Organometallic compounds-II

PG Semester I

Gauhati University

Lecture 5, 6, 7, 8

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Contents

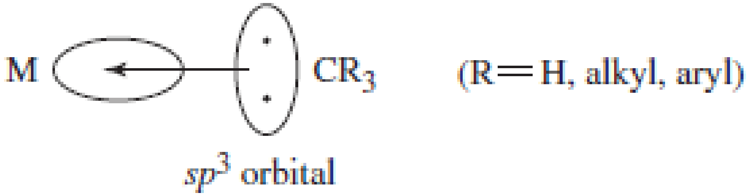
- Types of M-C bonds
- Synthesis and reactivity of metal alkyls,
- Synthesis and reactivity of metal carbenes
- Synthesis and reactivity of metal alkenes
- Synthesis and reactivity of metal alkynes
- Synthesis and reactivity of metal arenes
- Synthesis and reactivity of metallocenes and bent metallocenes

Metal Alkyls

- E. Frankland prepared the first σ-bonded organometallic compound-Diethyl zinc in 1848 by the reaction,

$$3C_2H_5I + 3Zn \rightarrow (C_2H_5)_2Zn + C_2H_5ZnI + ZnI_2$$

- W. J. Pope reported the first transition metal alkyl $PtMe_3I$ in 1907
- Alkyl groups bonded via covalent σ-interaction between the metal atom and the C -atom of the organic fragment.
- Alkyl groups with a H-atom on C-atom adjacent to the one that bonds to the metal are prone to decompose by a process known as β-hydrogen elimination.
- Choice of alkylating agent can affect the course of the reaction
- Transition metal alkyl complexes important for catalysts *e.g.* olefin polymerization and hydroformylation
- Problem is their weak kinetic stability



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- The M-C bond enthalpy decreases with increase in atomic number of main group elements but increase within a transition metal triad
- The M-C bond enthalpy of transition metal alkyls (150-300 $kJmol^{-1}$) is comparable to those of main group elements.
- On thermodynamic grounds, transition metal alkyls should be much more stable with few exceptions like Pb-alkyls (due to kinetic reason)

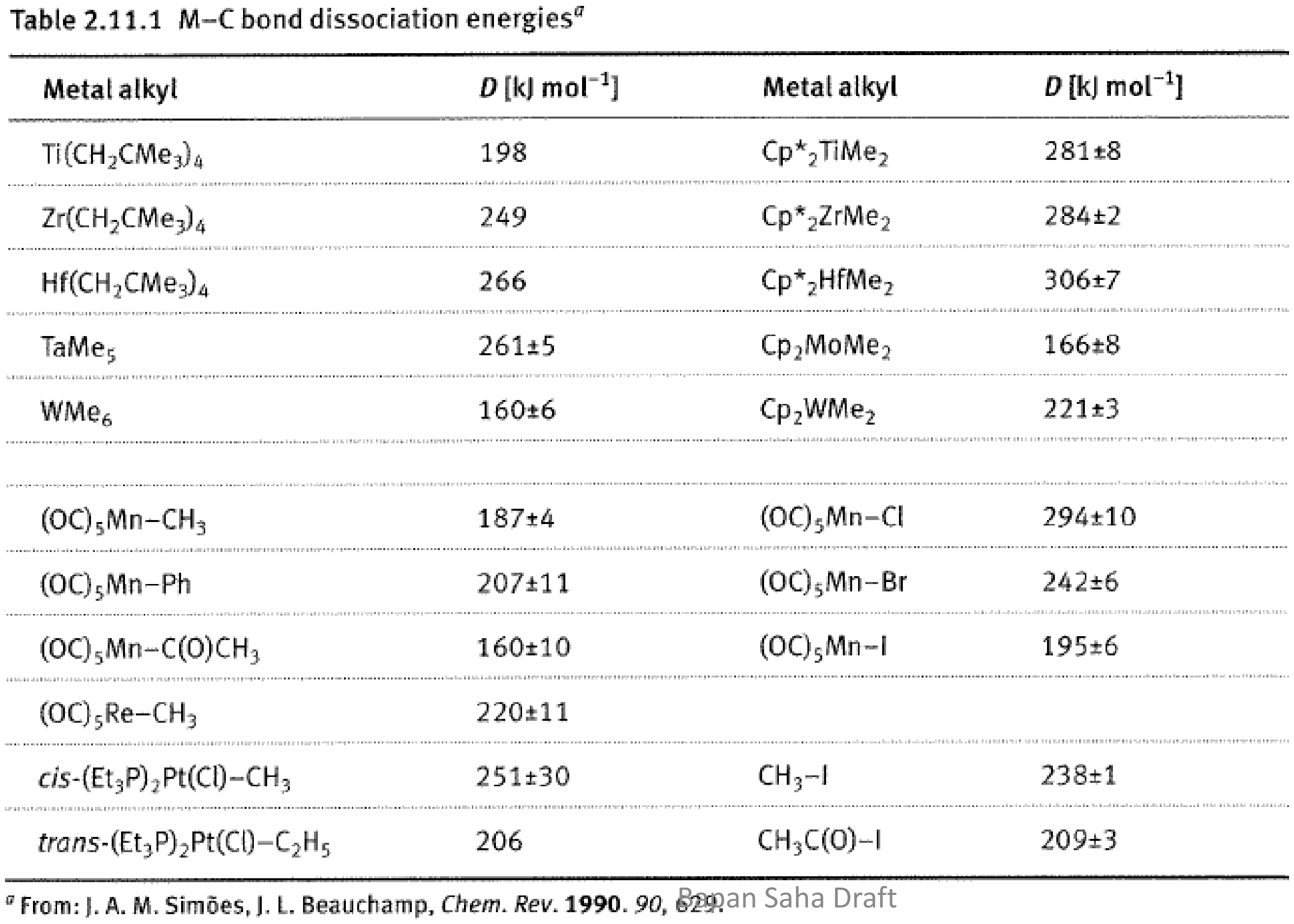


Table 2.11.1 M–C bond dissociation energies[a]

Metal alkyl	D [kJ mol^{-1}]	Metal alkyl	D [kJ mol^{-1}]
$Ti(CH_2CMe_3)_4$	198	$Cp^*{}_2TiMe_2$	281±8
$Zr(CH_2CMe_3)_4$	249	$Cp^*{}_2ZrMe_2$	284±2
$Hf(CH_2CMe_3)_4$	266	$Cp^*{}_2HfMe_2$	306±7
$TaMe_5$	261±5	Cp_2MoMe_2	166±8
WMe_6	160±6	Cp_2WMe_2	221±3
$(OC)_5Mn{-}CH_3$	187±4	$(OC)_5Mn{-}Cl$	294±10
$(OC)_5Mn{-}Ph$	207±11	$(OC)_5Mn{-}Br$	242±6
$(OC)_5Mn{-}C(O)CH_3$	160±10	$(OC)_5Mn{-}I$	195±6
$(OC)_5Re{-}CH_3$	220±11		
cis-$(Et_3P)_2Pt(Cl){-}CH_3$	251±30	$CH_3{-}I$	238±1
trans-$(Et_3P)_2Pt(Cl){-}C_2H_5$	206	$CH_3C(O){-}I$	209±3

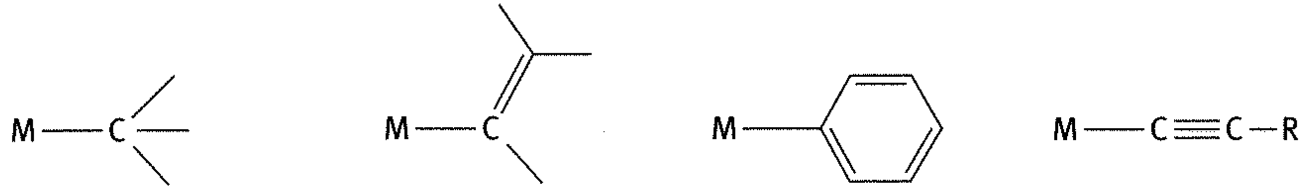
[a] From: J. A. M. Simões, J. L. Beauchamp, *Chem. Rev.* **1990**. *90*, 629.

Metal-methyl bonds are stronger than those of higher alkyls

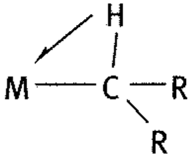
Types of Metal-alkyl bonding

- Most of the metal alkyls follow 18e rule [exceptions: few d^8-square planar complexes of Rh(I), Ir(I), Ni(II), Pd(II), Pt(II)]
- Sometime steric stabilization (bulky ligand prohibits the metal to bond with enough donor ligands, umbrella protecting the metal) play predominant role for which higher electron count is restricted. Also sometime referred as kinetic stabilization
- The metal ligand bonding of η^1-hydrocarbon ligands is a σ-interaction
- Methyl ligand can adopt surprising number of coordination mode.
- Terminal and bridging alkyl and aryl complexes are formed depending on the electron demand of the metal centers
- Electron deficient metals may, in addition to the M-C σ-bond, from bonding interactions with C-H bonds in a α, β, γ positions to the metal (agostic bonding)
- Benzyl ligands contain phenyl substituents that can donate some of the π-electron density to an electron-deficient metal center

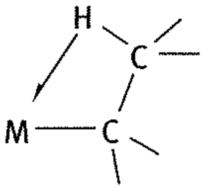
Terminal:



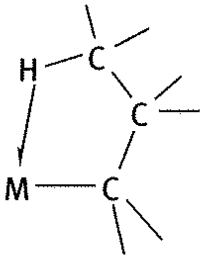
Alkyl bonding to electron-deficient metals:



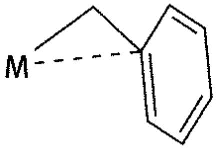
α-agostic



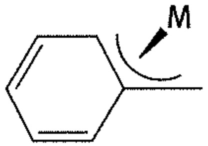
β-agostic



γ-agostic



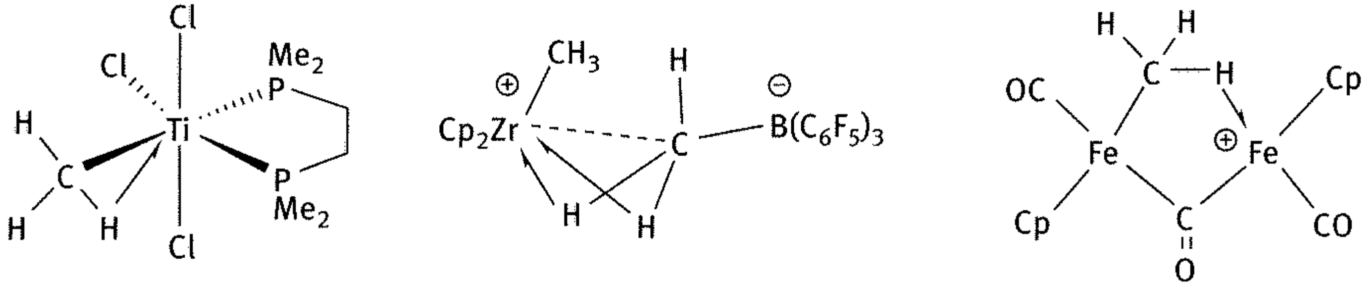
η^2-benzyl, indicated by narrow M–C–C angle



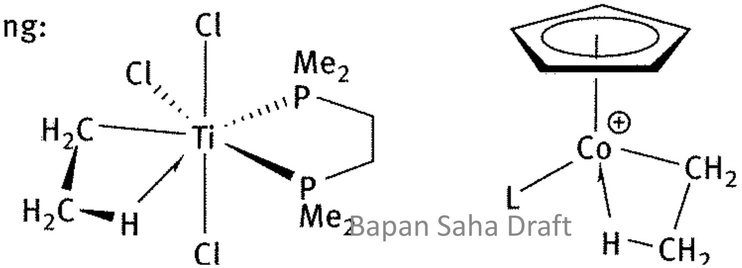
η^3-benzyl

Some examples of complexes with agostic bonding:

α-agostic bonding:



β-agostic bonding:



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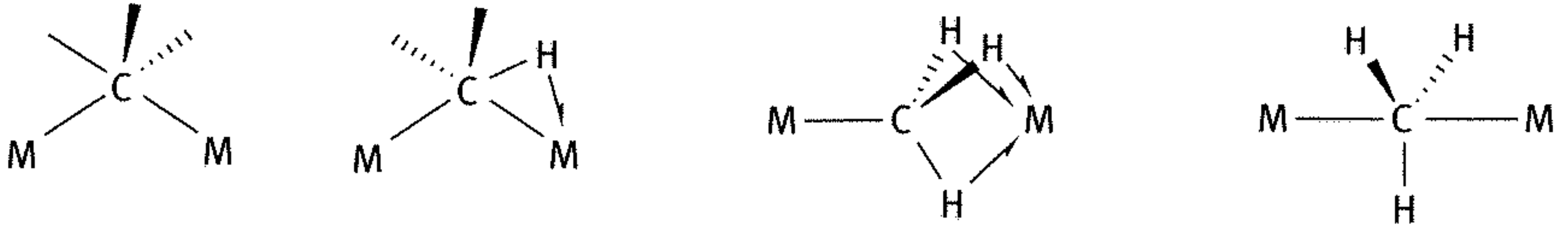
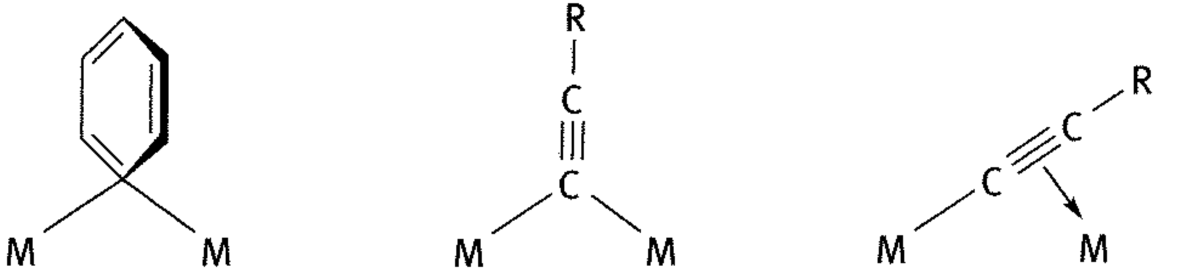
Bridging in highly electrophilic systems:



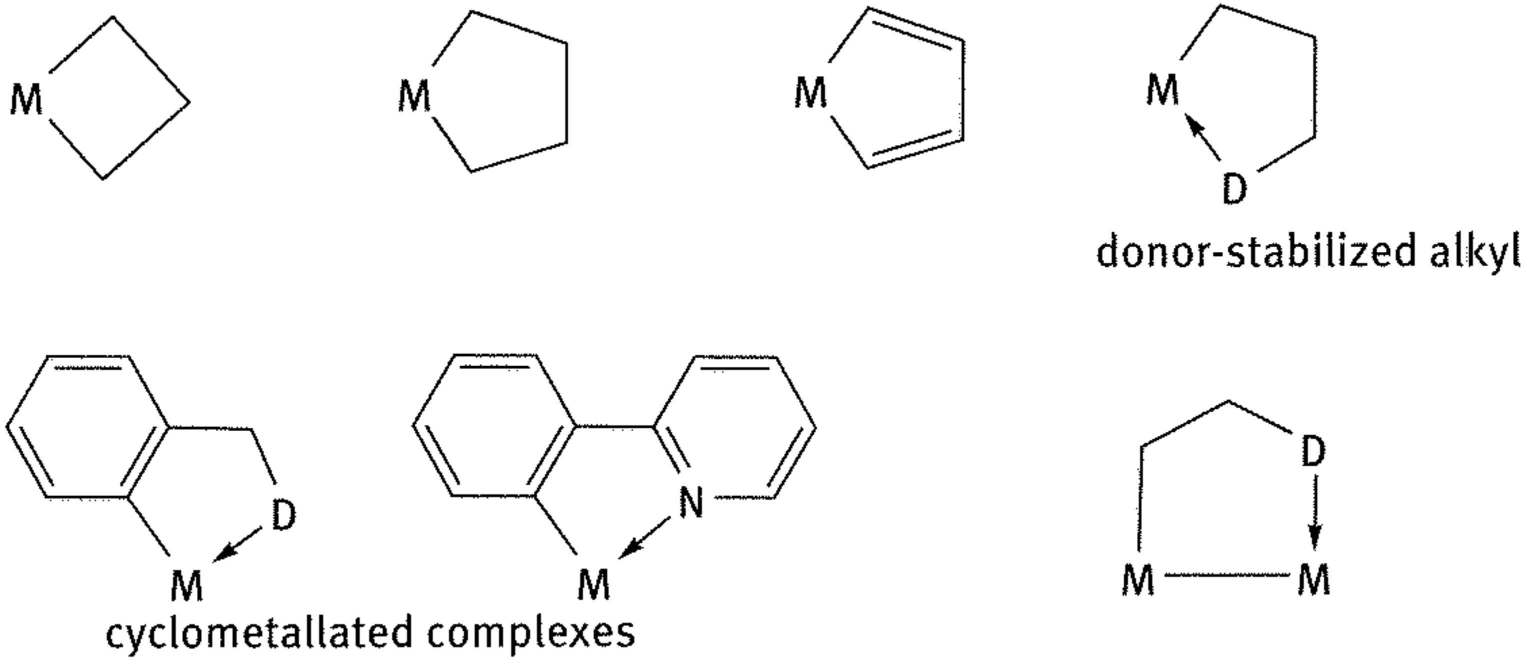
methyl bridges with single and multiple agostic M–H–C interactions

trigonal-bipyramidal 5-coordinate C in μ-CH_3 compounds



symmetrical and unsymmetrical bridging alkynyl

Bridging alkyls tend to form with electron-deficient metals, the bridge is often supported by a variety of agostic interactions

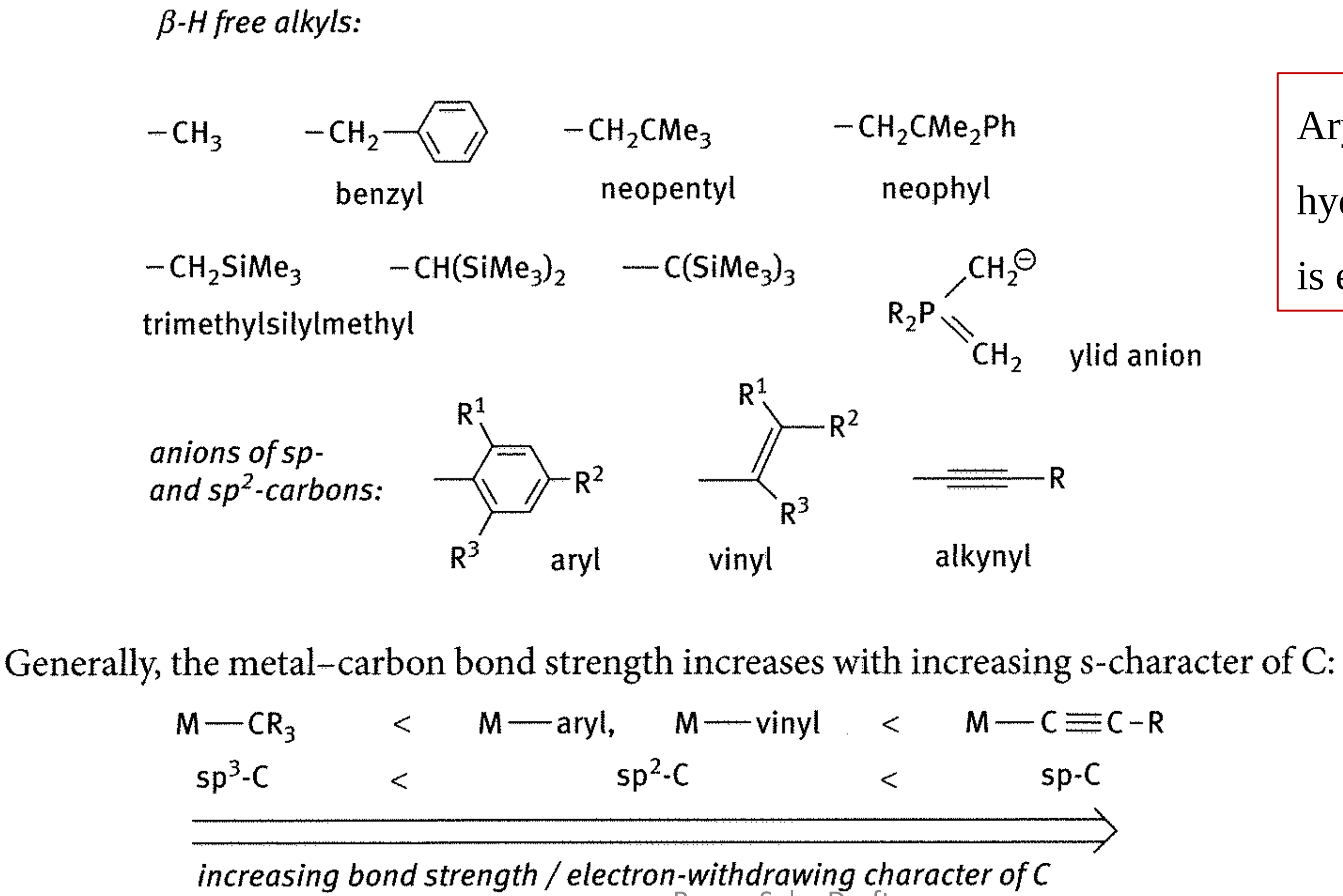


Metal alkyls can also form a variety of metallacycles. Five membered rings tend to be particularly stable. Metallacycles supported by a donor heteroatom are frequent.

Synthesis of metal alkyls

- By blocking of available coordination sites by donor ligands
- Using alkyl ligands stable to β-hydrogen elimination

Aryl and vinyl groups may have β-hydrogen but β-hydrogen elimination is energetically highly unfavorable



Generally, the metal–carbon bond strength increases with increasing s-character of C:

$$\underset{sp^3\text{-C}}{\mathrm{M{-}CR_3}} < \underset{sp^2\text{-C}}{\mathrm{M{-}aryl,\ M{-}vinyl}} < \underset{sp\text{-C}}{\mathrm{M{-}C{\equiv}C{-}R}}$$

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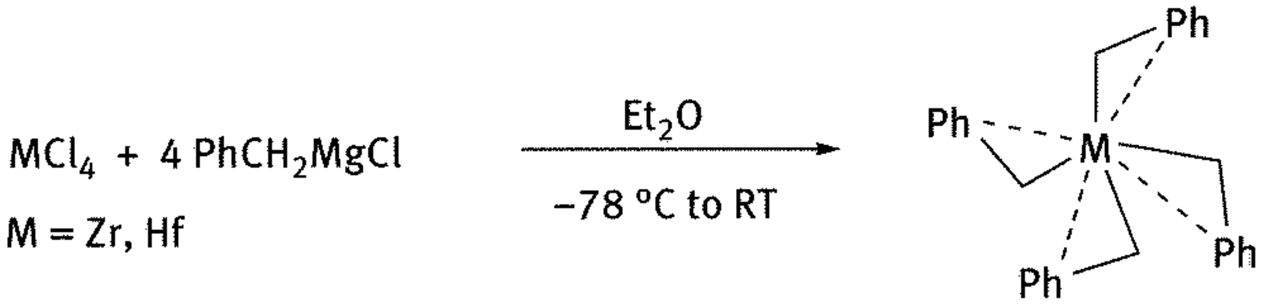
Synthesis of homoleptic metal alkyls

- Alkylation of transition metal halide

$$TiCl_4 + 2\,Mg(CH_2SiMe_3)_2 \xrightarrow[-78\,^{\circ}C \text{ to RT}]{Et_2O} Ti(CH_2SiMe_3)_4 + 2\,MgCl_2$$

8 VE, yellow, diamagnetic

- The alkylation of MCl_4 with benzylMgCl gives tetra alkyls $M(CH_2Ph)_4$



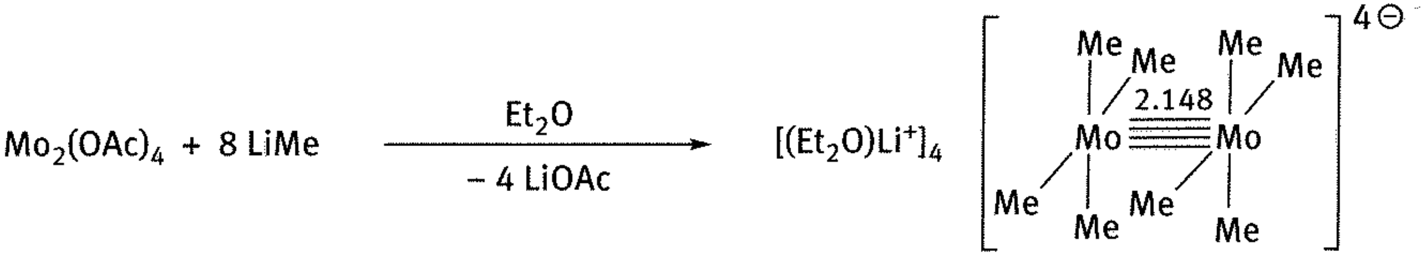
$$MCl_4 + 4\,PhCH_2MgCl \xrightarrow[-78\,^{\circ}C \text{ to RT}]{Et_2O}$$

M = Zr, Hf

$$WCl_6 + 3\,Al_2Me_6 \xrightarrow[-\,Me_2AlCl]{} WMe_6 \xrightarrow{LiMe} Li[WMe_7]$$

WMe_6: 12 VE, colourless, diamagnetic trigonal-prismatic, C_{3v}

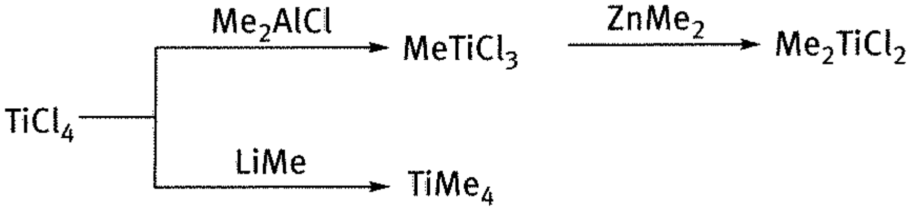
$Li[WMe_7]$: 14 VE anion, capped octahedron



$$Mo_2(OAc)_4 + 8\,LiMe \xrightarrow[-\,4\,LiOAc]{Et_2O} [(Et_2O)Li^+]_4 [Me_8Mo_2]^{4\ominus}$$

16 VE, M–M quadruple bond

- The alkylation strength of main group metal alkylating agents decreases with increasing electronegativity of the metal :LiR > RMgX > AlR_3 > R_2AlCl ~ ZnR_2
- Weaker alkylating agents lead to metal alkyl halides



- Mixed alkyl halides are often prepared by comproportionation

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

$$3\,Ti(CH_2Ph)_4 + TiBr_4 \longrightarrow 4\,TiBr(CH_2Ph)_3$$

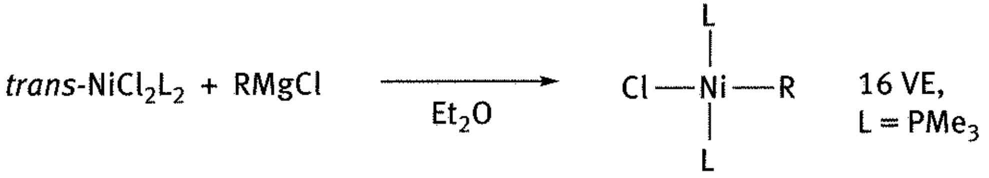
Synthesis of heteroleptic metal alkyls

1. **Alkylation of metal halides**

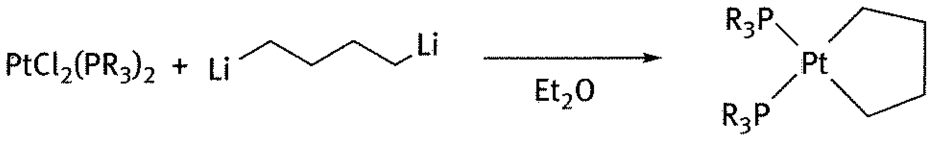
$$Cp_2MCl_2 + 2\ LiR \xrightarrow[-78\ ^\circ C\ \text{to RT}]{Et_2O} Cp_2MR_2 + 2\ LiCl$$

M = Ti, Zr, Hf

16 VE, yellow, diamagnetic



16 VE,
L = PMe$_3$

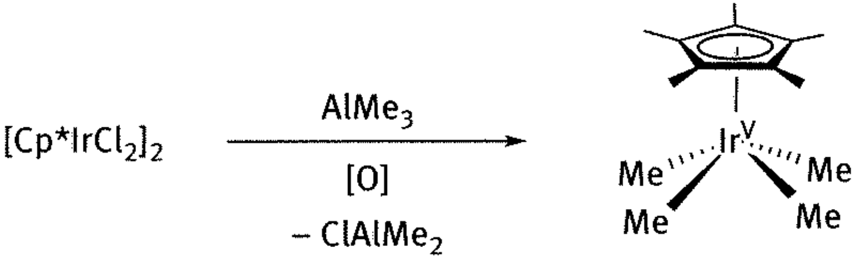


16 VE
colourless

- Alkylation may involve a change in oxidation state the driving force may be steric requirements or the attainment of an 18 VE configuration

$$Rh^{II}{}_2(OAc)_4 \xrightarrow[PMe_3]{MgMe_2} Rh^{III}Me_3(PMe_3)_3$$

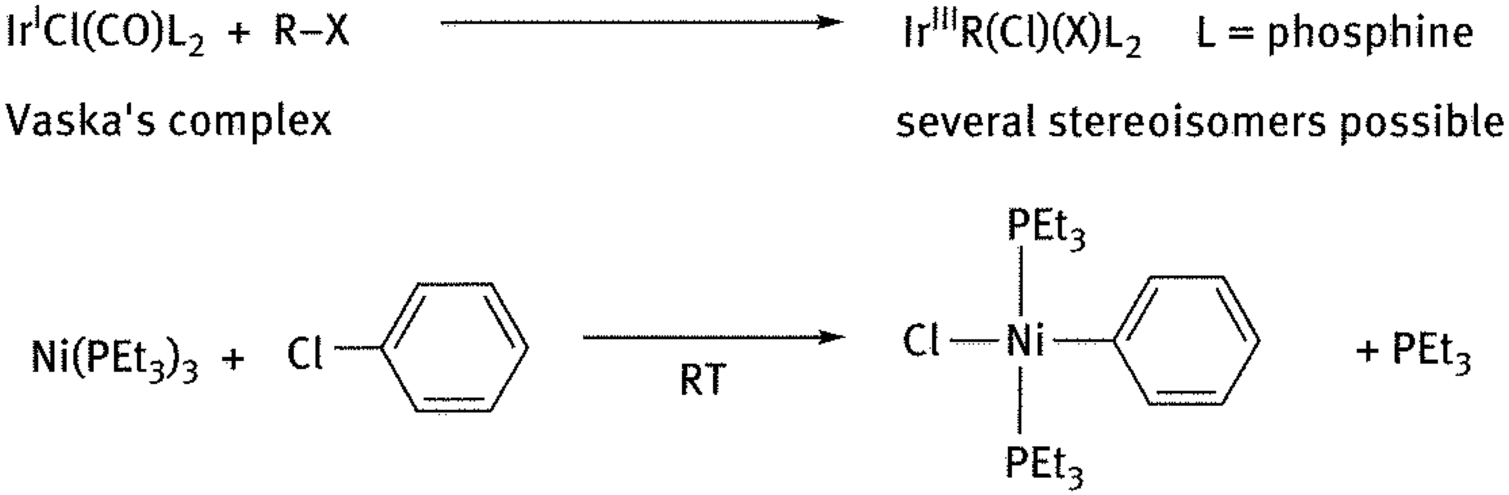
18 VE, diamagnetic



18 VE

2. Oxidative Addition

- The reaction is facilitated by electron donating ligands, which help to generate metal centers with energetically high lying occupied d-orbitals.
- Requires a covalently unsaturated, low-valent complex (16 e- or less)
- Phosphine or carbene complexes of M(I) (Co, Rh, Ir) and M(0) (Ni, Pd, Pt) metal centers are typical reaction partners
- Oxidative addition often involves changes in coordination geometry



