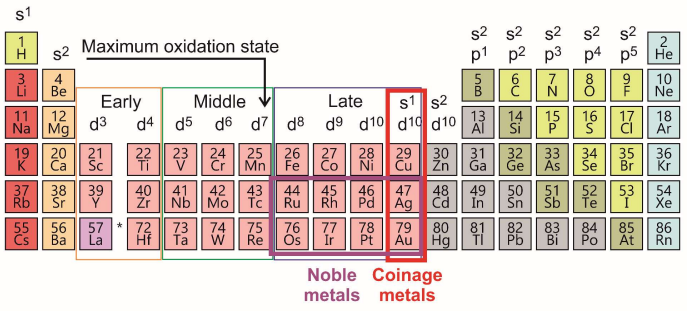
Transition metal organometallics

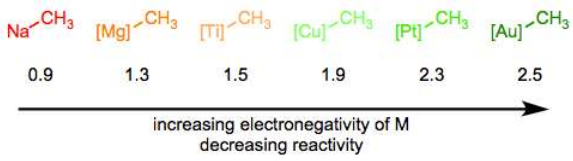
Reading: Crabtree, pages 69 - 162

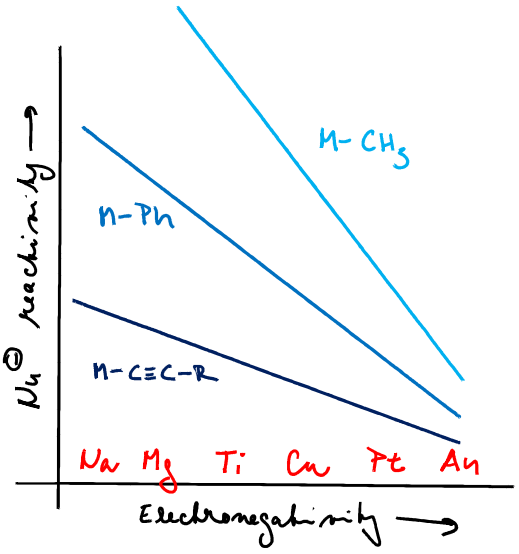
1

Transition metals



Noble metals:
High electronegativities
Covalent bonding to carbon
(Au-C bond is non-polar, stable to air and moisture)





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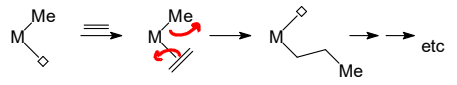
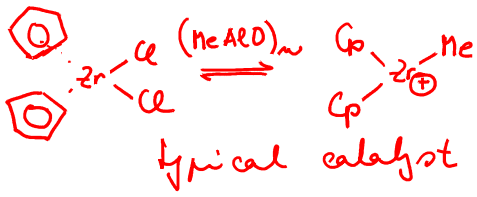
Early Transition Metals: Groups 3,4

Properties

- Strongly electrophilic and oxophilic
- Few redox reactions (exception: Ti)
- Nearly always < 18e
- Polar and very reactive M-C bonds (to alkyl and aryl)
- Few d-electrons:
  - preference for "hard" σ-donors (N/O/F)
  - weak complexation of π-acceptors (olefins, phosphines)

Typical catalysis: Polymerization

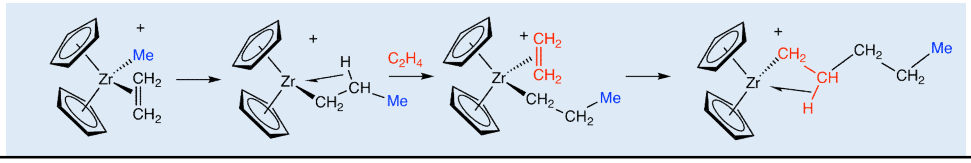




Electronegativities

C 2.55

Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65
Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 2.10	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69
La 1.10	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9



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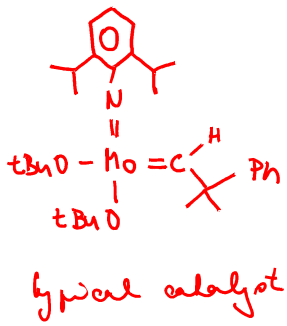
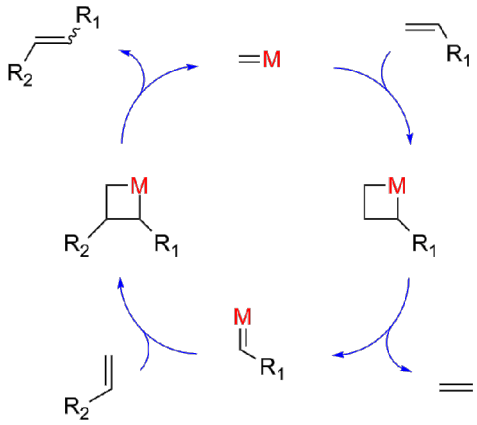
"Middle" Transition Metals: Groups 5-7

