

Organometallic Chemistry

C21J, 4 Lectures

Mohammed Bakir, Office #8

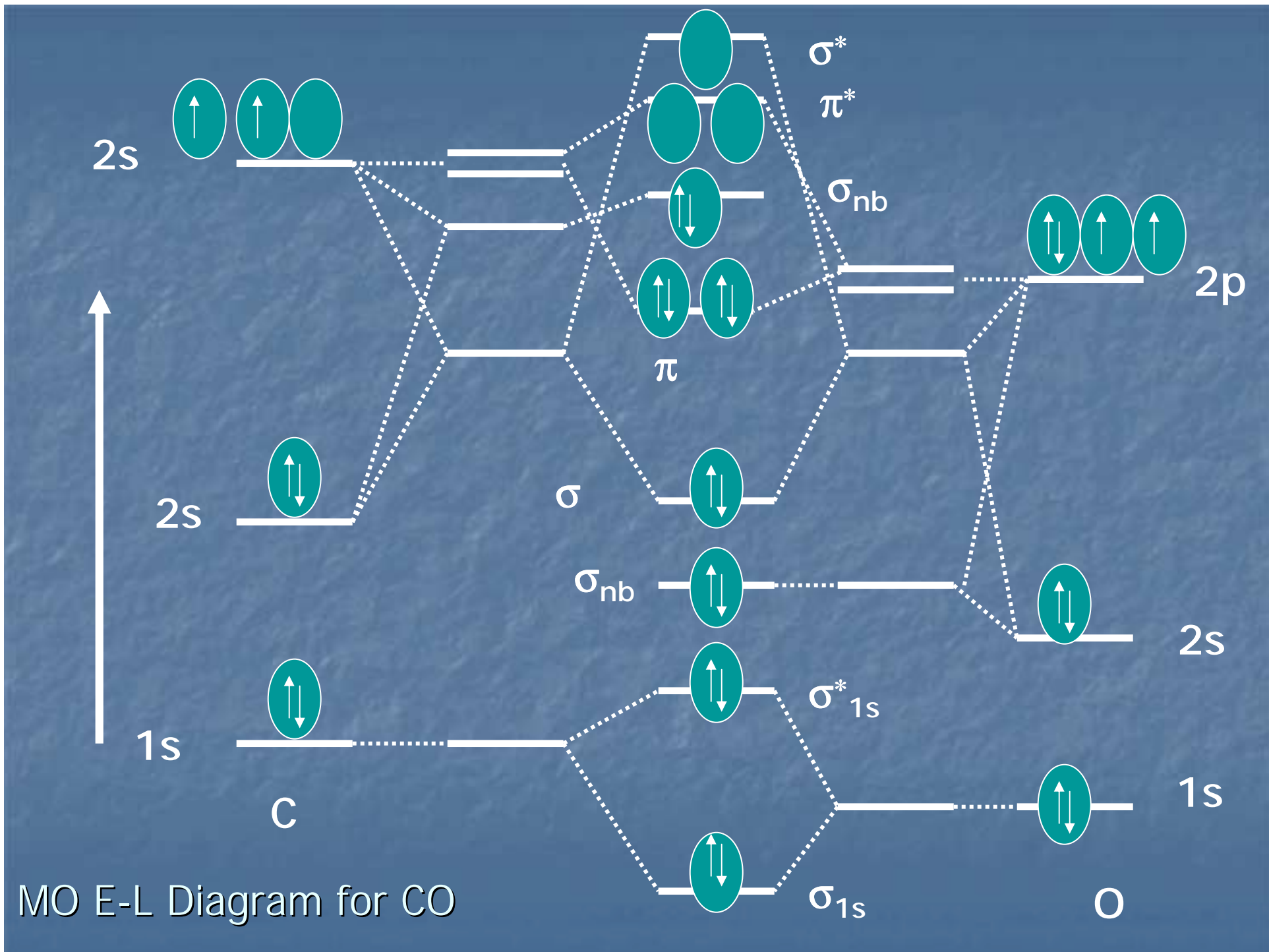
- Introduction
- Bonding
- π -acids
- Metal Carbonyl Compounds
- Organometallic Compounds
- Preparation and reactions of organometallic compounds.
- Reference: Chapters 10
- Textbook: B. Douglas, D. H. McDaniel, & J. J. Alexander, *Concepts & Models of Inorganic Chemistry*, 2nd edition, Wiley, New York

What is Organometallic?

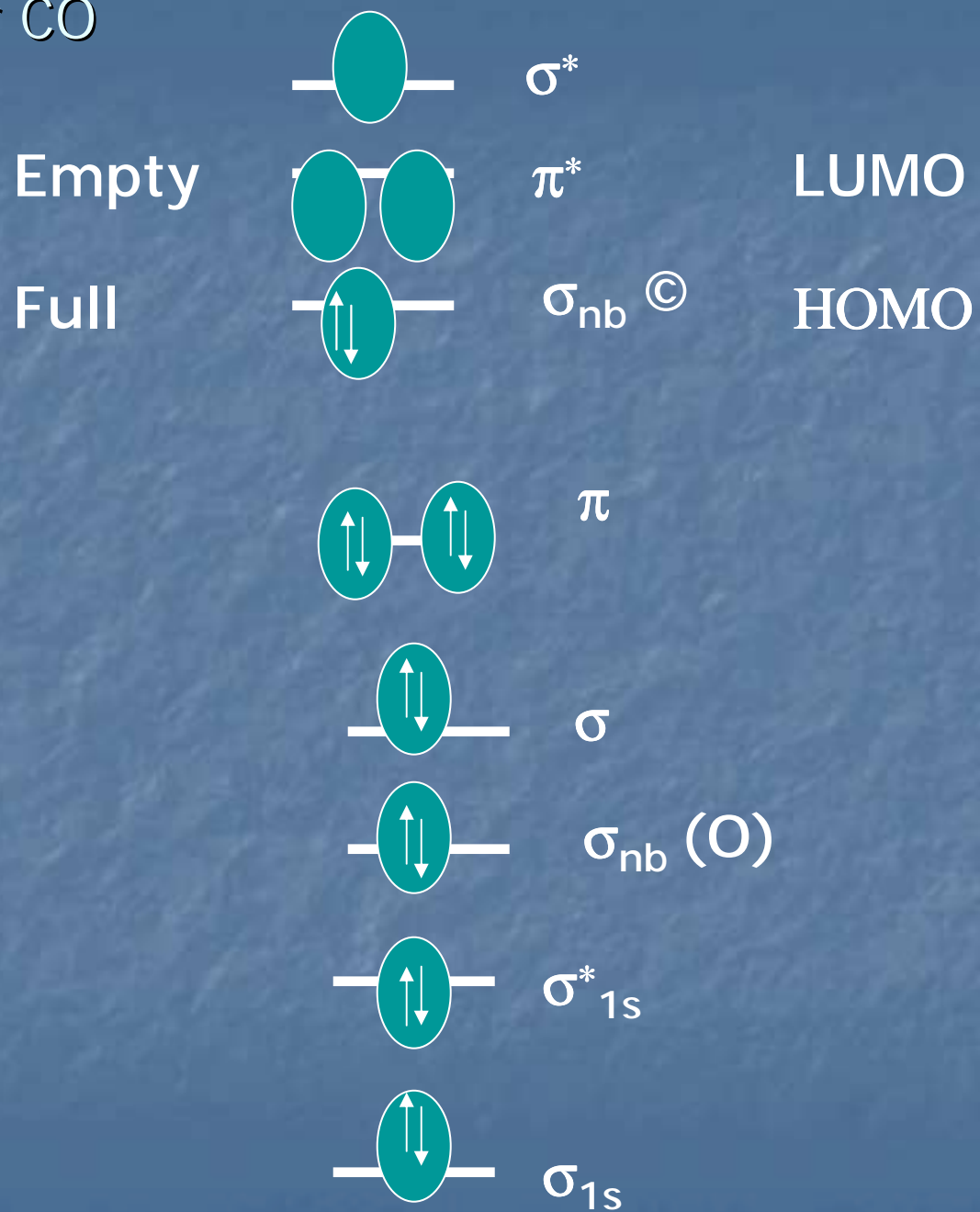
- Organometallic is the chemistry of M-C bond formation and reactivity.
- Although Zn-alkyls *e.g.* $\text{Zn}(\text{CH}_3)_2$ were prepared by Frankland in 1827, organometallic chemistry has undergone a renaissance in the last 50 years due to the importance of many organometallic compounds in many important chemical processes that include catalysis, sensors and others.

Metal Carbonyl Compounds

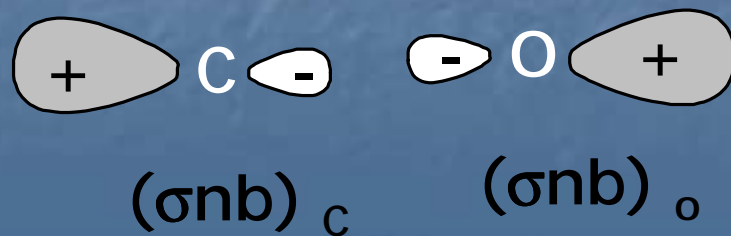
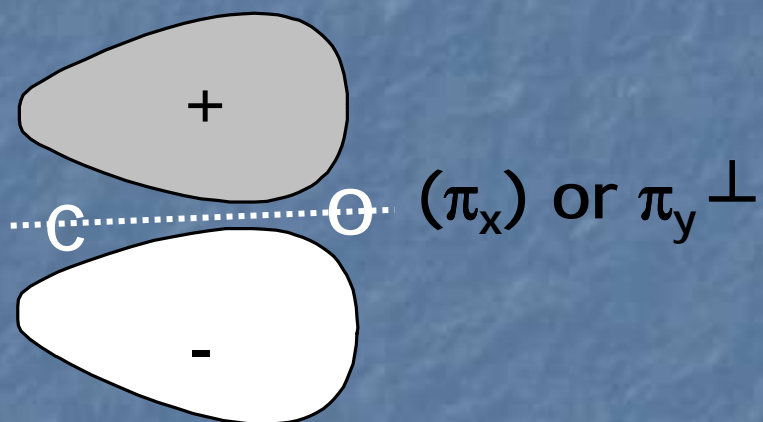
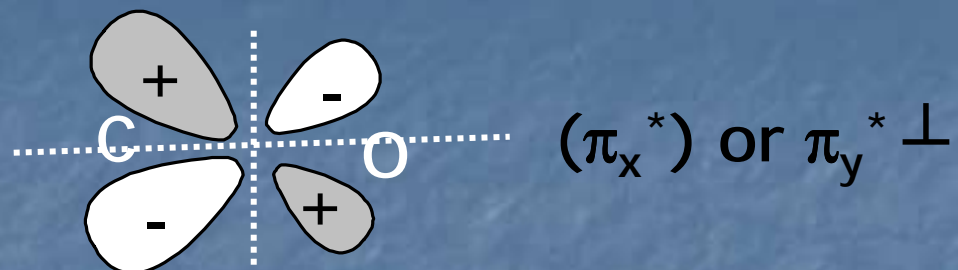
- π -acid Ligands.
- What are π -acid ligands?
- Ligands with a pair of electrons available for donation to the metal center and vacant orbital p , π^* , or d available for accepting electron density from the metal.
- e.g. CO, and PPh_3 where $\text{Ph} = \text{C}_6\text{H}_5$.



M.O. Diagram for CO



Sketches of the M.O. for CO



Metal Carbonyl Compounds

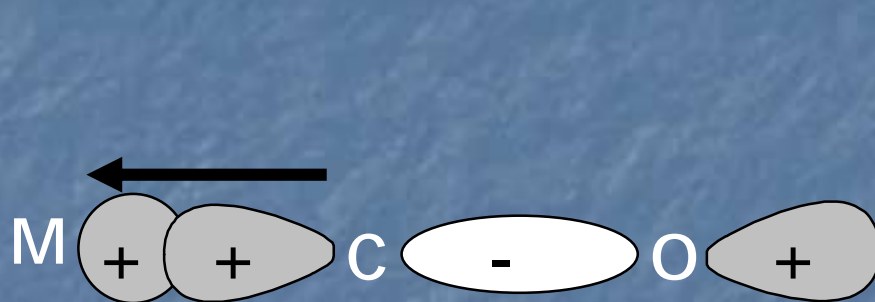
■ Requirements

- Metal should be in low oxidation state 0, 1 or 2; i.e. electron rich.
- Ligand should be a π -acceptor ligand, i.e. σ -donor or electron acceptor through empty p, π^* or d orbitals.