- Oxidative addition reaction with Ni, Pd and Pt complexes normally lead to the formation of M(II)-C bonds, widely used in Pd-catalyzed cross coupling reactions

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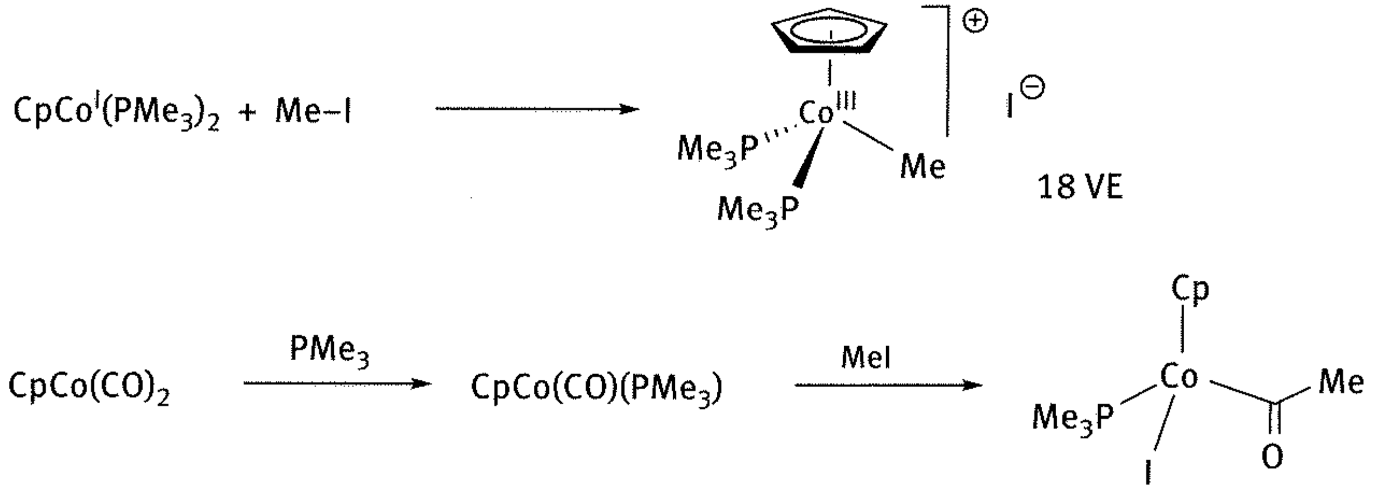
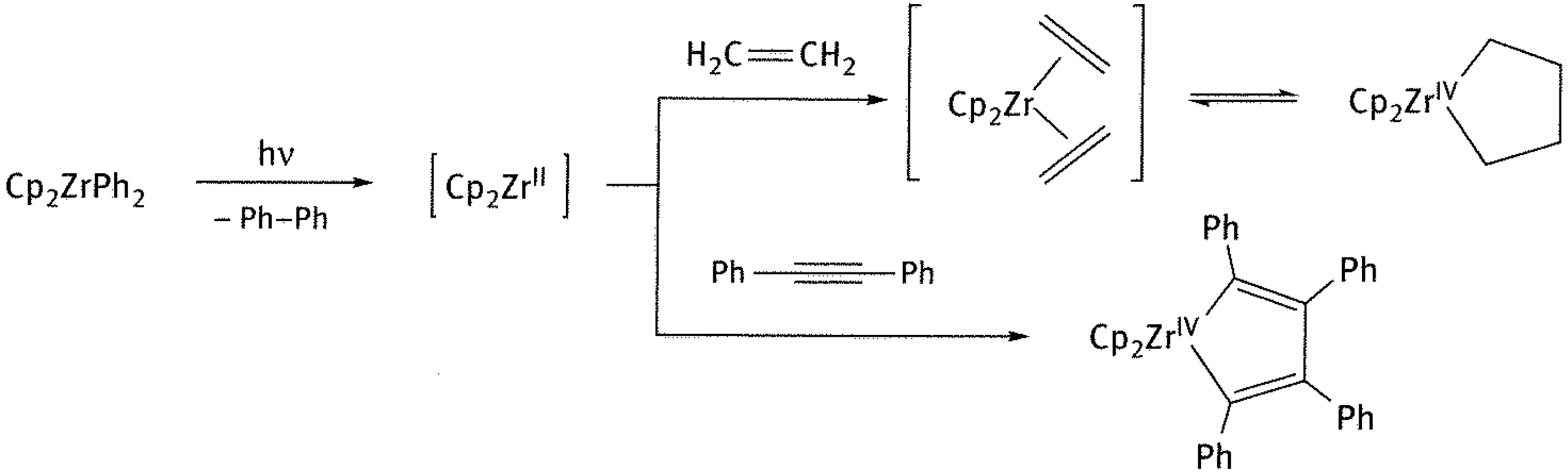
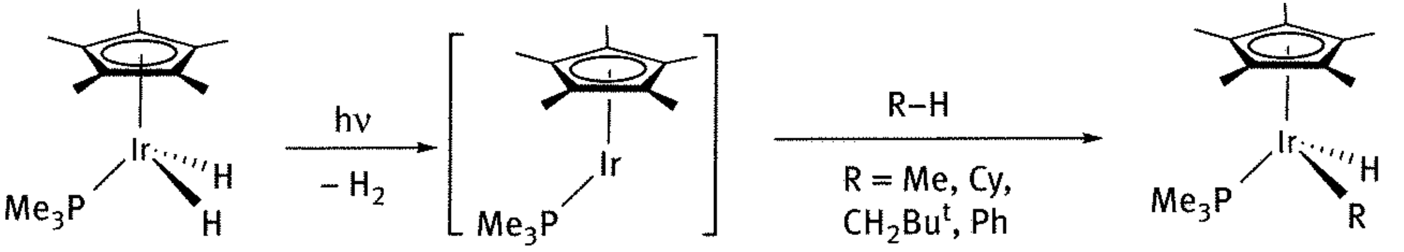
- Trialkyl phosphines can make the metal center highly basic, which aids oxidative addition

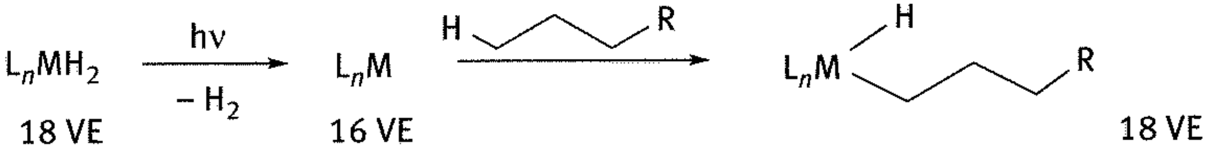


- Early transition metals with their high energy d-levels, show strong tendency to form complexes with metal in highest possible oxidation state



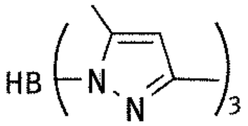
- Although most oxidative addition involves sp^2-C-H bonds, electron rich low valent metal centers (Ir) and other 16 e metal species with strong donor ligands are capable of oxidative additions of saturated hydrocarbons



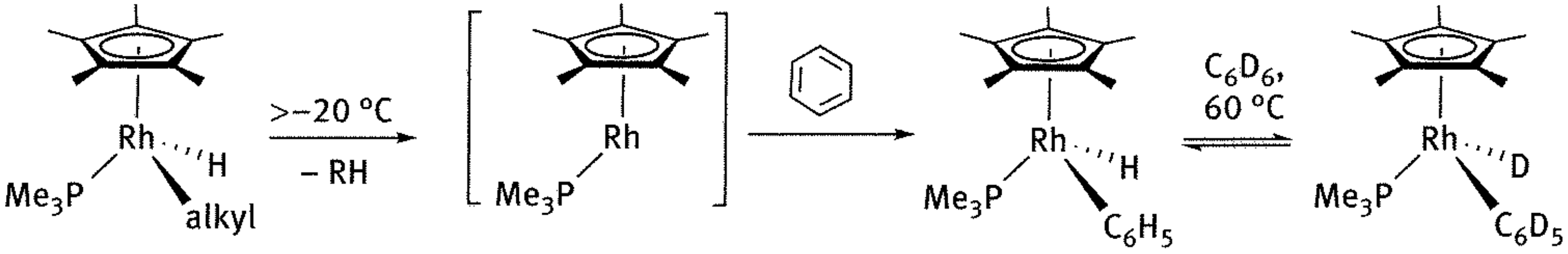


$ML_n = Fe(Me_2PC_2H_4PMe_2)_2$, $Cp^*Re(PMe_3)_2$, $Cp^*Rh(PMe_3)$, $Pt(Cy_2PC_2H_4PCy_2)$,

Tp*Rh(CNR); Tp* =



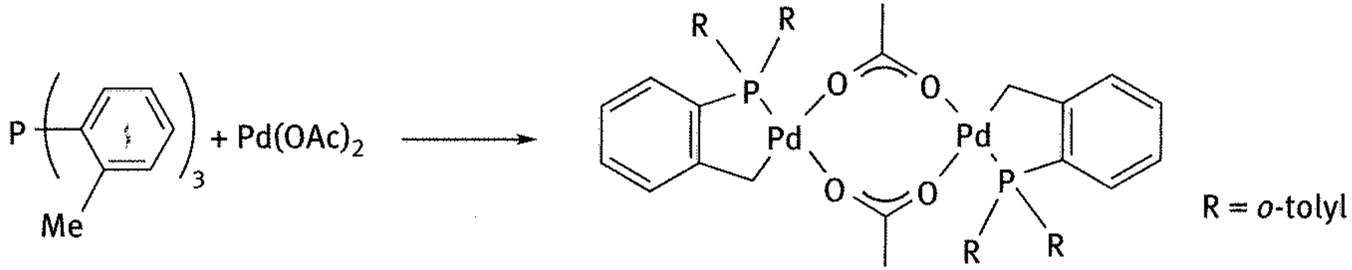
- Aromatic C-H bonds undergo oxidative additions more readily than aliphatic C-H bons

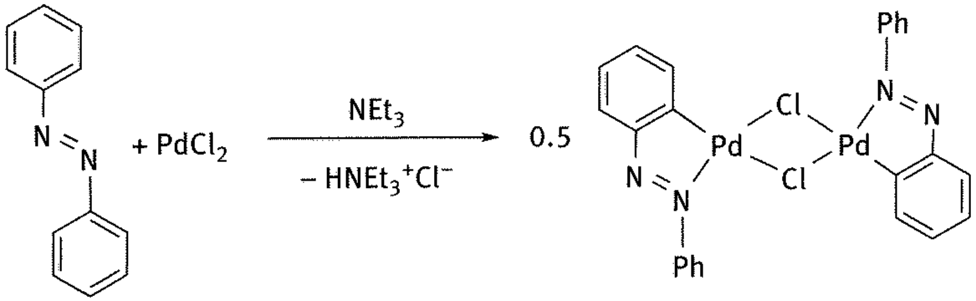


H/D exchange via reversible C–H addition/elimination

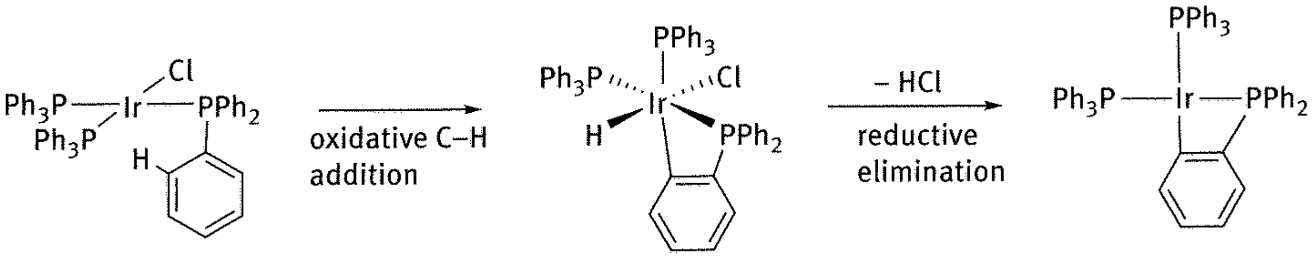
Electrophilic attack: Cyclometallation

- It occurs via the attack of an electrophilic metal center on an sp^2 C-H bond, followed by deprotonation
- Metal is in high oxidation state to act as an electrophile, and oxidation state does not change during this process
- Ortho metallation is common for Pd(II) compounds, widely explored in synthesis



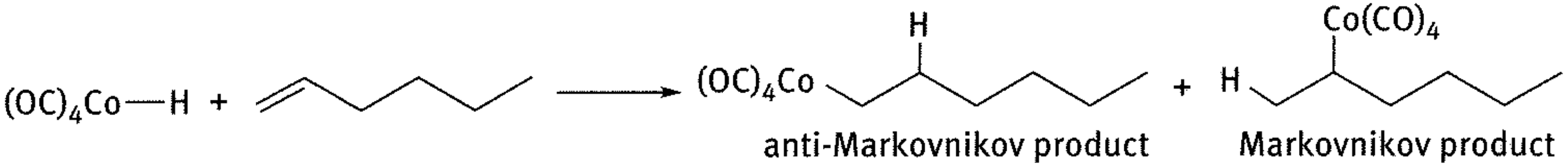


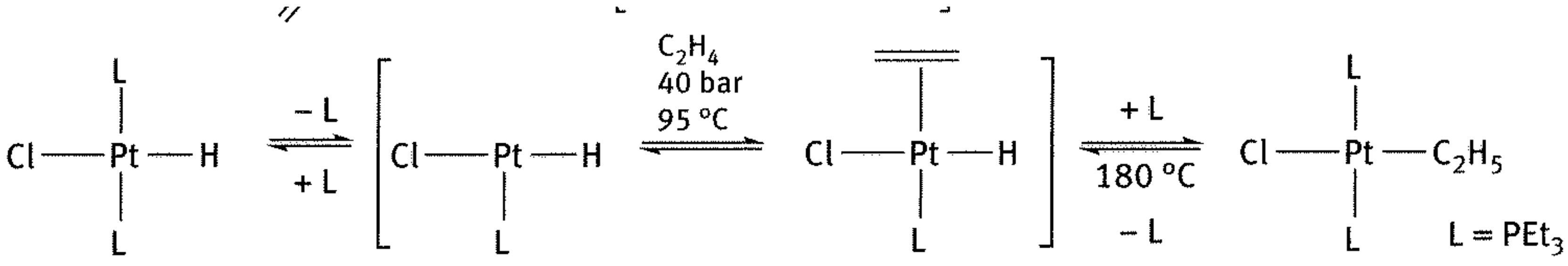
Cyclometallated complexes have widespread applications as sensors and in OLEDs

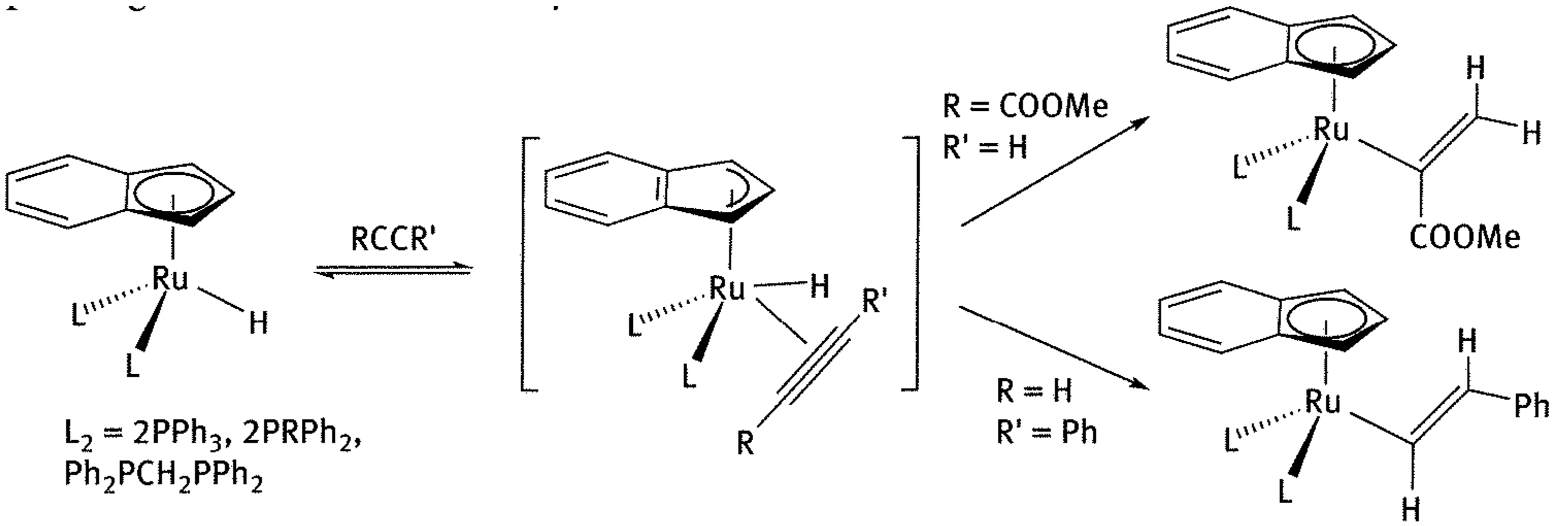


Insertion reaction

- Alkenes and alkynes readily insert into M-H bonds to give metal alkyls and metal vinyl respectively (key steps in hydrogenation, hydroformylation, carbonylation, polymerization

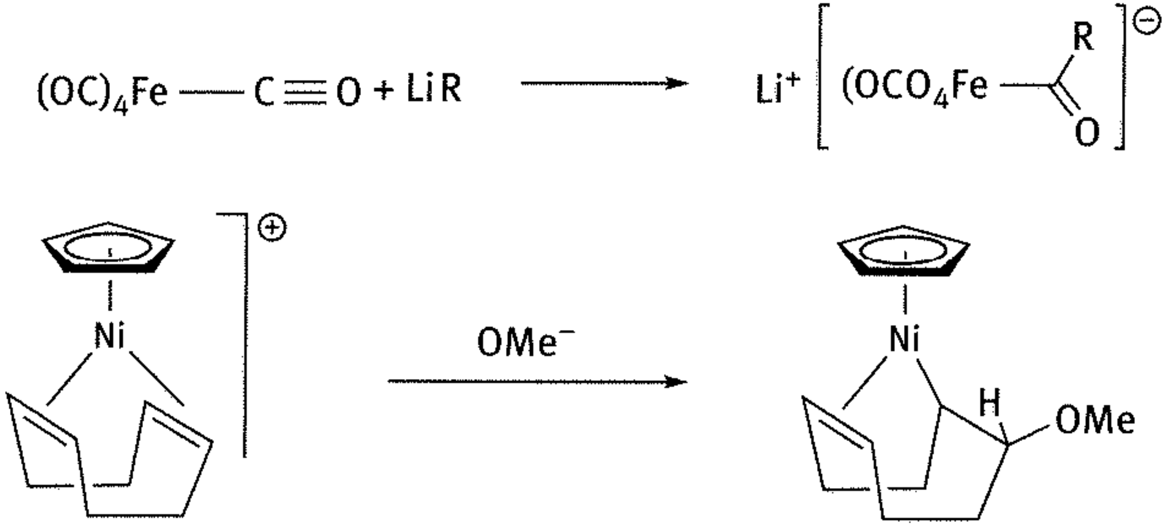




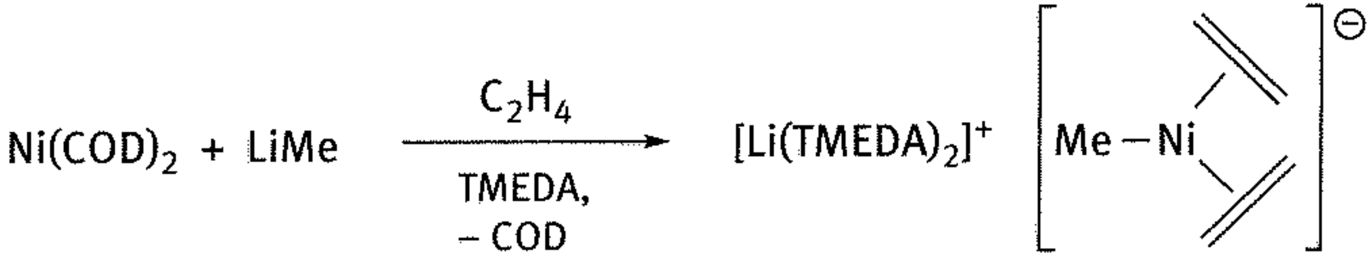


Nucleophilic attack

- Unsaturated polar bonds like CO, isocyanides, alkenes, alkynes are susceptible to nucleophilic attack to give M-C σ bond

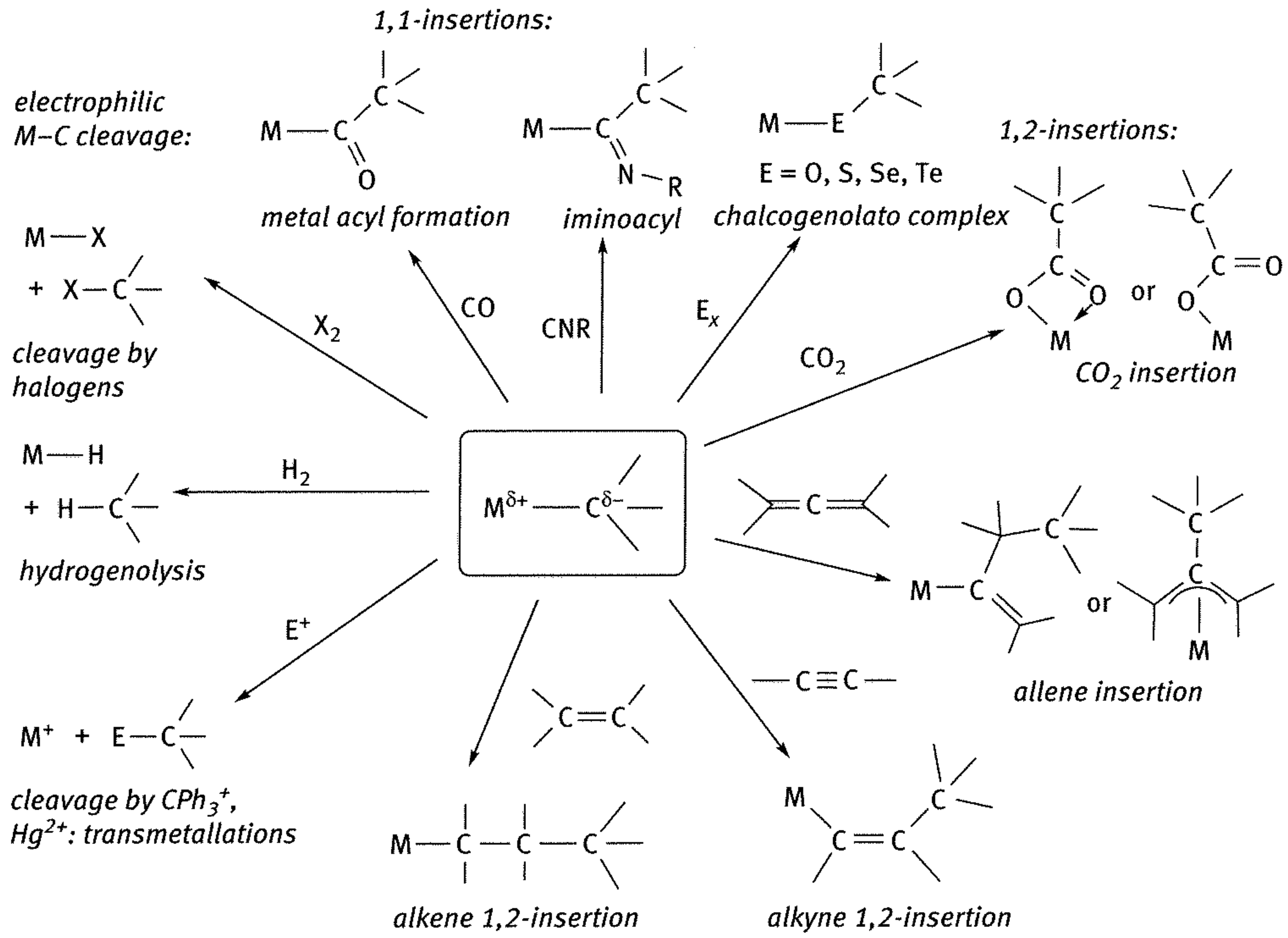


- Zero valent metals can also react with LiR under nucleophilic addition of the alkyl anion



Reactions

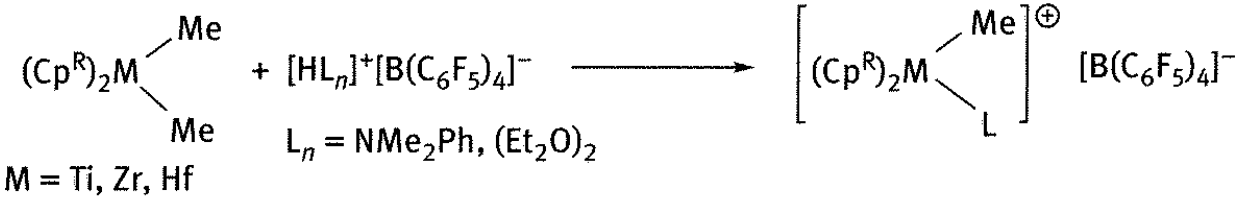
- The formation and breaking of metal-alkyl bonds is and integral part of most catalytic process.
- Can show M-C bond cleavage with electrophiles,
- M-C insertion with unsaturated organic molecules
- Reductive elimination with nucleophiles



- M-C bond cleavage reaction

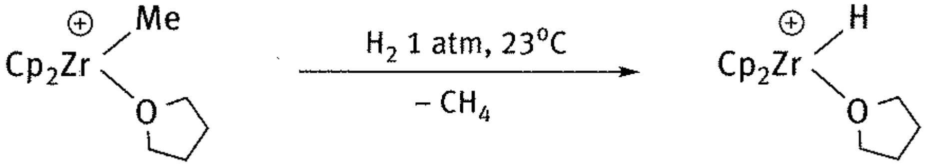
1. **Reaction with electrophile**: M-C σ-bonds react readily with electrophiles

$$Zr(CH_2Ph)_4 \xrightarrow[-\text{ toluene}]{Ar'OH} (Ar'O)Zr(CH_2Ph)_3 \xrightarrow[-\text{ toluene}]{Ar'OH} (Ar'O)_2Zr(CH_2Ph)_2$$



2. **Reaction with H_2**: Important in organometallic catalysis (synthetic method for preparation of metal hydrides)

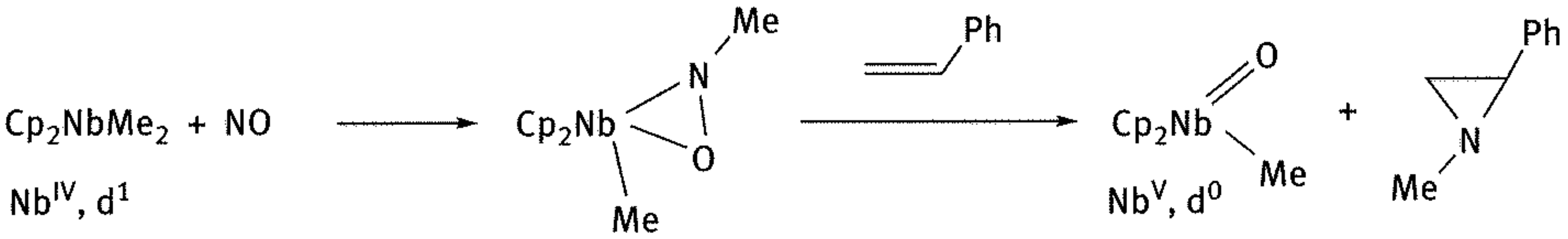
$$Cp^*{}_2ZrMe_2 \xrightarrow[-\,2\,CH_4]{H_2\text{ pressure}} Cp^*{}_2ZrH_2 + 2\,CH_4$$



$$(OC)_4Co{-}R \xrightarrow{H_2\text{ pressure}} (OC)_4Co{-}H + R\text{-}H$$

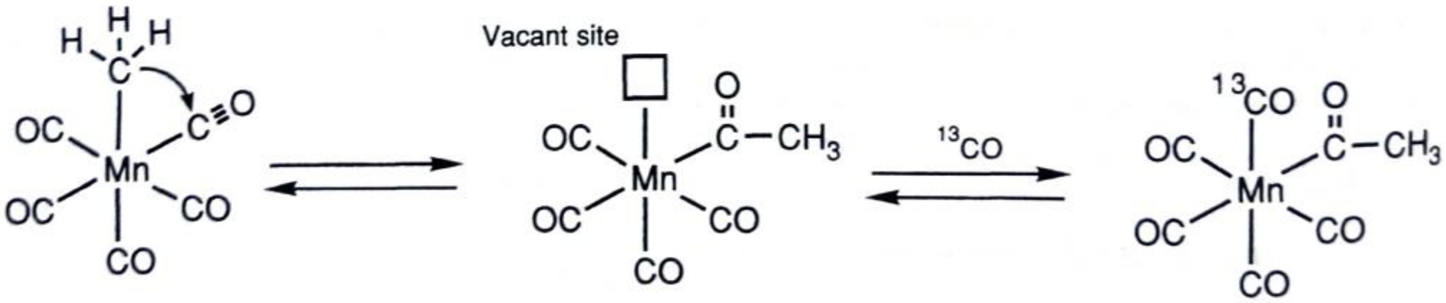
3. **Insertion of NO:** NO insertion takes place like CO with accommodation of NO unpaired electron. Diamagnetic metal alkyls react with NO under double insertion to give a metallacycle.

With paramagnetic alkyls oxidation usually results, and in presence of olefins the transfer of nitrene to the C=C double bond occurs

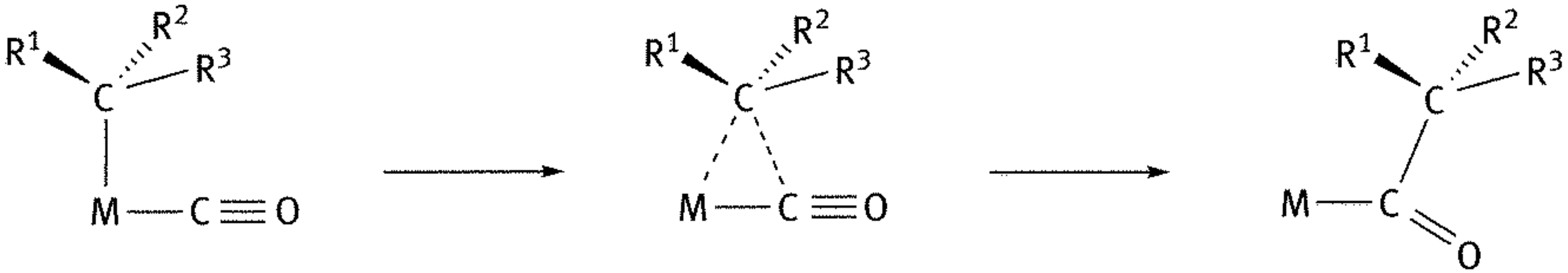


4. **Insertion of CO:** The insertion of CO into M-C bond to give acyl complexes.

