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

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)

\[ \text{Mn}(CO)_5^- + \text{CH}_2\text{CH} = \text{CH}_2\text{Cl} \rightarrow \text{OC-}\text{Mn-}\text{C=CH}_2 \text{H} + \text{Cl}^- \]

\[ \text{Fe} + \text{PPh}_3 \rightarrow \text{Fe-PPh}_3 \]

\[ \text{Ph}_3\text{P-}\text{Rh-Cl} + \text{CH}_3\text{I} \rightarrow \text{Ph}_3\text{P-Rh-Cl} \]

\[ \Delta \text{OC-Mn-CO} \rightarrow \text{OC-Mn-CH}_3 + \text{CO} \]
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\textsubscript{3})\textsubscript{2} + H\textsubscript{2} \rightarrow 

(b) (C\textsubscript{5}H\textsubscript{5})Mn(CO)\textsubscript{3} + AsPh\textsubscript{3} \xrightarrow{\Delta} CO + 

(c) (C\textsubscript{5}H\textsubscript{5})Fe(CO)\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3} \xrightarrow{\Delta} CH\textsubscript{2}CH\textsubscript{2} +
(d) $\text{K}[\text{Mn(CO)}_5] + (\text{C}_5\text{H}_5)\text{Fe(CO)}_2\text{Br} \rightarrow$

(e) $\text{cis-Re(CH}_3)(\text{PEt}_3)(\text{CO})_4 + ^{13}\text{CO} \rightarrow$

(f) $\text{PhCH}_2\text{Mn(CO)}_5 \xrightarrow{uv} \text{CO} +$

(g) $\text{V(CO)}_6 + \text{NO} \rightarrow \text{CO} +$

(h) $\text{cis-Ru(SiMe}_3)(\text{H})(\text{CO})_4 \xrightarrow{\Delta} \rightarrow$

(i) $2 \text{K}[(\text{C}_5\text{H}_5)\text{Mo(CO)}_3] + \text{SnCl}_2\text{Ph}_2 \rightarrow 2\text{KCl} +$
2. Catalytic cycles. Co$_2$(CO)$_8$ is used to form a 16-e catalyst HCo(CO)$_3$ that can convert alkenes (CH$_2$CHR) 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. CH₃CHRCHO
B. RCH₂CH₂CHO
C. H₂
D. RCH₂CH₂CH₂OH
E. RCH₂CH₂C(O)C(O)CH₂CH₂R
F. HCHO

(V) Assume R = H for this question. Suppose a competing reaction also takes place in Step 3 in which H₂ is oxidatively added to Co(CO)₃CH₂CH₂R 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.
1. Which of these involves reductive elimination

(a) Rh(Cl)(PPh$_3$)$_3$ + CH$_3$I $\rightarrow$ trans-Rh(Cl)(PPh$_3$)$_3$(CH$_3$I)
(b) NH$_4$[Re(CO)$_5$] + CH$_3$I $\rightarrow$ Re(CO)$_5$CH$_3$ + NH$_4$I
(c) (C$_5$H$_5$)Fe(CO)$_2$CH$_2$CH$_3$ $\rightarrow$ CO + (C$_5$H$_5$)Fe(CO)(H)(p-CH$_2$CH$_2$)
(d) (C$_5$H$_5$)Mn(CO)$_3$ + PPh$_3$ $\rightarrow$ CO + (C$_5$H$_5$)Mn(CO)$_2$(PPh$_3$)
(e) NH$_4$[Ni(CH$_3$)(CO)$_3$] + HI $\rightarrow$ CH$_4$ + NH$_4$[Ni(CO)$_3$I]

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$_5$H$_5$)Fe(CO)$_3^+$
(d) (C$_5$H$_5$)$_2$Fe
(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