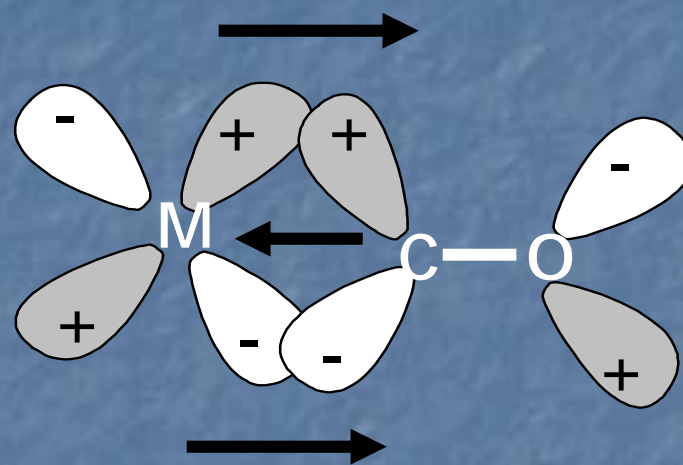
Bonding

- Sequence of bonding
- A pair of electrons is donated from the π -acid to the metal center
- The excess electron density around the metal center is donated back to the empty orbitals on the ligand.

Synergic Bonding



Ligand → Metal σ bonding



Metal → ligand π -back bonding
(one of a mutual \perp is shown)

The back donation to the π^* orbitals should strongly affect the bond order of $\text{C}\equiv\text{O}$.

IR data can be correlated C-O bond order.

π -acid Ligands

- Examples of 2-e⁻s donors & have empty orbitals of π -symmetry include isocyanides CNR and carbenes :C(X)(Y) have empty $2p_z$ orbital.
- π -acids without C, NO⁺ (isoelectronic with CO), :phosphines PR₃, arsines AsR₃, stibenes SbR₃, bipyridine (bipy) and phenanthroline (Phen)
- Bipy & phen possess π^* orbital \perp molecular plane.

The Effective Atomic # Rule or the 18e⁻ Rule

- The rule predicts the stability of organometallic compounds and simply states that stability is attained or gained when all of the bonding and non-bonding orbitals are occupied.
- The rule is useful in predicting the stoichiometry of stable species and also reactivity patterns.
- CO donates 2e⁻ to the system from the σ_{nb} orbitals on C.

Metal Carbonyl Compounds

- M-C≡O's are important for their rich properties and applications in many industrial processes that include catalysis, medical diagnostics and molecular sensors.
- Mond Process, 1890
- $\text{Ni}(\text{CO})_4 \rightarrow \text{Ni}^0 + 4\text{CO}$
- $\text{Fe}(\text{CO})_5 \rightarrow \text{Fe}^0 + 5\text{CO}$

Mononuclear Metal Carbonyls

- $M(\text{CO})_x$ –hydrophobic (lacking affinity for water, i.e. water insoluble), volatile, soluble in non-polar solvents.

- e.g.

$\text{V}(\text{CO})_6$	O_h
$\text{Cr}(\text{CO})_6$	O_h
$\text{Mo}(\text{CO})_6$	O_h
$\text{W}(\text{CO})_6$	O_h
$\text{Fe}(\text{CO})_5$	tbp
$\text{Ru}(\text{CO})_5$	tbp
$\text{Ni}(\text{CO})_4$	T_d

Mononuclear Metal Carbonyls

- Stable homoleptic carbonyls of transition metal elements can be predicted using the EAN rule.
- Vanadium- ^{23}V $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
- V^0 $5 e^-$
- $6 \times \text{CO}$ $12 e^-$
- $1 \times 1e^-$ $1e^-$
- Total $18e^-$

- Stable $\text{V}(\text{CO})_6^-$

Metal carbonyls

- $M = \text{Cr, Mo, \& W} - 3d^4 4s^2$
- $M^0 = 6 e^-$
- $6 \times \text{CO} = 12 e^-$
- Total = 18 e-
- Stable $M(\text{CO})_6$ –stable

Mn, Tc, Re

$MO = 7$

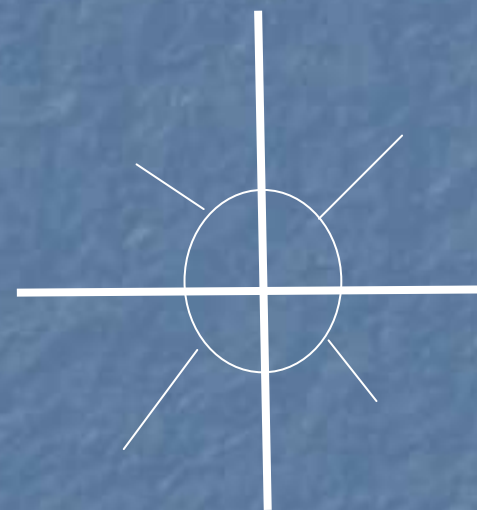
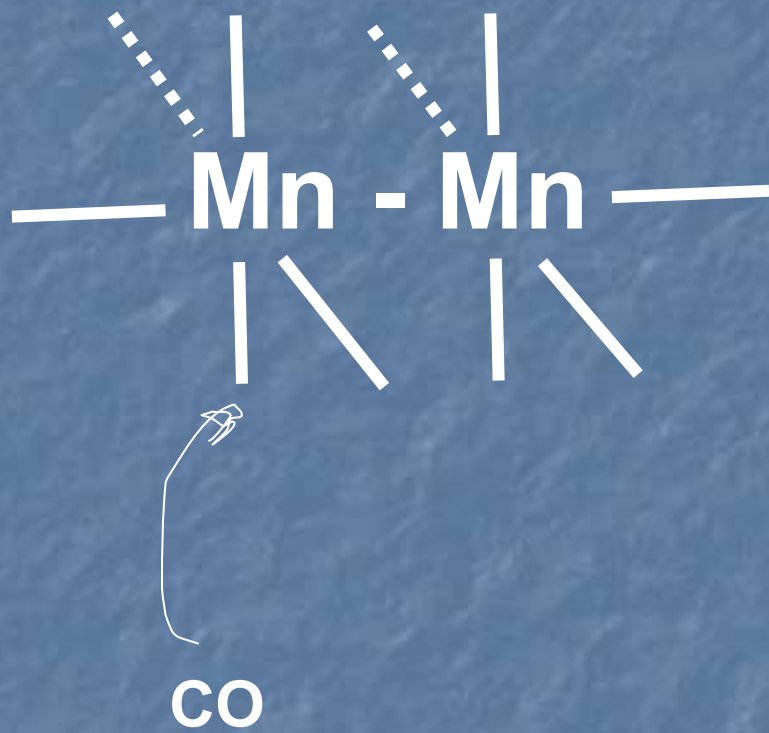
∴ Need 11 e-

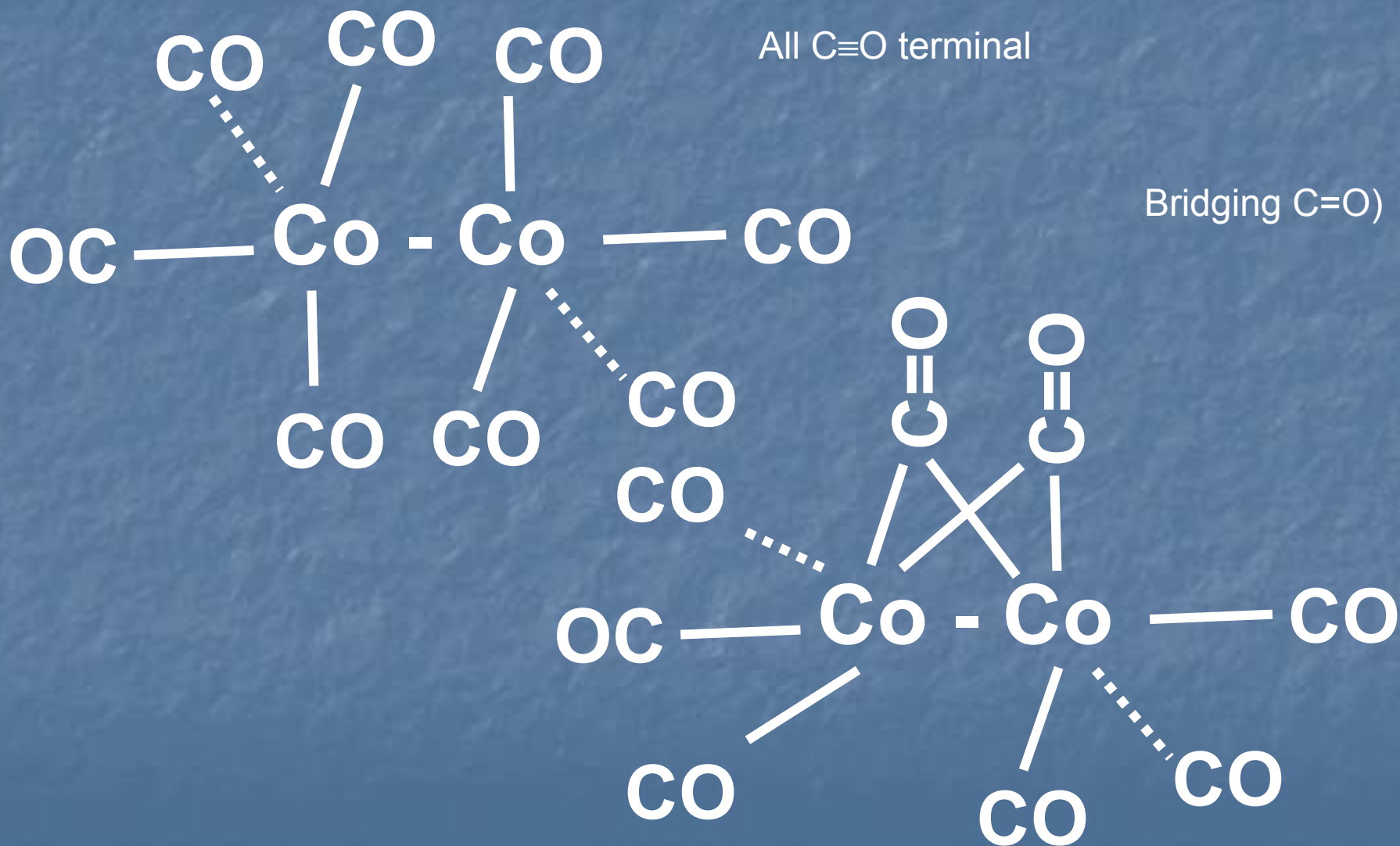
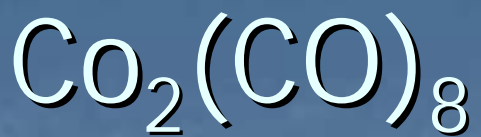
∴ Possibilities