- It involves migration of alkyl ligand to a coordinated CO ligand
- Migration represents an intramolecular nucleophilic attack by alkyl on a coordinated unsaturated electrophile

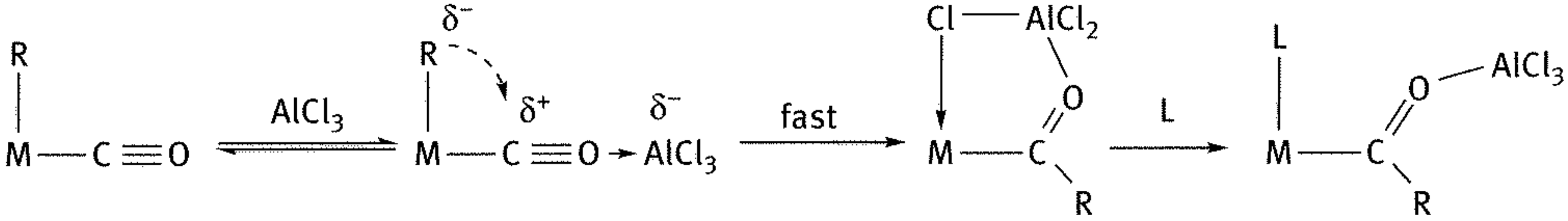


- If the alkyl ligand is chiral, the migration step proceeds with the retention of configuration

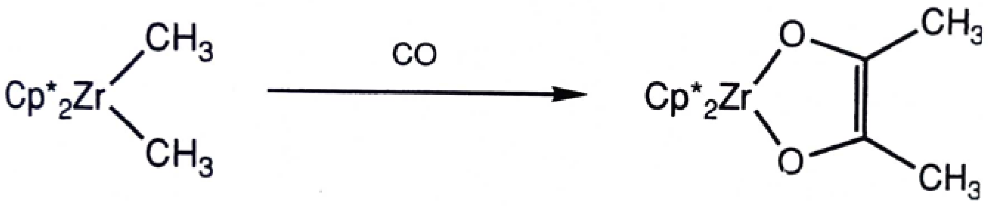


- The reaction is reversible, on heating a CO ligand again cis to the acyl group dissociates and allows migration of methyl back to metal

- Presence of Lewis acid accelerates the rate of alkyl migration
- Lewis acid coordinates to the O-terminus of a CO ligand, thereby increasing the polarity and also stabilize the acyl product
- The intermediate may also be stabilize if the metal halide Lewis acid coordinates to the site vacated by the migrated ligand



- Double carbonylation of metal dialkyls may lead to C-C coupling (Fischer –Troposch reaction)



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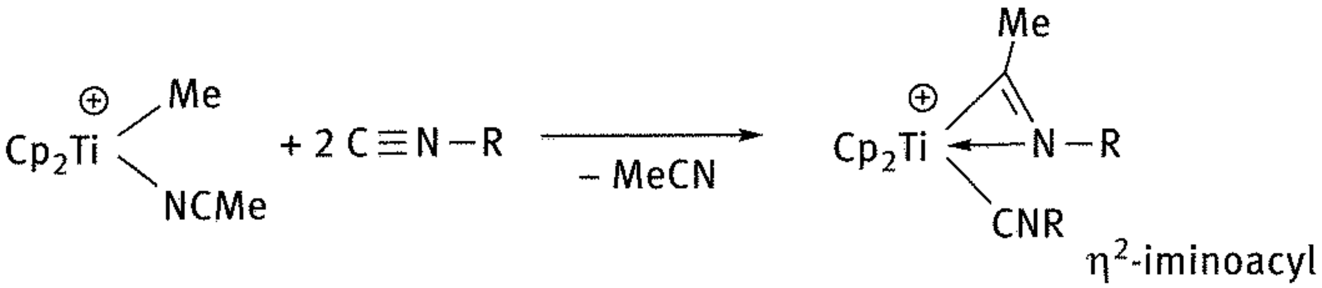
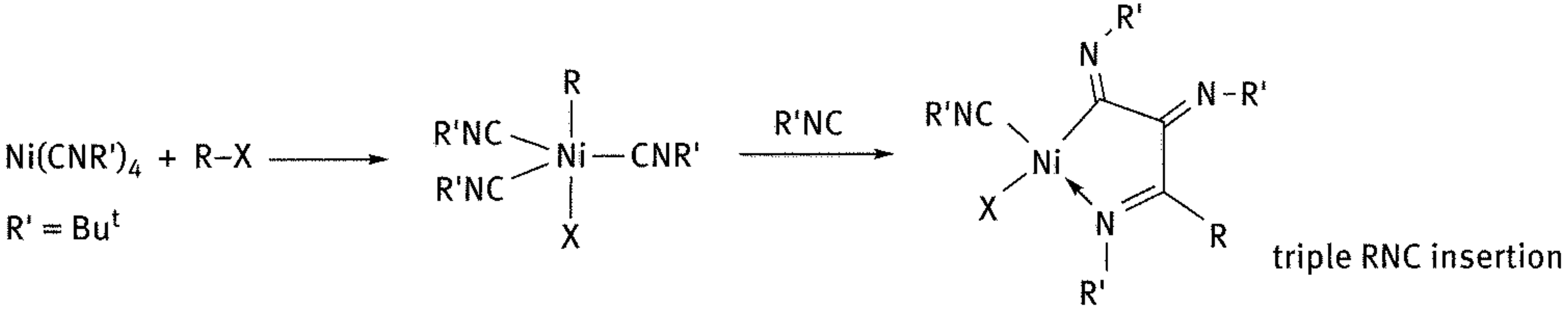
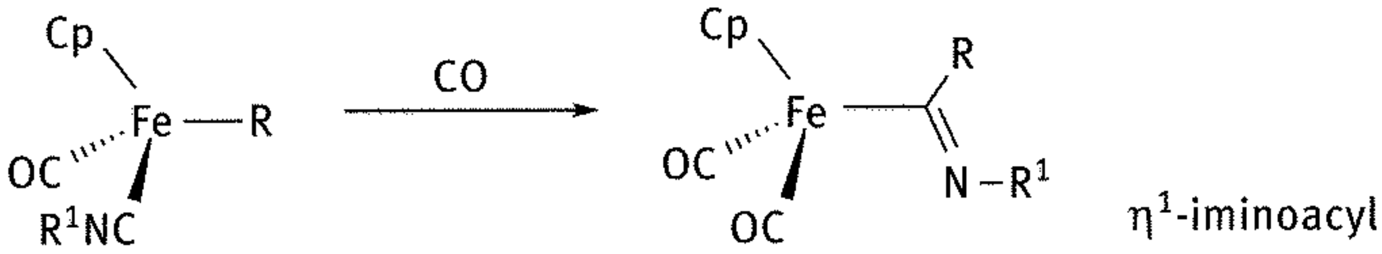
5. **Insertion of isocyanide:** Isocyanides are closely analogous to CO and generally undergo similar reactions

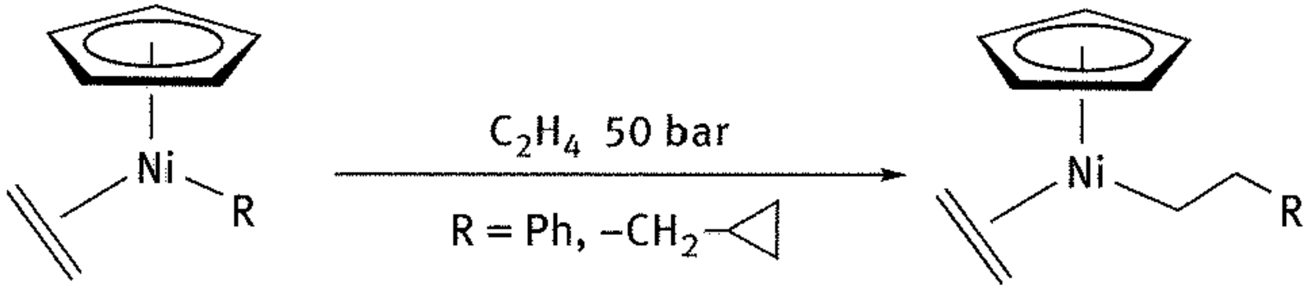




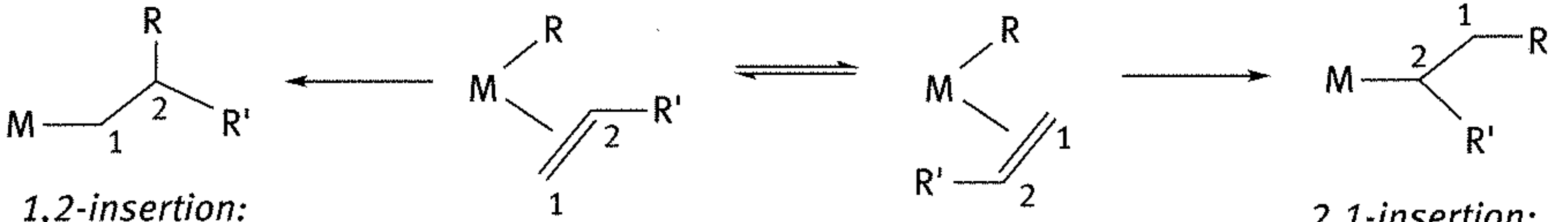
- Where there is a competition between CO and RNC insertion, formation of iminoacyl prevails



6. **Insertion of alkene and alkynes**: Insertion of alkene into metal alkyl is one of the most important catalytic industrial process: polymerization of olefins



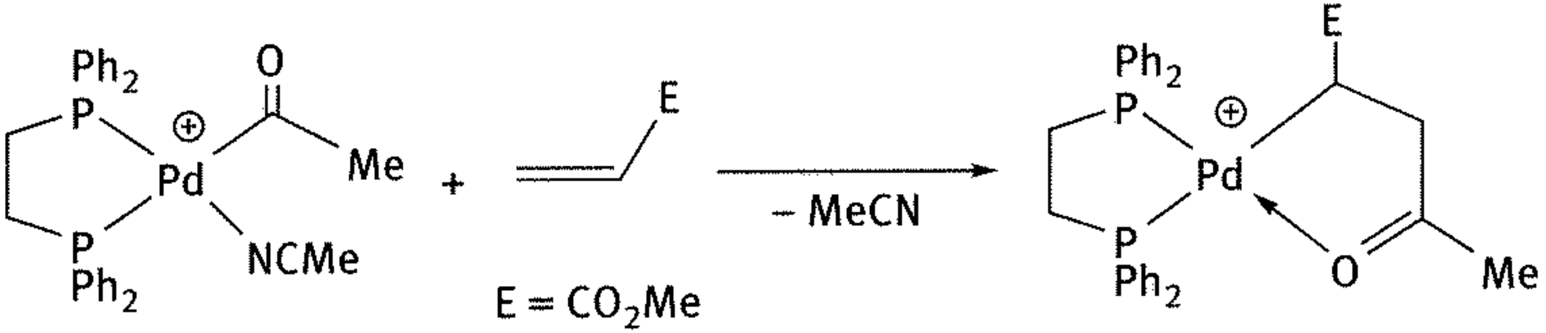
- Activated alkenes insert even into metal-acyl bonds: ethylene-CO polymerization catalyzed by Ni and Pd complexes. Antimarkonikoff’s product is preferred for primary metal alkyls



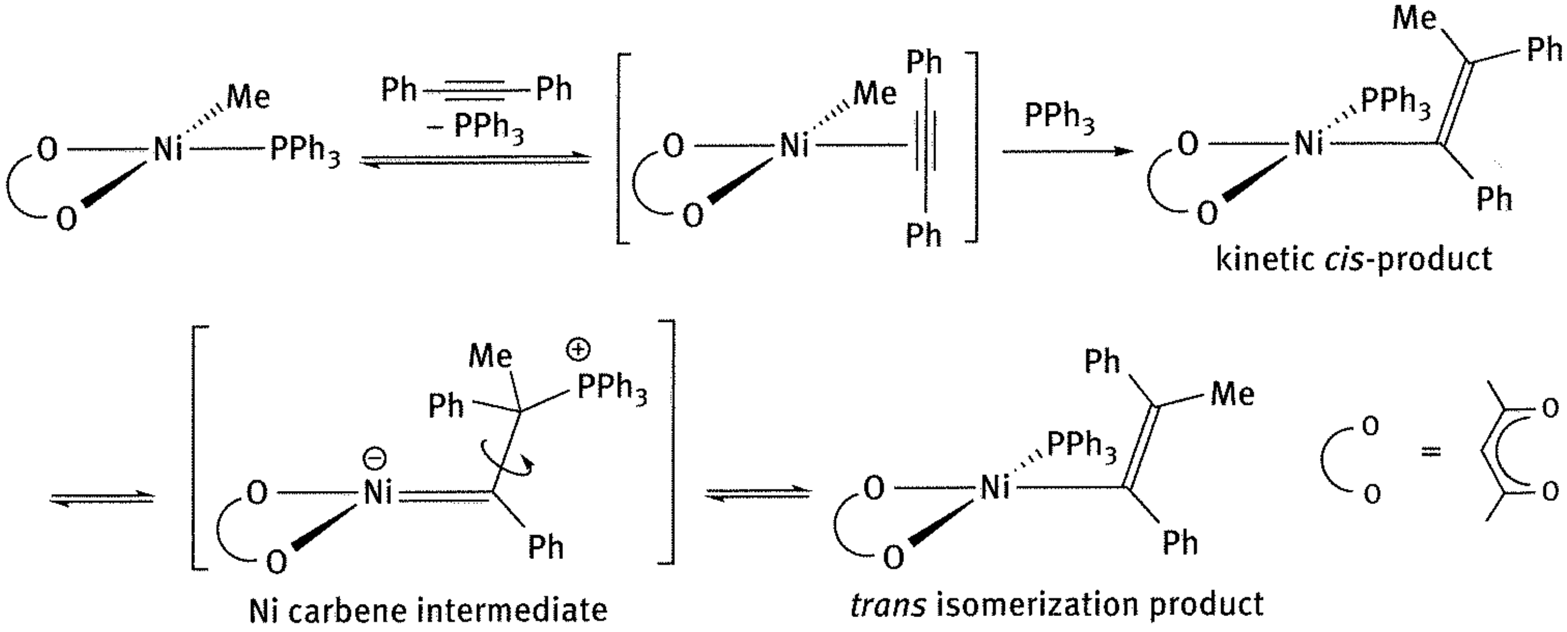
1,2-insertion:
linear
anti-Markovnikov

2,1-insertion:
branched,
Markovnikov product
R' = electron-withdrawing

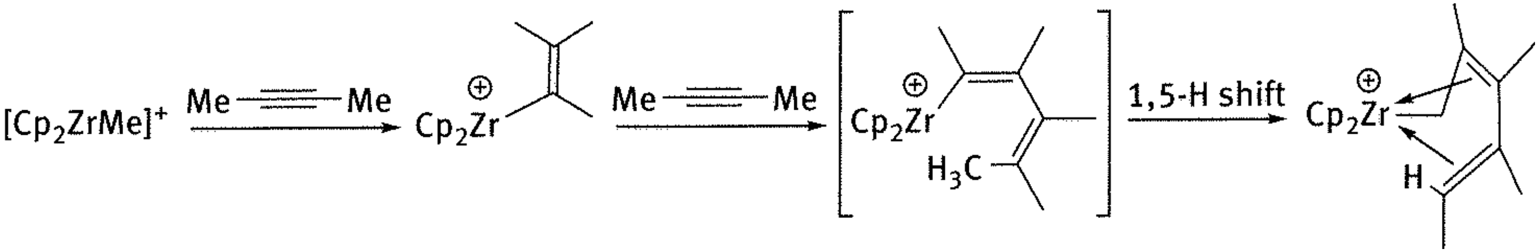
- The C=O function of the acyl ligand stabilizes the insertion by chelate formation



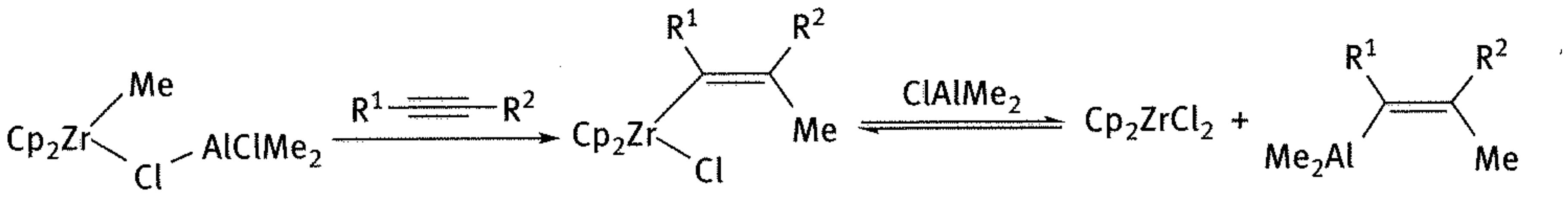
- Insertion of alkynes into M-C bonds in square planar Ni(II) complexes proceed via ligand substitution

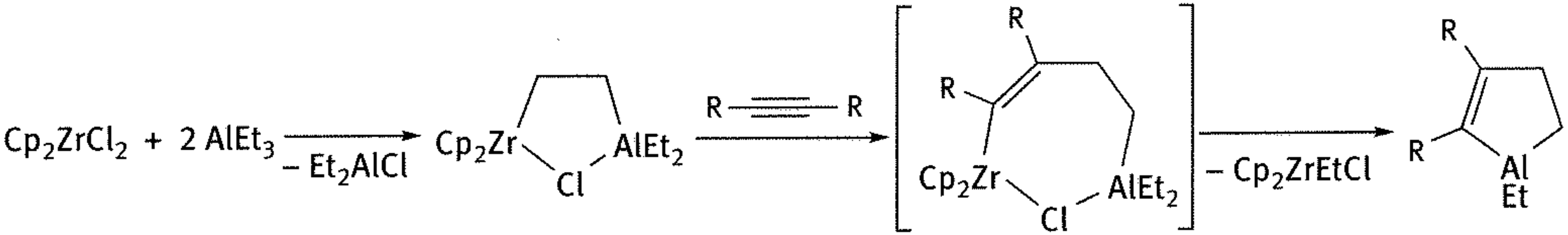


- Multiple insertion of alkynes have been observed to give complexes free of coordinated dienyl ligands, depending on the electronic characteristics of the metal center

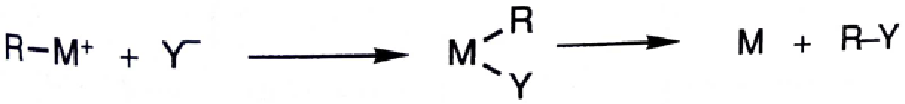


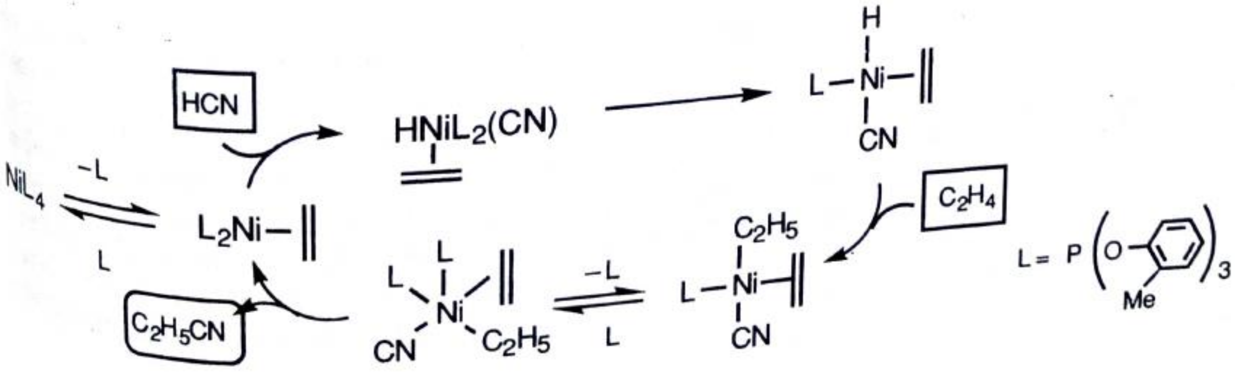
- Alkyne insertion into Zr-C bonds are the key mechanistic step in Negishi-type alkyne carboalumination reactions





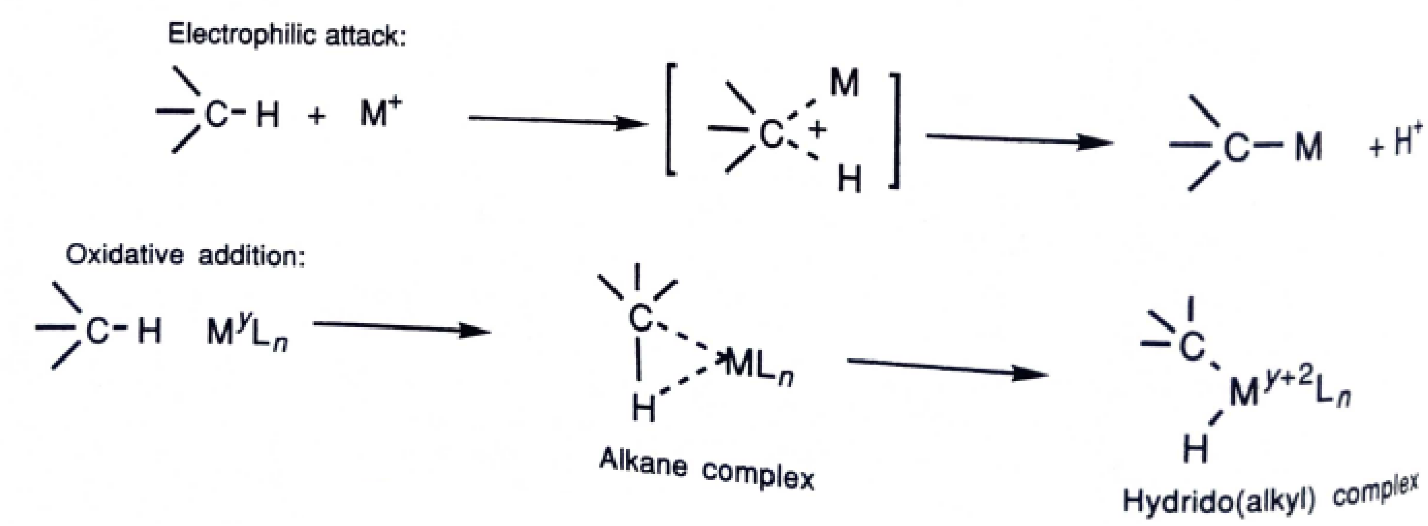
Reaction with nucleophiles: Attack of a nucleophile on a metal alkyl often induces reductive coupling, it's a part of catalytic cycle. Leads to functionalization of alkene (hydrocyanation of alkene)





Insertion of metals with C-H bond: C-H bonds are generally unreactive in saturated hydrocarbons. In unsaturated, it is relatively more reactive. Two processes are possible.

- Electrophilic attack on C-H, involving metals in high OS and oxidative addition of C-H bond to a coordinatively unsaturated metal center.
- They may proceed intra or intermolecularly.
- Step 1: interaction of a metal center with C-H bond or C-H hydrogen (α- and β-hydride elimination
- In electron deficient metal systems M…H-C represents ground state and more stable. The term agostic has been used to describe this mode of bonding



Bonding

- Most of the metal alkyl complexes follow 18e rule with few exceptions to few d^8-square planar complexes of Rh(I), Ir(I), Ni(II), Pd(II) and Pt(II)
- Sometime steric stabilization (bulky ligand prohibits the metal to bond with enough donor ligands, umbrella protecting the metal) play predominant role for which higher electron count is restricted. Also sometime referred as kinetic stabilization.

Metal alkenes

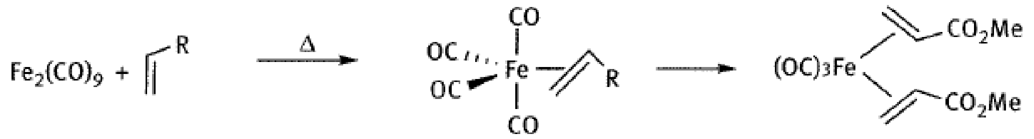
- Alkene complexes of metals constitute one of the important classes of coordination compounds.
- The metals are found in low oxidation states owing to the more favorable interaction with the soft π-electron donors
- The majority of metal alkene complexes contain other ligands. However, complexes with only the metal and organic ligands (olefins) are also known.
- Alkene complexes are often made by displacement of CO or halide ion by an alkene.
- **Zeise's salt,** the first synthesized organometallic compound, W. C. Zeise, 1827
- **Zeise's method:** By dehydration of ethanol. The dimer $[Pl(C_2H_4)Cl_2]_2$ is obtained first and the original salt is obtained by treating the concentrated dimer with KCl.

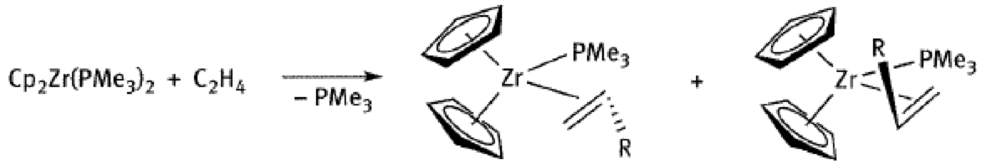
$$K_2[PtCl_4] + C_2H_5OH \rightarrow K[PtCl_3(\eta^2\text{-}C_2H_4)]$$

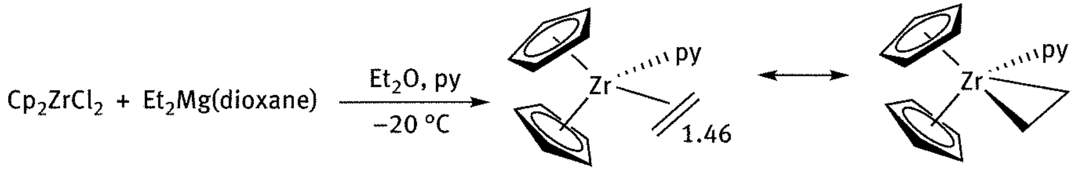
- **Smoother condition:** By treating $K_2[PtCl_4]$ with ethylene in presence of catalytic amount of $SnCl_2$, with $[PtCl_3(SnCl_3)]^{2-}$ being the intermediate.

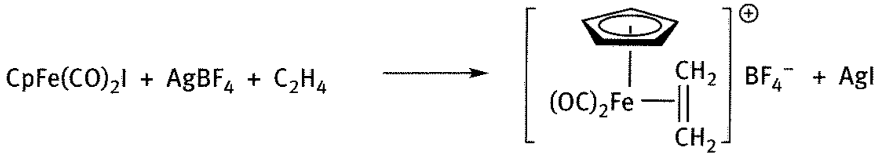
$$K_2[PtCl_4] + C_2H_4 \xrightarrow{SnCl_2} K[PtCl_3(C_2H_4)] + KCl$$

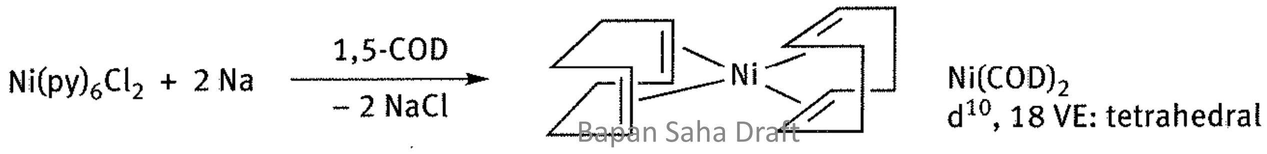
Synthesis:











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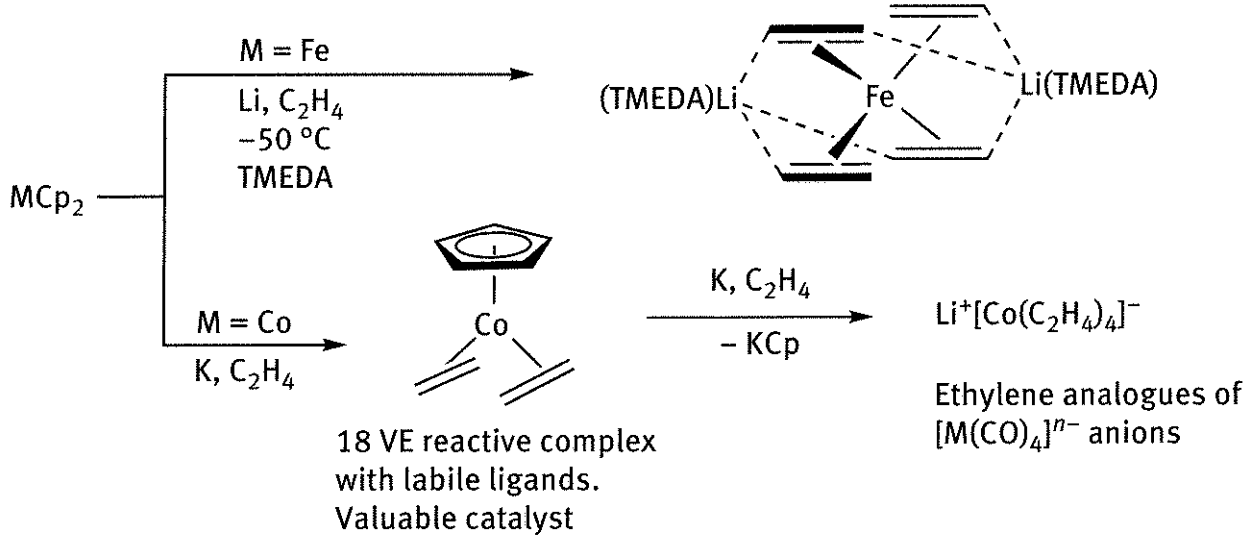
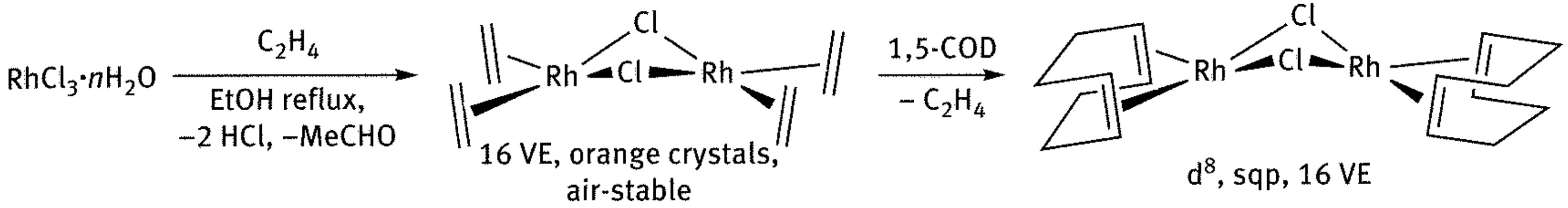


$Li^+[Co(C_2H_4)_4]^-$

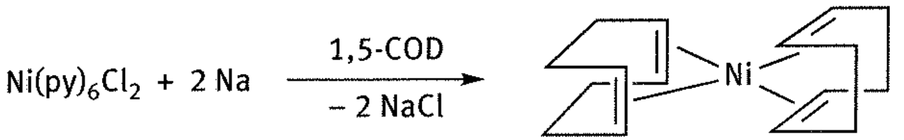
18 VE reactive complex
with labile ligands.
Valuable catalyst

Ethylene analogues of
$[M(CO)_4]^{n-}$ anions

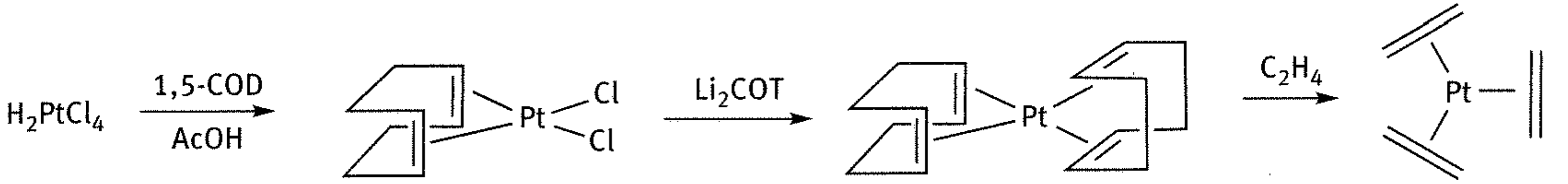


16 VE, orange crystals,
air-stable

d^8, sqp, 16 VE



$Ni(COD)_2$
d^{10}, 18 VE: tetrahedral



d^8, sqp, 16 VE

Pt(0), d^{10}, 16 VE
trigonal-planar,

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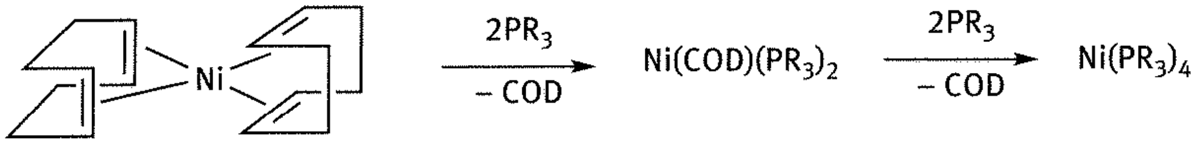
Reaction

