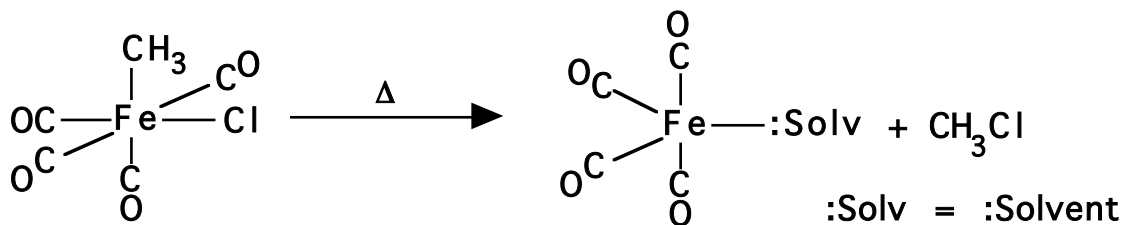
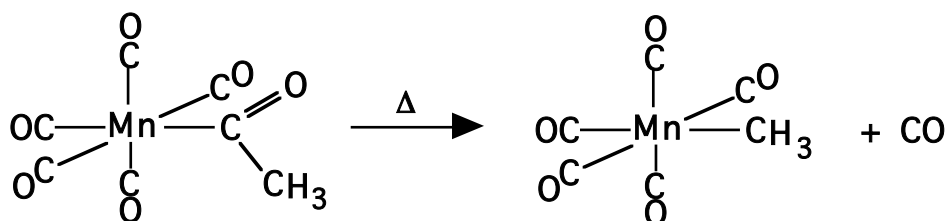
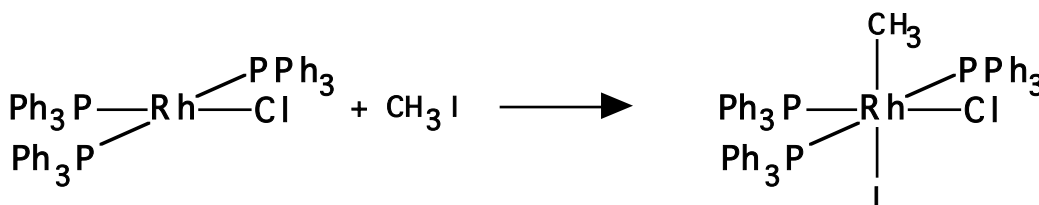
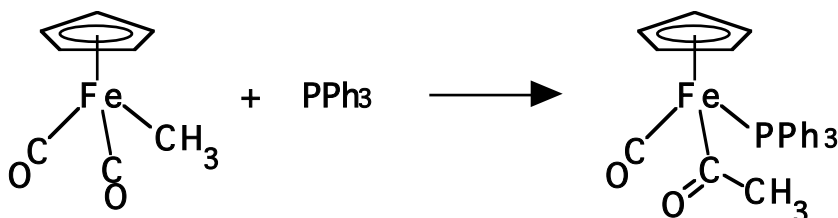
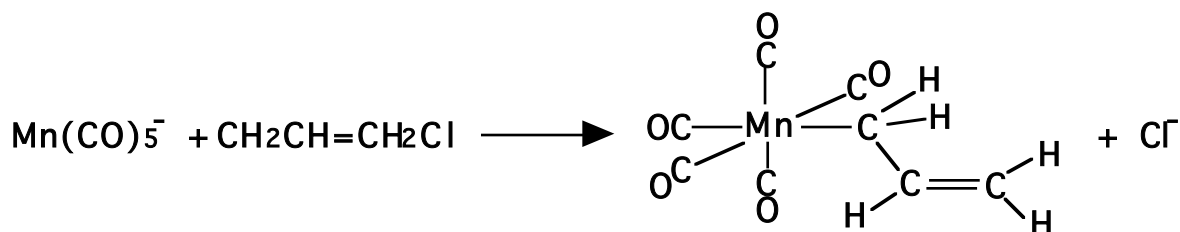
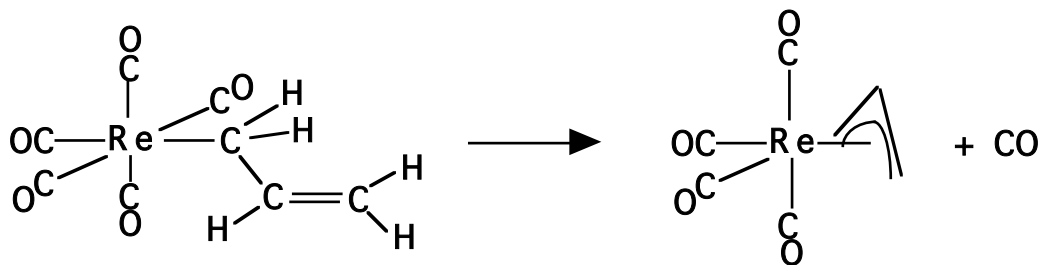