∴ 1. $M(\text{CO})_5^-$

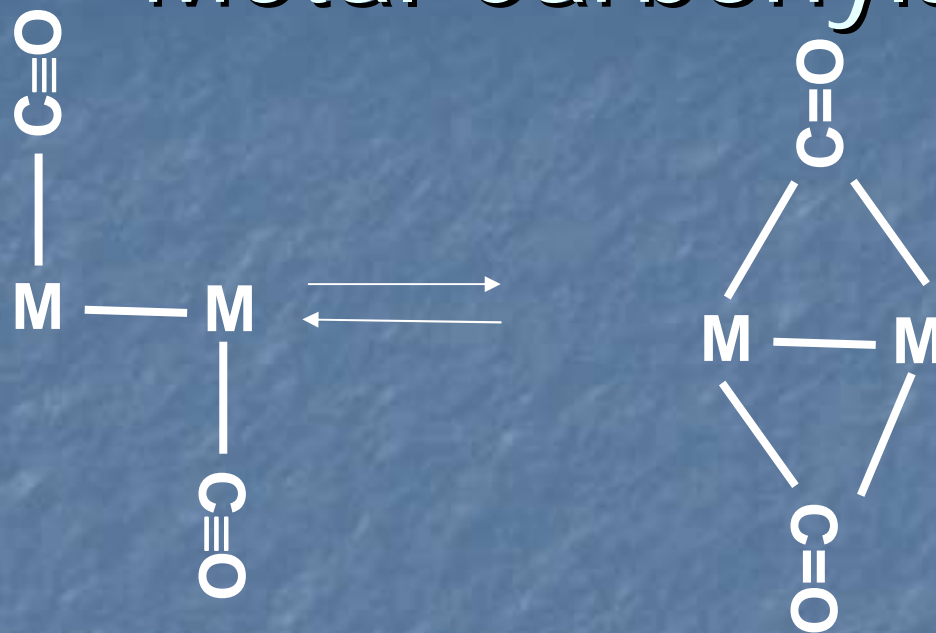
∴ 2. $M(\text{CO})_6^+$

∴ 3. $(\text{CO})_5M-M(\text{CO})_5$ Metal metal bond donates
1e to each metal





Metal Carbonyls

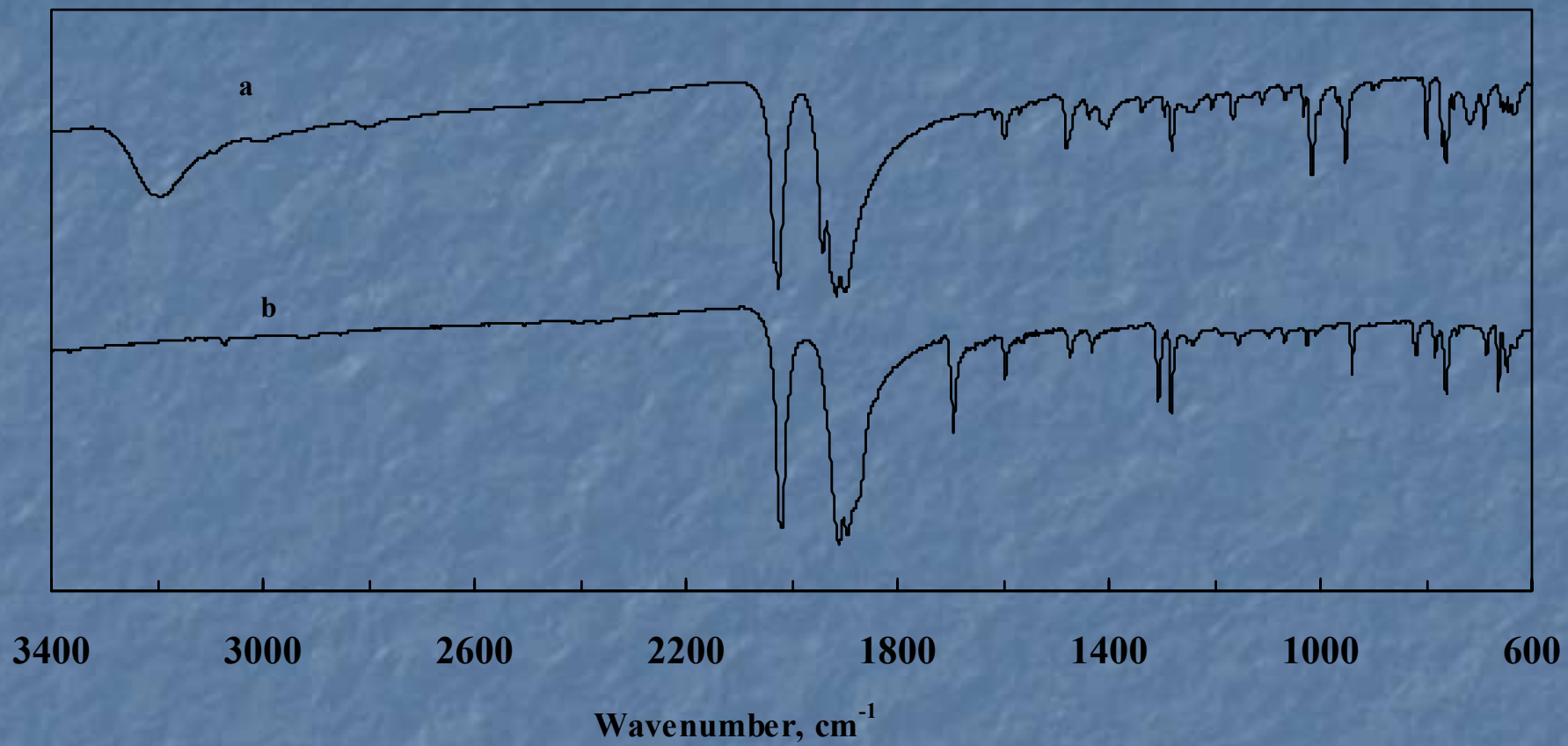


I.R. $\nu(\text{C}\equiv\text{O}) \sim 2150 - 1850 \text{ cm}^{-1}$

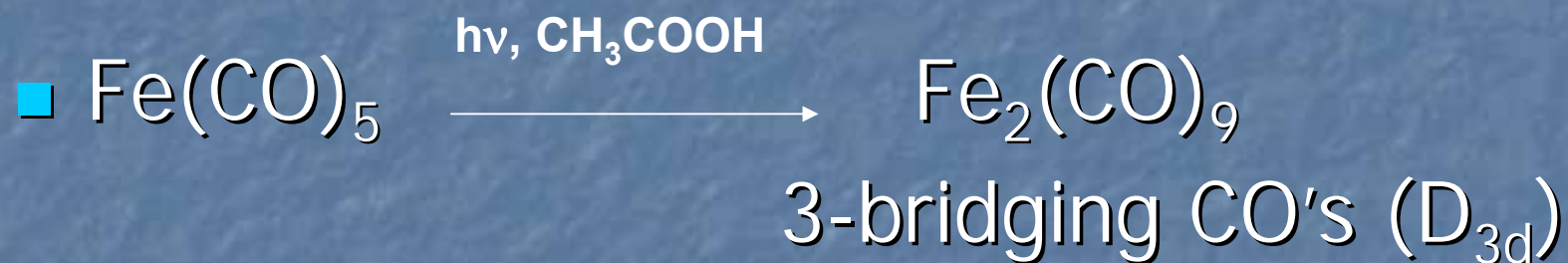
$\nu(\text{C}=\text{O}) - 1850 - 1750 \text{ cm}^{-1}$

$\nu(\text{C}-\text{O}) \sim < 1600 \text{ cm}^{-1}$

fac-Re(CO)₃(dpk.oxime)Cl and fac-Re(CO)₃(dpk)Cl



$M_2(CO)_9$



M = Ru, Os



- Higher nuclearity



- $M = Fe, Ru, Os$

- $3 M = 24 e^-$

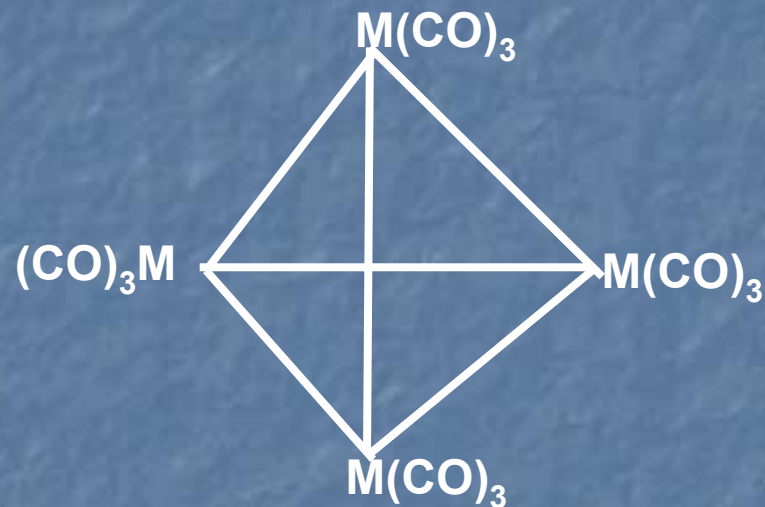
- $12 CO = 24 e^-$

- Need $3 \times 18 = 54e^-$ for EAN

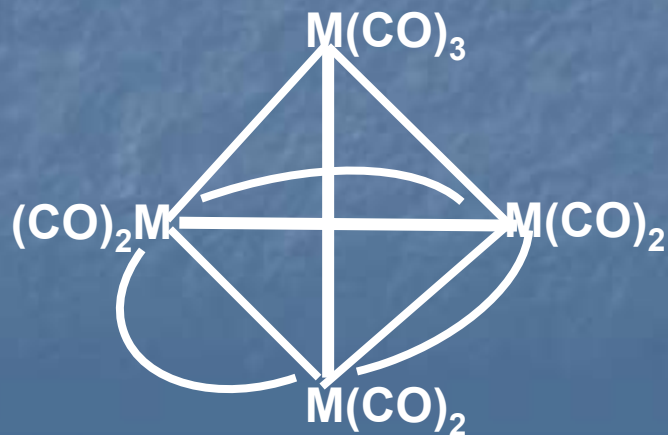
- $6e^-$ short, then need 3 (M-M) bonds



- $4 \times M = 36 e^-$
- $12 CO = 24 e^-$
- Total = $60 e^-$
- Need $4 \times 18 = 72 e^-$
- \therefore need $6(M-M)$ bonds



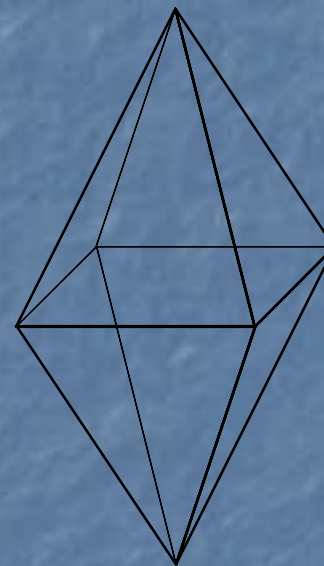
= bridging CO





- $6 \times \text{Rh} = 54$
- $16 \times \text{CO} = 32$
- Total 86

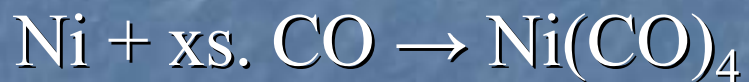
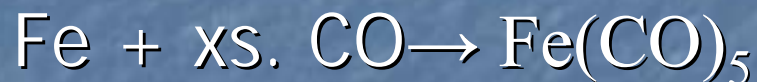
- $6 \times 18 = 108$, then
need 22 electrons, i.e.
11 M-M bonds



Preparation of metal carbonyl Compounds

- Two procedures are used
 - Direct reaction of a metal with CO

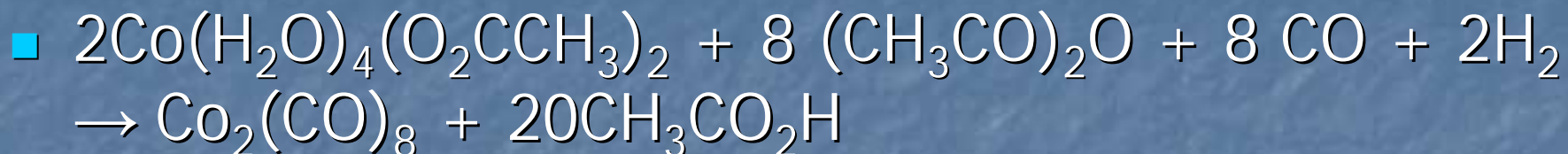
e.g. $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$.



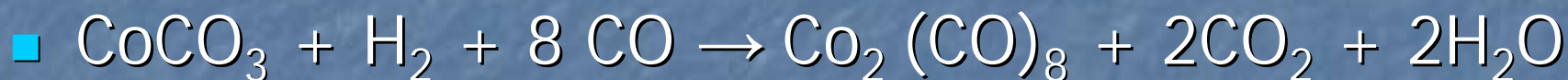
Note only Ni & Fe are prepared this way, xs. \equiv excess.