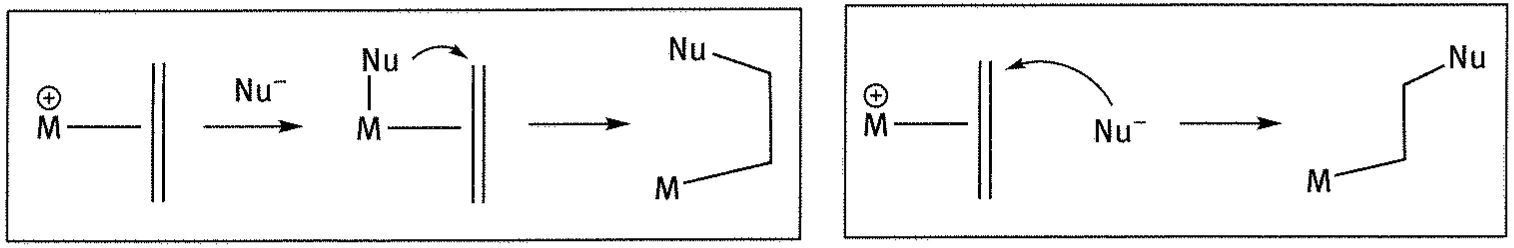
Ligand substitution

- Addition of an alkene to 16-electron Vaska's complex $\textit{trans}\text{-Ir(CO)Cl(PPh}_3)_2 + R_2C{=}CR_2 \longrightarrow \text{Ir(CO)Cl}(\eta^2\text{-}C_2R_4)(\text{PPh}_3)_2$

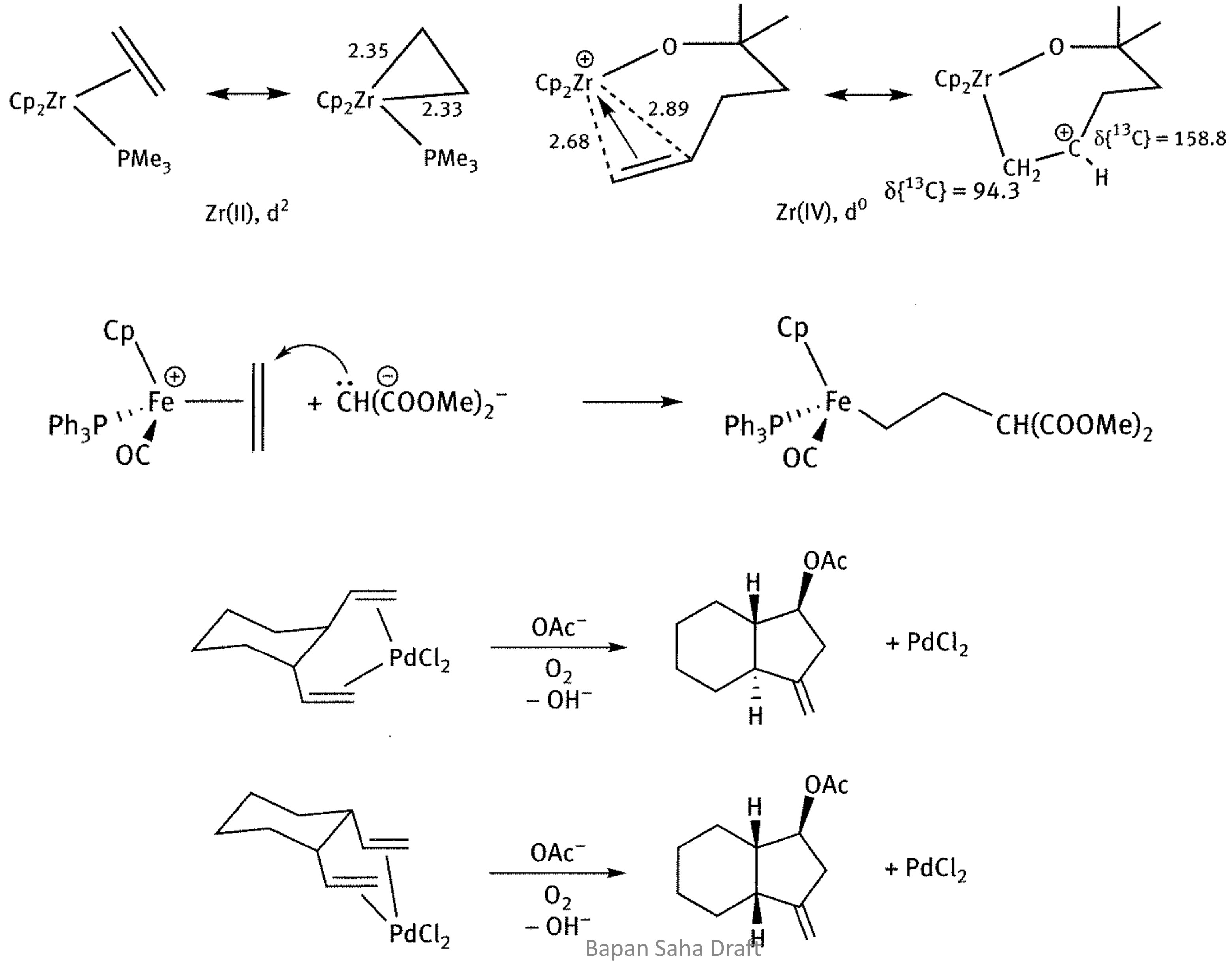


$$\underset{\text{solid}}{\text{Ni(PEt}_3)_4} \rightleftharpoons \underset{\text{solution}}{\text{Ni(PEt}_3)_3 + \text{PEt}_3}$$

- **Reaction with Nucleophiles:** The most important consequences of metal olefin bonding is that this coordination makes low polarity C=C substrate highly susceptible to nucleophilic attack



- Nucleophilic attack occurs in both intermolecular or intramolecular fashion



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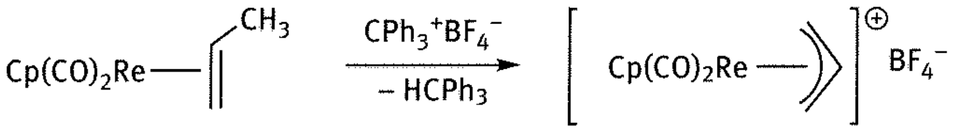
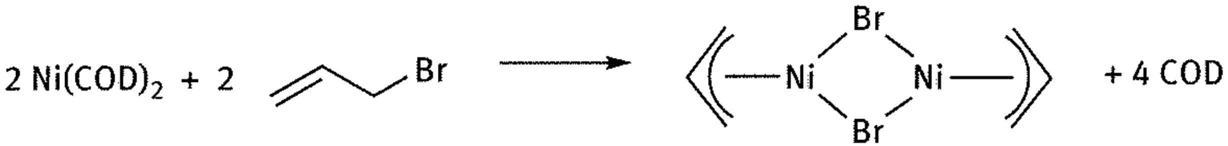
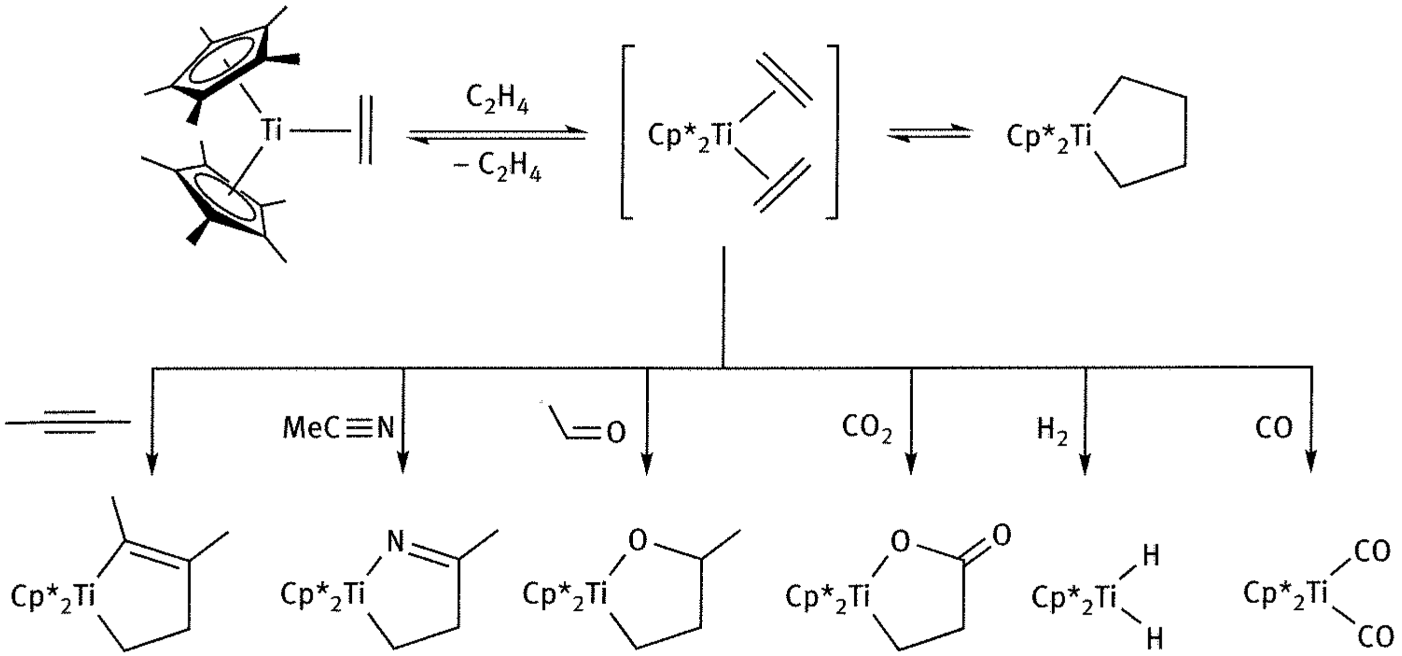
Reaction with electrophiles

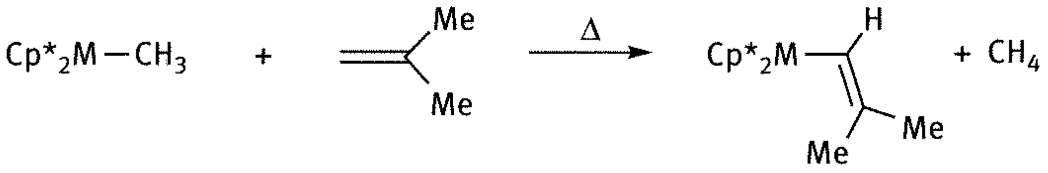




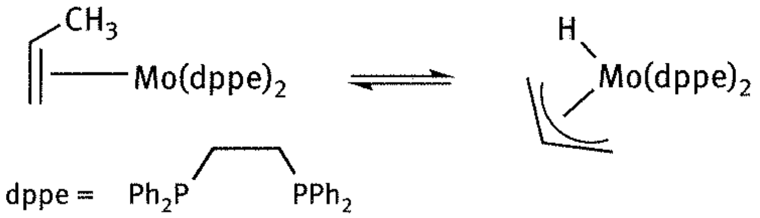


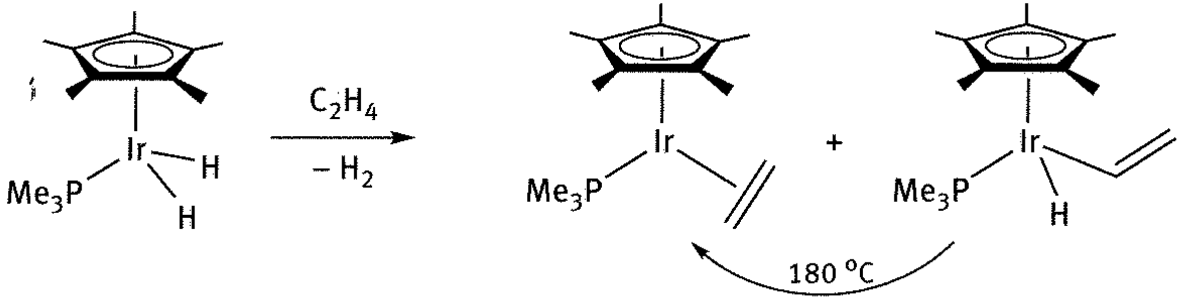
C-H activation reaction

- Highly electrophilic metal centres may react with alkenes under C-H bon cleavage (lanthanide complexes are common)



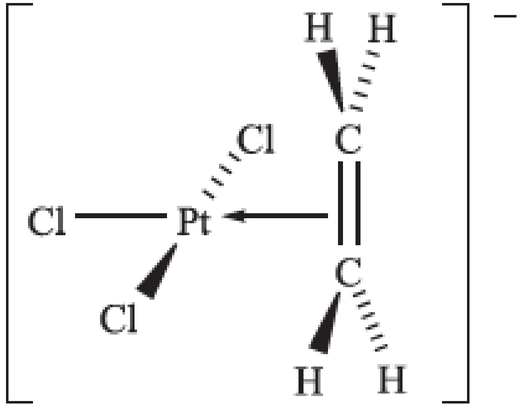
- If the energy difference between the olefin complex and C-H activation product is small, both the type of compounds may be in equilibrium





Structure of Zeise's salt

- $[PtCl_3(\eta^2\text{-}C_2H_4)]^-$ ion contains a square planar (or pseudo-square planar) Pt(II) center and in the solid state, the ethene ligand lies perpendicular to the coordination 'square plane', thereby minimizing steric interactions.
- Pt-Cl bond trans to C_2H_4 (234 pm) is longer than the cis Pt-Cl bonds (~230 pm)
- Pt-C bonds are equidistant from Pt atom (~213pm).
- The C-C distance, 137 pm, is slightly longer than in free ethylene (134 pm), indicating some dπ-pπ* back-bonding.
- Back-bonding is also indicated by a bending of the four hydrogen atoms away from the Pt atom

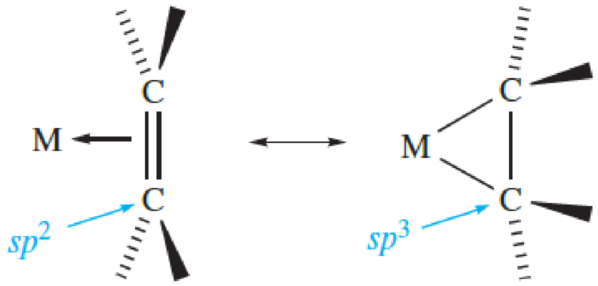


C-C = 137pm

Pt-C = 213pm

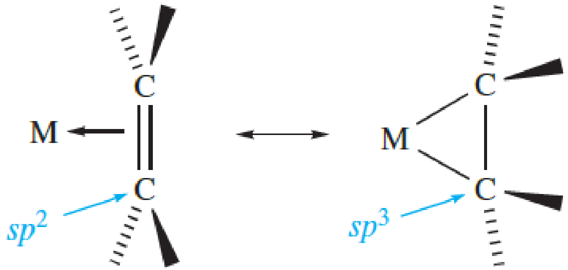
Pt-Cl$_{trans}$ = 234pm

Pt-Cl$_{cis}$ = 230 pm

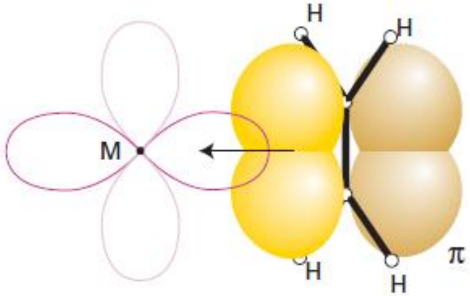


Bonding in metal-alkene/Zeise's salt (Dewar Chatt Duncanson model)

- Alkenes (C_2H_4) normally bond side-on to a metal atom (Pt) with equidistant C-atoms and other groups on the alkene (C_2H_4) lying perpendicular to metal (Pt) plane and two C-atoms.
- The electron density of the C=C π-bond can be donated to an suitable empty orbital (d_{x2-y2}) on the metal (Pt) atom to form a σ-bond.
- Simultaneously, a filled metal d orbital (d_{yz}, T_{2g}) can donate electron density back to the empty π* orbitals of the alkene to form a π-bond (Dewar Chatt Duncanson model).
- These effects tend to reduce the C-C bond order (elongated C-C distance) and rehybridizing C-atoms to sp^3, indicated by the bending of H-atoms away from the metal (Pt).



rehybridization



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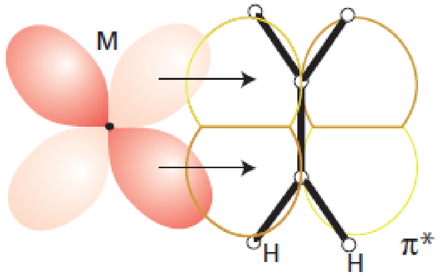
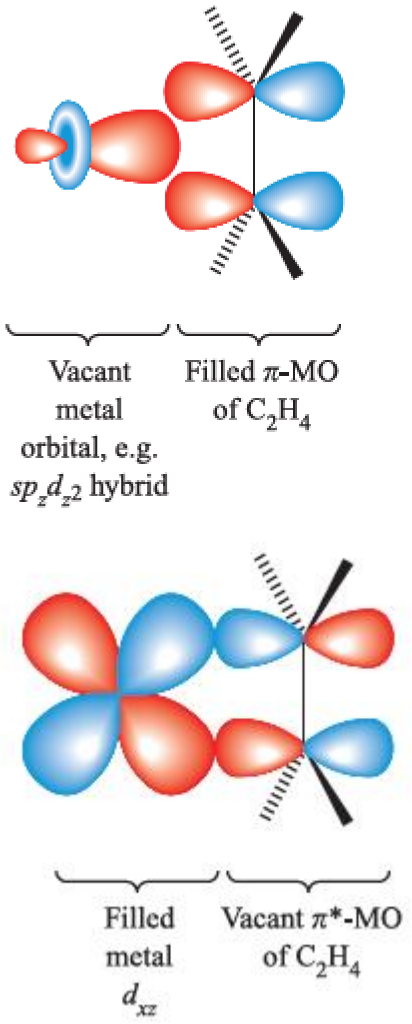
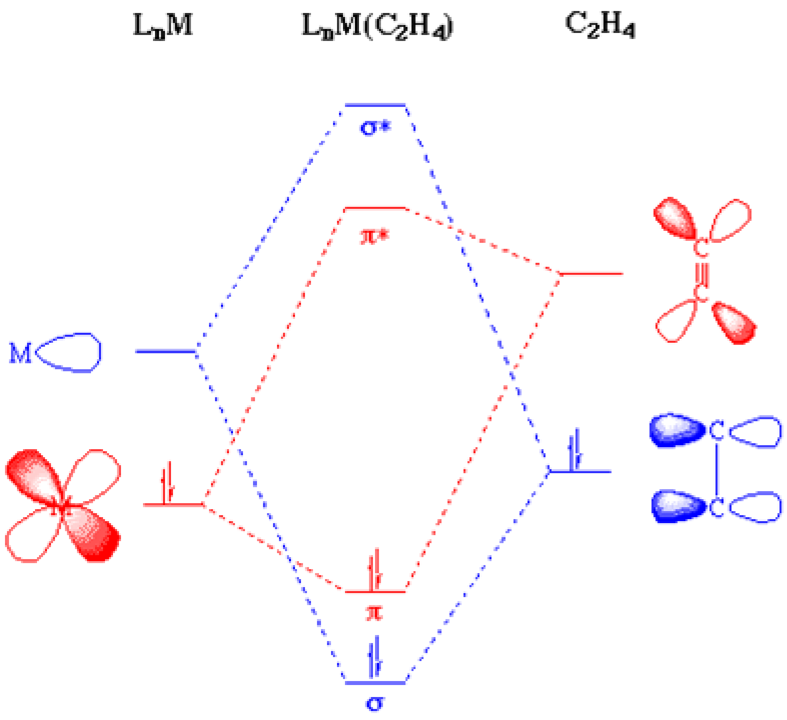
Pt(d_{x2-y2}) ← π(C_2H_4)



Pt(d_{yz}) → π*(C_2H_4)

- Greater the electron density back-donated into the π* orbital on the alkene, the greater the reduction in the C=C bond order





Dewar-Chatt-Duncanson model

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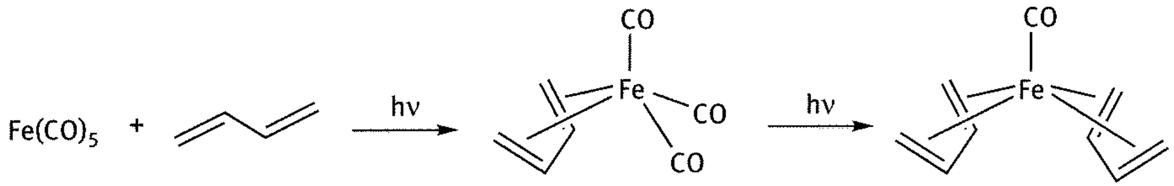
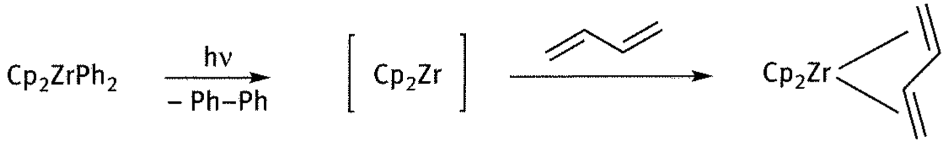
Synthesis of diene complexes

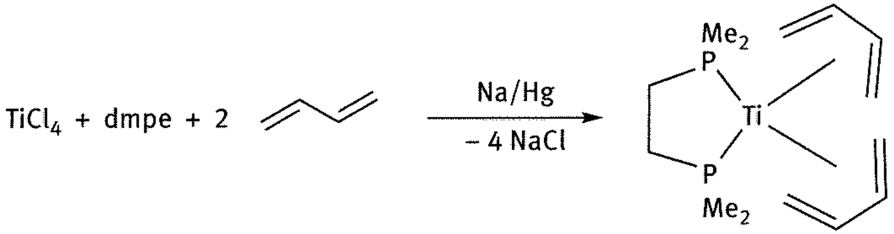
By photolysis:





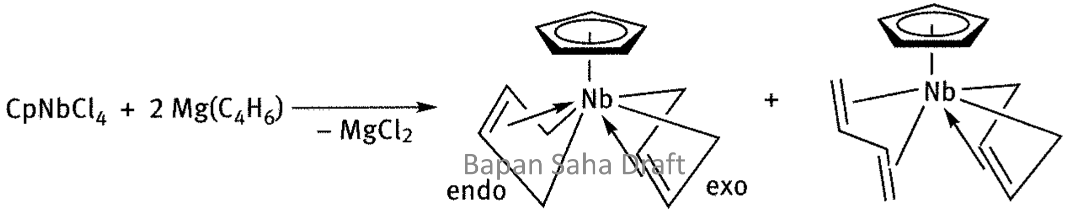
highly reactive
14 VE intermediate

By reduction:



By alkylation:

Magnesium butadiene (2-butene-1,4-diylmagnesium) acts as alkylating agent to give diene complexes:



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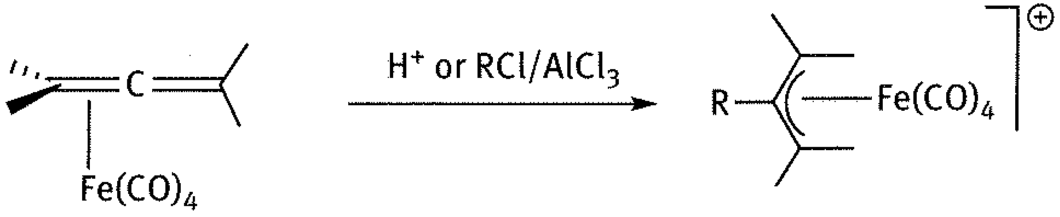
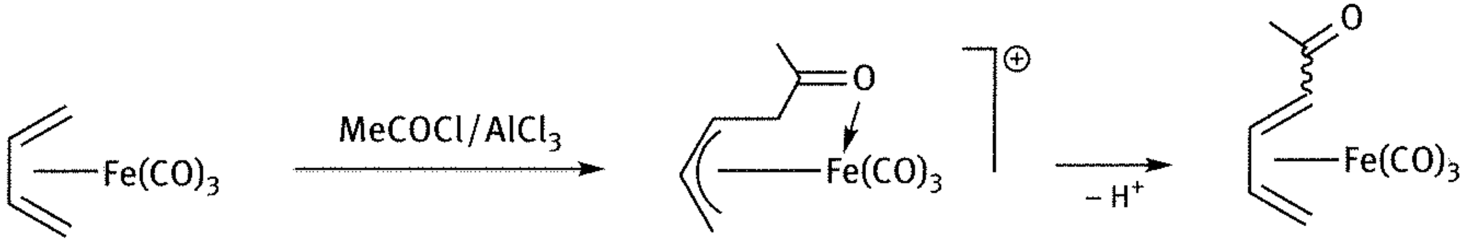
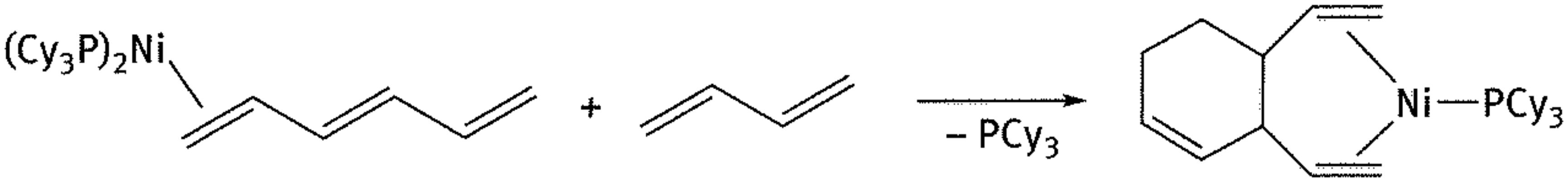
Reactions of conjugated diene

- Reaction with electrophiles





- 4+2 cycloaddition

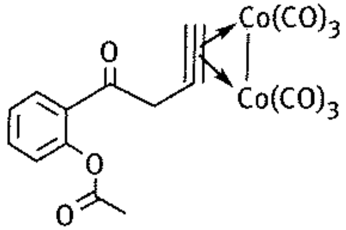


Metal alkynes

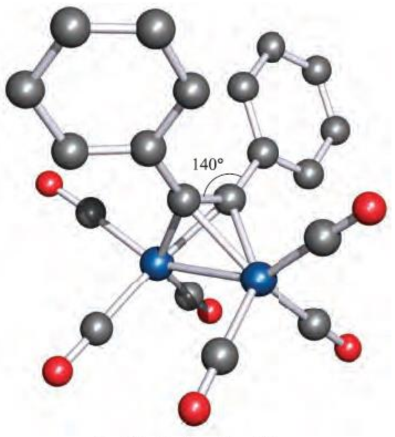
- With two π-bonds (two fully occupied π-MOs), alkynes can behave as two/four-electron donors. When side-on to a single metal atom, the η^2-C≡C triple bond is best considered as a two-electron donor, with the π* orbitals accepting electron density from M-atom
- With strongly electron-withdrawing groups, the substituted alkyne (ligand) becomes an excellent π-acceptor and displace other ligands like phosphines
- Substituted alkyne forms stable polymetallic complexes acting as a four-electron donor. For example, η^2-diphenylethyne-(hexacarbonyl)dicobalt(0), in which we can view one π-bond as donating to one of the Co atoms and the second π-bond as overlapping with the other Co atom. Alkyl or aryl group adds to the stability.

$$Co_2(CO)_8 + PhC{\equiv}CPh \longrightarrow Co_2(CO)_6(C_2Ph_2) + 2CO$$

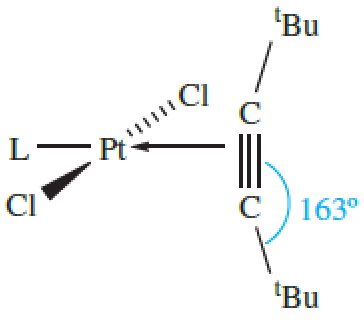
Co alkyne complex with anti-tumour activity



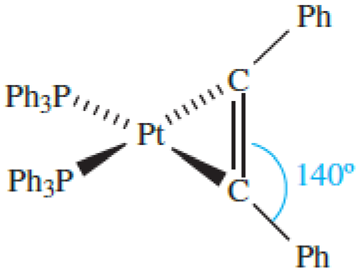
- In this Co-complex, the alkyne acts as a 4-electron donor, forming a metallacycle (as shown below); the C≡C bond length increased to 136 pm (almost double bond). A decrease in the alkyne C-C-C_R bond angle accompanies the change in bonding mode (as shown below). The resulting complex is a Co_2C_2 cluster
- The bonding in a monometallic alkyne complex is similar to alkene complex, but allowing for the participation of the two orthogonal π-MOs.
- C≡C bond length in a free alkyne is 120 pm and, in complexes, this lengthens to 124–137pm depending on the mode of bonding.



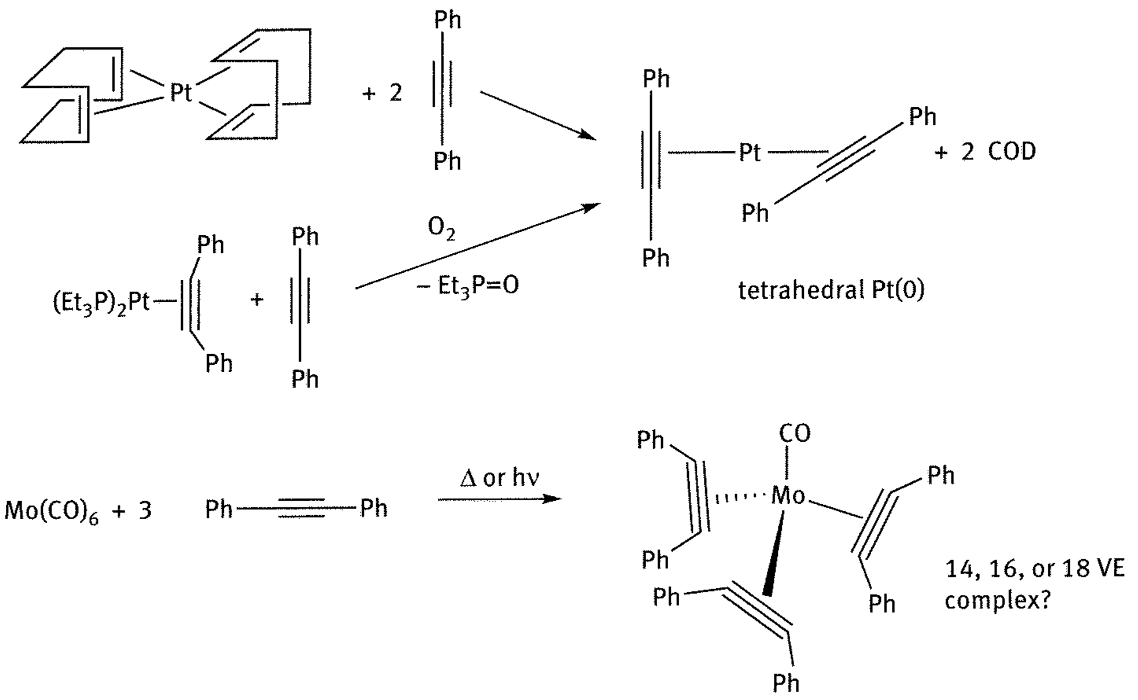
C—C in Co_2C_2-unit = 136pm



L = 4-$MeC_6H_4NH_2$



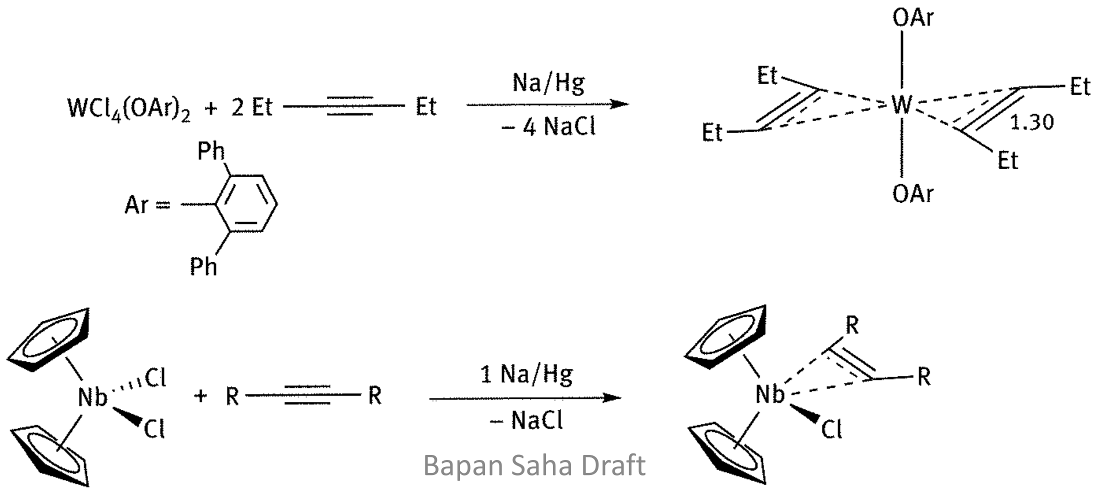
Synthesis of metal alkenes



tetrahedral Pt(0)

14, 16, or 18 VE complex?