Properties

- Many accessible oxidation states
- Mostly 18e
- Ligands strongly bound
- Strong, not very reactive M-C bonds
- Preference for σ-donor/π-acceptor combinations (CO)



Typical catalysis: Alkene and alkyne metathesis



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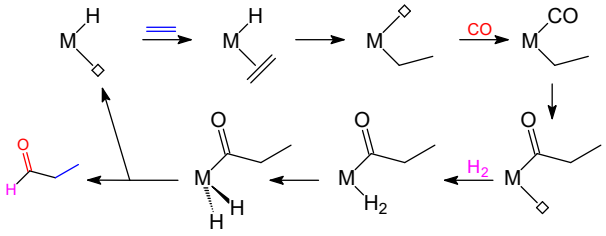
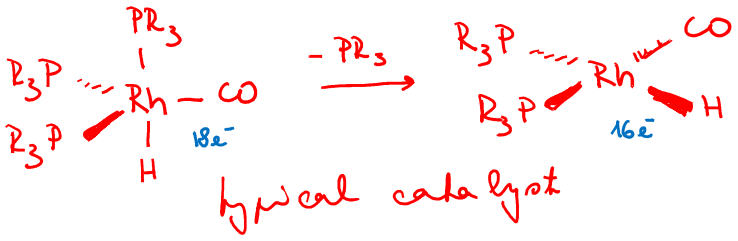
Late Transition Metals: Groups 8-10 (and 11)

Properties

- Many accessible oxidation states
- Mostly 18e or 16e
  16e common for square-planar complexes
- Easy ligand association/dissociation
- Weak, not very reactive M-C bonds
- Even weaker, reactive M-O/M-N bonds
- Preference for σ-donor/weak π-acceptor ligands (phosphines)

Typical catalysis: Hydroformylation





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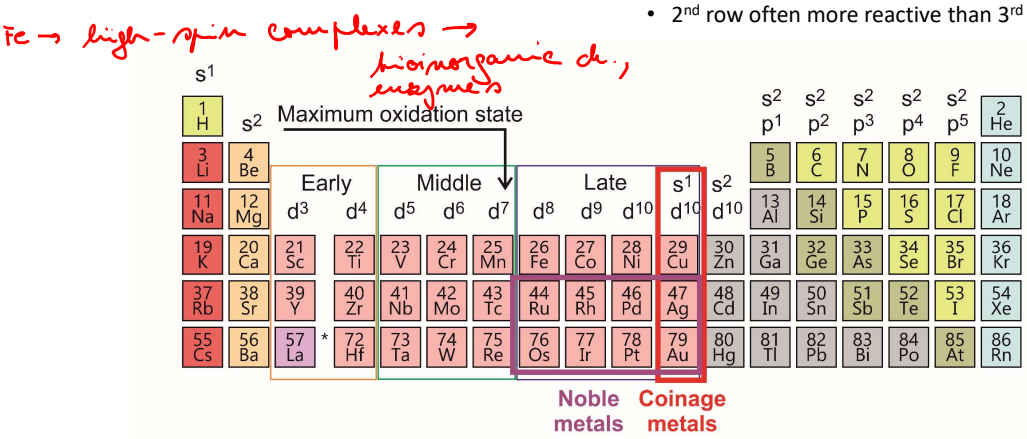
Going down...

1st row:

- often unpaired electrons
- different spin states (HS/LS) accessible
- "highest possible" oxidation states not very stable
  - MnO_4^- is a strong oxidant

2nd and 3rd row:

- nearly always "closed shell"
- virtually same atomic radii
- highest oxidation states fairly stable
  - ReO_4^- is hardly oxidizing
- 2nd row often more reactive than 3rd row



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M-H and M-C σ-bonds

M—H Hydride

M—C Alkyl

M—C Vinyl (alkenyl)

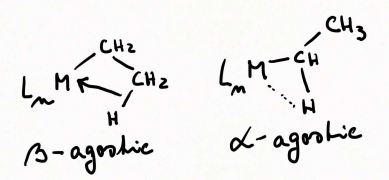
M—C≡C— Acetylide (alkynyl)

M Aryl

- Transition M-C bonds can be strong
- Many attempts to prepare TM-alkyl compounds failed
  →Formation in competition with decomposition pathways (kinetics vs. thermodynamics)

understood ~ 1960-1970s
→ until then: TM-C bond – weak
→ difficult to prepare
(main group M-C known – last lecture)
1973 Wilkinson prepared WMe_6

BDE (W-C) ~ 39 kcal/mol → strong bond
⇒ kinetics was to blame (β-H elimin.)
once understood → new area of chemistry



Agostic alkyls: C-H bonds
- Coordinatively unsaturated complexes

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Synthesis of metal alkyls

- R^-: nucleophilic attack on the metal (transmetallation)

