Organometallic Chemistry

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- Cyclic mechanism (monometallic and bimetallic)

- Different type of ligands and metals

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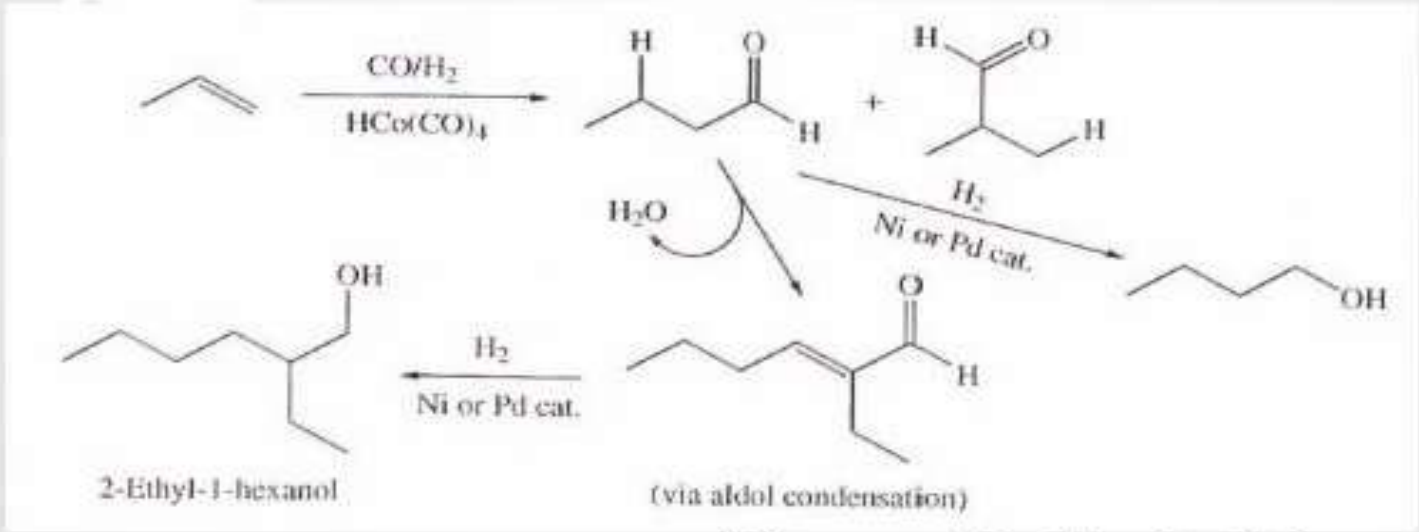
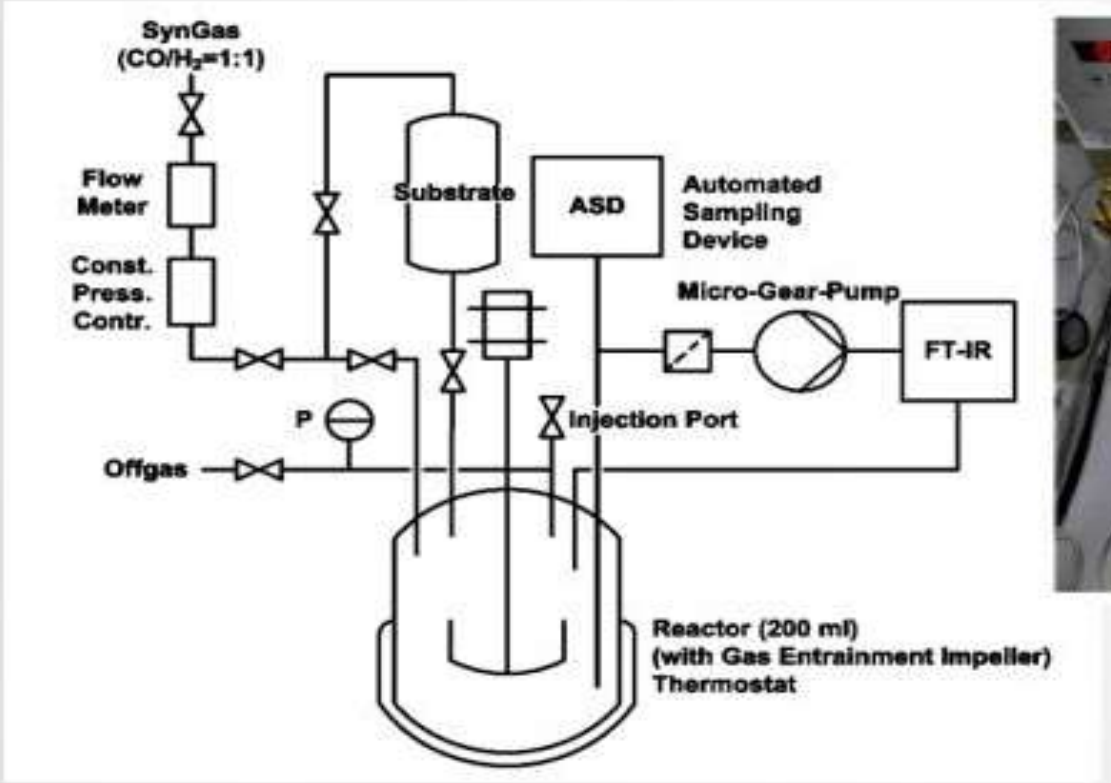
Introduction