- Reductive Carbonylation of metal salts using a reducing agent or CO as a reducing agent.
e.g.

Reductive Carbonylation



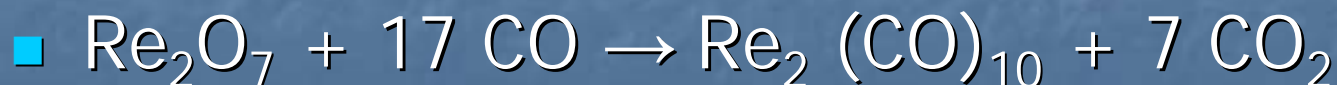
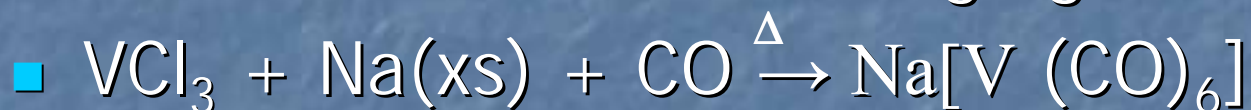
H_2 is the reducing agent



H_2 is the reducing agent



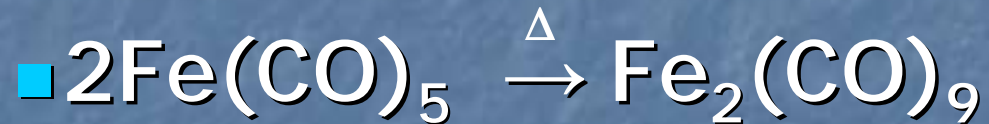
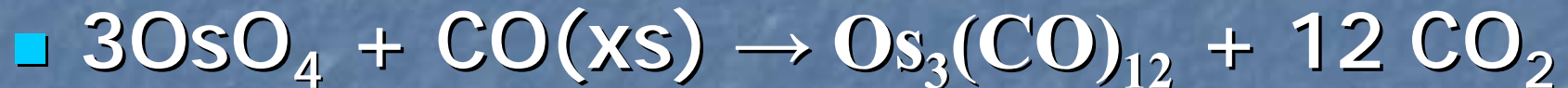
Al is the reducing agent



CO is the reducing agent

Polynuclear Carbonyls

- Higher carbonyls can be prepared from the thermolysis or photolysis of lower carbonyls



Substituted Carbonyls & Carbonylate Anions

- The carbonyl group in metal carbonyls are labile and can be replaced with of other ligands.
- The EAN rule can be used to predict the stability of the substitution product.
- e.g.
- $\text{Cr}(\text{CO})_6 + \text{CNR} \rightarrow \text{Cr}(\text{CO})_5(\text{CNPh}) + \text{CO}$
- $\text{Ir}_4(\text{CO})_{12} + 2 \text{PPh}_3 \rightarrow \text{Ir}_4(\text{CO})_{10}(\text{PPh}_3)_2 + 2 \text{CO}$
- $\text{Mo}(\text{CO})_6 + \text{Br}^- \rightarrow \text{Mo}(\text{CO})_5\text{Br}^- + \text{CO}$

Lewis Bases & # of valence e's

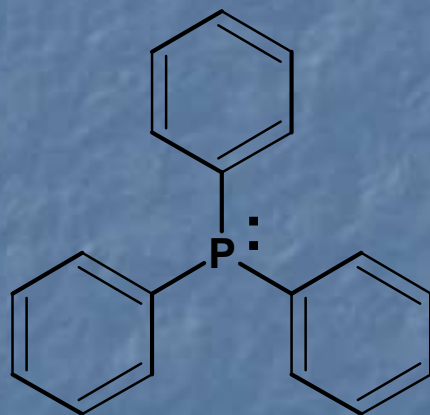
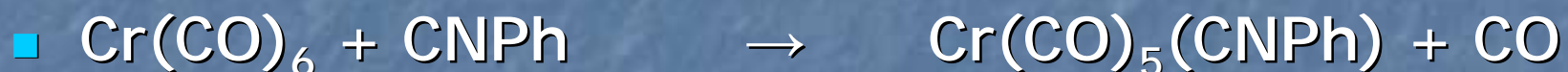
- H^- , X^- , NCS^- , CN^- where $\text{X} = \text{halide}$ = $2e^-$ donor
- CO , CNR , NO^+ , PR_3 , P(OR)_3 , AsR_3 , NR_3 , SbR_3 , SR_2 ,
: CXY
= $2e^-$ donor ligands
- R^- , C(O)R^- , Ar^-
ligands
= $2e^-$ donor
- NO
= $3e^-$ donor Ligand

Metal Carbonyls Reactions 1

1. Direct Substitution

- $2 e^- \equiv 1 \text{ CO}$

- e.g.



Triphenylphosphine

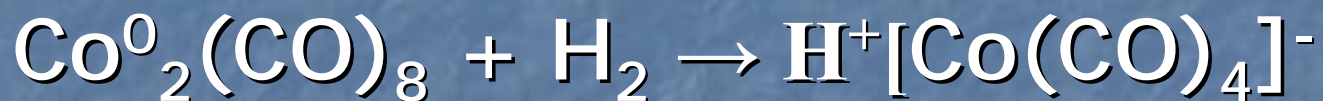
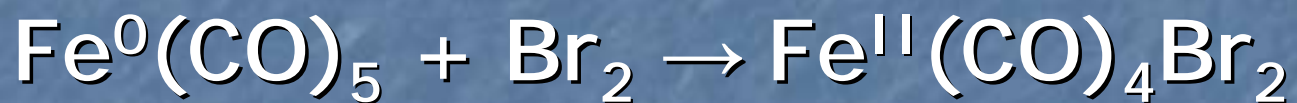
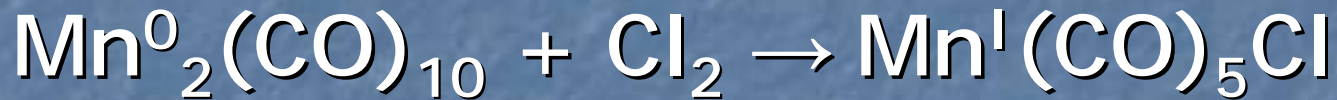
PPh_3



Isonitrile, R = Aryl or alkyl

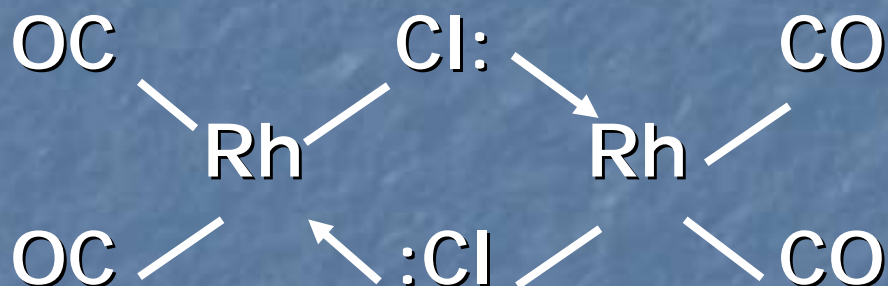
Metal Carbonyl Reactions 2

2. Oxidation



Substitution Reactions 3

3. Rearrangements



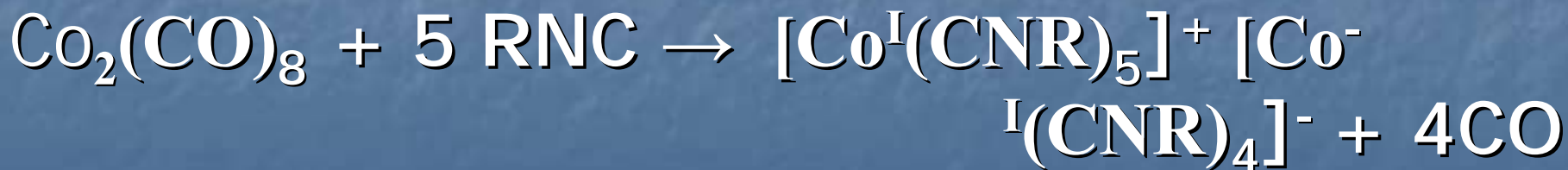
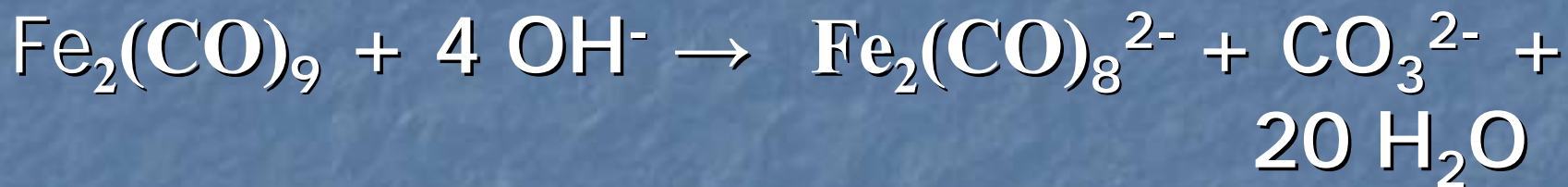
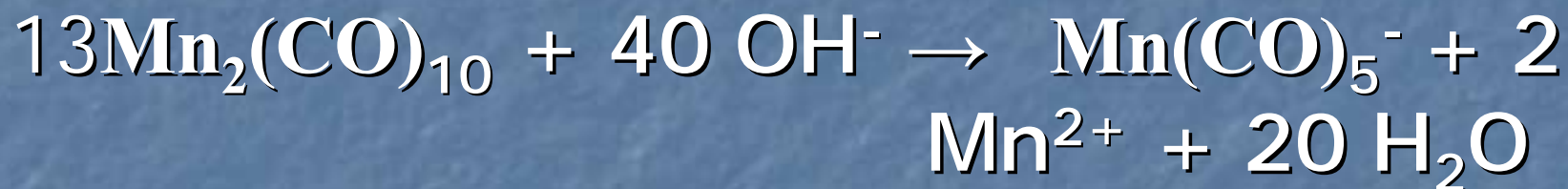
Bridging chloride in this case is 3 e⁻ donor, explain? And predict if EAN is satisfied!