By reduction: Note that alkyne complexes may also arise from the reductive coupling of CO ligands.



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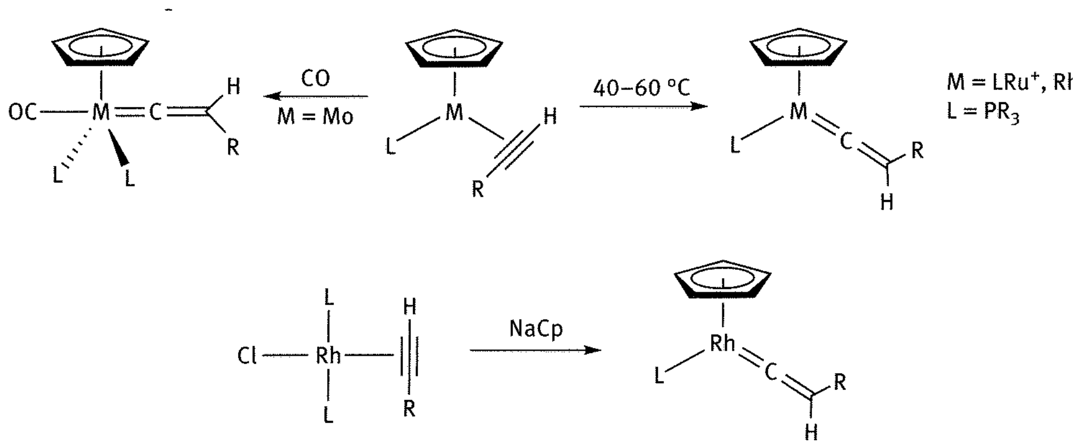
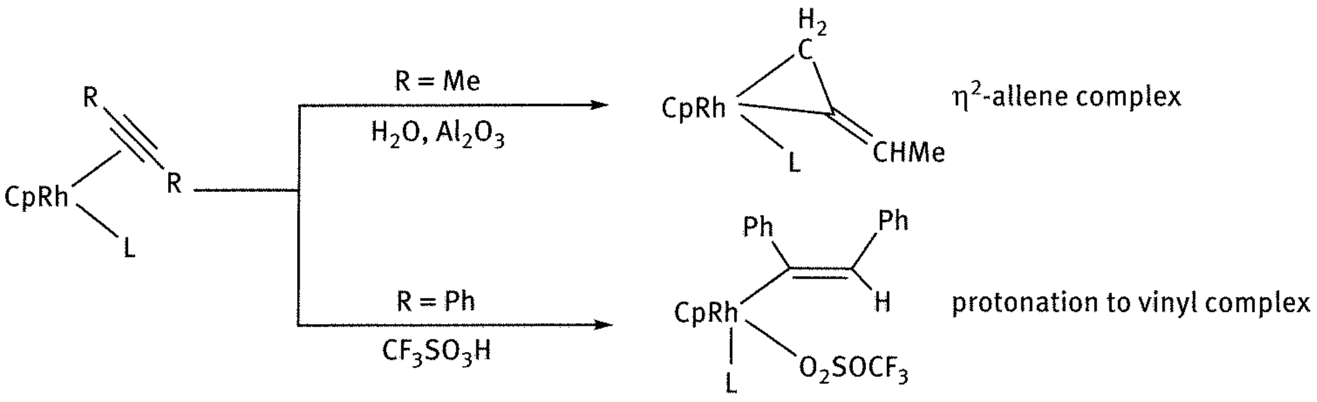
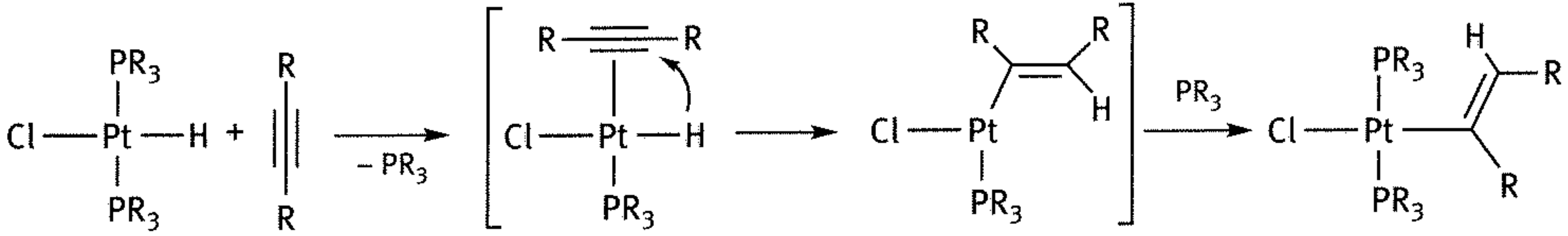
Reactions of metal alkynes

- Alkyne complexes can rearranges to vinylidene or allene complexes





- Alkynes undergo a multitude of insertion reactions. The reaction with M-H bonds gives vinyl complexes via cis-insertion



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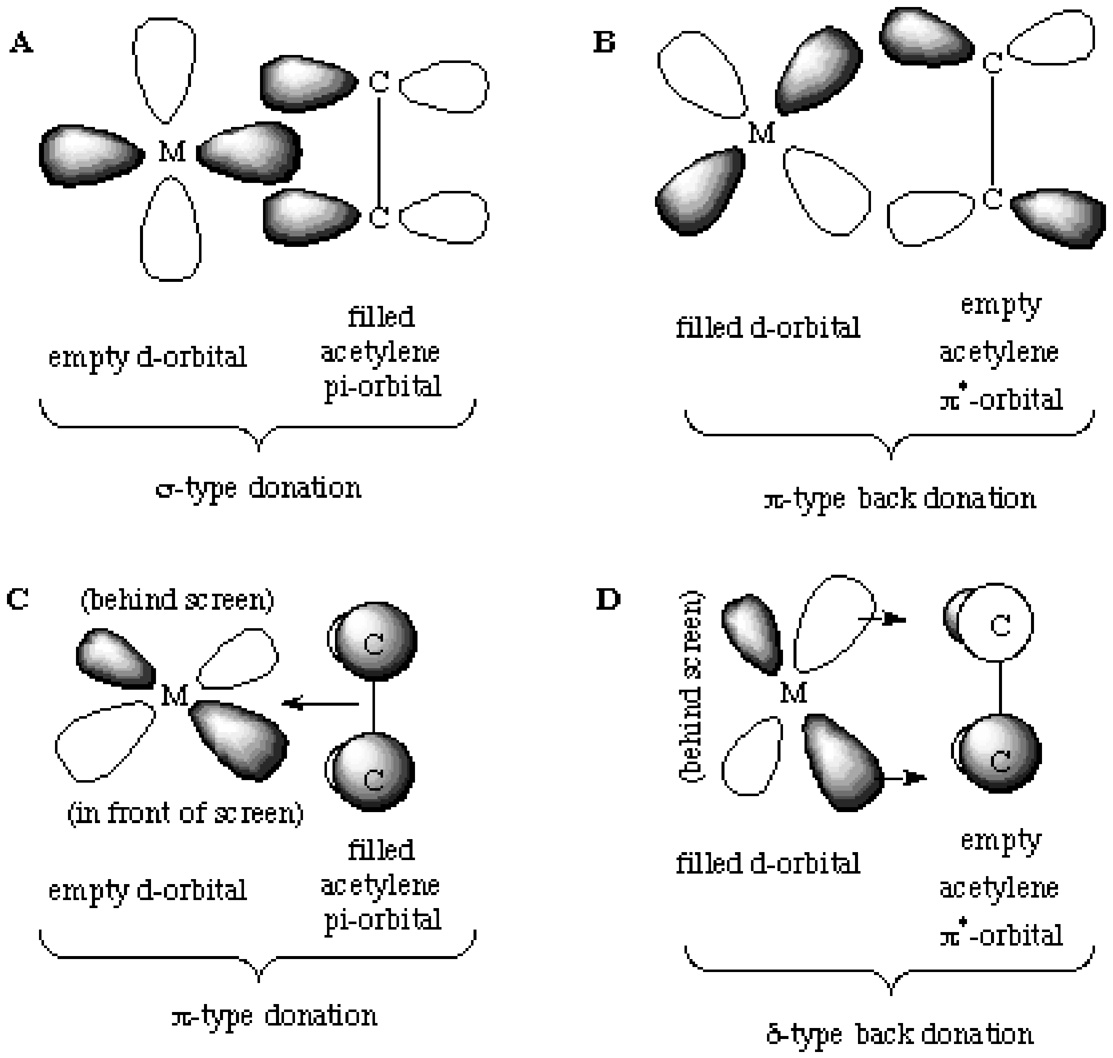
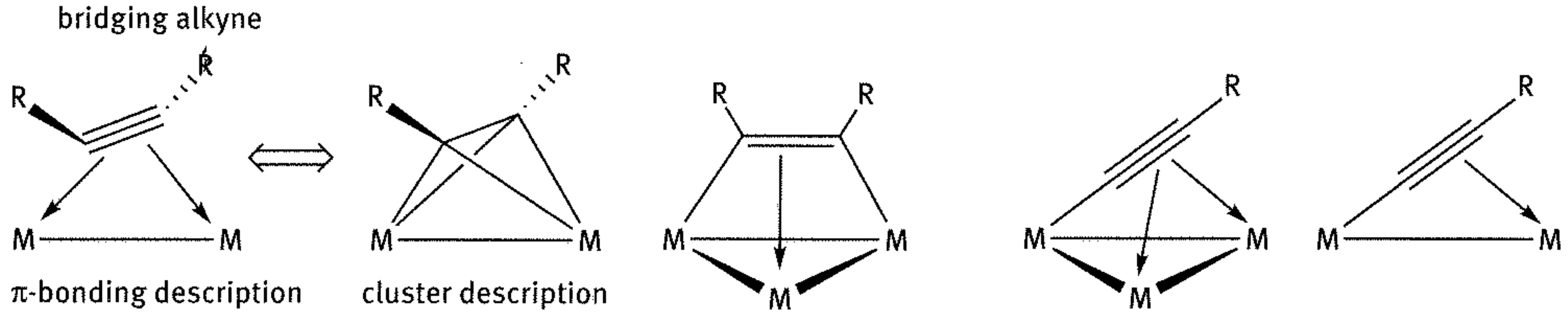
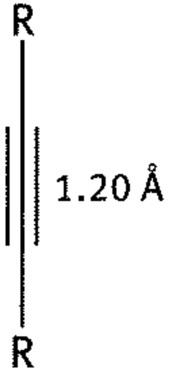
Alkyne ligands

- Alkynes tend to be more electropositive-bind more tightly to a transition metal than alkenes, alkynes will often displace alkenes
- Difference is 2 or 4 electron donor. σ-type (A) including a π-back bonding (B)
- The orthogonal set can also bind in a pi-type fashion using orthogonal metal d-orbital (C)
- The back-donation to the antibonding orbital (D) is a delta-bond-the degree of overlap is quite small - contribution of D to the bonding of alkynes is minimal
- The net effect π-donation-alkynes are usually non-linear in TM complexes

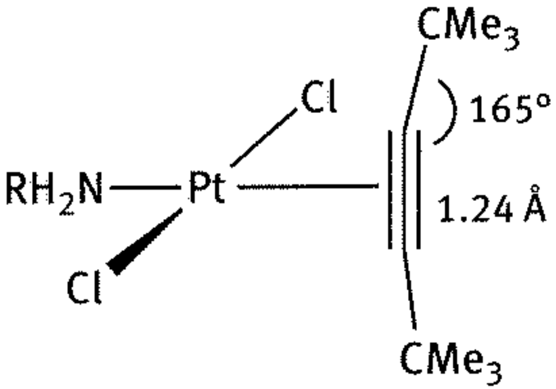






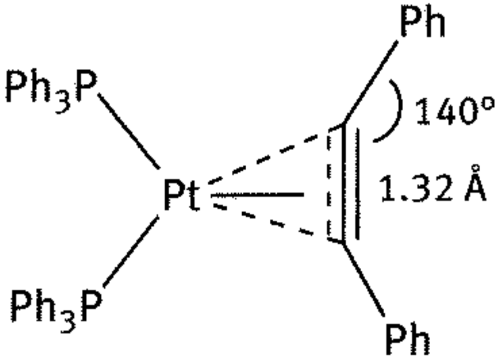
free alkyne

ν_{CC} 2190–2260 cm^{-1}



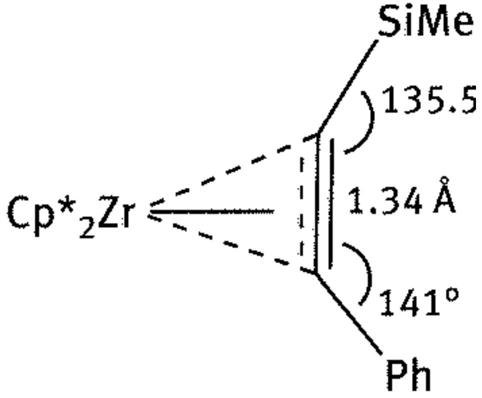
Pt^{II}, d^{8}

ν_{CC} 2028 cm^{-1}



Pt^{0}, d^{10}

ν_{CC} 1750 cm^{-1}



Zr^{II}, d^{2}

ν_{CC} 1618 cm^{-1}

- Deviation from linearity depend upon the metal electron count and its propensity to back bonding

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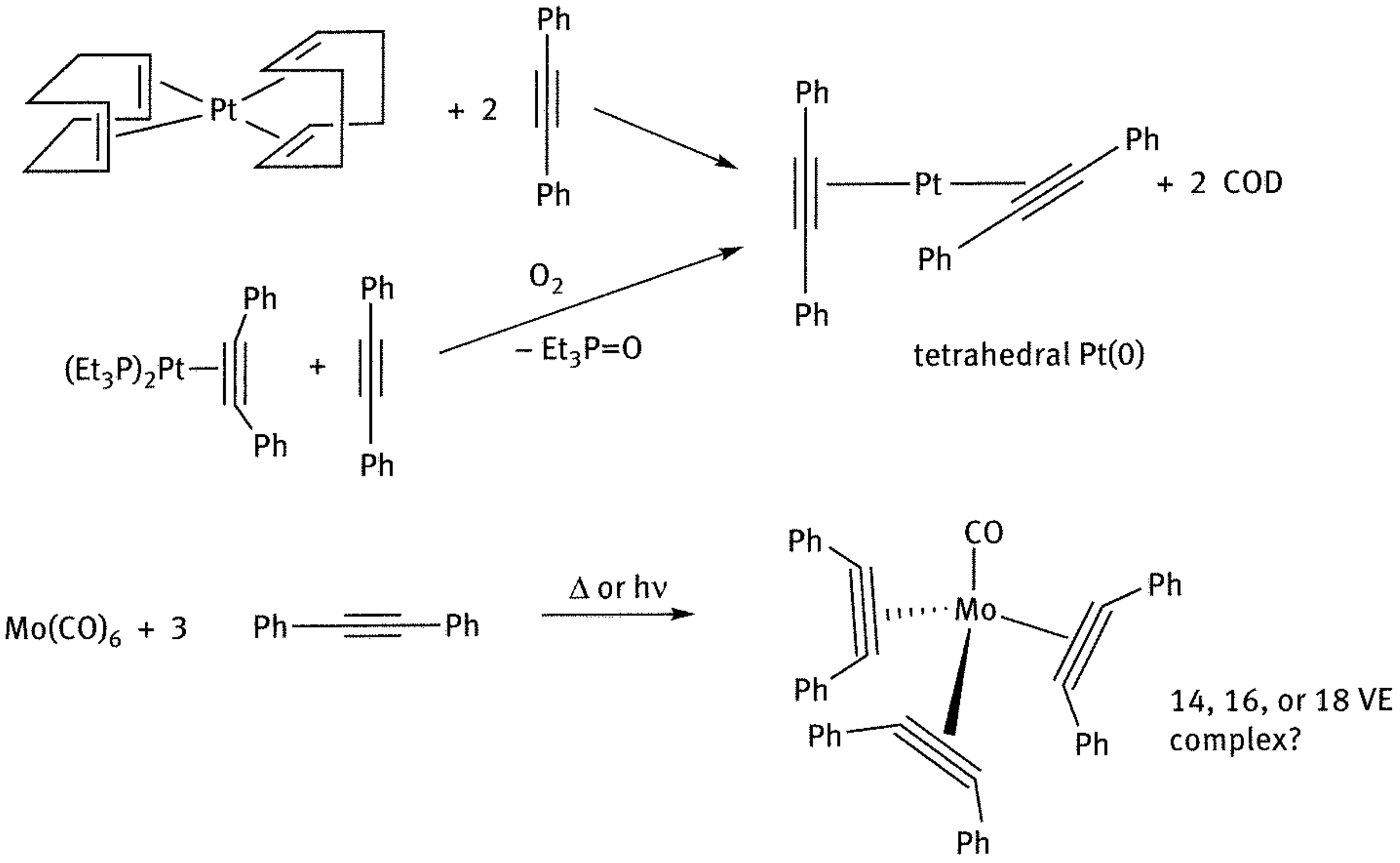
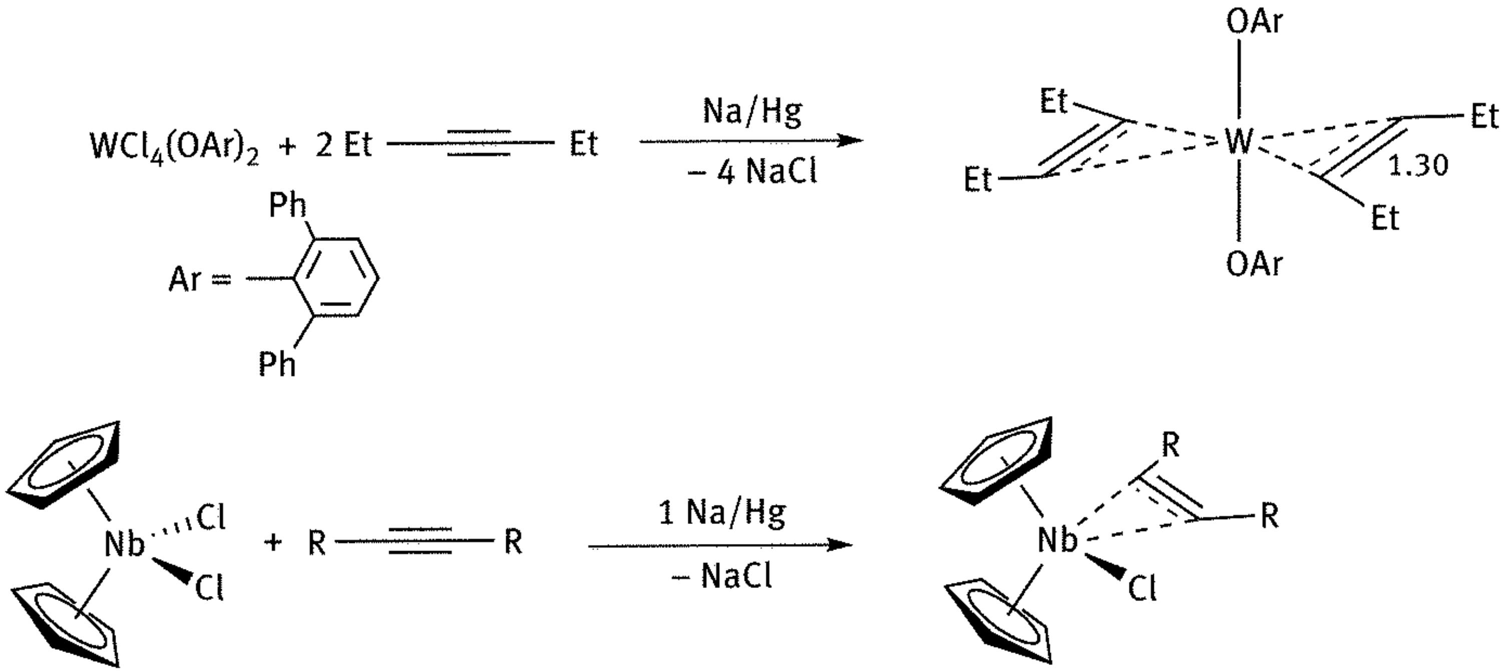
Synthesis:

- Primarily prepared by ligand substitution



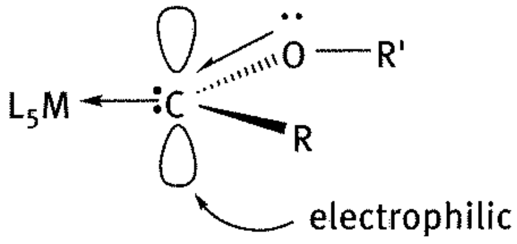
Reductive coupling of CO ligand



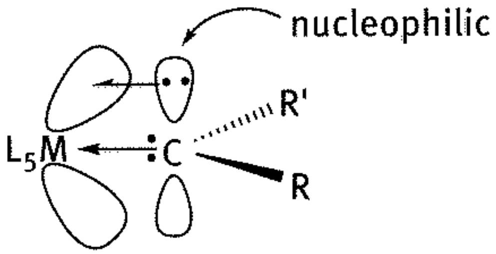
Metal carbenes (alkylidene) complexes

- Carbene (alkylidene) complexes possess a M=C double bond (two electron donors)
- Carbene complexes of the type $(OC)_5M{=}C(R)(OR^/)$ with M=Cr, Mo, W was first reported by E. O. Fischer in 1964
- These are derived from the coordination of a carbene $:CR_2$ to a metal center, they are known as carbene complexes
- The metal in these complexes is in low oxidation state, and bonding is similar to that of metal carbonyl.
- Majority of carbene complexes contain one or two highly electronegative heteroatoms like O, N, or S directly attached to the carbene carbon
- Another group of M=C compounds with highly oxidized metal center was reported by R. R. Schrock ($Cp_2Ta(CH_3)(CH_2)$), termed as alkylidene complex
- These carbenes can be regarded as CR_2^{2-} dianion, can be regarded as π-as well as σ-donors
- The term alkylidene is now adopted for all $M{=}CR_2$ complexes
- M-C multiple bond is common for metals that from M-M multiple bonds readily

Fischer carbene	**Schrock carbene**
Good π-acceptors	Good σ and π-donors
Fischer carbenes are electron deficient at the C-atom and is of electrophilic nature	Due to strong back bonding, carbene C-atom is electron rich and of nucleophilic nature.
Metal atom possesses a low oxidation state e.g., Fe(0), Mo(0), Cr(0)	Formed by early d-block metal in a high oxidation state e.g., Ti(IV), Ta(V)
At least one highly electronegative heteroatom such as O, N and S is present	H or alkyl as substituent. No heteroatom is present
Electron count is preferably 18	Electron count vary within 10-18



'Fischer carbene'



'Schrock carbene'

- M=C bond is readily formed by Ta, Cr, Mo, W & Re.
- Mononuclear M=C complexes of Fe, Co & Ni triads are less common
- M=C bond formation by Ti, Zr & Hf are exceptions only, cannot form M≡C bond

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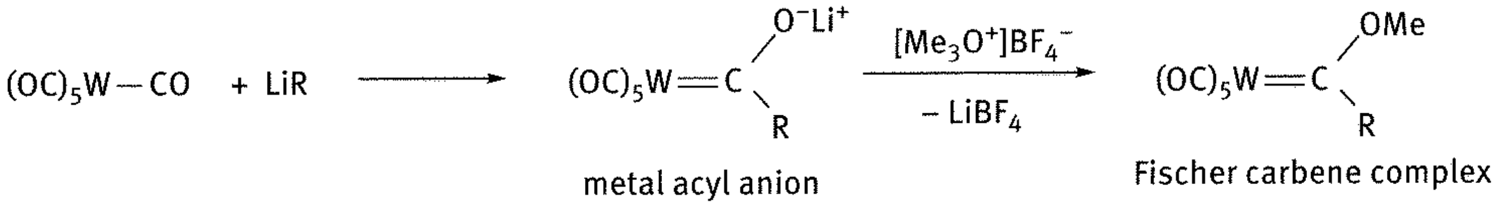
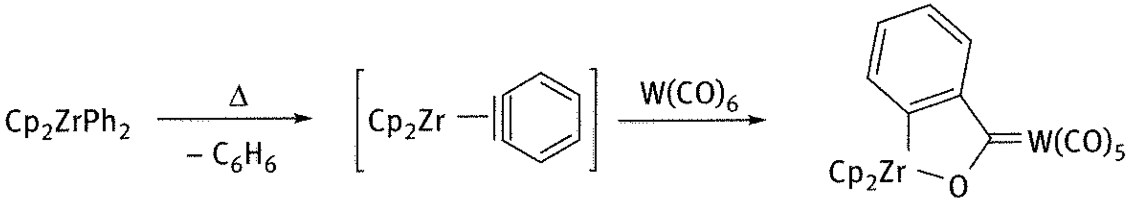
Preparation of Fischer complexes

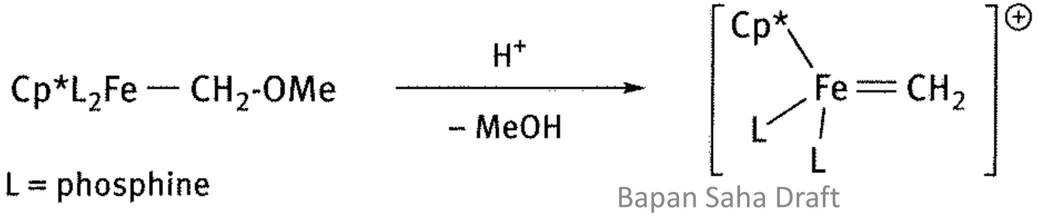
- Carbenes can also be made by nucleophilic attack on a carbonyl C-atom followed by alkylation



- Reduction of coordinated CO with reactive Zr(II) complexes (Zr acts both as alkylating agent and Lewis acid). This routes give access to carbene complexes of variety of metals



- From heteroatom substituted alkyl complexes



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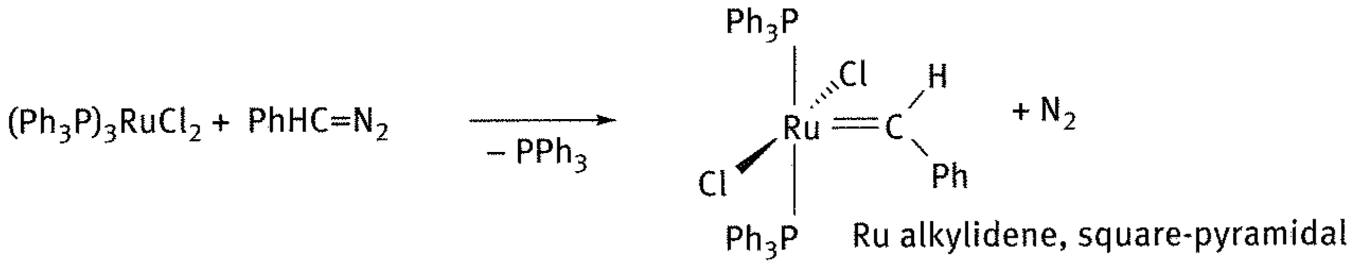
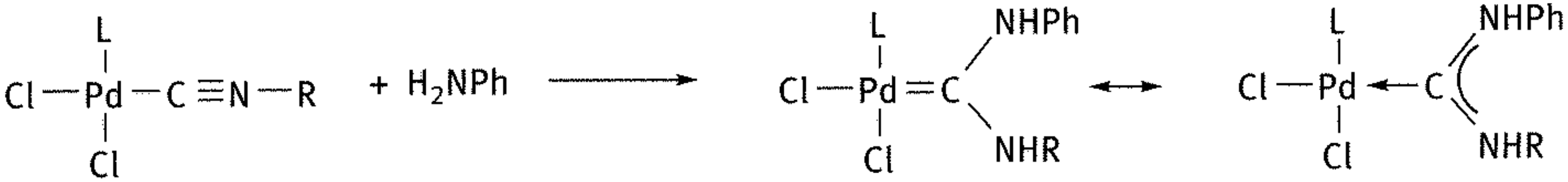
- From diazoalkane