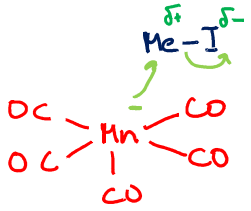
$$TiCl_4 + 4\ PhCH_2MgCl \longrightarrow Ti(CH_2Ph)_4 + MgCl_2$$

$$WCl_6 + 6\ MeLi \longrightarrow WMe_6 + 6\ LiCl$$

$$NbCl_5 + 2\ ZnMe_2 \longrightarrow NbMe_2Cl_3 + 2\ ZnCl_2$$

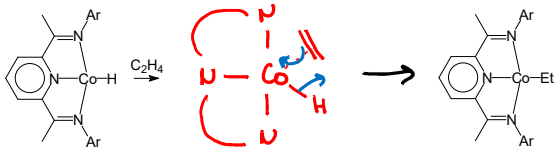
- R^+: electrophilic attack on the metal

$$Mn(CO)_5^{\ominus} \xrightarrow{MeI} MeMn(CO)_5$$

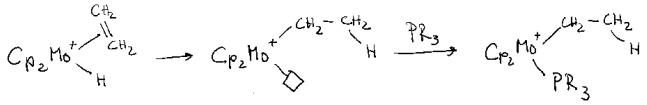


$$CpFe(CO)_2^{\ominus} \xrightarrow[-PhI]{Ph_2I^{\oplus}} CpFe(CO)_2Ph$$

- Insertion (reverse β-elimination)



Formed as intermediates
Equilibrium concentration (reverse elimination!)
→ sufficient for catalytic reaction
Metal alkyls can be trapped using ligands:



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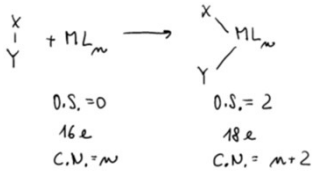
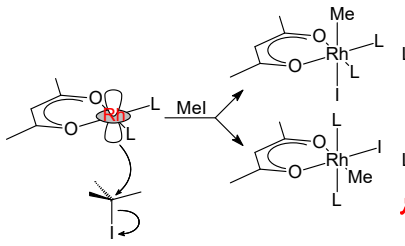
Synthesis of metal alkyls

- Oxidative addition



  - XY = H_2, R_3C-H, Cl-H, Ar-Cl, RCO-Cl, Cl-Cl, Me-I, R_3Si-H, …
  - different possible mechanisms
  - often starts with electrophilic attack

more π-acidic → equatorial



less π-acidic → axial

PR_3 → strong σ-donor → Rh – e⁻-rich → nucleophilic → S_N2 type reaction with Me-I

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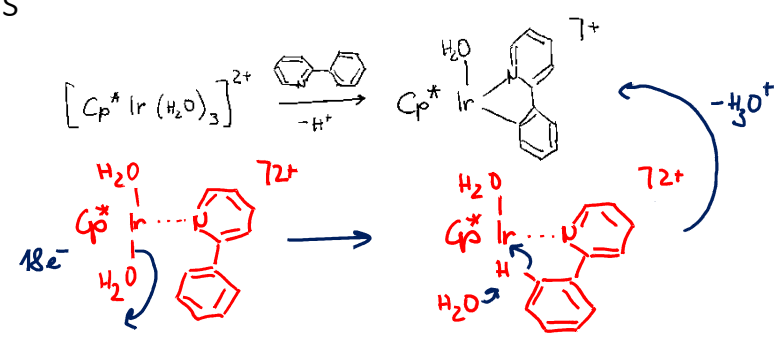
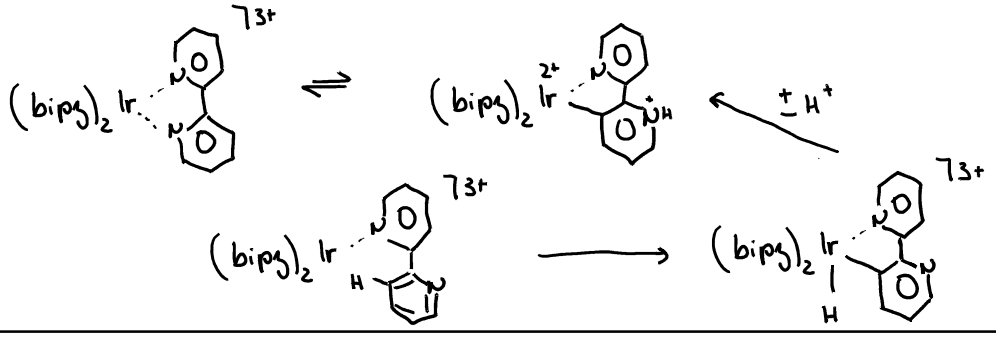
Synthesis of metal alkyls