- **What is hydroformylation?**
  - produces aldehyde from alkene via
  - addition of a CO and H_2 to a alkene



"Organometallic Chemistry", Spessard and Miessler

Experimental setup with reactor system



A: autoclave unit
C: IR transmission cell
P: micro-gear pump
S: FTIR spectrometer

Chem. Rev. 2012, 112, 5675- 5732

2. Metathesis reactions (exchange of partners)

$$4MeLi + SiCl_4 \longrightarrow SiMe_4 + 4LiCl$$

The electronegative halide ends up with the most electro-positive metal, so that the new organometallic compound has less polar M-C bonds and is less reactive.

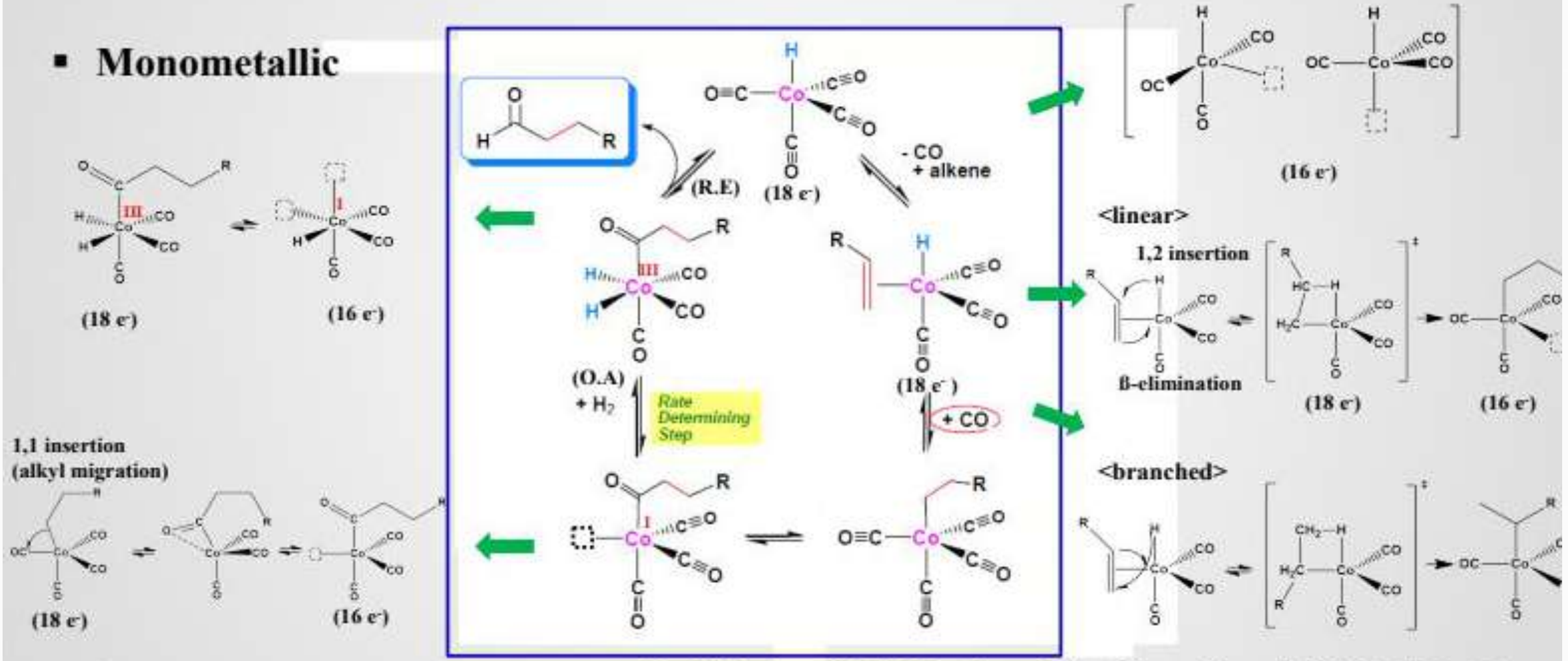
e.g

$$2MeLi + CuI \xrightarrow{Et_2O} Me_2CuLi + LiI$$

"Gilman reagent"