Reactivity of Organometallics

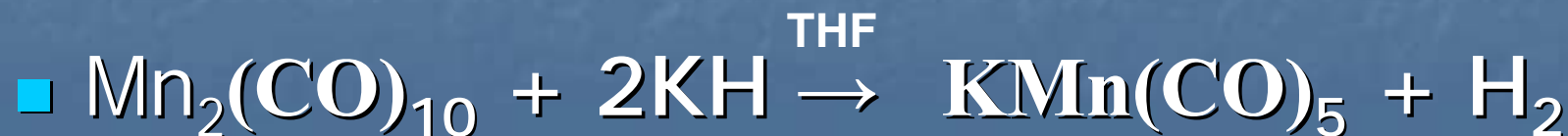
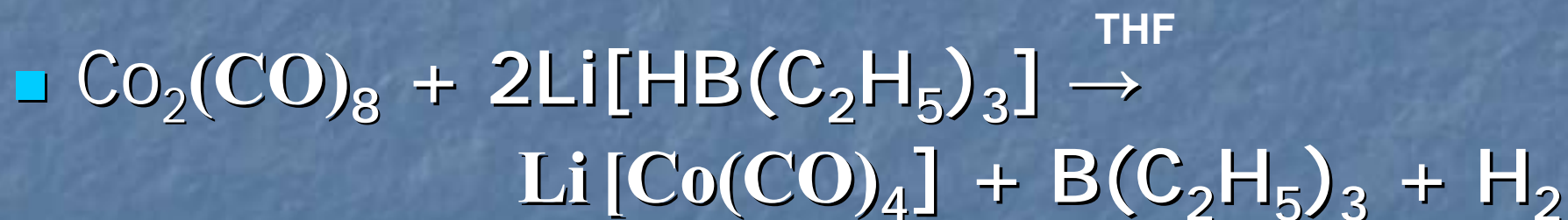
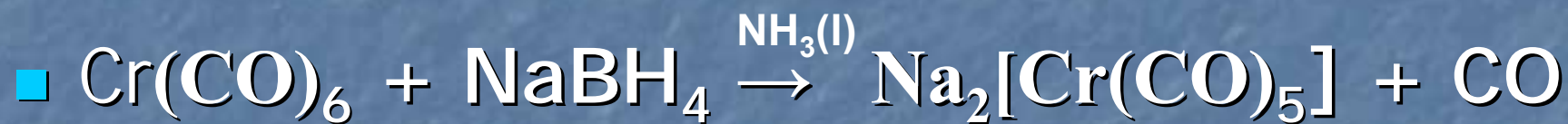
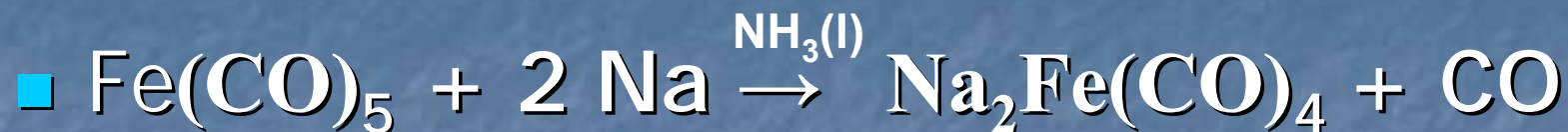
- $2\text{Mn}(\text{CO})_5\text{Cl} \xrightleftharpoons[\text{+CO, pressure}]{\Delta, -\text{CO}} \text{Mn}_2(\text{CO})_8(\mu\text{-Br}_2)$
- $\text{Re}_2(\text{CO})_{10} + \text{Cl}_2 \rightarrow \text{Re}_2(\text{CO})_8(\mu\text{-Cl}_2)$
- $[\text{Rh}(\text{CO})_2(\mu\text{-Cl})] + 2 \text{PPh}_3 \rightarrow$
 $\textit{trans}\text{-Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl} + \text{CO}$

Carbonylate Anions

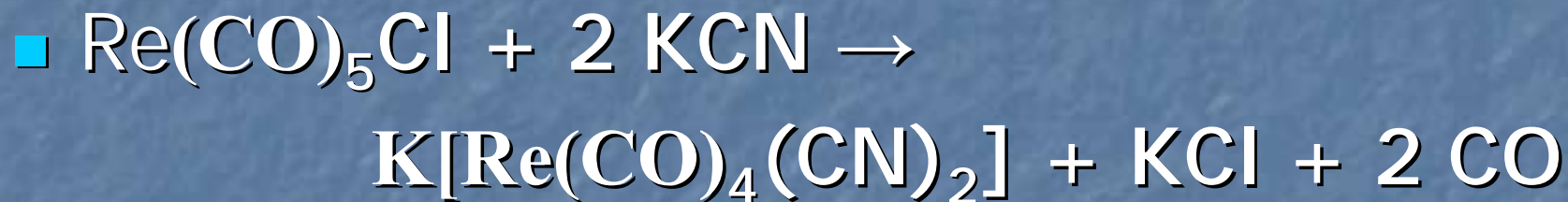
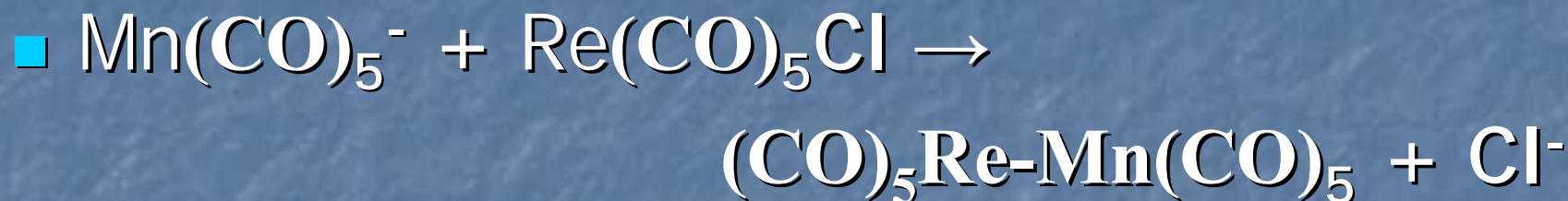
- Synthesis
- Reaction of metal carbonyls with base.
- e.g.



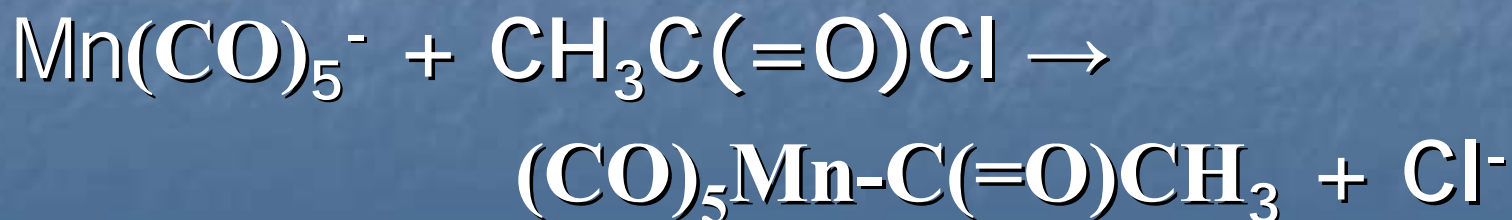
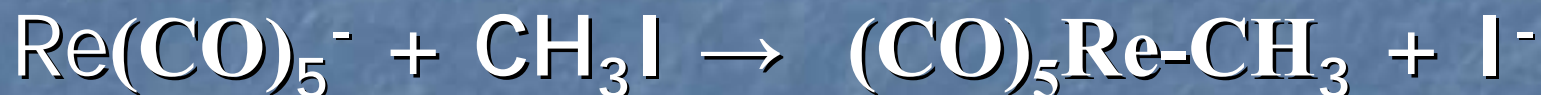
Reaction of Metal Carbonyls with a reducing agent



Reactions of Metal Carbonyls with Anions



- Reactions with alky, acyl halides



Protonation of Carbonylate anions

- $\text{Mn}(\text{CO})_5^- + \text{H}^+ \rightarrow \text{H-Re}(\text{CO})_5$
- $\text{Fe}(\text{CO})_4^{--} + \text{H}^+ \rightarrow \text{H-Fe}(\text{CO})_4^-$
- $\text{H-Fe}(\text{CO})_4^- + \text{H}^+ \rightarrow \text{H}_2\text{-Fe}(\text{CO})_4$

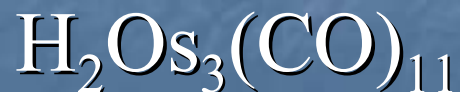
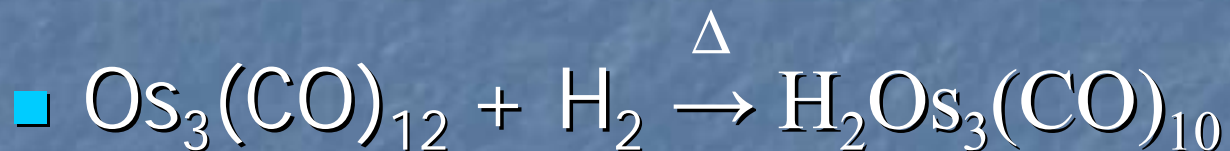
Oxidation States

- Always consider the metal in its zero oxidation state.
- e.g.
- H-Mn(CO)_5
- Br-Mn(CO)_5
- $\text{CH}_3\text{-Mn(CO)}_5$
- Mn in oxidation state of zero,
- \therefore H, CH_3 , Br all donate $1 e^-$.

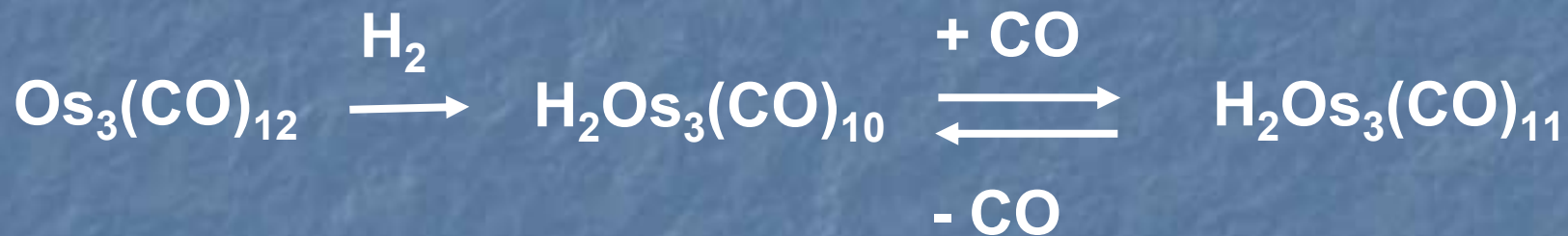
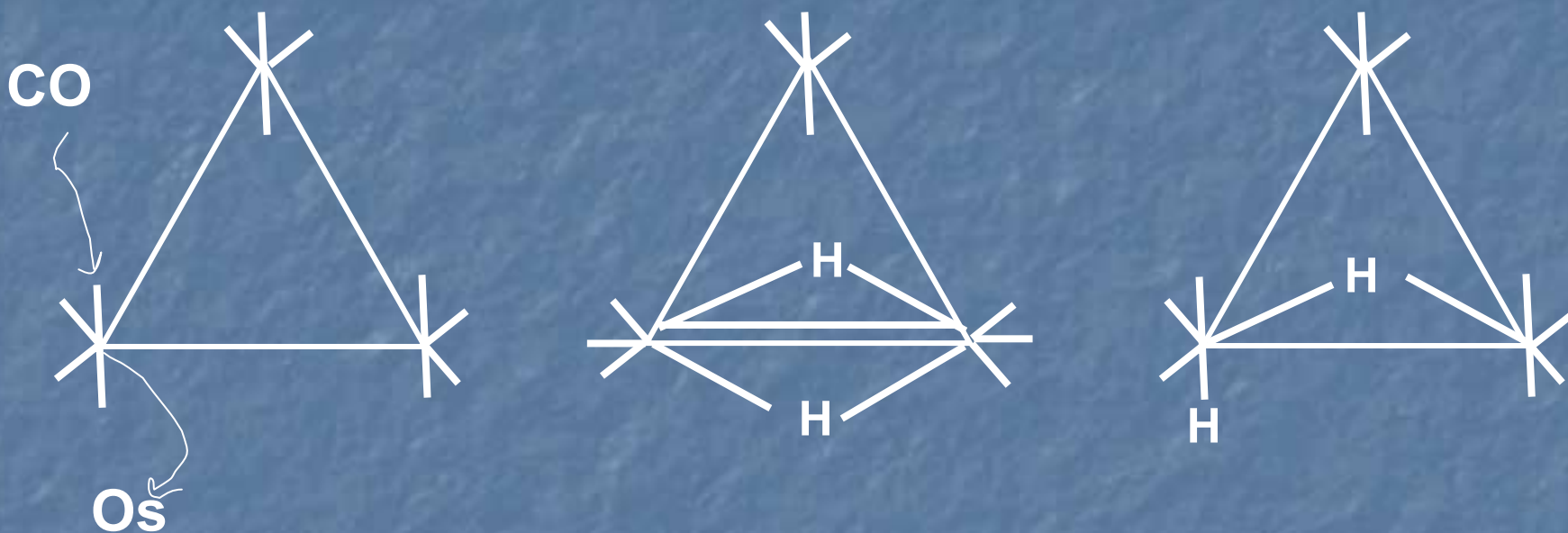
Reactivity of polynuclear Carbonyls

- 1 CO \equiv 2 e⁻; \therefore if 1 CO is removed then you need to replace it with two 1 e⁻ donors such as H, CH₃, Br