- Cyclometalation
  - Chelation to form metal aryls



  - Rollover cyclometalation



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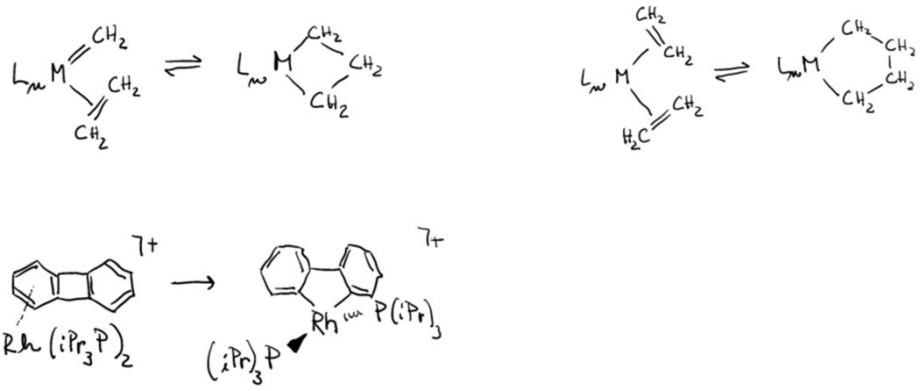
Metallacycles

- Cyclic alkyls
- Often intermediates (dimerization and trimerization reactions)
- β-hydrogen bonds are not accessible in small metallacycles



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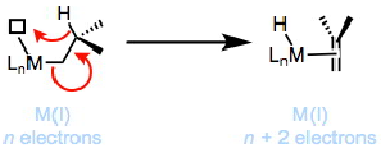
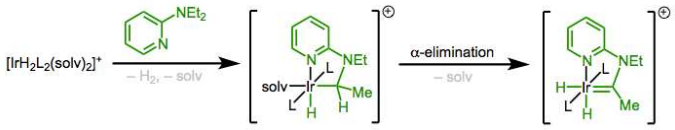
Decomposition of metal alkyls

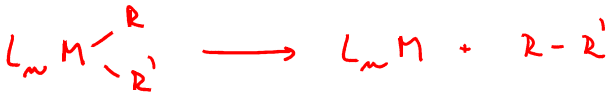
- Dominant: β-hydrogen elimination
  - β-carbon atom **must have hydrogen**
  - M-C-C-H unit must be able to adopt ~**syn-coplanar** configuration
  - A **vacant site on the metal** cis to the alkyl must be accessible (labile ligand)
  - Rapid for d^2 and higher metals
    – back donation of d-electrons to the C-H bond
    → weakens the bond and facilitates hydrogen transfer
  - **Slow for d^0 metals** (incl. main group)



- Alternatives:
- homolysis
- α/γ/δ-eliminations
- reductive elimination
  (especially with H or another alkyl)

α-elimination





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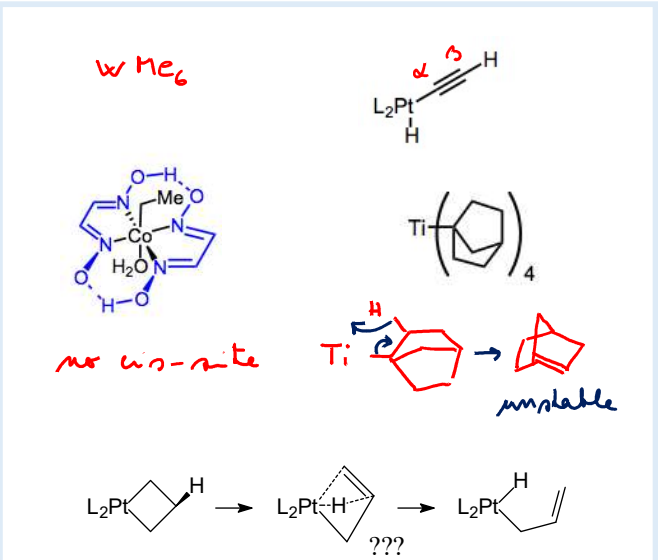
How to prevent β-hydrogen elimination ?

- No β-hydrogen : CH_3, CH_2CMe_3, CH_2SiMe_3, CH_2Ph
- No empty site *cis* to alkyl
- Product of elimination unstable
- Planar transition state inaccessible

  even for 5-membered metallacycles

  β-elimination is difficult !
  (basis of selective ethene *tri*merization)



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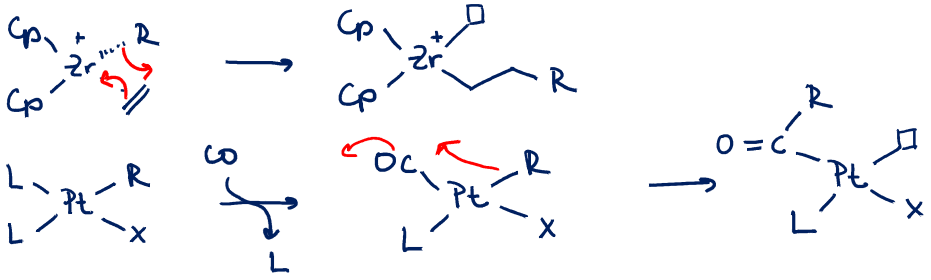
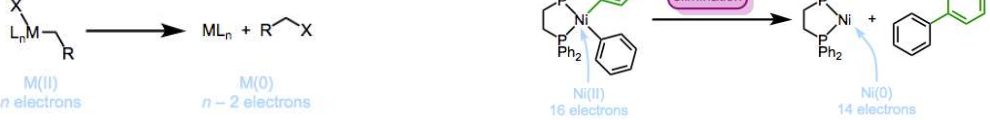
Reactions of metal alkyls

