CH_3I \rightarrow Re(CO)_5CH_3 + NH_4I$

(c) $(C_5H_5)Fe(CO)_2CH_2CH_3 \rightarrow CO + (C_5H_5)Fe(CO)(H)(p\text{-}CH_2CH_2)$

(d) $(C_5H_5)Mn(CO)_3 + PPh_3 \rightarrow CO + (C_5H_5)Mn(CO)_2(PPh_3)$

(e) $NH_4[Ni(CH_3)(CO)_3] + HI \rightarrow CH_4 + NH_4[Ni(CO)_3I]$

2. Which of these compounds would be most likely to undergo nucleophilic substitution?

(a) $Ir(CO)(Cl)(PPh_3)_2$

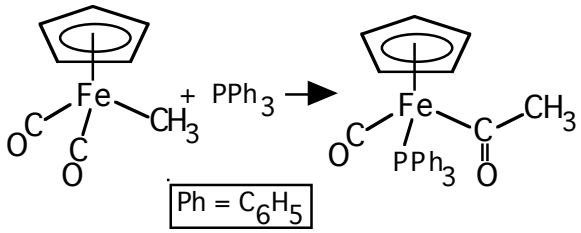
(b) $Re(CO)_5^-$

(c) $(C_5H_5)Fe(CO)_3^+$

(d) $(C_5H_5)_2Fe$

(e) $Cr(CO)_6$

3. The following reaction can be classified as




(a) oxidative addition

(b) nucleophilic displacement

(c) insertion (alkyl migration)

(d) substitution

(e) reductive elimination

*Answers: E, B, C*