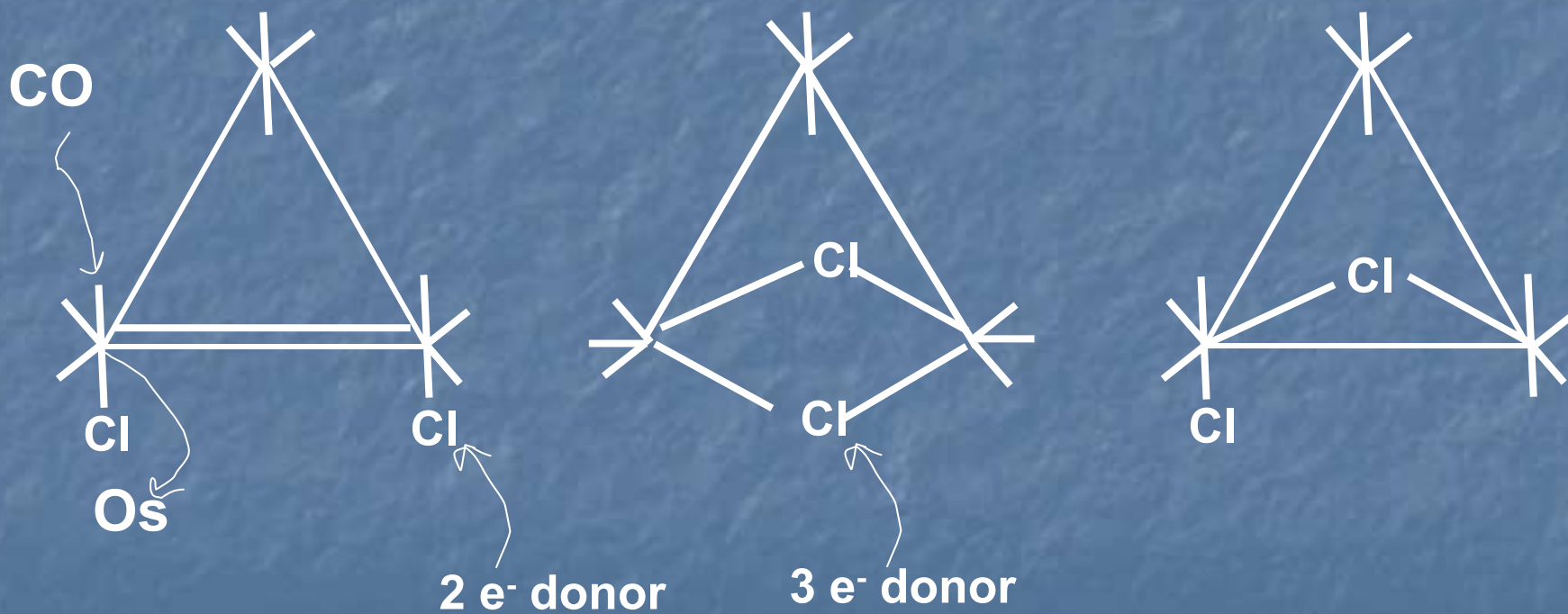
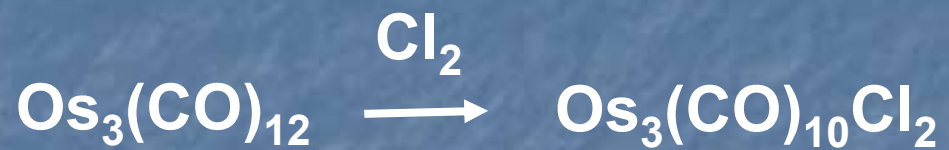
- e.g. Os₃(CO)₁₂



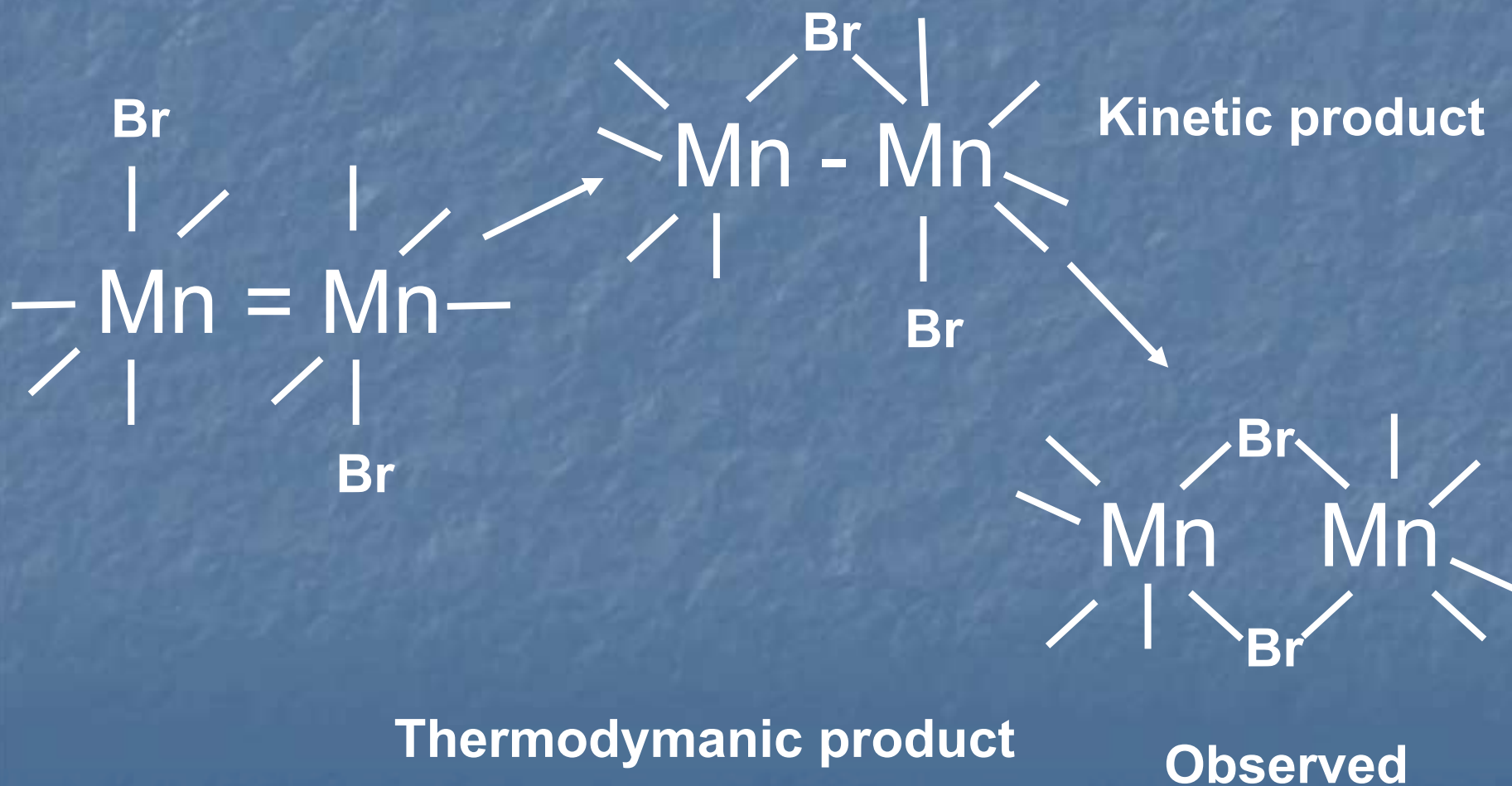
Bonding



Bonding

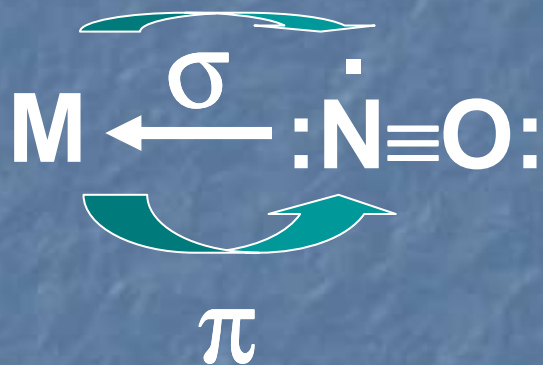


Bonding



Nitric Oxide Ligand

- NO has a very similar M.O. diagram to that of CO, except that it contains one extra electron in the π^* orbital.

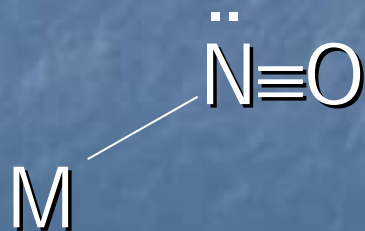


3 e^- are donated to the M.O. scheme of the complex by NO. In this case L-N-O bond $\sim 170 - 180^\circ$.

NO is 3 e^- donor;
 $\therefore \text{NO}^+$ is 2 e^- donor
 \therefore *i.e.* $\text{NO}^+ \equiv \text{CO}$, *i.e.* isoelectronic

Compounds of NO

- $\text{Co}(\text{CO})_4\text{NO}$; $\text{Mn}(\text{CO})_4\text{NO}$; $\text{Fe}(\text{CO})_2(\text{NO})_2$.
- EAN ? Check.
- Bent M-NO, with M-N-O bond angle of 110-120°, then NO is 1 e⁻ donor.

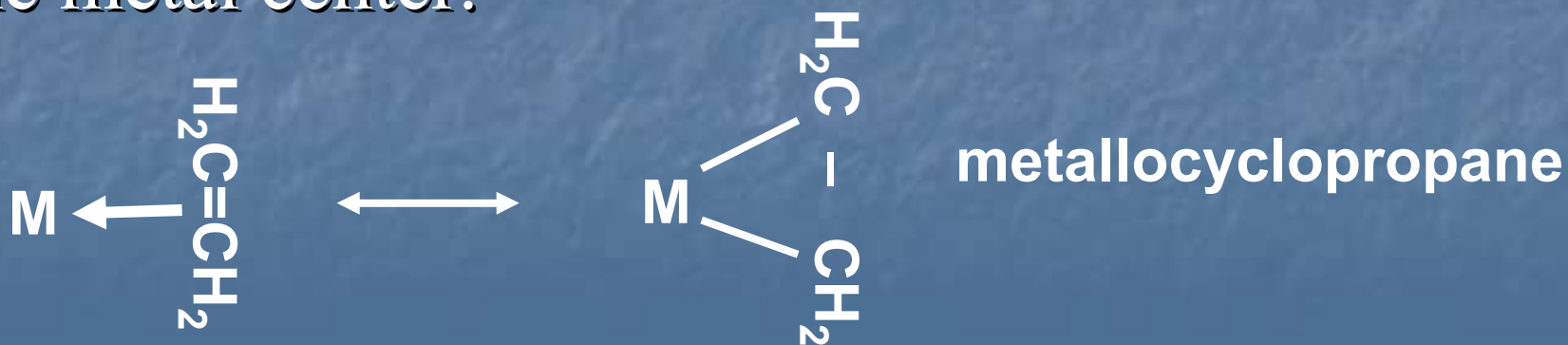


Bonding of Organic Ligands to Metals

- Olefin Compounds
- Zeises' Salt



The bonding is best described by the Dewar-Chatt Mode. The olefin here is a total of 2 e- donor to the metal center.



Acetylene

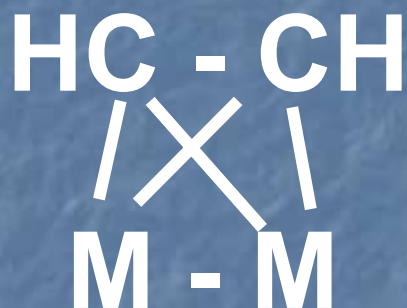
- As in the case of olefins, acetylene can use one of its p-bonds or both to coordinate to metal atoms. Note each π -bond is $2e^-$ donor.