## Day 22. Organotransition Metal Chemistry II: Organometallic Reactions

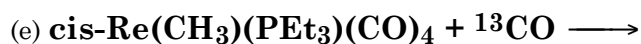
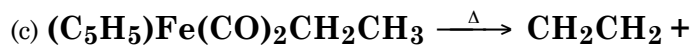
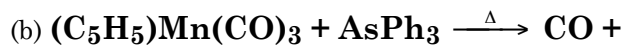
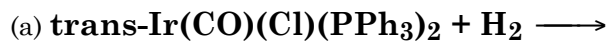
1. Classify the following reactions by their type. The choices are:

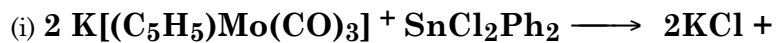
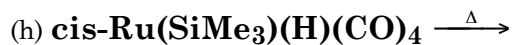
- |   |                                     |
|---|-------------------------------------|
| 1. Ligand dissociation/substitution.      | 4. Nucleophilic displacement        |
| 2. Oxidative addition                     | 5. Insertion (alkyl migration)      |
| 3. Reductive elimination (opposite of #2)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



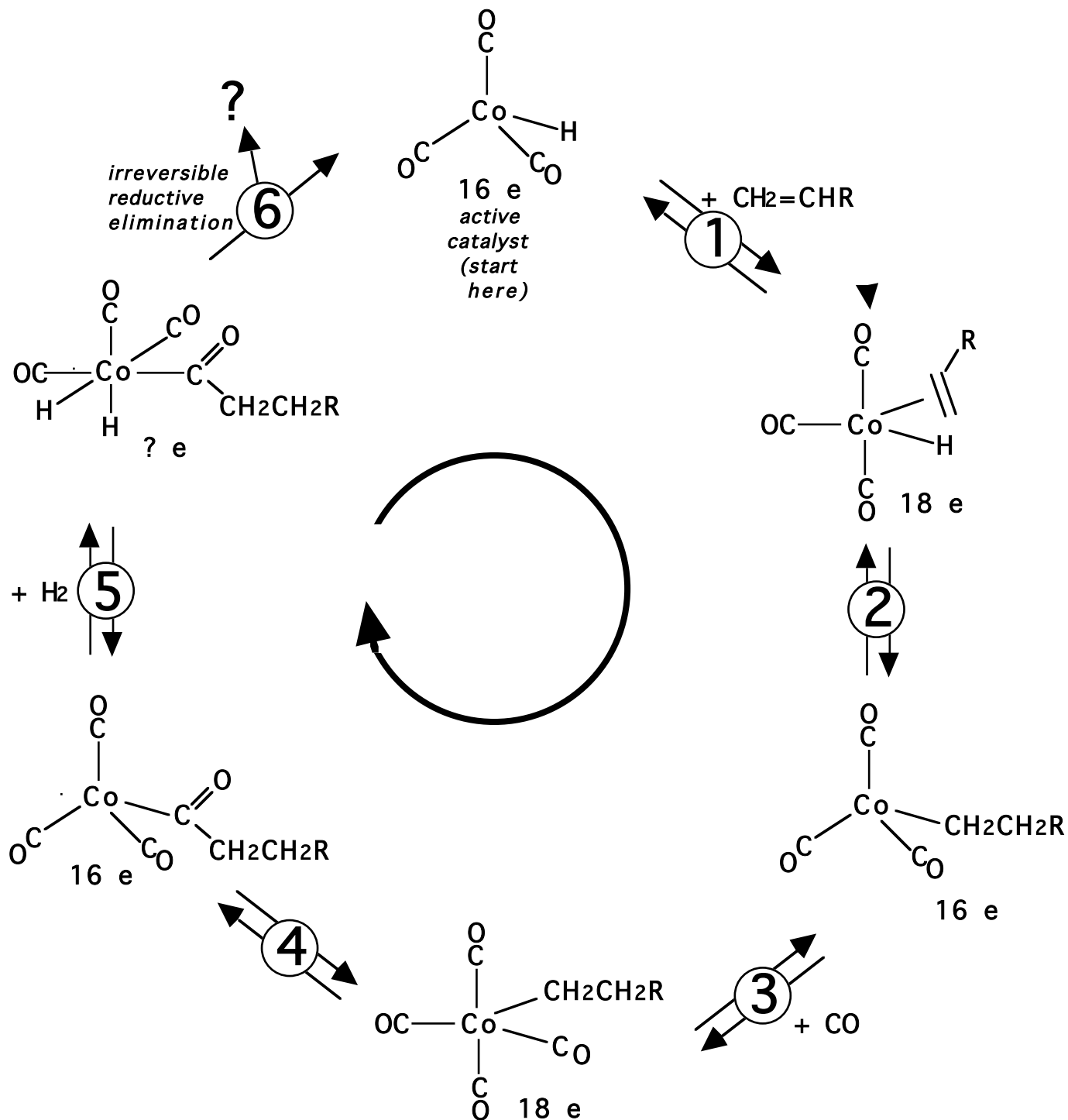


3. Predict the products of the following reactions. Start by sketching the reactants. Also sketch the products. In each case, state the reaction type that you are using (See list in previous problem.) Count electrons to justify your answer. Sketch structures as you go.