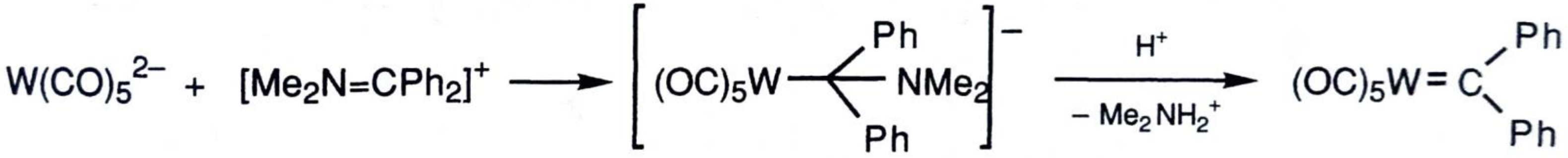


Ru alkylidene, square-pyramidal

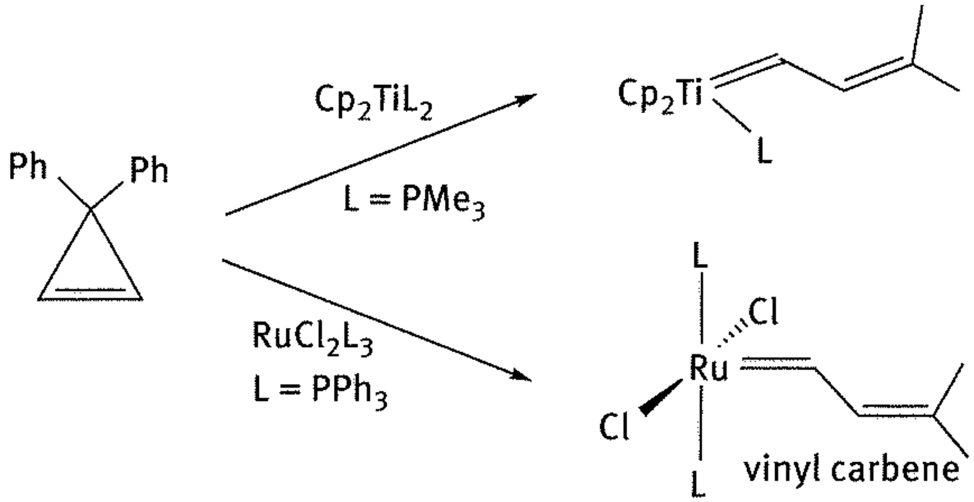
- From isocyanides



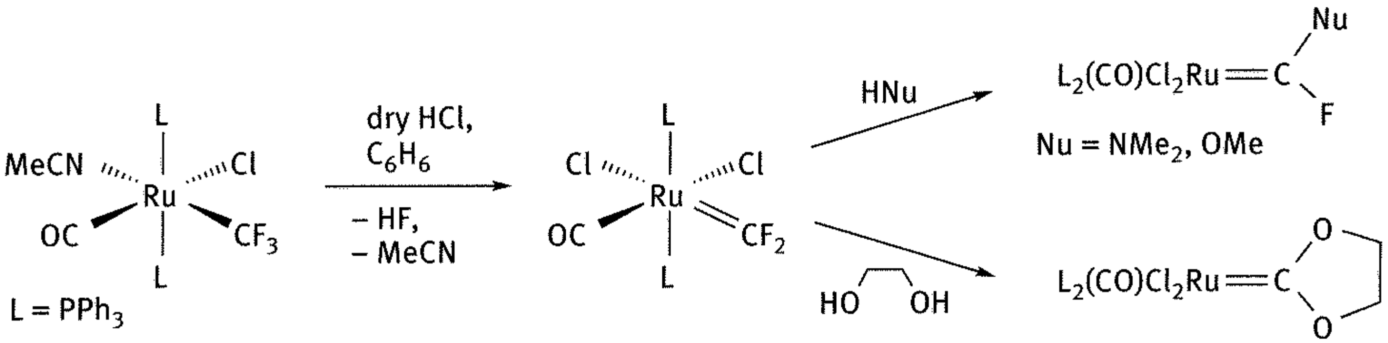
- Reaction of metal carbonyl anion with iminium salt to give heteroatom free carbene complexes



- From activated olefins



- From dihalocarbenes by halide substitution



$$Ru(CO)(PPh_3)_3 + CCl_4 \longrightarrow L_2(CO)Cl_2Ru{=}CCl_2$$

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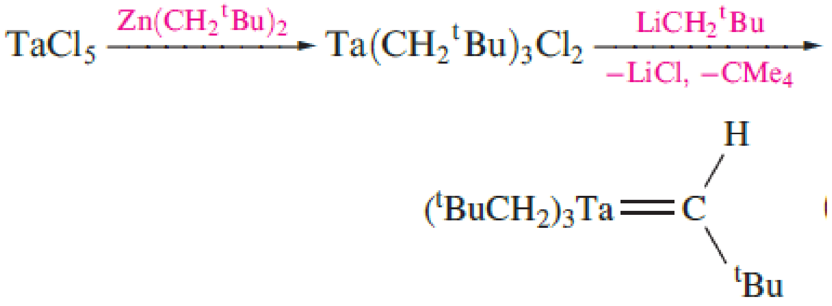
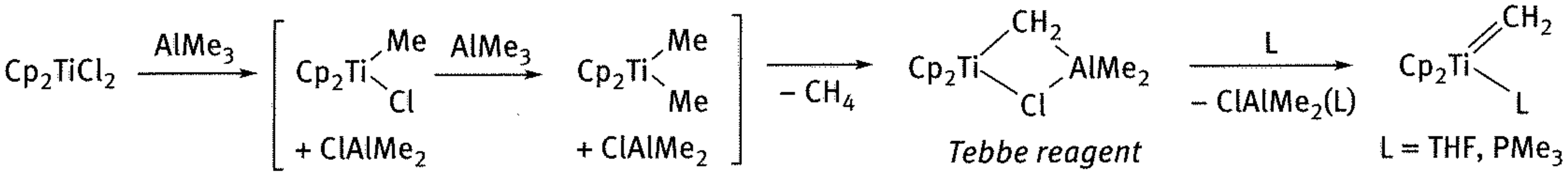
Preparation of Schrock complexes

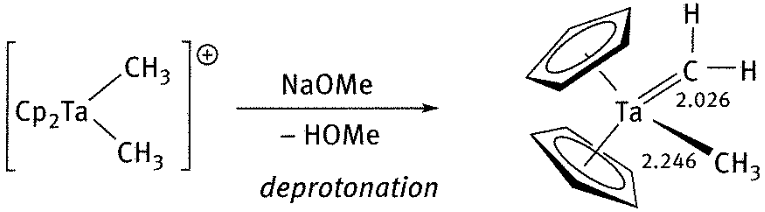
- Early d-block metal complexes with α-hydrogen atoms undergo α-hydrogen abstraction to yield carbene (alkylidene). Abstraction of a second α-hydrogen atom (if any) gives a carbyne complex

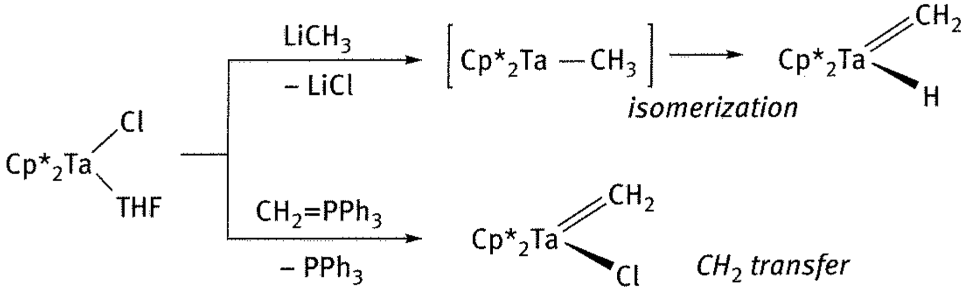


- Reaction of Cp_2TiCl_2 with $AlMe_3$ forms $TiCH_2$ complex, stabilized by complexation to Me_2AlCl (knows as Tebbe reagent (synthetic applications)

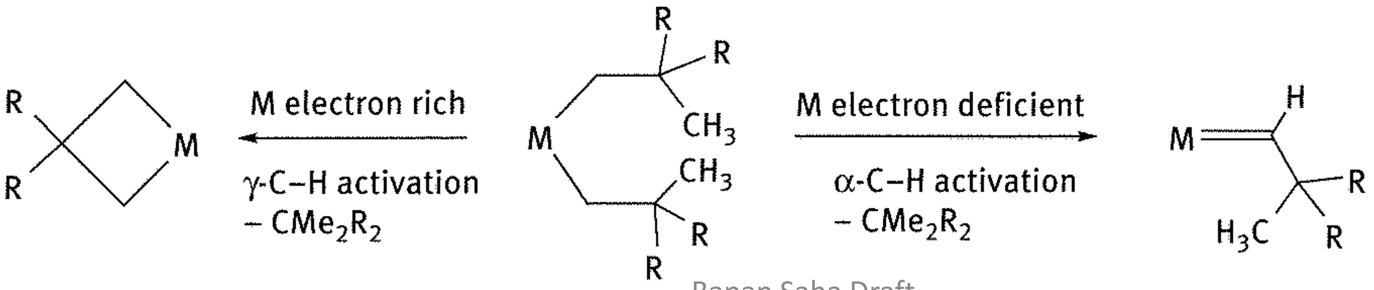


- Reaction of $[Cp_2TaMe_2]^+$ with NaOMe lead to deprotonation of one Me-ligand giving a methylene complex





- Electron rich noble metal complexes under sterically congested conditions tend to form metallacycles by γ-C-H activation, early transition metals undergo α-H abstraction to give M=CHR species



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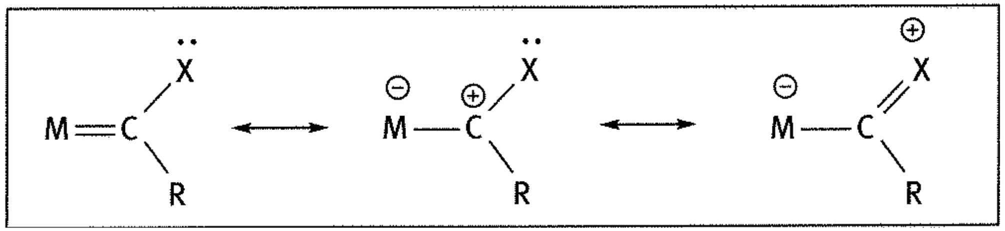
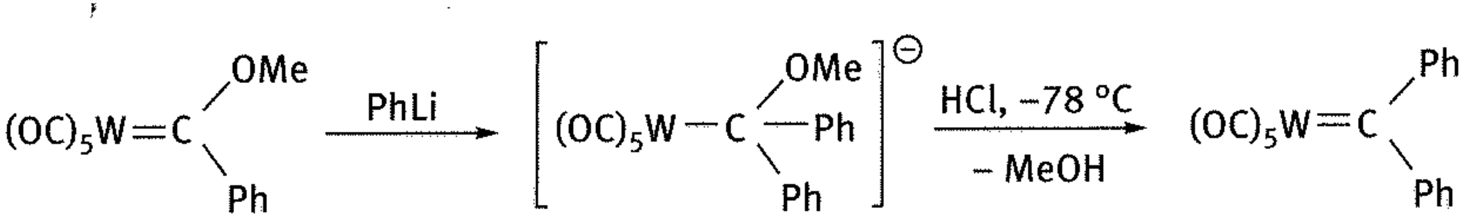
Reactions of carbene complexes

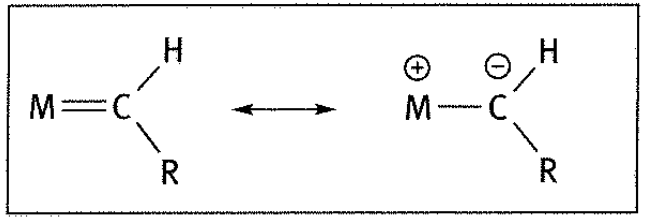
- **Reactions with electrophiles:** Alkylidene complexes of the type LnM=CR_2 is similar to ketones O=CR_2 and ylide (Wittig) $R_3P=CR_2$ and hence undergo reactions that are similar to ketones and ylides.
- **Reactions with Bronsted acids:** Alkylidene complexes reacts with Bronsted acids, leading to interconversion of alkylidene to alkylidyne and vice versa
- **Alkylidene transfer:** Alkylidene ligands undergoes intermolecular exchange reactions
- **Alkylidene-alkyl coupling reaction:** Alkylidene ligands react with nucleophiles either intra or intermolecularly to give new C-C bond (Fischer-Troposch reaction)
- **Reactions with alkynes:** Reaction of alkylidenes with unsaturated organic molecules is exploited in organic synthesis (insertion and cyclization)
- **Tebbe reagent:** It is the protected form of the unstable $Cp_2Ti=CH_2$, undergoes reactions complementary to ylides.
- Ability of alkylidenes to form metallacycles, used in olefin metathesis and in formation of alkylidene bridged heteronuclear metal clusters.

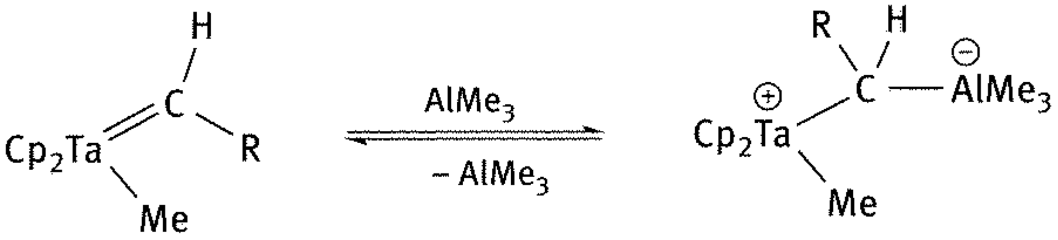
- Fishers' carbene (nucleophilic attack), can be described by the following resonance forms, which show the role of the heteroatom as electron pair donor





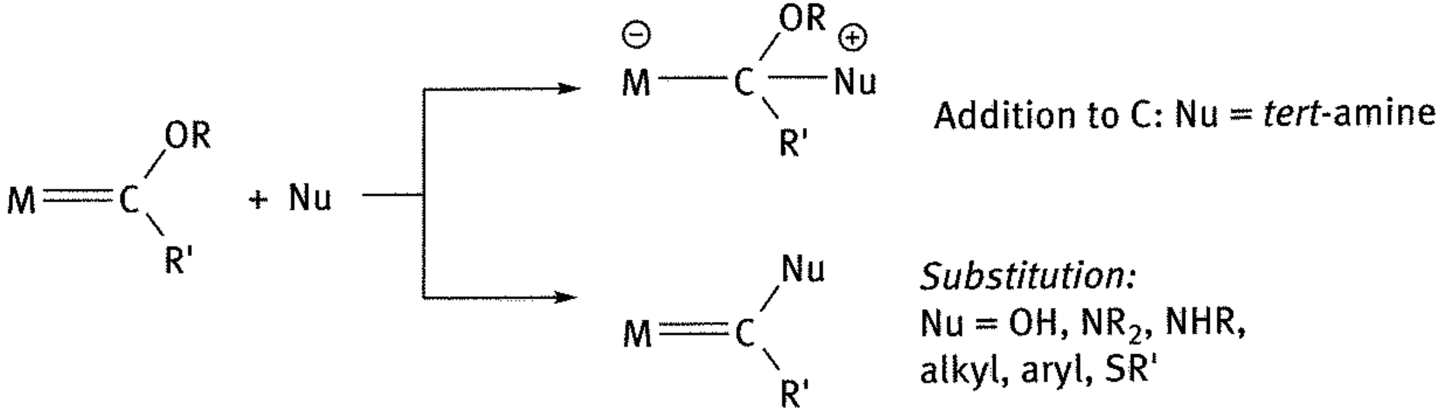
- Schrock-type carbenes (electrophilic attack), with the above two resonance pair giving a bonding description



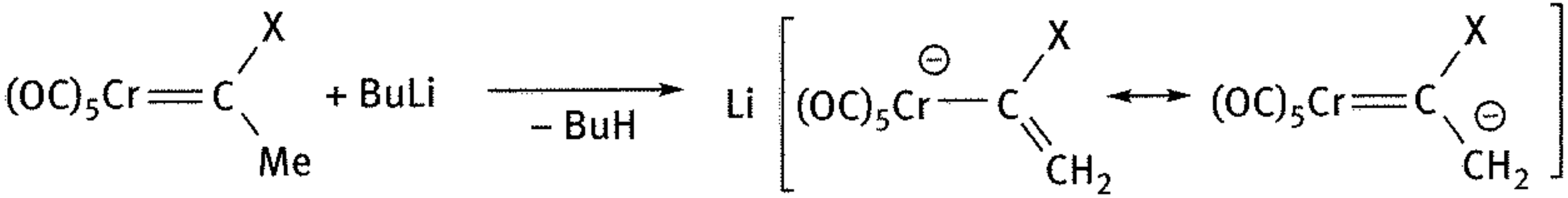


- The M=C bonds are longer than typical MC_{CO} bonds, but shorter than MC single bonds. This implies some degree of (d–p)π-character (indicated by resonance).

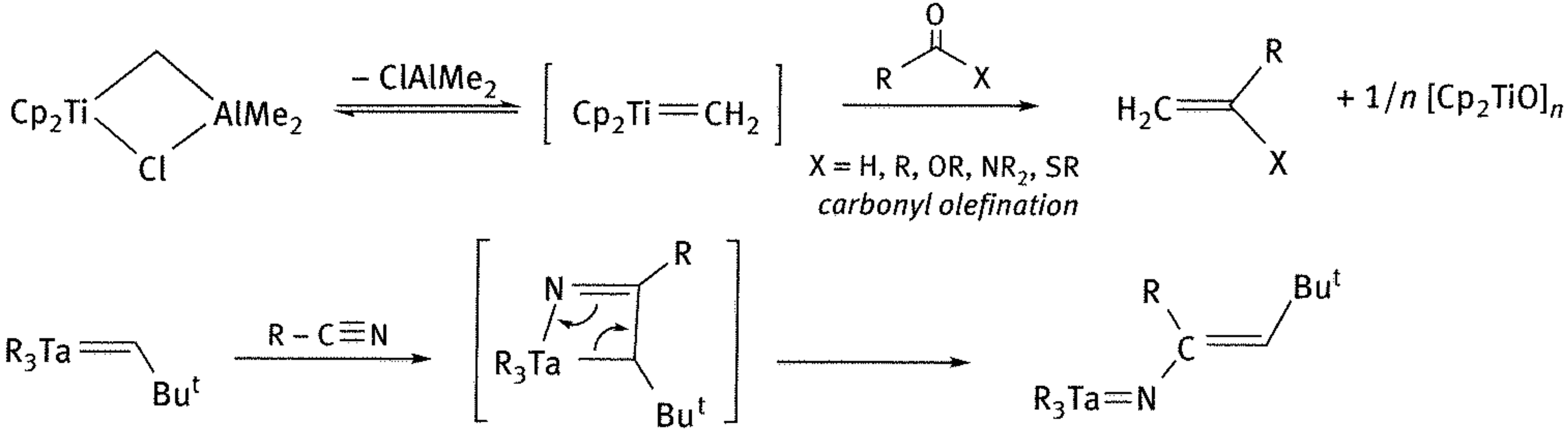
- Fischer carbenes primarily show nucleophilic substitution at the carbene-C and carbene transfer (cyclopropanation)



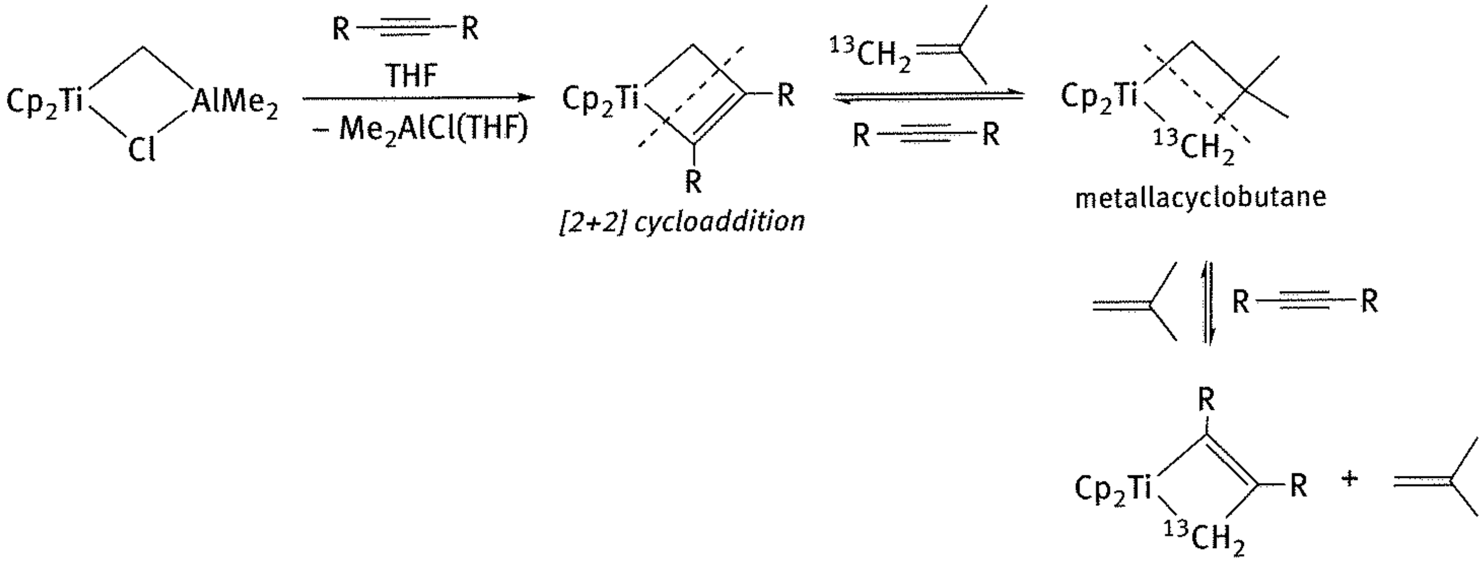
- Lithium alkyls may also deprotonate methyl substituted carbenes to give nucleophilic metal carbonyl metal enolate anions



- Alkylidene complexes of early transition metals (d^0) can act like Wittig reagents and convert C=O functions into olefins. Other hetero-alkenes and alkynes also give products where M=C bond is replaced by M-heteroatom bonds

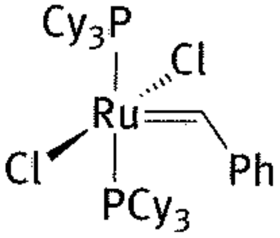


- More important however are [2+2] cycloadditions to give metallacycles: the basis of olefin metathesis reactions. (Tebbe reagent) (details you see from 300-303 olefin mathethsis

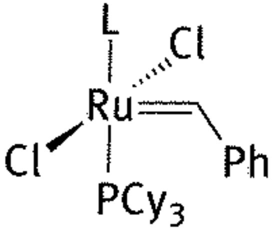


Ruthenium carbene

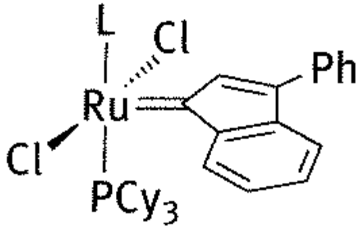
- Ru complexes $L_2Cl_2Ru{=}CHR$ (L= donor ligand) form a large family of alkene metathesis complexes, widely used in organic synthesis
- Another type of catalyst is based on benzylidene ligands with ortho ether substituents



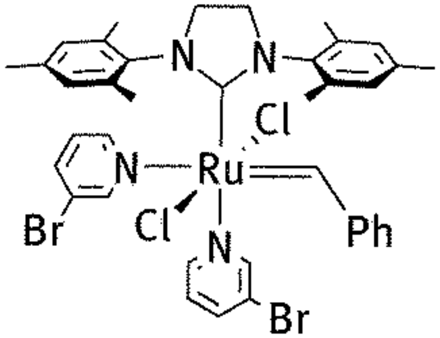
Grubbs 1st generation



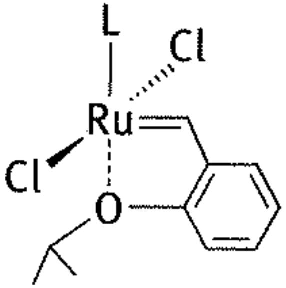
Grubbs 2nd generation



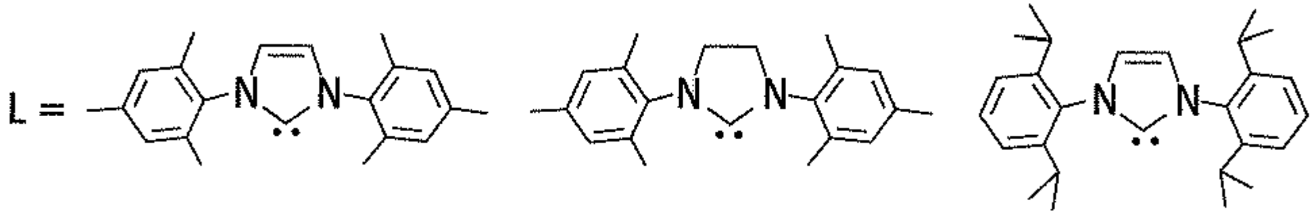
Ru indenylidene



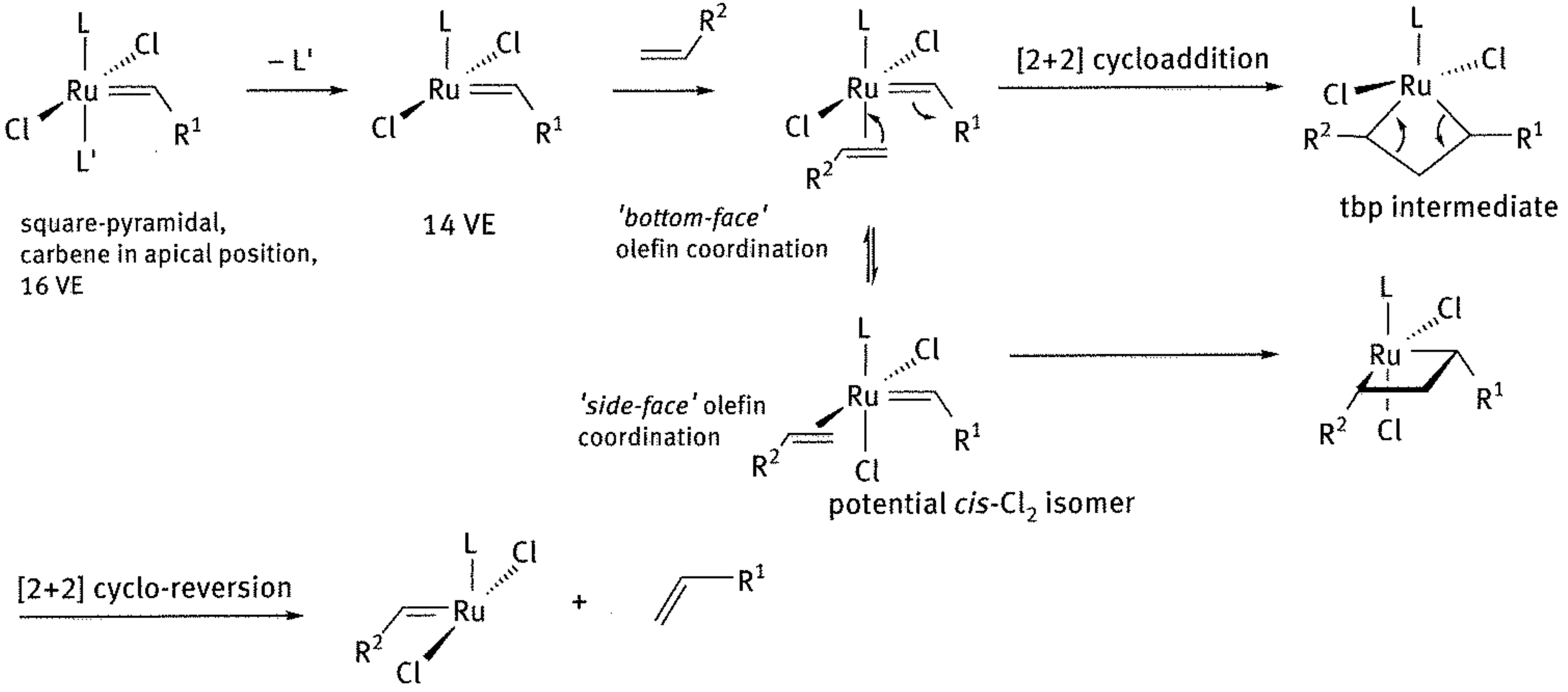
Grubbs 3rd generation



Hoveyda, Blechert



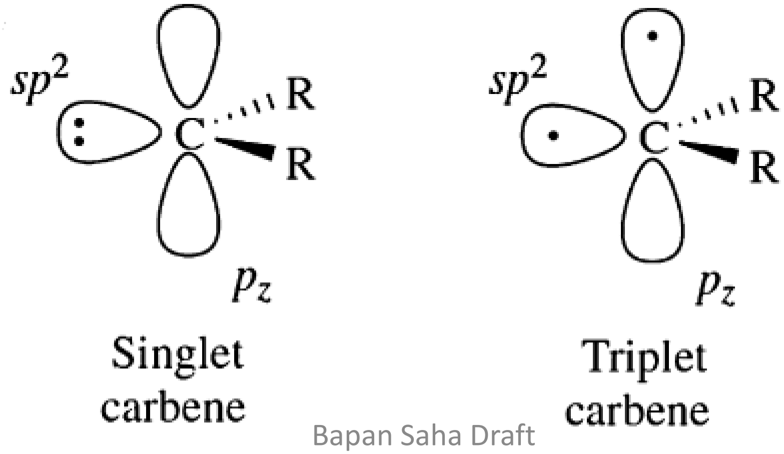
- The reaction with olefins follows the [2+2] cyclo addition pathway, proceeds via trigonal bipyramidal structure
- Stereochemistry of intermediates and transition states are influenced by the ligands and the reaction medium



- *Olefin metathesis: Details see from books*

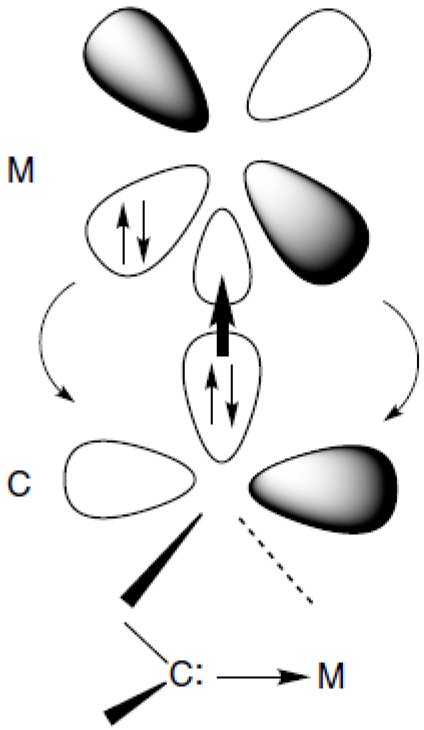
Types of Carbene

- Carbene C-atom has six electrons with two different structural arrangements.
- Bent arrangement with the two groups ($4e^-$), the two remaining electrons are paired and one empty p orbital, singlet carbene (S=0, Fischer carbene).
- C-electron pair of singlet carbene is suitable for M-L σ- bond formation. Empty p-orbital accepts electron density from M and stabilizes the electron-poor C-atom
- Linear arrangement with the two groups ($4e^-$), the two remaining electrons are unpaired in two p orbitals, triplet carbene (S=1, Schrock carbene)

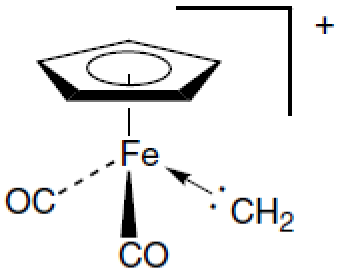


Bonding in carbene complexes

- The formal double bond in carbene is quite similar to that in alkenes.
- In carbene complex, the metal *d*-orbital forms a π-bond with carbene C-atom.
- The pair of electrons in the sp^2-orbital may be donated to a metal to form σ-bond, and an empty p_z-orbital is present to accept π-electron density
- Filled *d*-orbitals of the metal may donate electrons to p_z-orbital to give a M-C double bond.
- The M-C bond order is in between 1 and 2
- Each triplet carbene is housing an unpaired electron overlapping with two metal d-orbitals, each of which provides electron.