- Insertion, of both polar and non-polar C=X bonds:
  - olefins, acetylenes, allenes, dienes
  - (ketones etc)
  - CO, isocyanides



- Reductive elimination



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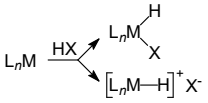
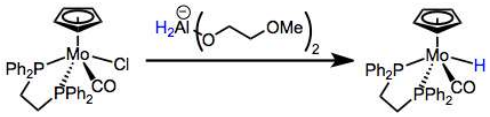
Synthesis of metal hydrides

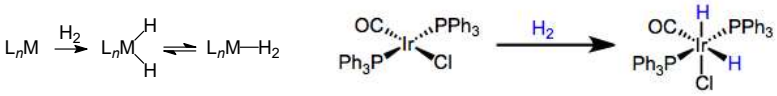
- Protonation / oxidative addition



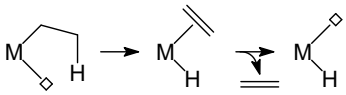
- From hydride donors

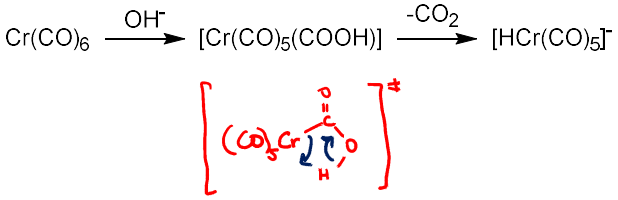


- From H_2



- β-elimination





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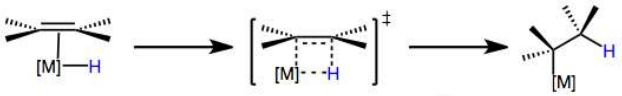
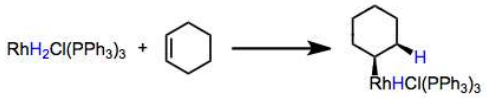
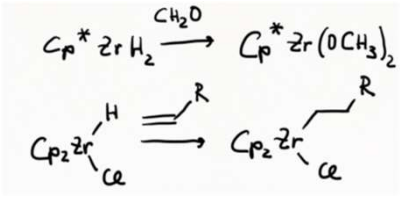
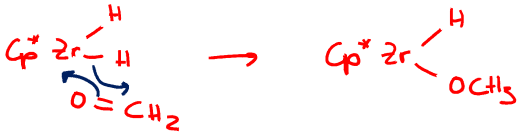
Reactivity of metal hydrides

- "Hydride is the smallest alkyl"
- Can react as H^+ or H^-
  - $HCo(CO)_4$ nearly as acidic as H_2SO_4
  - Cp_2ScH gives H_2 with acids, alcohols, ...
- Insertion reactions
  - CO insertion rare (endothermic!)
  - hydrogenations









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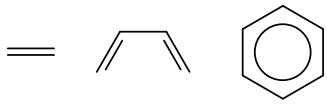
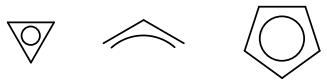
The other ligands...

- Common ligands for transition metals: π ligands, CO, phosphines



- General characteristic: σ-donating, π-accepting, "soft"



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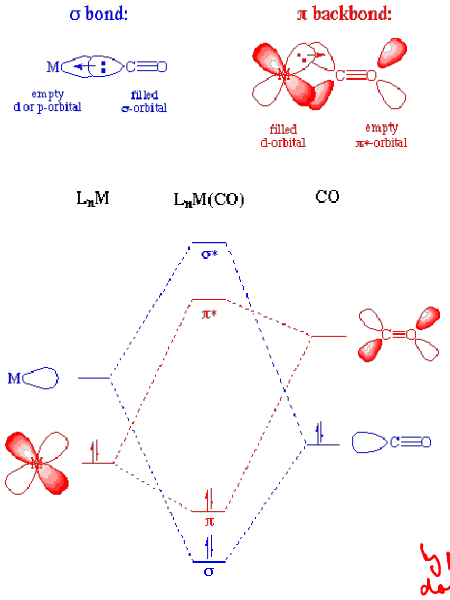
CO ligand

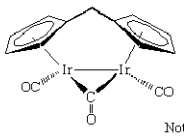


Back-bonding involves an antibonding orbital of CO

- Bonding interaction
- C-O bond gets weaker:

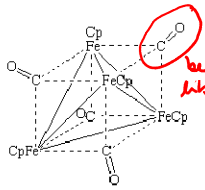
Free C≡O	Terminal carbonyls d_{CO} = 1.12-1.18Å
d_{CO} = 1.128Å	$Ni(CO)_4$ ν_{CO} = 2057 cm^{-1}
ν_{CO} = 2143 cm^{-1}	$(PR_3)_2ClIr(CO)$ ν_{CO} = 1960 cm^{-1}
	$Co(CO)_4^-$ ν_{CO} = 1886 cm^{-1}

μ_2-Bridging carbonyls d_{CO} = 1.17-1.22Å



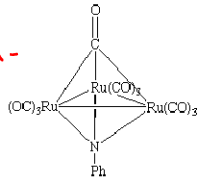
ν_{CO} = 2002(s), 1959(w), and 1776(m) cm^{-1}
d_{CO} (bridge) = 1.207(58) Å
d_{CO} (terminal) = 1.177(59) Å
^{13}C: δ 203.4 (terminal), 171.40 (bridge)
Notice that the C=O bond is ⊥ to the M-M bond

μ_3-Bridging carbonyls d_{CO} = 1.17-1.22Å



typical double bond

ν_{CO} = 1620 cm^{-1}
d_{CO} = 1.197(7) - 1.209(7) Å



ν_{CO} = 2104(m), 2070(s), 2032(vs) 2011(s) 1978(w), 1743 cm^{-1}

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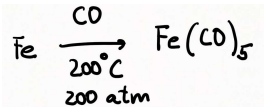
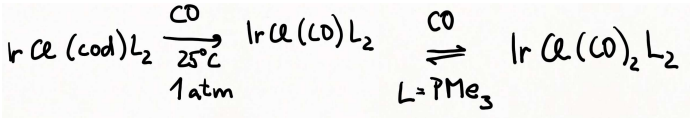
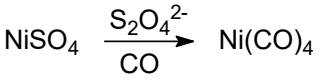
Synthesis of CO complexes

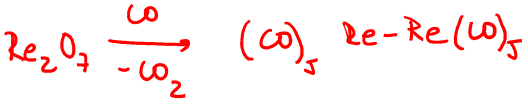
- Reaction of low-valent metals with CO





- Reaction of high-valent metal with CO and a reducing agent





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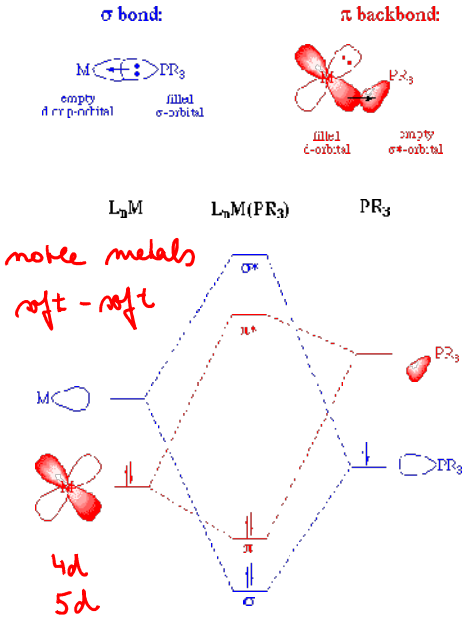
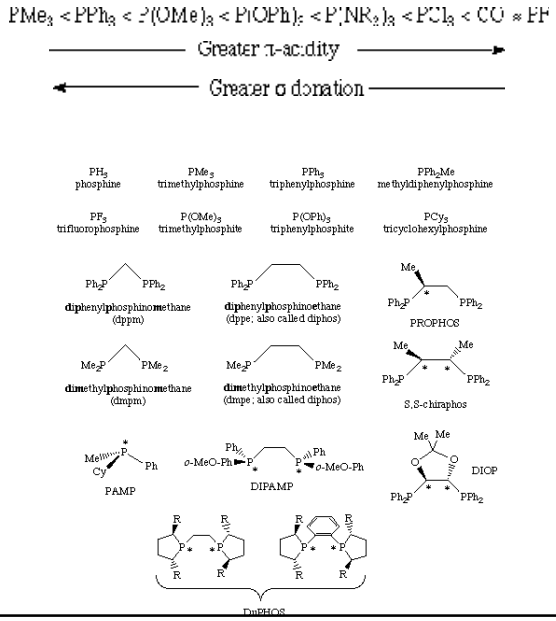
Phosphines (phoshites, polydentate phosphines)





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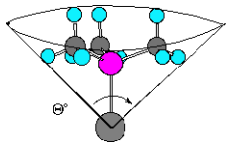
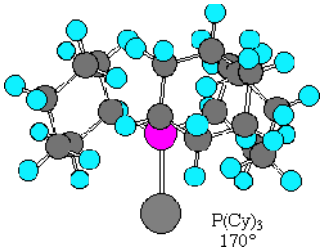
Phosphines (phoshites, polydentate phosphines)