5. (14 points)  $\text{Co}_2(\text{CO})_8$  is used to form a 16-e catalyst  $\text{HCo}(\text{CO})_3$  that can convert alkenes ( $\text{CH}_2\text{CHR}$ ) plus  $\text{CO}$  and  $\text{H}_2$  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 | D. Nucleophilic Displacement   |
| B. Oxidative addition               | E. Insertion (alkyl migration) |
| C. Reductive elimination            | F. Retro-insertion             |

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

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

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

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

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

- |  |  |
|--|--|
| A. $\text{CH}_3\text{CHRCHO}$          | D. $\text{RCH}_2\text{CH}_2\text{CH}_2\text{OH}$                   |
| B. $\text{RCH}_2\text{CH}_2\text{CHO}$ | E. $\text{RCH}_2\text{CH}_2\text{C(O)C(O)CH}_2\text{CH}_2\text{R}$ |
| C. $\text{H}_2$                        | F. $\text{HCHO}$   |

(V) Assume  $\text{R} = \text{H}$  for this question. Suppose a competing reaction also takes place in Step 3 in which  $\text{H}_2$  is oxidatively added to  $\text{Co(CO)}_3\text{CH}_2\text{CH}_2\text{R}$  instead of  $\text{CO}$  addition as shown in the figure. We would expect to see traces of:

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

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

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

(VII) Assume  $\text{R} = \text{H}$  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

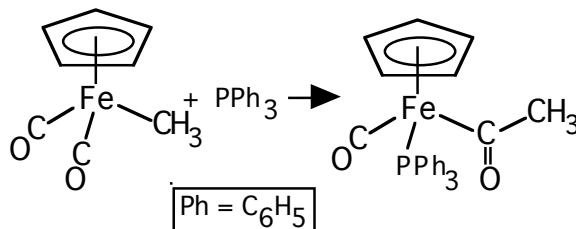
1. Which of these involves reductive elimination

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

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

- (a)  $\text{Ir}(\text{CO})(\text{Cl})(\text{PPh}_3)_2$
- (b)  $\text{Re}(\text{CO})_5^-$
- (c)  $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_3^+$
- (d)  $(\text{C}_5\text{H}_5)_2\text{Fe}$
- (e)  $\text{Cr}(\text{CO})_6$

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

## Answers Worksheet Two

### 1. First Row:

carbonyl, pi-allyl

carbonyl, carbene

pi-benzene (or pi-arene), carbonyl

### Row 2:

pi-cyclopentadienyl, carbonyl, alkene

pi-cyclopentadienyl, carbonyl, metal-metal bond

carbonyl, diene

### Row 3:

pi-cyclopentadienyl, carbonyl, alkyl

pi-cyclopentadienyl, carbonyl, nitrosyl, hydride

carbonyl, phosphine, chloro

### Row 4:

pi-cyclopentadienyl, carbonyl, acyl

pi-cyclopentadienyl, carbonyl, sigma-cyclopentadienyl

carbonyl, carbyne

2. 4, 5, 2, 6, 1, 1

3.

(a) oxidative addition of non-polar molecule gives trans-Ir(CO)(Cl)(PPh<sub>3</sub>)<sub>2</sub>(H)<sub>2</sub> (hydrides go cis)

(b) substitution of CO ligand by triphenylarsine: (C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>2</sub>(AsPh<sub>3</sub>)

(c) retro-1-2-insertion (beta-hydrogen elimination) (C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>(H)

(d) nucleophilic substitution (double displacement) forms Fe-Mn bond in this case: (C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>5</sub> + KBr

(e) alkyl migration converts a regular CO into an acyl CO: cis-Re(COCH<sub>3</sub>)(PEt<sub>3</sub>)(CO)<sub>3</sub>(13CO)

(f) PhCH<sub>2</sub>Mn(CO)<sub>4</sub> (Tough one! The benzyl group goes from sigma-bonded 1e donor to a 3e pi-allyl type in which one double bond from the C<sub>6</sub>H<sub>6</sub> is used to form the allyl

(g) V(CO)<sub>5</sub>(NO) NO is linear. 3e and the complex is octahedral, 18e!

(h) Reductively eliminates HSiMe<sub>3</sub> and the identity of the Ru products are uncertain -- thermal conditions are hard on organometallic compounds

(i) Ph<sub>2</sub>Sn[(C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub>]<sub>2</sub> Note: the chlorides groups on SnPh<sub>2</sub>Cl<sub>2</sub> were replaced by (C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub><sup>-</sup> via nucleophilic substitution