singlet carbene, L ligand



Pettit

$Fe^+ \leftarrow CH_2 \longleftrightarrow Fe{-}CH_2^+$

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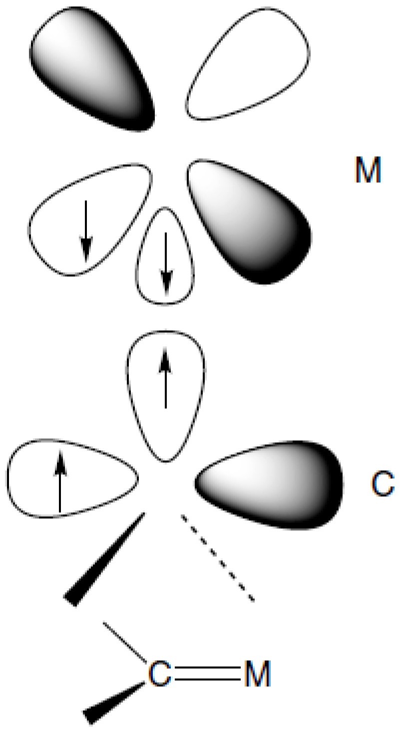
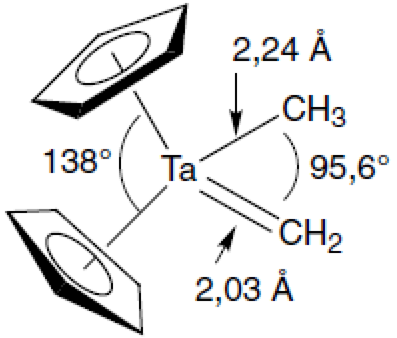
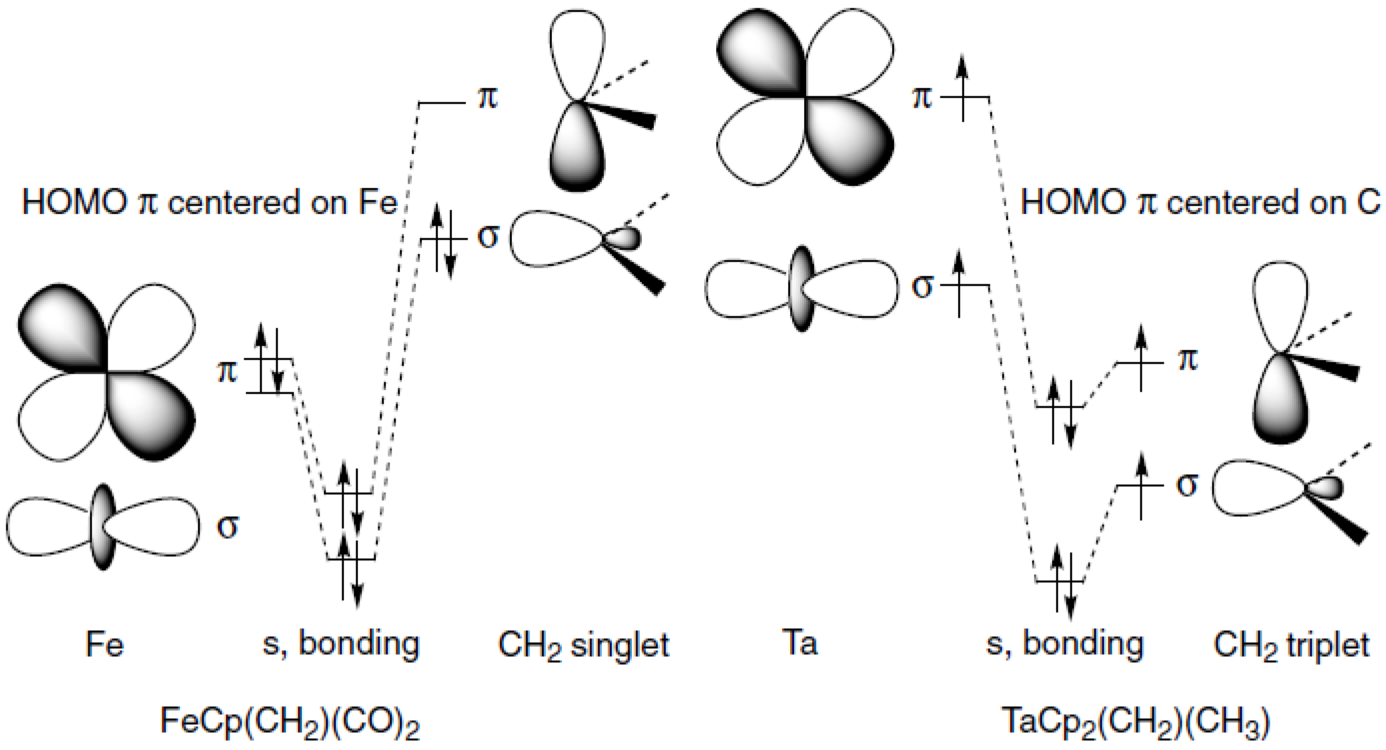


triplet carbene, X_2 ligand

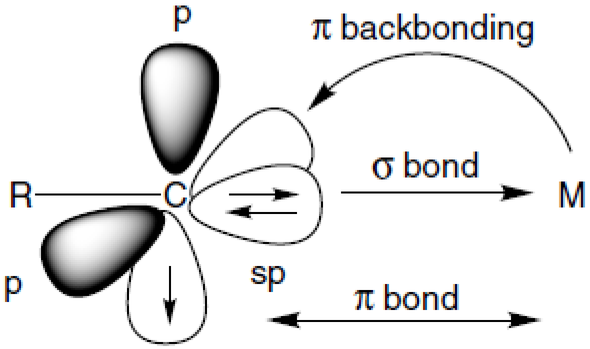


Schrock

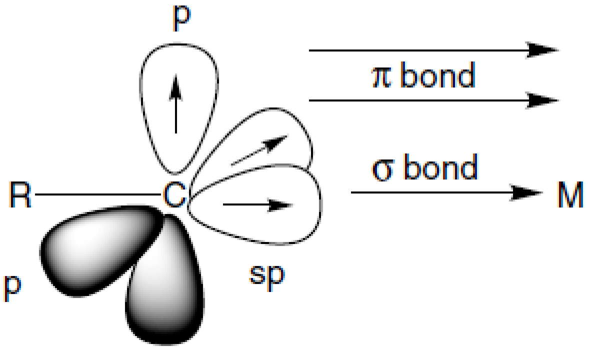
$Ta{=}CH_2 \longleftrightarrow Ta^+{-}CH_2^-$



Two methylene complexes of opposite polarities



Fischer carbyne (RC is a LX ligand)



Schrock carbyne (RC is a X_3 ligand)

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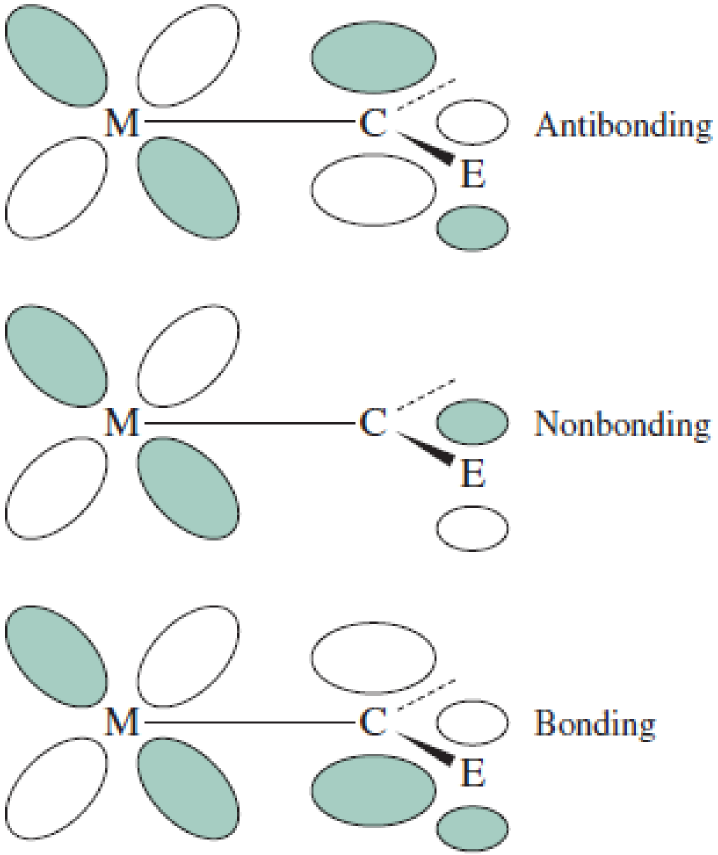
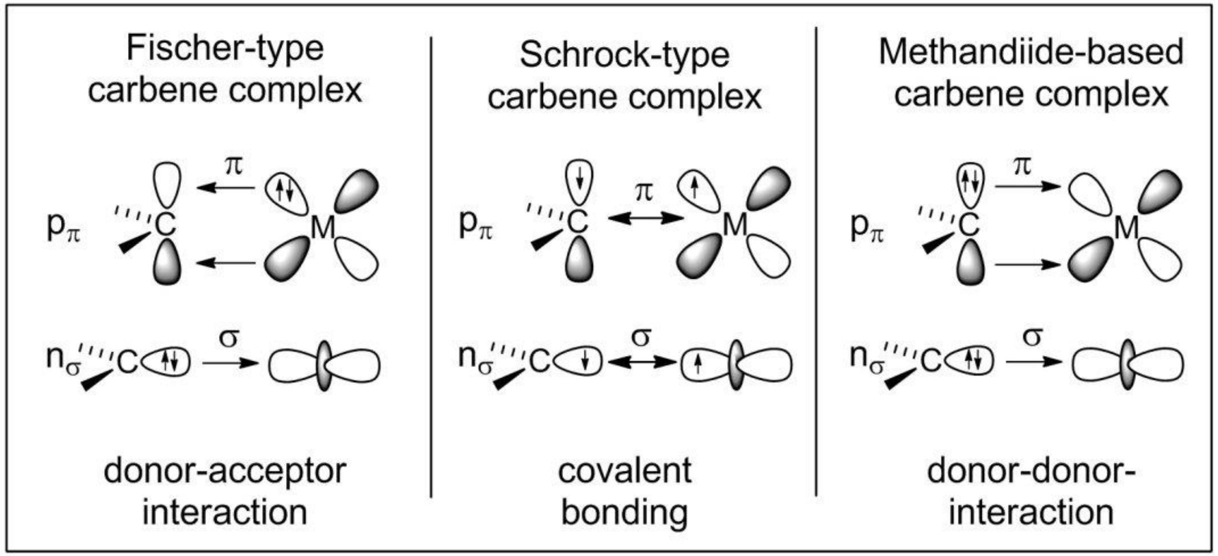
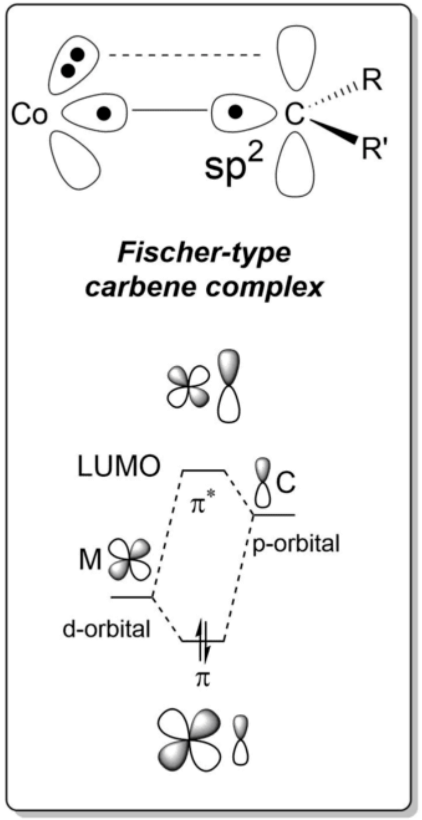
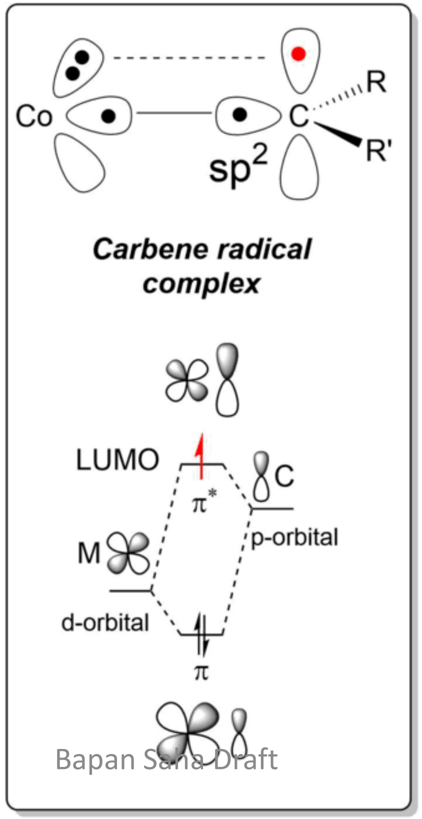
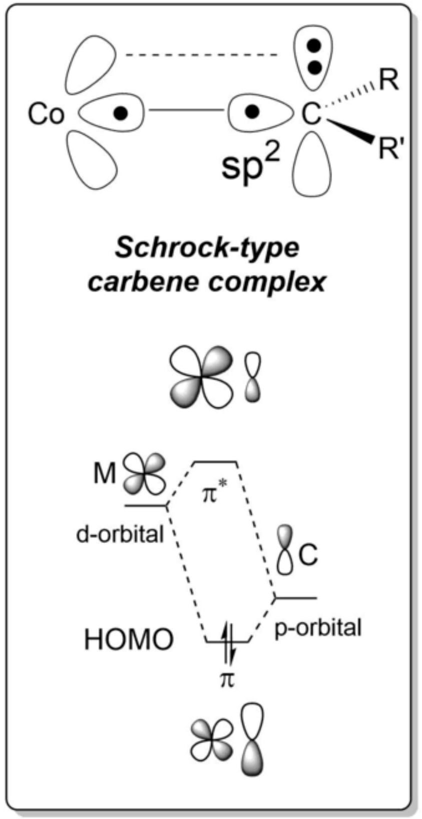


Delocalized Pi Bonding in Carbene Complexes, E = highly electronegative O, N, or S









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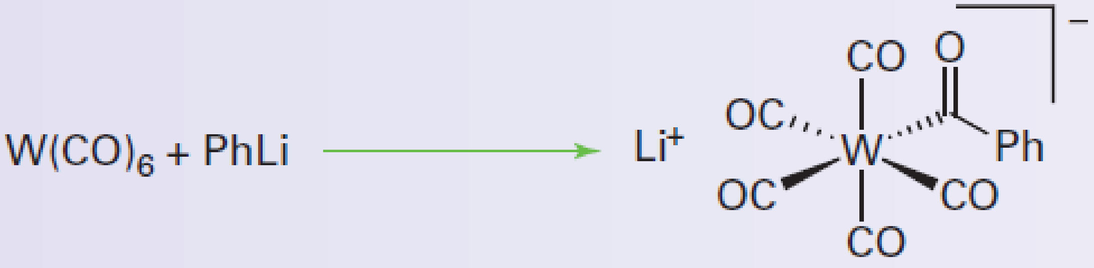
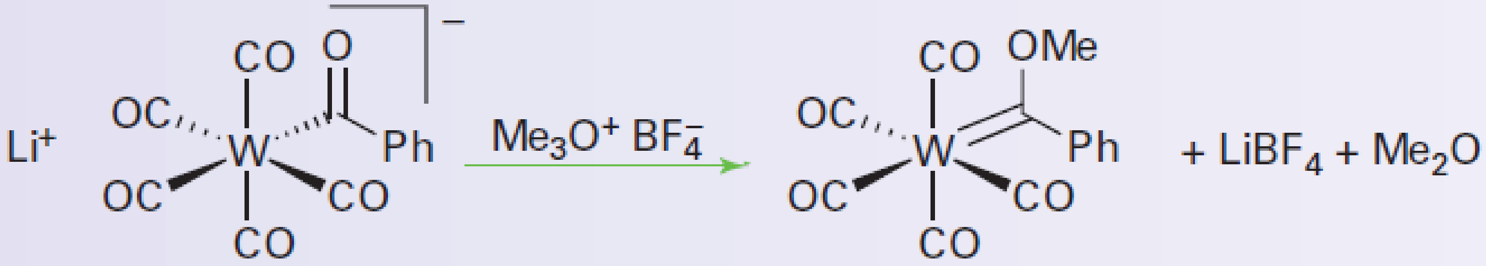
Propose a set of reactions for the formation of $[W(C(OCH_3)Ph)(CO)_5]$ starting with hexacarbonyltungsten(0) and other reagents of your choice.

Answer We know that CO ligands in hexacarbonyltungsten(0) are susceptible to attack by nucleophiles, and therefore that the reaction with phenyllithium should give a C-phenyl intermediate:

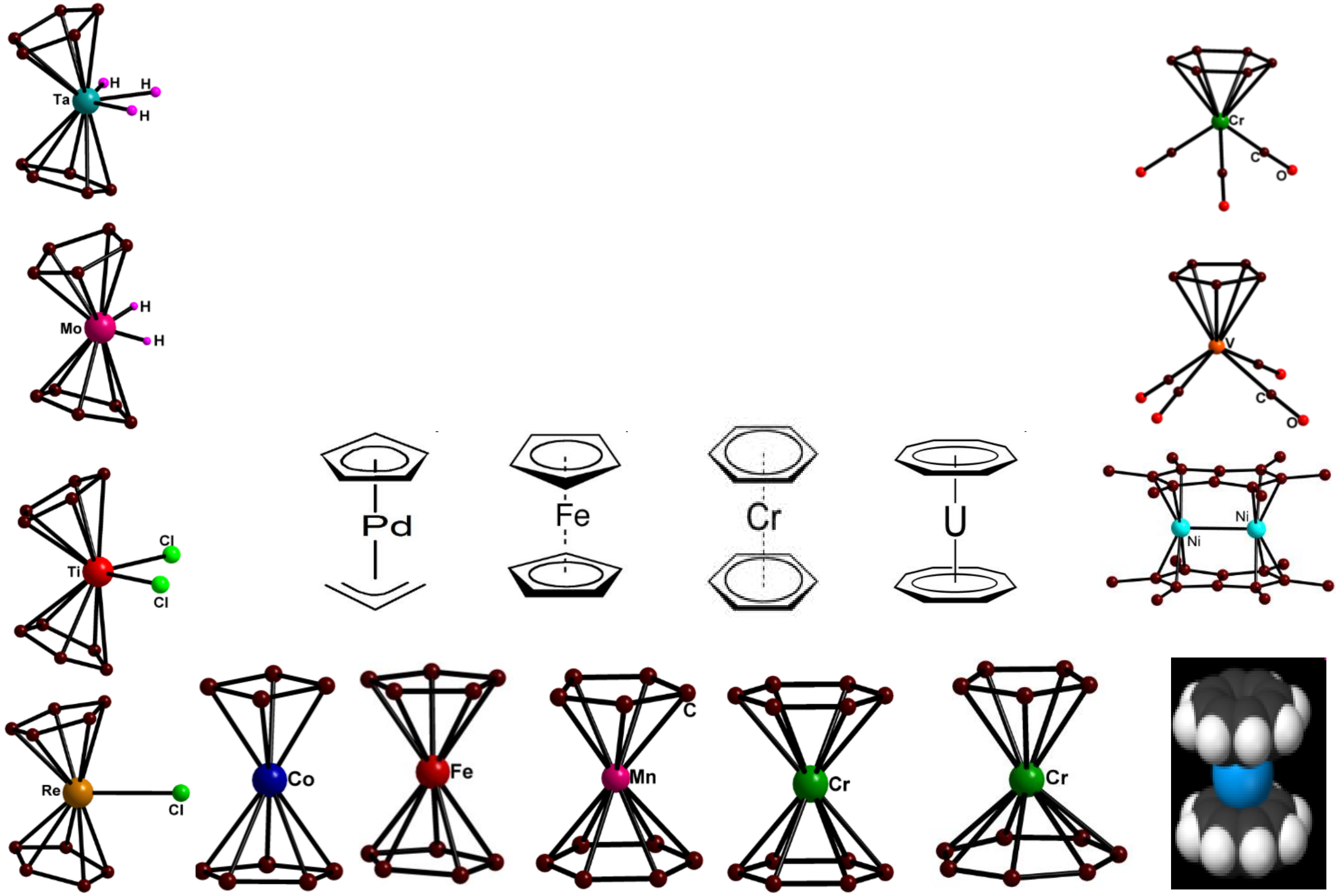


This anion can then react with a carbon electrophile to attach an alkyl group to the O atom of the CO ligand:



Self-test 22.6 Propose a synthesis for $[Mn(COCH_3)(CO)_4(PPh_3)]$ starting with $[Mn_2(CO)_{10}]$, PPh_3, Na, and CH_3I.

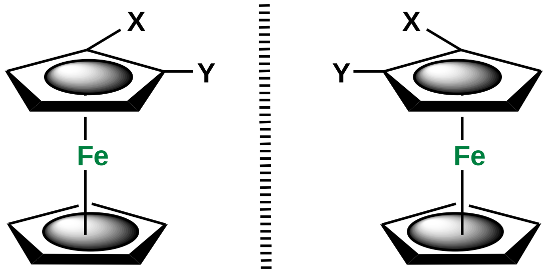
Metal- Sandwich compounds



Hapticity of sandwich compounds varies from 1-8

Why metal – sandwich compounds are important?

- Transition metal/metal ion embedded inside an organic matrix: Makes a metal ion soluble even in hydrocarbon solvents. E.g. ferrocene is soluble in hexane while Fe^{2+} as such is not. Outcome: a hydrocarbon soluble additive/catalyst
- Coordination to an electropositive metal often changes the reactivity and electronic properties of the π system bound to it (benzene vs ferrocene)
- A sterically protected metal site where a wide range of catalytic applications are possible such as alkene polymerization
- Metal sandwich compounds are excellent substrates to make planar chiral compounds. Applications as chiral catalysts in asymmetric catalysis



Non- super-imposable mirror images

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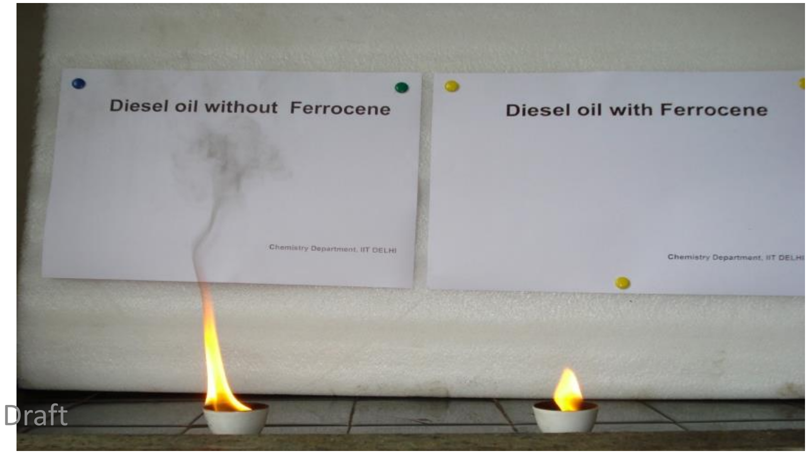


Metallocenes

- Bonding theory proposed to be in between a metal and π-orbitals of ligand.
- Metallocene name come from their similarities with aromatic molecules.
- Cyclopentadienyl complexes are of three types viz. metallocene (MCp_2), bent metallocene with additional ligands [($Cp_2M(A)(B)(C)$] and half sandwich complexes $CpML_z$
- In metallocene, metal ions is sandwiched between two Cp rings, $(Cp)_2M$, 18e rule is not mandatory.
- All the C-C bond lengths in each of these bound ligands are identical, ligands are aromatic.
- The first metallocene to be discovered was ferrocene ($FeCp_2$) and also known V(II), Cr(II), Mn(II), Co(II) and Ni(II)
- **General method**: All except $(\eta^5\text{-}C_5H_5)_2V$ (VCl_3 is used), other 3d metal sandwiches can be prepared by treating MCl_2 with alkali metal cyclopentadienides

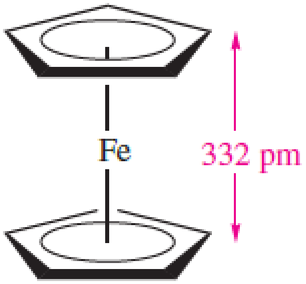
$$MCl_2 + 2\,Na^+Cp^- \xrightarrow[\text{Et}_2\text{O or THF}]{} MCp_2 + 2\,NaCl$$

$M = V, Cr, Mn, Fe, Co, Ni$

$$Ni(acac)_2 + 2\,CpMgBr \xrightarrow[\text{Et}_2\text{O}]{} NiCp_2 + 2\,MgBr(acac)$$

Ferrocene

- $(Cp)_2Fe$ is the best-known cyclopentadienyl complex
- It is a diamagnetic, orange solid (MP 393 K) and obeys 18-electron rule
- In the gas phase, the two cyclopentadienyl rings are eclipsed
- The structure of $(\eta^5\text{-}C_5H_5)_2Fe$ in the solid state, originally believed to be staggered
- Now it is viewed to be nearly eclipsed with rotational angle of 9° between the Cp rings.
- In case of substituted Cp rings, the barrier to rotation is higher, and staggered orientation is favored in gas and solid phase.



Preparation

- The Fe(III) is first reduced by the Grignard reagent to Fe(II) which then reacts to form ferrocene

$$Fe^{3+} \xrightarrow{CpMgX} Fe^{2+} \xrightarrow{CpMgX} (n^5\text{-}C_5H_5)_2Fe$$

- Cyclopentadiene itself is acidic enough so that potassium hydroxide will deprotonate it in solution and then reaction with $FeCl_2$ leads to the formation of $(\eta^5\text{-}C_5H_5)_2Fe$

$$2KOH + 2C_5H_6 + FeCl_2 \xrightarrow{DMSO} Fe(C_5H_5)_2 + 2H_2O + 2KCl$$

- Alternatively., $(\eta^5\text{-}C_5H_5)_2Fe$ can be synthesized by

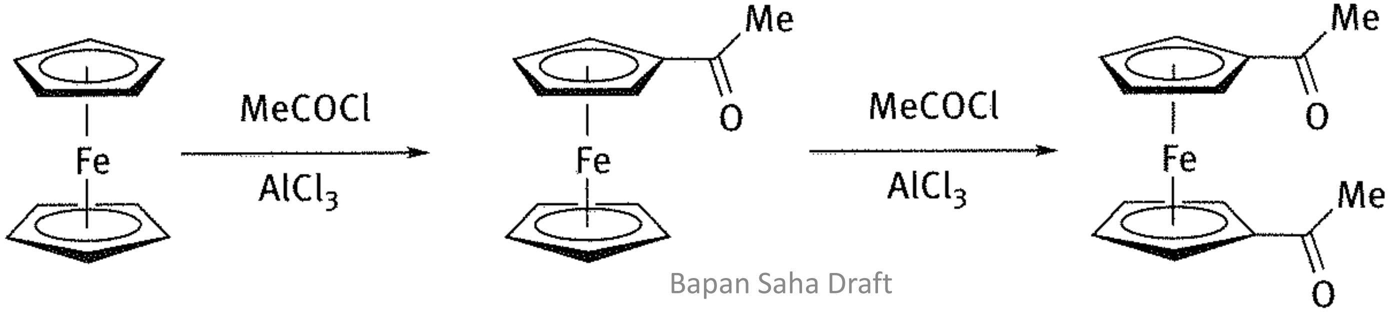
$$MCl_2 + 2C_5H_6 + 2Et_2NH \longrightarrow (\eta^5\text{-}Cp)_2M + 2[Et_2NH_2]Cl$$
$$(M = Fe, Ni)$$

Reactions of metallocene

- Electron deficient metallocenes will add ligands to gain a higher electron count
- Electron rich metallocenes are redox active and show reversible 1-e oxidations and reductions
- The reactivity of 18e metallocenes is dominated by modification of the Cp ligands, without affecting the metallocene structure itself
- Electron rich metallocenes show ligand exchange behavior to achieve an 18e configuration

- Protonation occurs at the Fe(II) center is indicated by the appearance of a signal at -2.1 ppm in the 1H NMR spectrum of $(\eta^5\text{-}C_5H_5)FeH^+$.