Phosphine Ligand	Cone Angle
PH_3	87°
PF_3	104°
$P(OMe)_3$	107°
PMe_3	118°
PMe_2Ph	122°
PEt_3	132°
PPh_3	145°
PCy_3	170°
$P(t\text{-}Bu)_3$	182°
$P(mesityl)_3$	212°





more bulky ligands
→ more stable complexes
→ better reactivity control

- chiral phosphines
  → enantioselective synthesis

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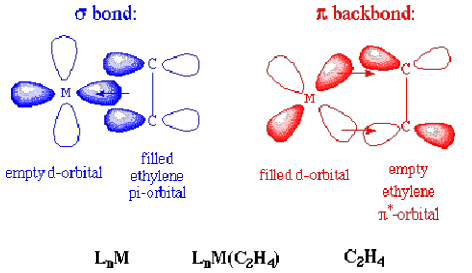
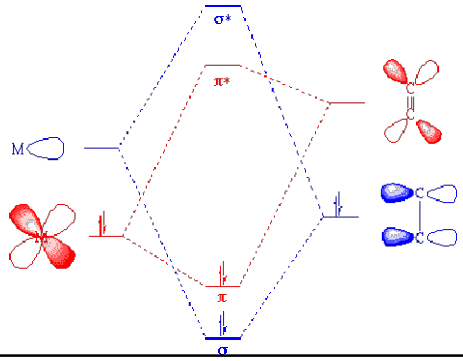
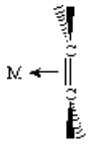
π ligands



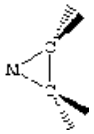
L_nM $L_nM(C_2H_4)$ C_2H_4



Alternative view:

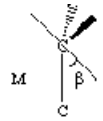


simple alkene adduct β = 90°



metallacyclopropane β = 30°

	$d_{C=C}$	β
C_2H_4	1.337	90°
$K[PtCl_3(C_2H_4)]$	1.375	74°
$Cp^*_2Ti(C_2H_4)$	1.438	55°
$(PPh_3)_2Pt(C_2F_4)$	1.44	50°
C_2H_6	1.54	36°



β is the angle between a vector perpendicular to the CH_2 plane and the C-C bond

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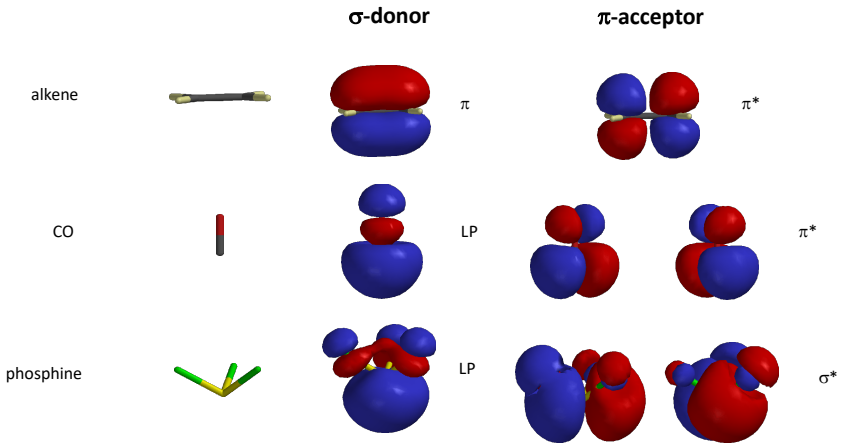
Donor and acceptor orbitals



σ-donor character:
phosphines > alkenes, CO

π-acceptor character:
CO > alkenes > phosphines

Depends strongly on the substituents on P, C=C !

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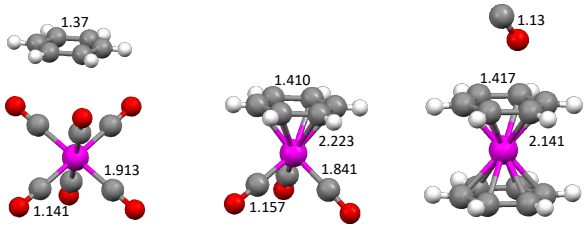
Synthesis of π-ligand complexes

- Substitution at low-valent metals:
  generate empty site(s) in presence of free ligand

$$Cr(CO)_6 \xrightarrow[C_6H_6]{\text{reflux in}} Cr(CO)_3(C_6H_6)$$



$$PtCl_4^{2-} \xrightarrow{C_2H_4} [PtCl_3(C_2H_4)]^- + Cl^-$$

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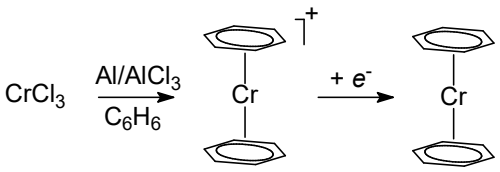
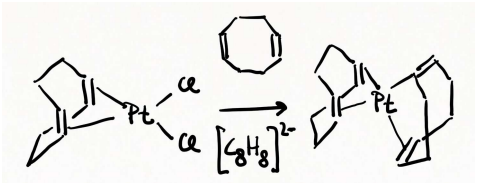
Synthesis of π-ligand complexes