Note: this type of bonding is not common

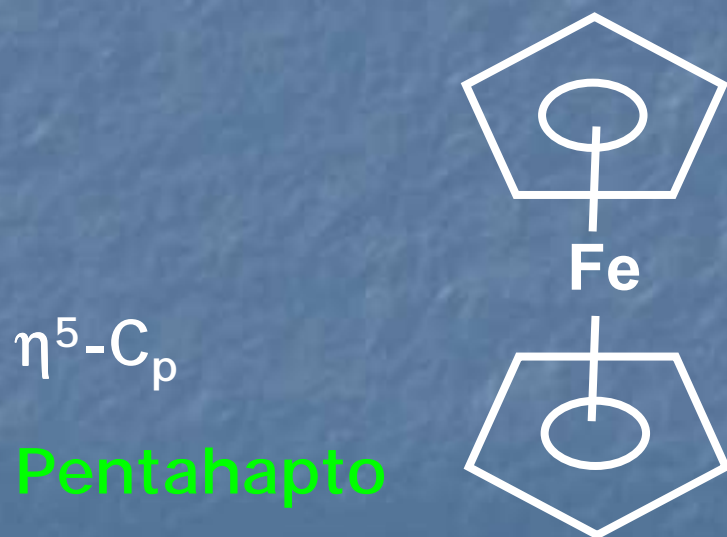
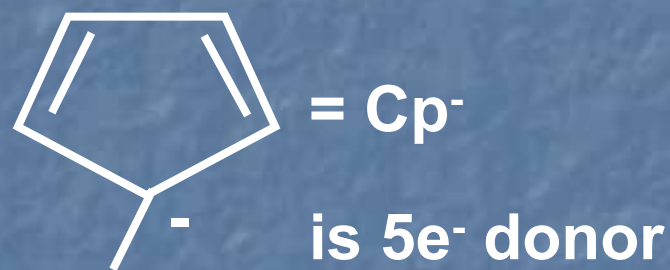
Acetylene (ac) Bonding

- Bridging acetylene bonding is more common
- e.g.
- $\text{Co}_2(\text{CO})_8 + \text{HC} \equiv \text{CH} \rightarrow \text{Co}_2(\text{CO})_6(\text{ac})$

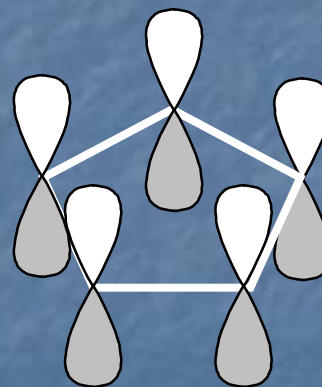


Conjugated Olefin Systems

- Ferrocene
- $\text{FeCl}_2 + 2 \text{NaCp} \rightarrow \text{FeCp}_2$

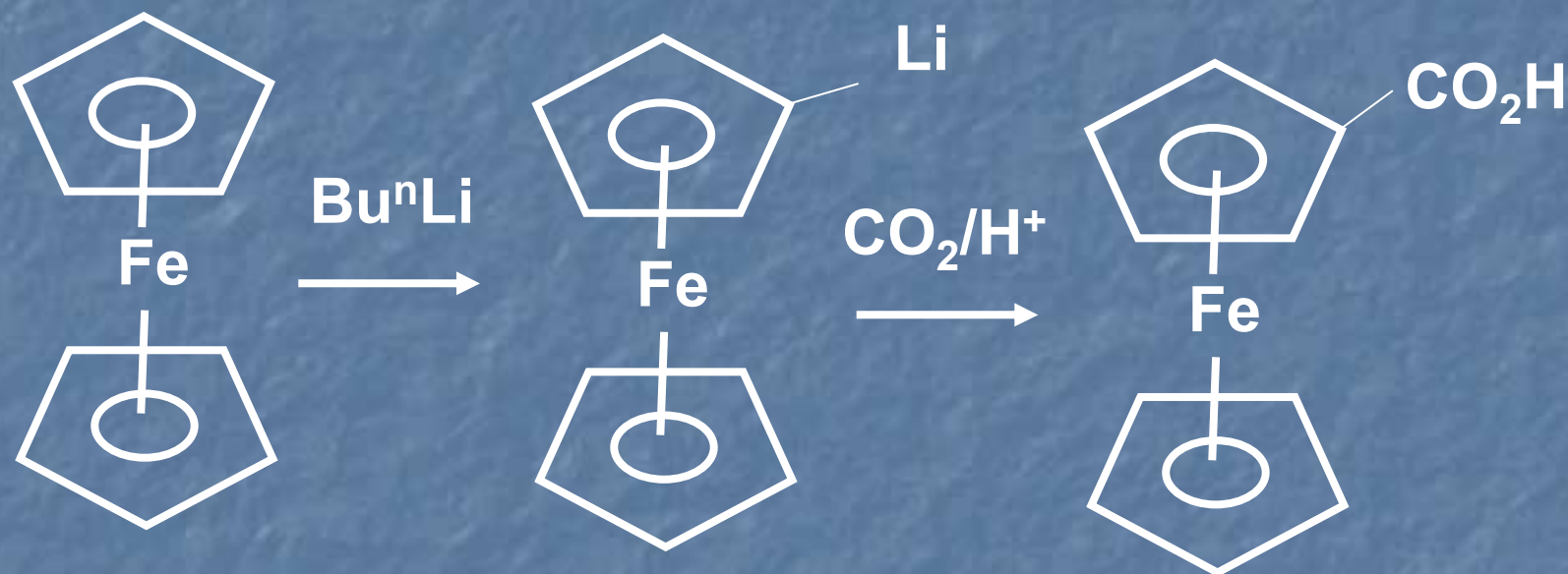


Staggered=sandwich

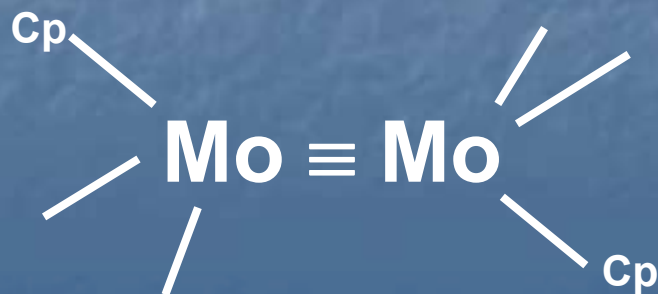
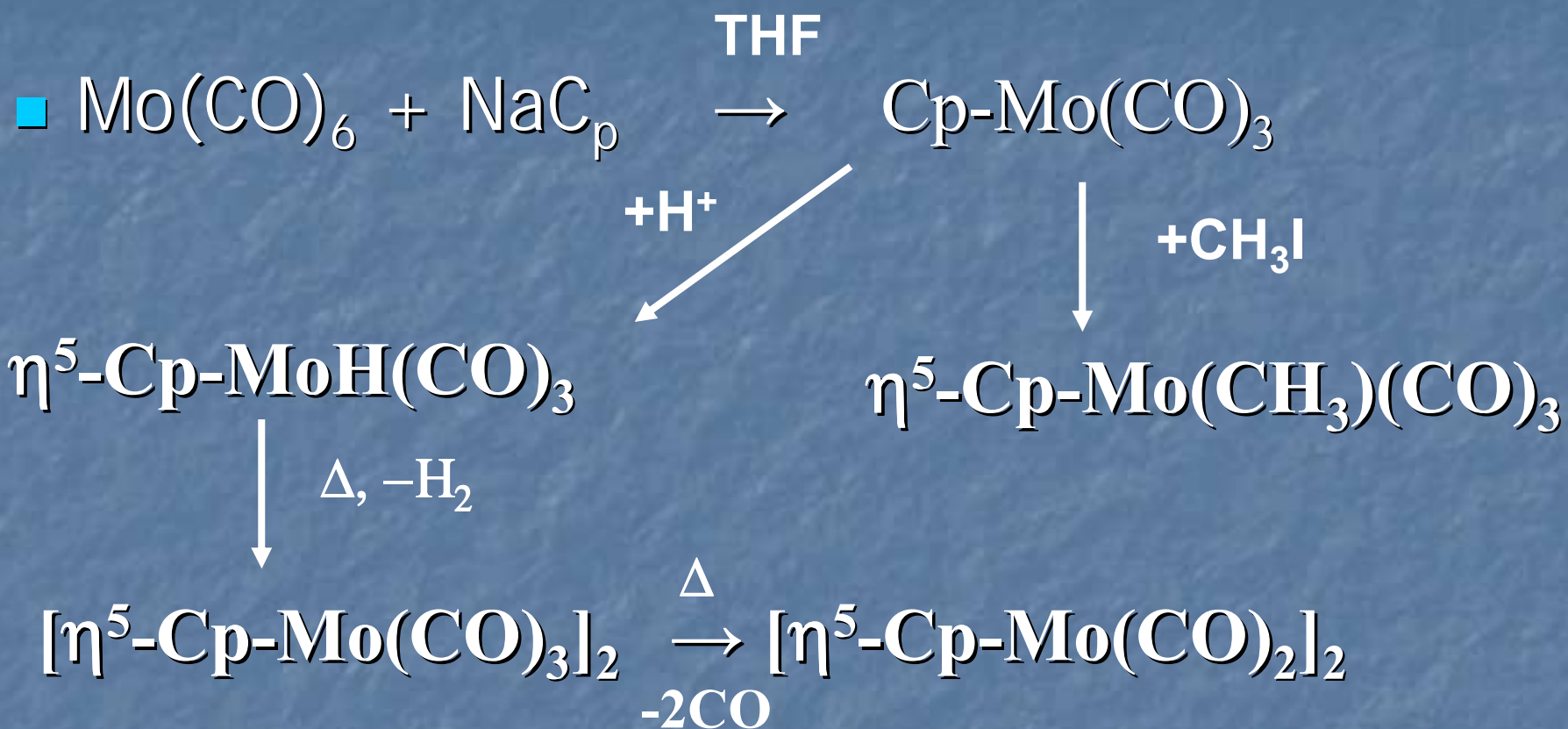


Reactions of C_p -compounds

- With Organometallics

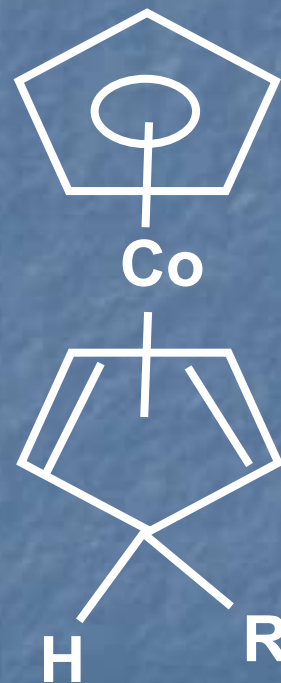


Reactions of Cp-compounds



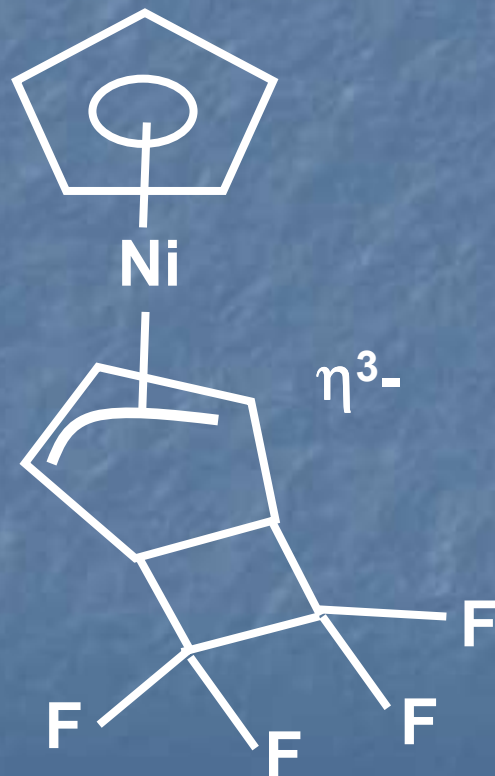
Reactions of C_p-compounds

- Nucleophilic Addition
- $\text{CoCp}_2 + \text{CH}_3\text{Br} \rightarrow \text{Co}(\eta^5\text{-Cp})(\eta^4\text{-C}_5\text{H}_5\text{R}) + \text{Br}^-$



