Introduction to Organometallic Chemistry
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Module VIII

This module deals with useful catalytic and Stoichiometric reactions

32. Hydrogenation reactions
33. Addition of HX to olefins
34. Reactions with CO insertion
35. Organometallics promoted C-X coupling
36. Organometallic polymerization
37. C-H activation

1. The water gas shift reaction (CO + water ➔ CO_2 + H_2) is promoted by $Fe(CO)_5$. Write a suitable catalytic cycle for this reaction.

2. A sample of 3-octene in toluene was treated with $HRh(CO)_3PPh_3$ (1%). A mixture of olefins were found to be present in the sample after 4 days. Explain giving intermediates the reason for this observation. Why are not all isomers formed in equal amounts.

3. Explain the following observations (If there are several possible explanations, give all of them)

A. tris(isobutyl)aluminum reacted with propylene to give isobutylene.
B. $Ru(acac)_3$ + H_2 + CO (excess) → gives an organometallic complex.

4. Reaction of $CpCo(PR_3)_2$. With RI and CO results in the formation of RCOI. Write a catalytic cycle for this reaction.

5. The Wilkinson hydrogenation catalyst $RhCl(CO)(PPh_3)_3$ sometimes isomerises the olefins during the hydrogenation process. Write a reasonable scheme indicating the various intermediate involved.

6. Give at least two different ways by which transition metals isomerise olefins. Give suitable examples for each of these catalytic processes: identify the steps.
    A. Imagine you are part of a company which wants to make terminal olefins from a mixture of olefins. What criteria would you use to choose the right complex.
    B. What complex would be suitable for making high boiling olefins from butene.

7. Write a catalytic cycle for the conversion of ethylene to acetaldehyde using a suitable transition metal catalyst. Explain each step.
   What would be the product if the reaction was carried out in D_2O?

8. Outline a catalytic synthesis for 2-vinyl pyridine from simple starting materials.

   (a) Give the catalytic cycle identifying the elementary process involved in each step.
   (b) If there are plausible side products in the reaction identify them.

9. What is the product formed in the following reactions

(a) $Ph - C \equiv C - Ph$ + cat.$PdCl_2$

(b) $CrCl_3 + C_6H_6 + Al + AlCl_3$ at RT

(c) Cr(gas) + 1,4 dimethoxy naphthalene -196^oC

(d) Acetylene + $Ni(acac)_2$

(e) Quadricyclane + $[Rh(CO)_2Cl]_2$ + CO

10. Write down the steps involved in the reaction of vinyl bromide with styrene to 1-phenyl butadiene in the presence of $PdCl_2$ and PPh_3 .
11. What is the product formed when $(Cp)_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Al(Me)_2$ is reacted with (a) cyclohexene, (b) cyclohexanone.
12. Comment on the observation that most organometallic catalysts have a 4d or 5d metal rather than a 3d metal.
13. What are the two major reasons given for very large activation energies for the breaking of C-H bonds by transition metals.