- Reduction of high-valent metals





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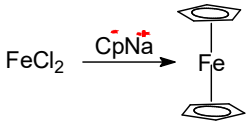
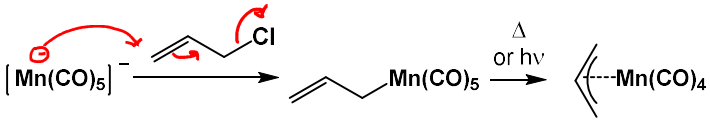
Synthesis of π-ligand complexes

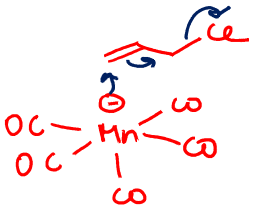
Anionic ligands:

- nucleophilic attack of an anionic ligand (Cp^-)

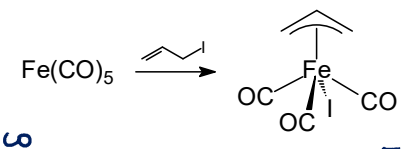


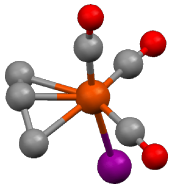
- substitution

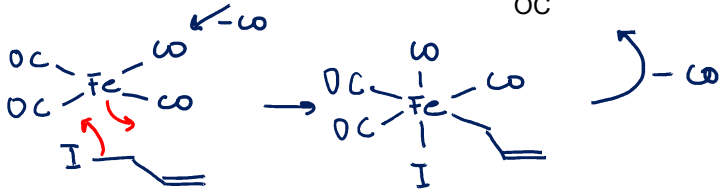




- oxidative addition (allyl)







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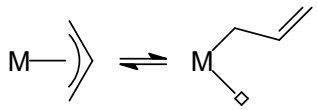
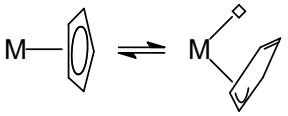
Change of hapticity

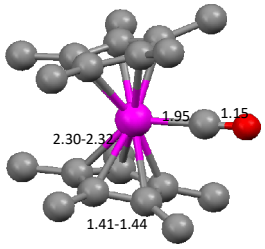


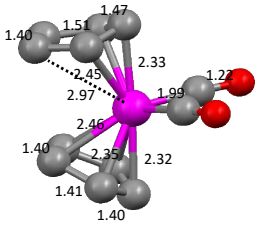
σ/π allyl



ring slippage

- More than 18 e ?





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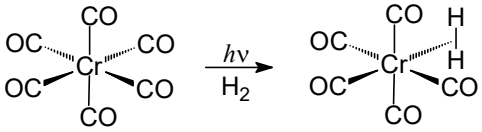
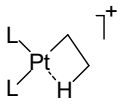
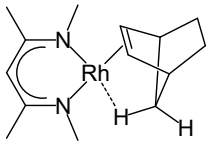
σ complexes

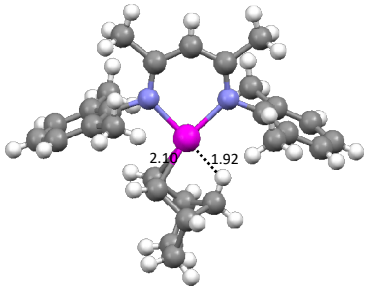
- A σ bond as 2-electron donor for a metal.
- H_2 complexes (non-classical hydrides)



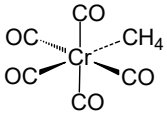
- Agostic C-H bonds
  - Usually intramolecular







  - Sometimes intermolecular



In "matrix"
Characterized by IR

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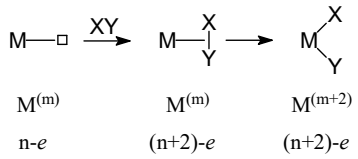
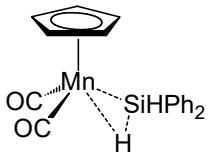
σ complexes

A σ complex is an (arrested) intermediate for oxidative addition:



Stable σ complexes are formed when the metal is not π-basic enough to enable completion of the addition.

- Y-H bonds (Y does not have lone electron pairs)
  Si-H, B-H, P-H, …



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What did you learn today?

- Early-middle-late TMs – different reactivity, different use
- Metal-alkyls
  - β-elimination
  - agostic bonds
  - synthesis (nucleophilic attack, electrophilic attack, insertion, oxidative addition, cyclometalation)
  - decomposition (β-hydrogen elimination, homolysis, reductive elimination)
  - reactivity (insertion, reductive elimination)
- Metal-hydrides
  - synthesis (protonation, hydride transfer, H_2 addition, β-hydrogen elimination)
  - reactivity (H^+ and H^- transfer, hydrogenation)
- Other ligands:
  - CO, π-complexes, σ-complexes, phosphines
  - synthesis, properties
  - σ-bonding, π-back-bonding (σ-basicity, π-acidity)

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