Hydroformylation Mechanism

- **Monometallic**



R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, 1961, 83, 4023

Cobalt Catalyst

- **Kinetics**

$$\frac{d(\text{aldehyde})}{dt} = k[\text{alkene}][\text{Co}][\text{H}_2][\text{CO}]^{-1}$$

- inversely proportional to CO concentration because CO dissociation from the coordinatively saturated $18e^-$ species is required

- using a 1:1 ratio of H_2/CO, the reaction rate is independent of pressure

- $HCo(CO)_4$ is only stable under certain minimum CO partial pressures at a given temperature

-

- CO pressure ↑ → reaction rate ↓ & high ratio of linear to branched product

- CO pressure ↓ → reaction rate ↑ & branched alkyl ↑ (reverse ß-elmination)

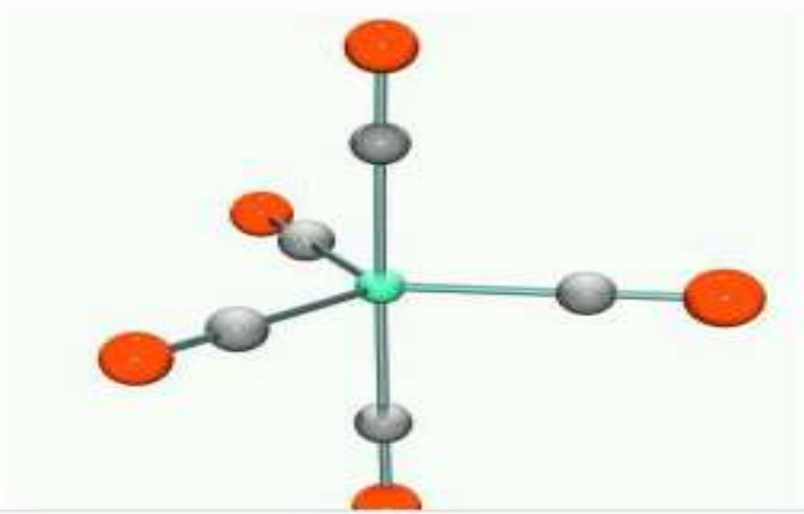
This polarisation of the M-C bond is extremely useful in synthesis

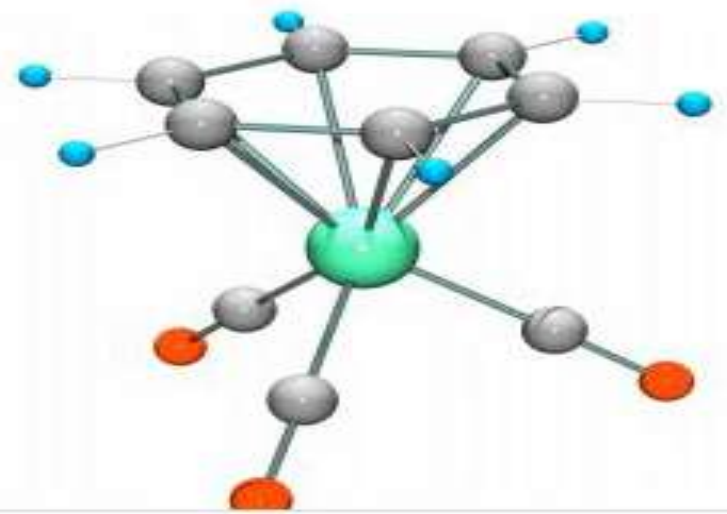
$R_2C^{\delta+}=O^{\delta-} + LiCH_3 \rightarrow R_2MeC\text{-}OLi \xrightarrow[\text{hydrolysis}]{} R_2MeC\text{-}OH$

ketone/aldehyde → alcohol

A huge variety of organic molecules can be bonded to metals, especially transition metals.

Examples include : alkyl & aryl groups, alkenes, alkynes, CO (carbonyls)






THANK YOU

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