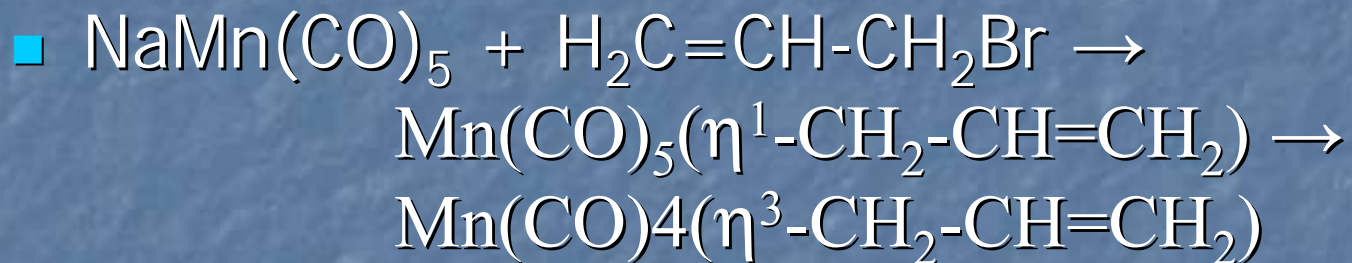
Reactions of C_p-compounds

- Addition reactions [2 + 2] cycloaddition
- $\text{NiCp}_2 + \text{F}_2\text{C}=\text{CF}_2 \rightarrow \text{Ni}(\eta^5\text{-Cp})(\eta^3\text{-C}_5\text{H}_3\text{C}_2\text{F}_4)$

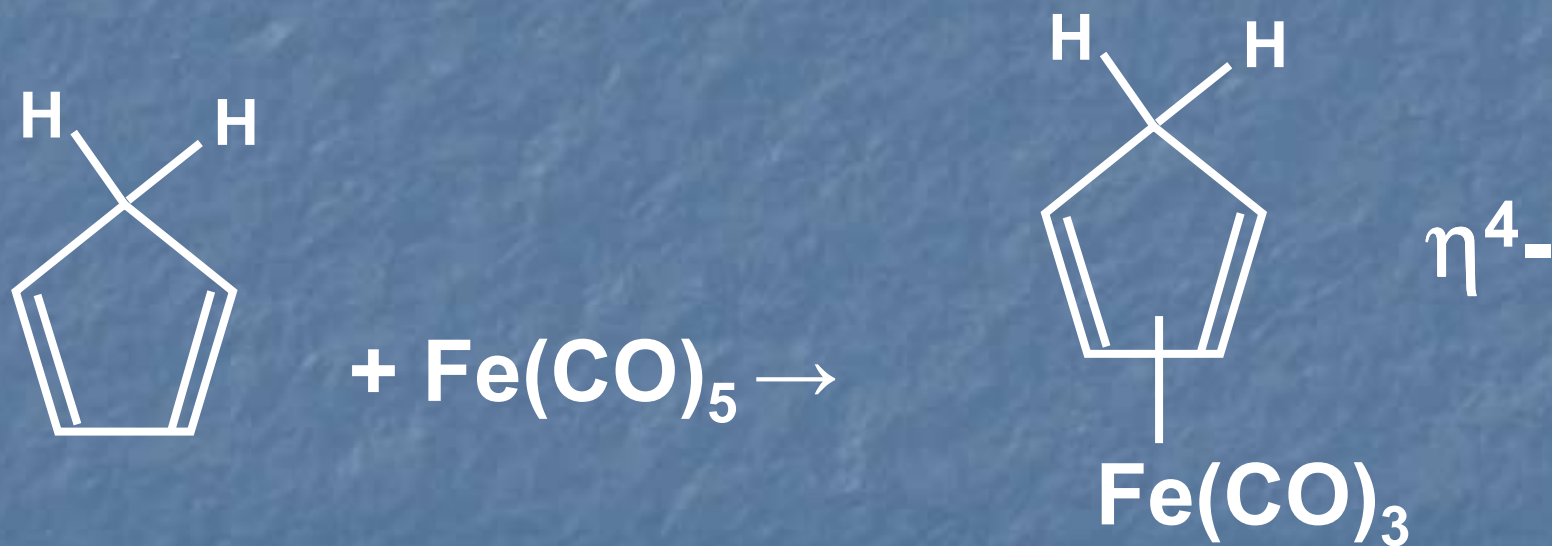
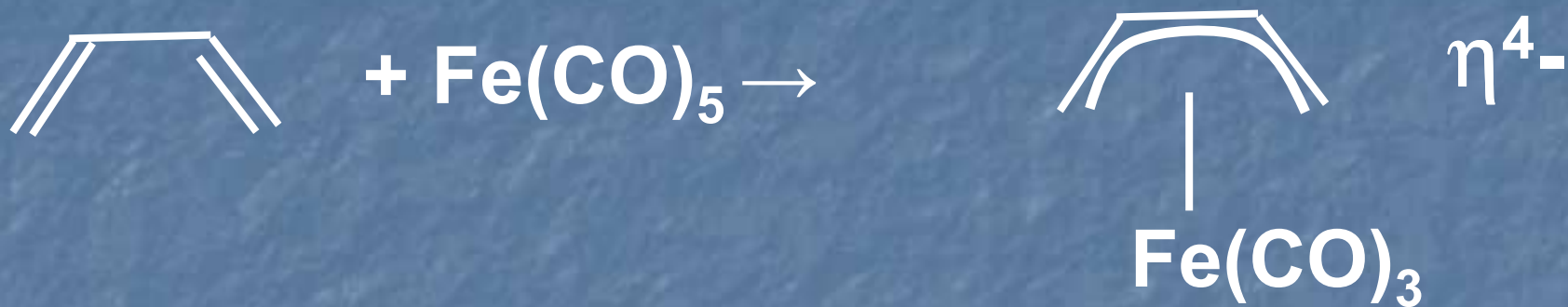


Other systems

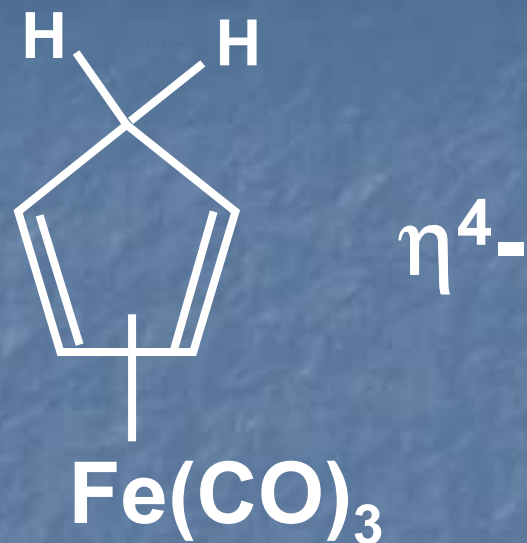
- Allyls



Other systems



Reactions

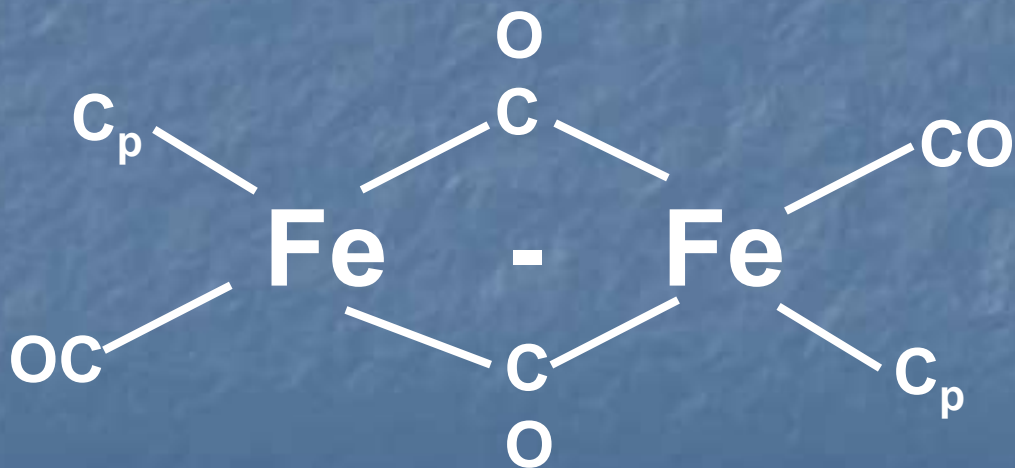


- CO



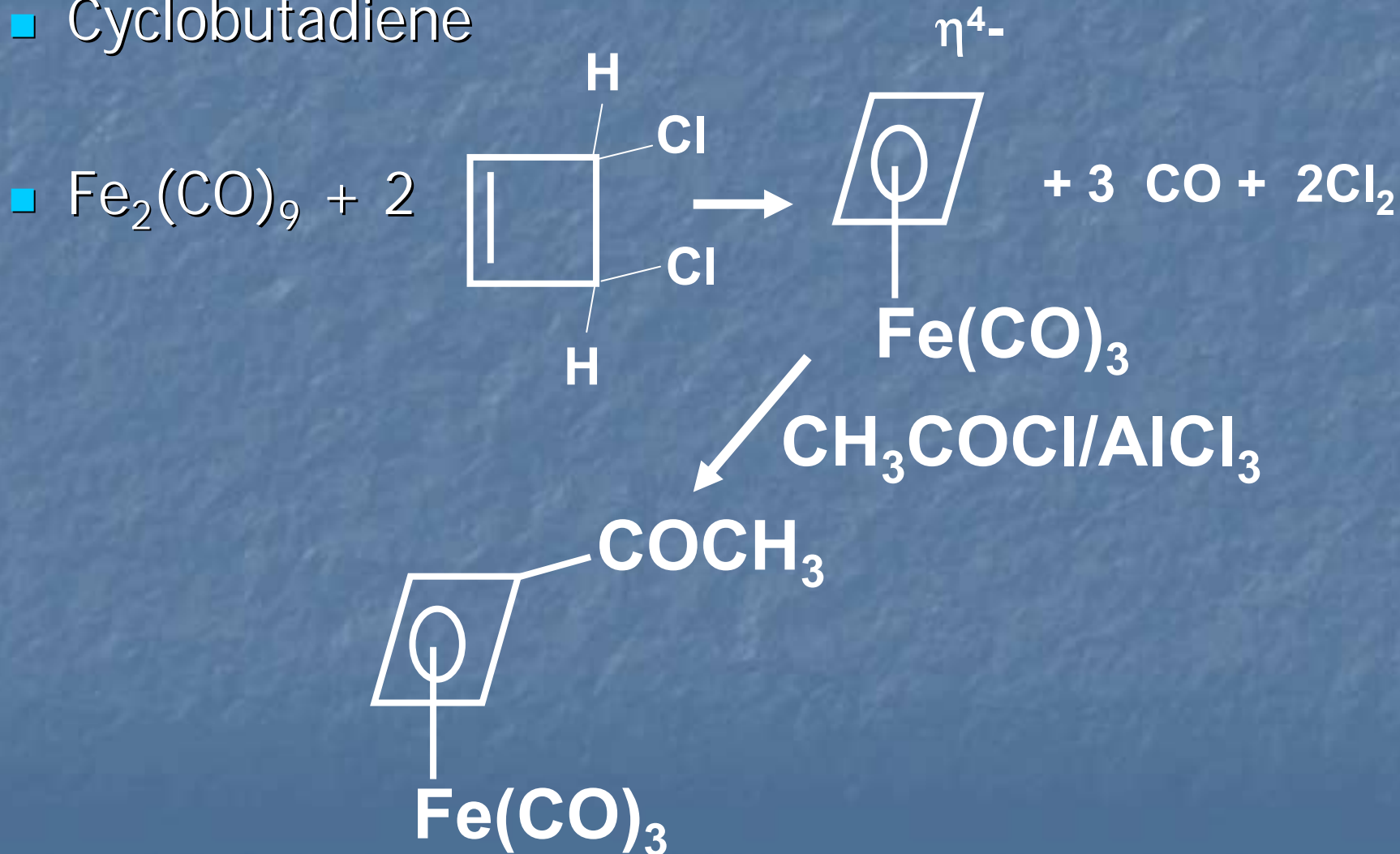
Δ

- H_2



Other ring systems

- Cyclobutadiene



Other ring systems

- Benzene