Friedel Crafts' acylation of ferrocene is even more facile than benzene: the name coined due to similarity with benzene



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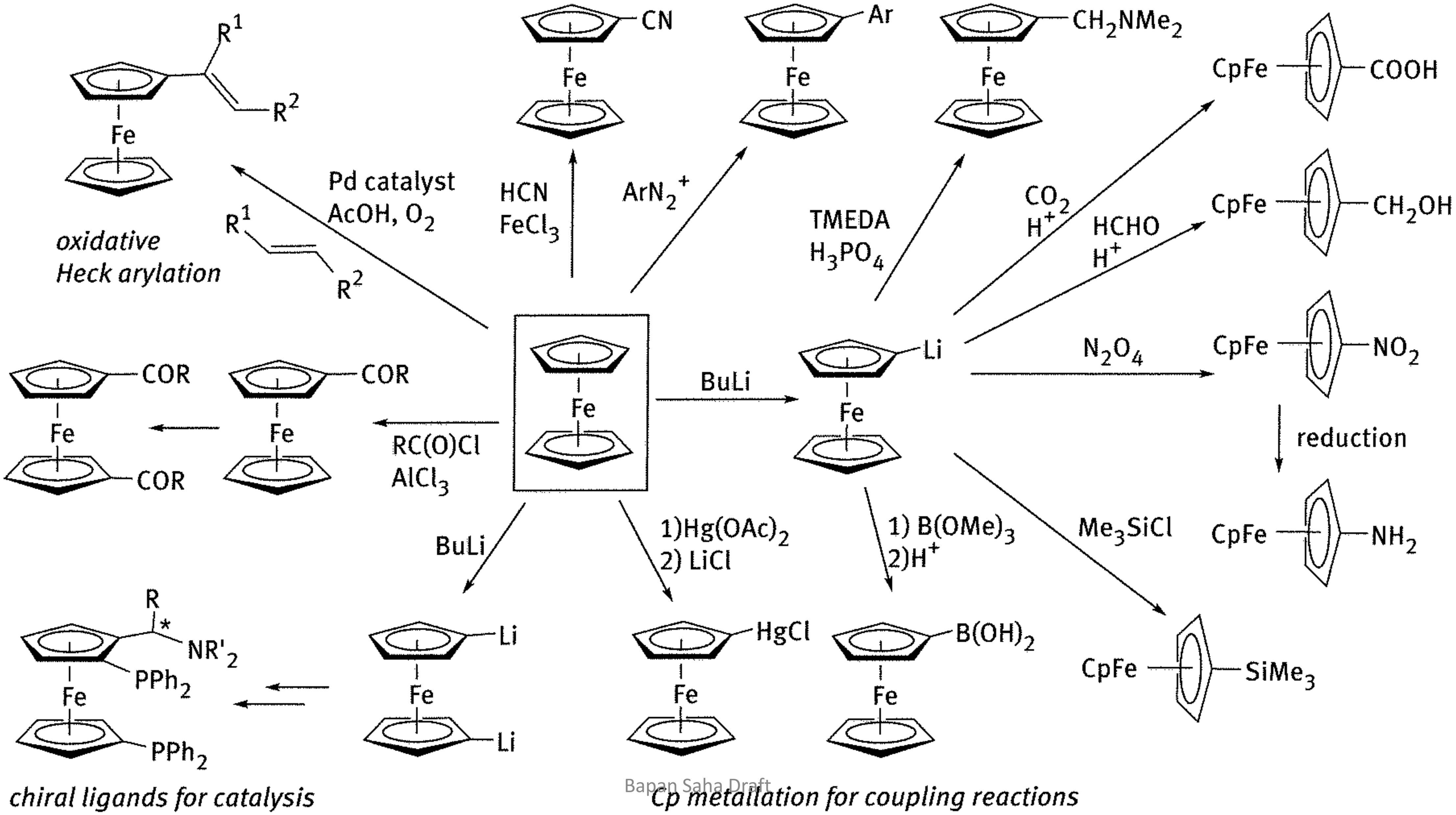
Reactions of ferrocene

- Substitution on the Cp ring



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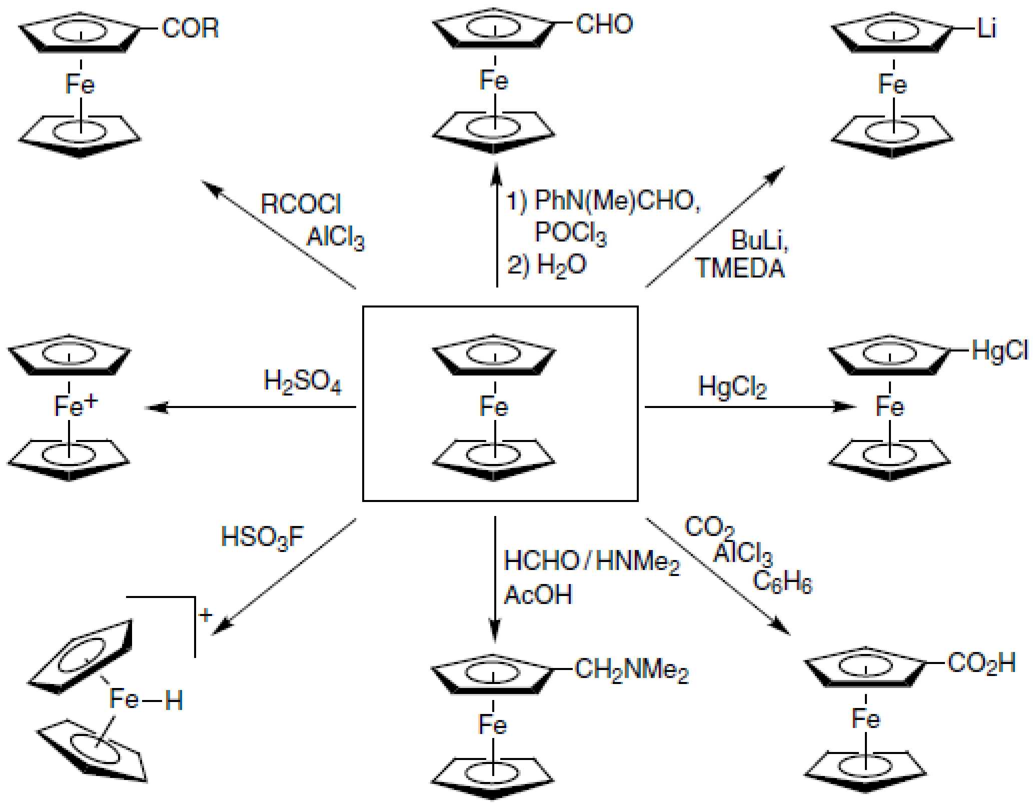
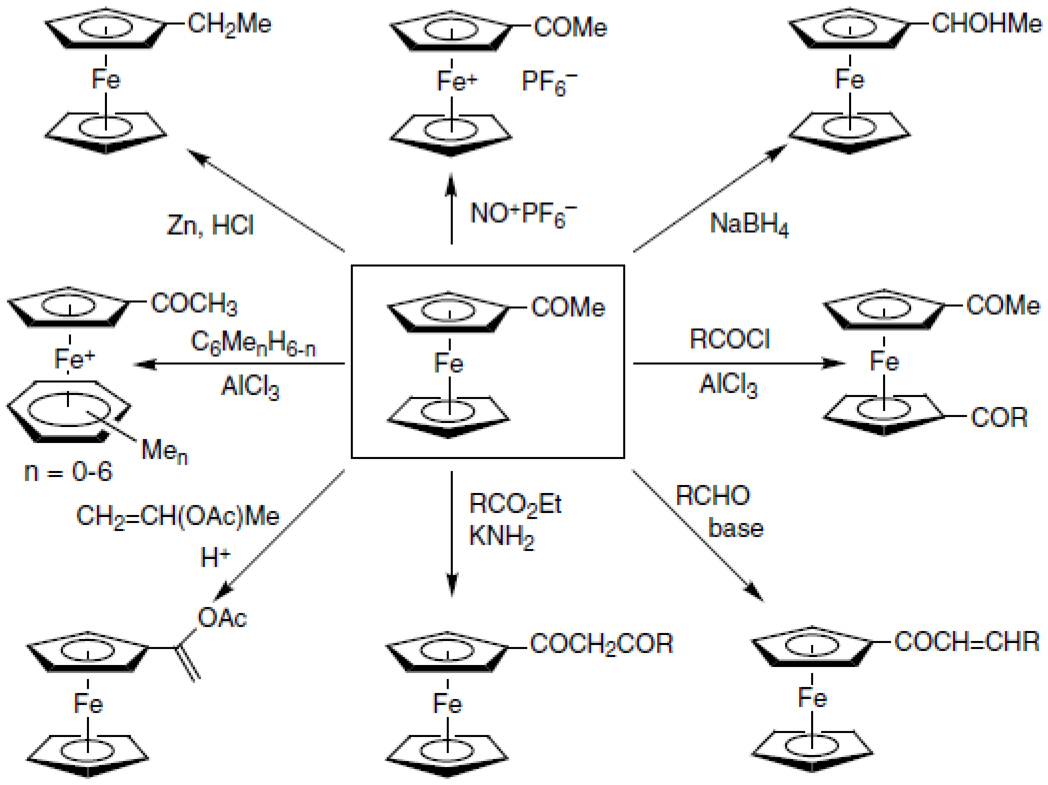
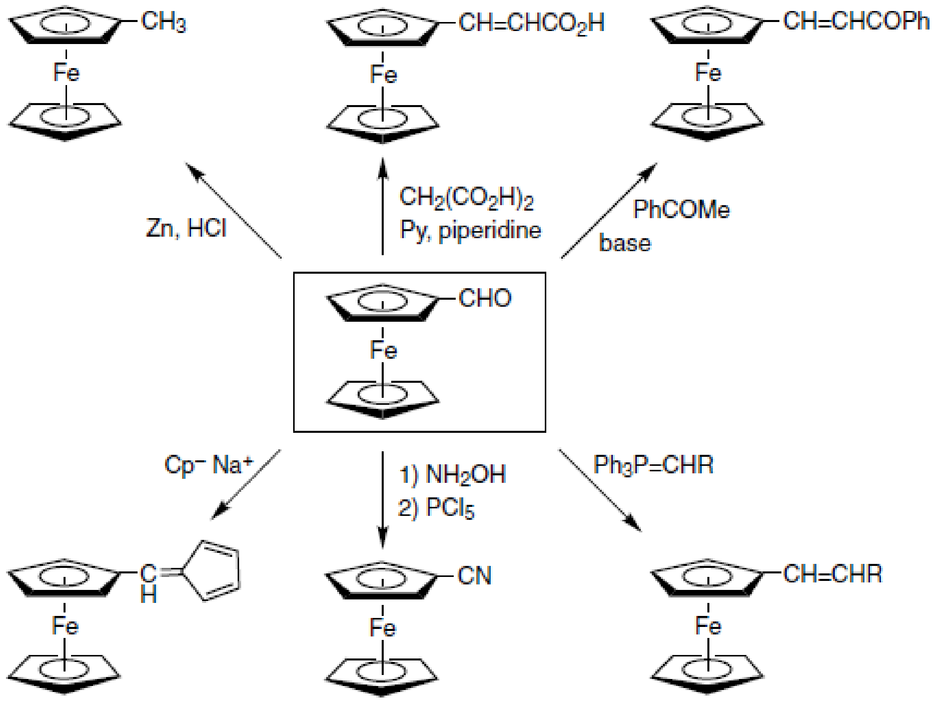
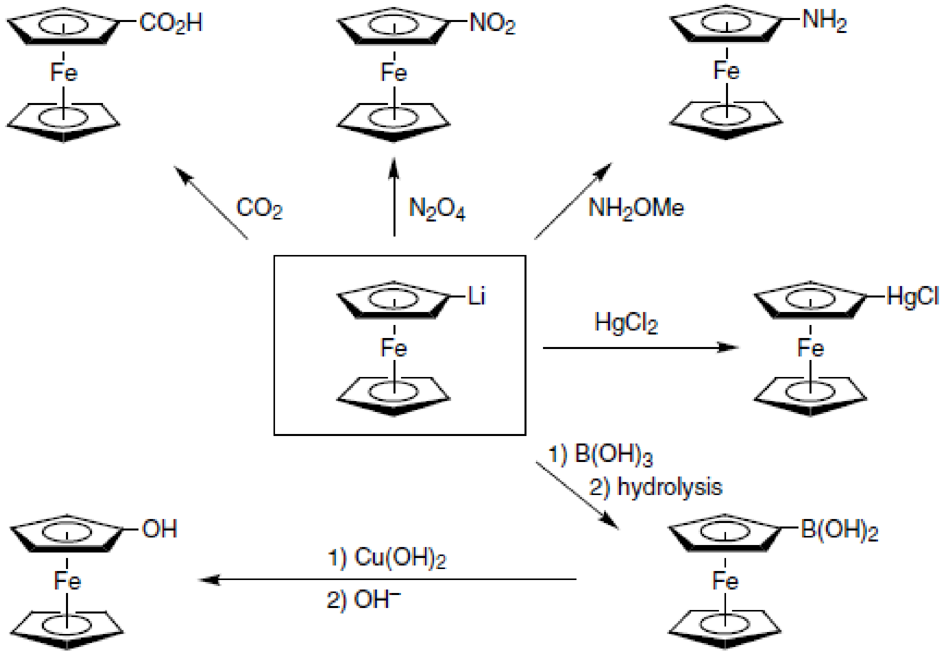
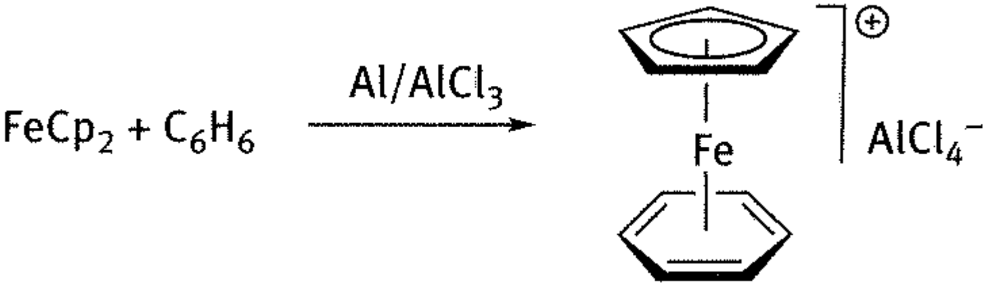

COR
Fe
RCOCl
AlCl3
CHO
Fe
1) PhN(Me)CHO,
POCl3
2) H2O
Li
Fe
BuLi,
TMEDA
Fe+
H2SO4
Fe
HgCl2
HgCl
Fe
HSO3F
+
Fe—H
HCHO / HNMe2
AcOH
CH2NMe2
Fe
CO2
AlCl3
C6H6
CO2H
Fe


CH2Me
Fe
Zn, HCl
COMe
Fe+
PF6−
NO+PF6−
CHOHMe
Fe
NaBH4
COCH3
Fe+
Men
n = 0-6
C6MenH6-n
AlCl3
COMe
Fe
RCOCl
AlCl3
COMe
Fe
COR
CH2=CH(OAc)Me
H+
OAc
Fe
RCO2Et
KNH2
COCH2COR
Fe
RCHO
base
COCH=CHR
Fe

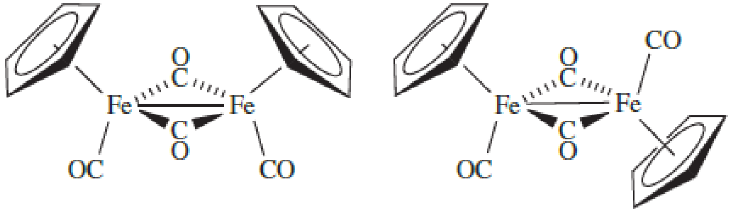

CH3
CH=CHCO2H
CH=CHCOPh
Fe
Zn, HCl
CH2(CO2H)2
Py, piperidine
PhCOMe
base
CHO
Cp⁻ Na⁺
1) NH2OH
2) PCl5
Ph3P=CHR
C
H
CN
CH=CHR


CO2H
NO2
NH2
Fe
CO2
N2O4
NH2OMe
Li
HgCl2
HgCl
1) B(OH)3
2) hydrolysis
OH
1) Cu(OH)2
2) OH⁻
B(OH)2

- A general method for exchanging one Cp ring in ferrocene by an arene is the treatment of $FeCp_2$ with a mixture of the arene, $AlCl_3$ and Al-powder to give corresponding cationic mixed ligand sandwich complex (18-electron center).



- Reactions between metal carbonyls and cyclopentadiene usually yield mixed ligand complexes, e.g. $Fe(CO)_5$ reacts with C_5H_6 to give $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$. Two isomers viz. cis and trans have been confirmed in solid state with Fe-Fe distance of 253 pm (Fe-Fe single bond, 18 electrons)



cis-isomer *trans*-isomer

- In solution at 298 K, both the cis- and trans-forms are present and the terminal and bridging ligands exchange by an intramolecular process

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- The dimer $(\eta^5\text{-Cp})_2Fe_2(CO)_4$ is commercially available and is a valuable starting material in organometallic chemistry. Reactions with Na or halogens cleave the Fe-Fe bond giving useful organometallic reagents which are exemplified below.

$$(\eta^5\text{-Cp})_2Fe_2(CO)_4 + 2Na \longrightarrow 2Na[(\eta^5\text{-Cp})Fe(CO)_2]$$

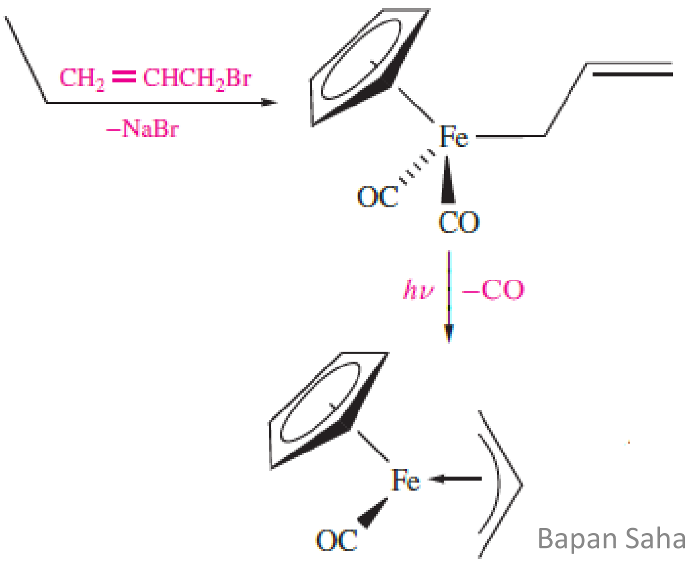
$$(\eta^5\text{-Cp})_2Fe_2(CO)_4 + X_2 \longrightarrow 2(\eta^5\text{-Cp})Fe(CO)_2X$$

$$X = Cl, Br, I$$

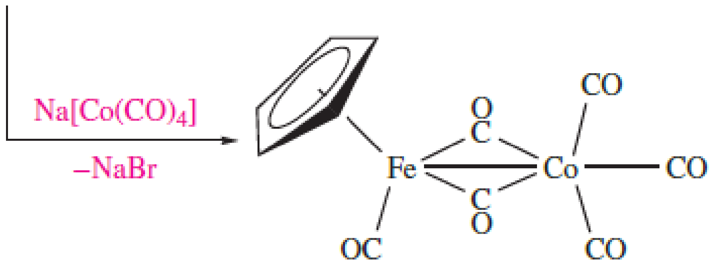
$$Na[(\eta^5\text{-Cp})Fe(CO)_2] + RCl \longrightarrow (\eta^5\text{-Cp})Fe(CO)_2R + NaCl$$

e.g. R = alkyl

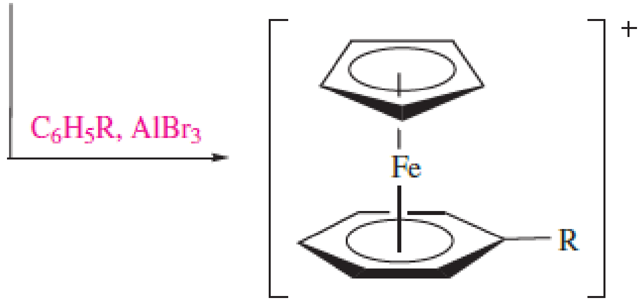
$Na[(\eta^5\text{-Cp})Fe(CO)_2]$



$(\eta^5\text{-Cp})Fe(CO)_2Br$



$(\eta^5\text{-Cp})Fe(CO)_2Br$



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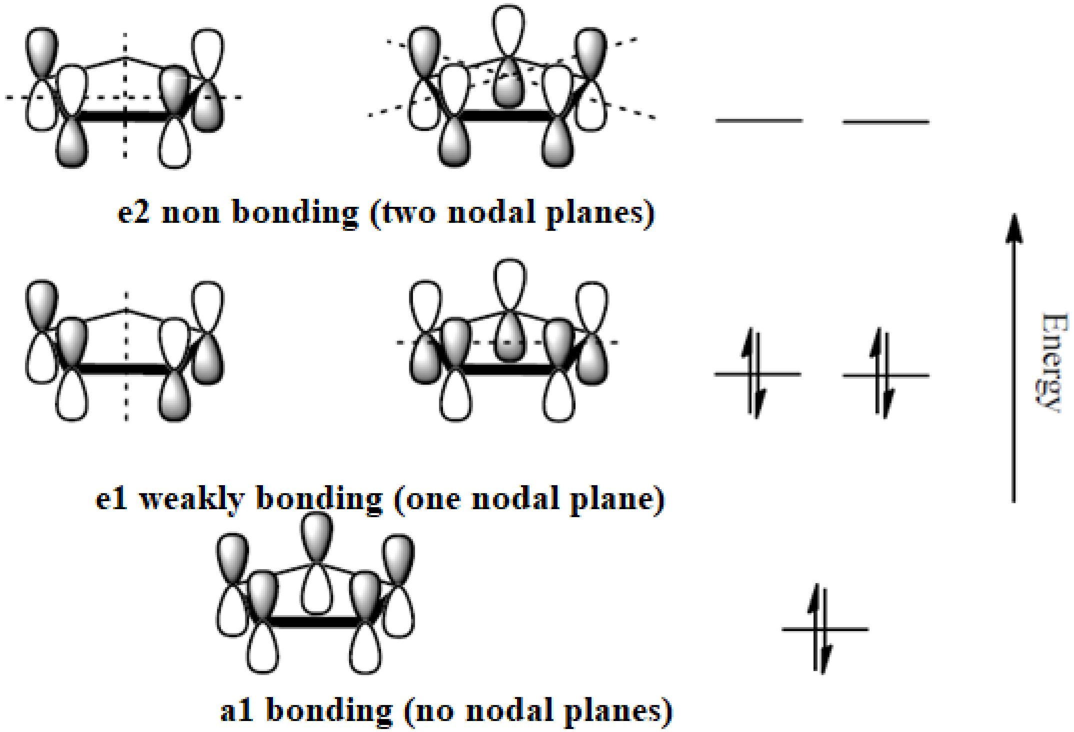
Structure and bonding in Ferrocene (early 1950s)

- The two cyclopentadienyl (Cp) rings of ferrocene may be orientated in the two extremes of either an eclipsed (D_{5h}) or staggered (D_{5d}) conformation
- Ground state structures of ferrocene may be either D_{5h} or D_{5d} (energy barrier of rotation about Fe-Cp axis is very small)
- The primary orbital interactions occur between d-orbitals of Fe and π-orbitals of the Cp ligand
- The D_{5d} point group representations simplify the symmetry matching of ligand molecular orbitals and metal atomic orbitals.
- In D_{5d} symmetry, there is a center of symmetry and there will be centro-symmetric (g) and anti-symmetric (u) combinations
- The five p-orbitals on the planar Cp^- ring (D_{5h} symmetry) can be combined to produce five molecular orbitals.

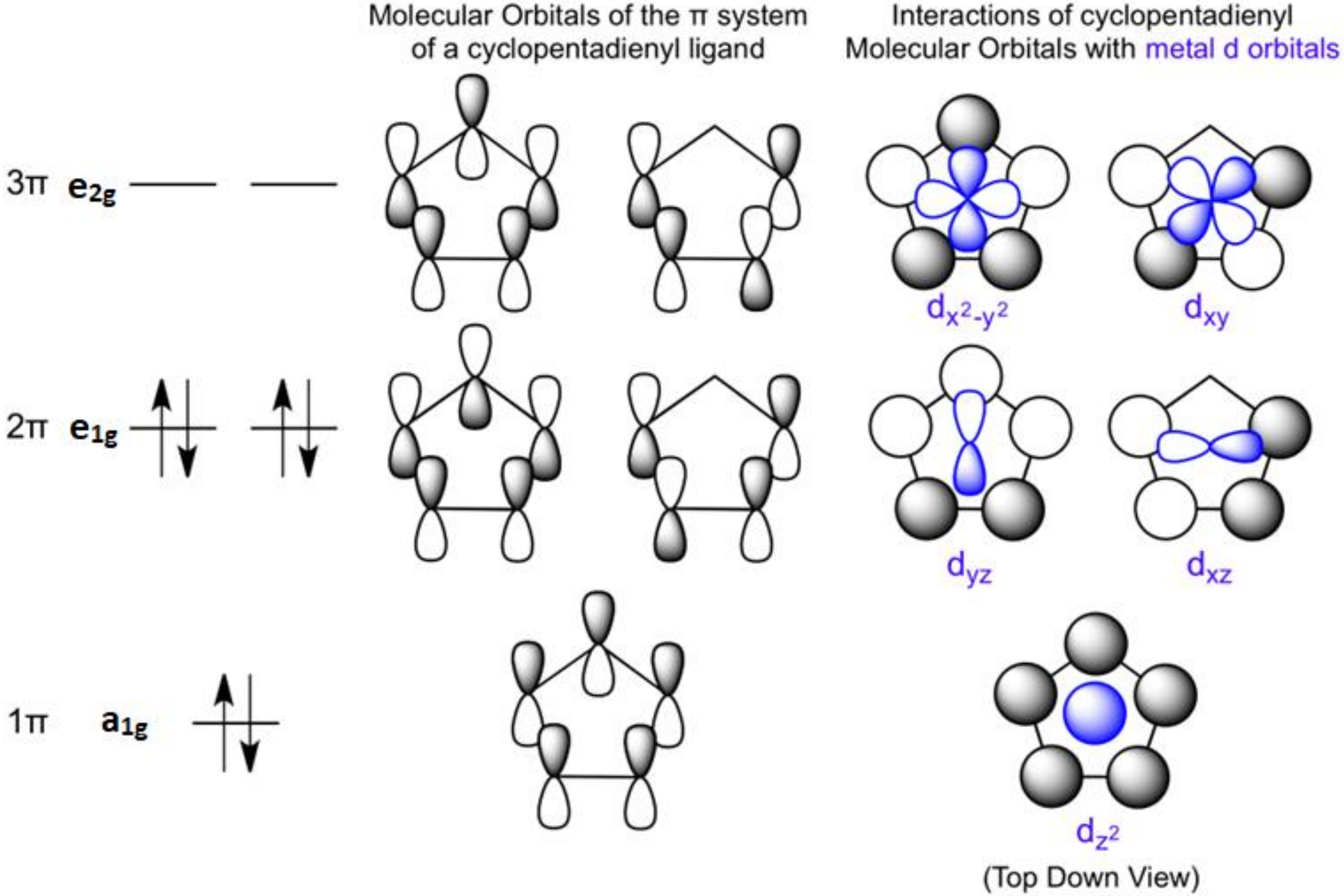
- For (η^5-Cp)$_2$M, such as ferrocene, the π-orbitals of the two Cp ligands are combined pairwise to form the symmetry-adapted linear combination of molecular orbitals (SALC's), resulting in three different Ligand Group Orbitals (LGOs)

1. A low lying filled bonding pair of *a*1g and *a*1u symmetry
2. A filled weakly bonding pair of *e*1g and *e*1u symmetry
3. An empty anti-bonding pair of *e*2g and *e*2u symmetry.

- Metal orbitals of suitable symmetry interact with SALC orbitals and give MOs of (η^5-Cp)$_2$Fe.



The π-molecular orbitals of the cyclopentadienyl ring (D_{5h})



- a_{1g} (σ) orbitals are very stable & interact very little, poor σ-donor
- Only e_{1g} orbitals of ligand matches with 3d orbitals (dyz, dzx) that form two strong π-bonds
- e_{2g} (π) orbitals are very high in energy & interact and interact little, poor π-acceptor

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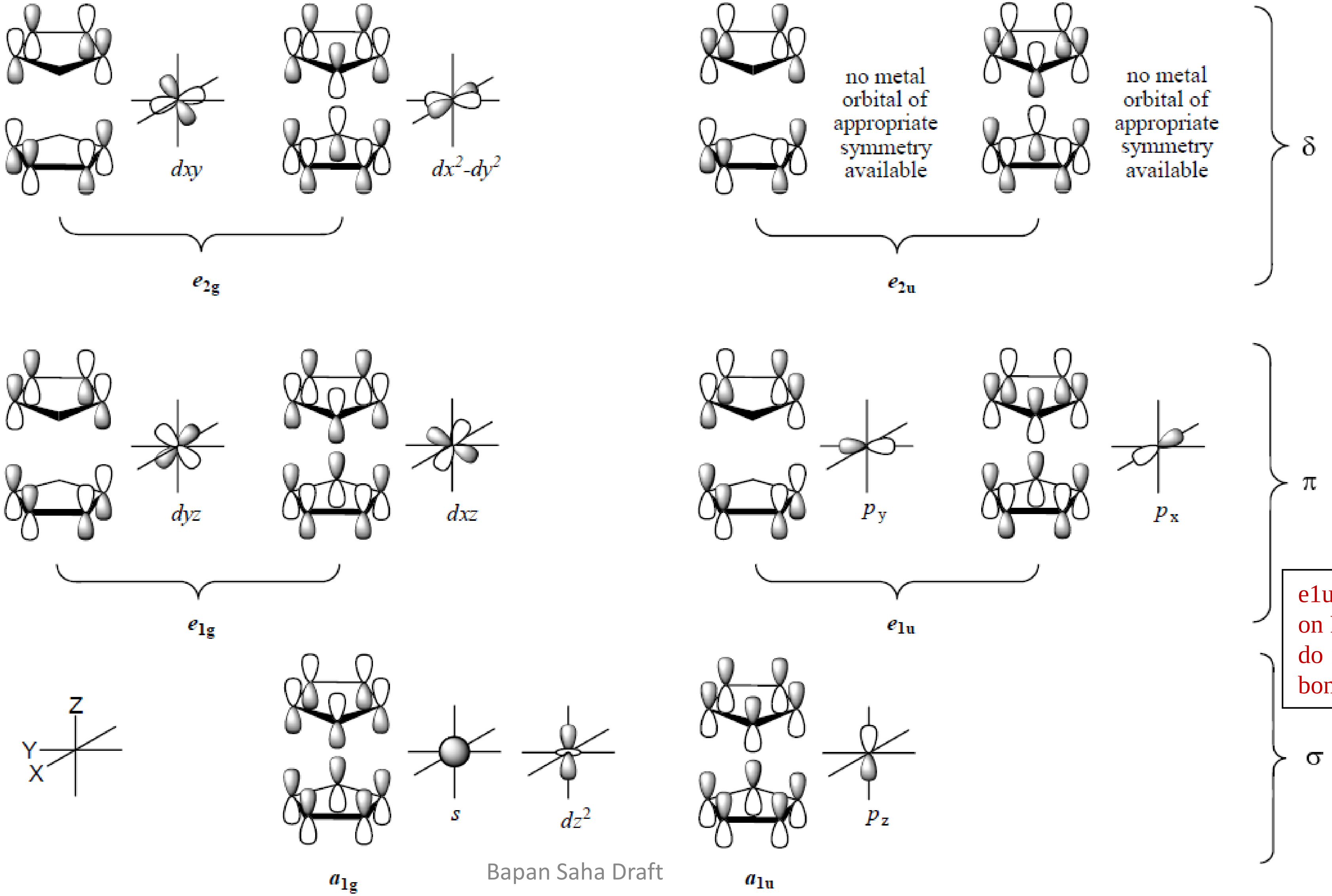
- Metal orbitals of suitable symmetry interact with SALC orbitals and give MOs of (η^5-Cp)$_2$Fe.

Symmetry matching of SALC orbitals with the metal atomic orbitals



e2g (π) orbitals are very high in energy & interact and interact little, poor π-acceptor.

Only e1g orbitals of ligand matches with 3d orbitals (dyz, dzx) that form two strong π-bonds

a1g (σ) orbitals are very stable & interact very little, poor σ-donor

e1u and a2u (4p) orbitals on Fe are at a high energy, do not contribute much to bonding

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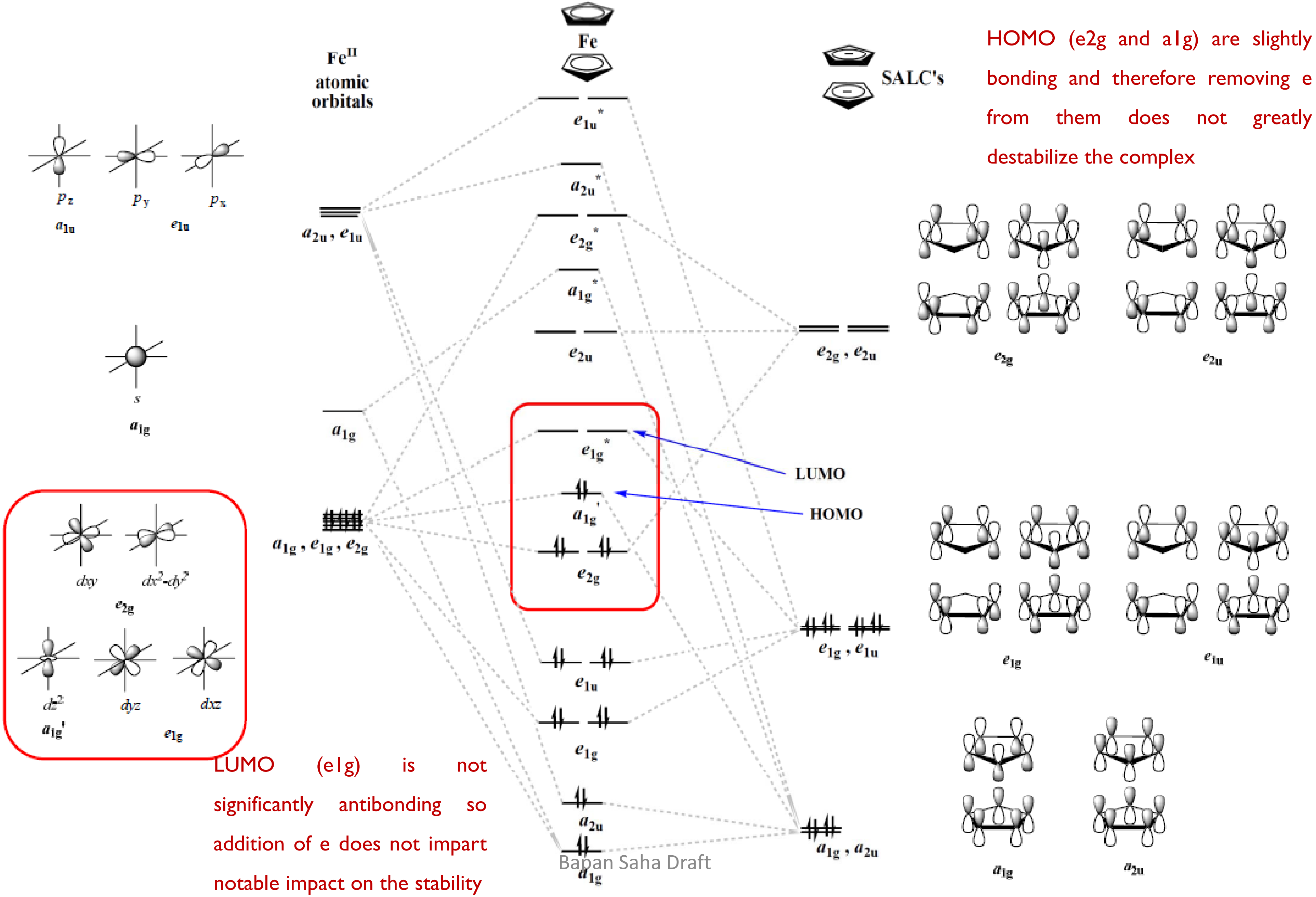
A qualitative molecular orbital diagram for ferrocene (D_{5d})



HOMO (e2g and a1g) are slightly bonding and therefore removing e from them does not greatly destabilize the complex

LUMO (e1g) is not significantly antibonding so addition of e does not impart notable impact on the stability

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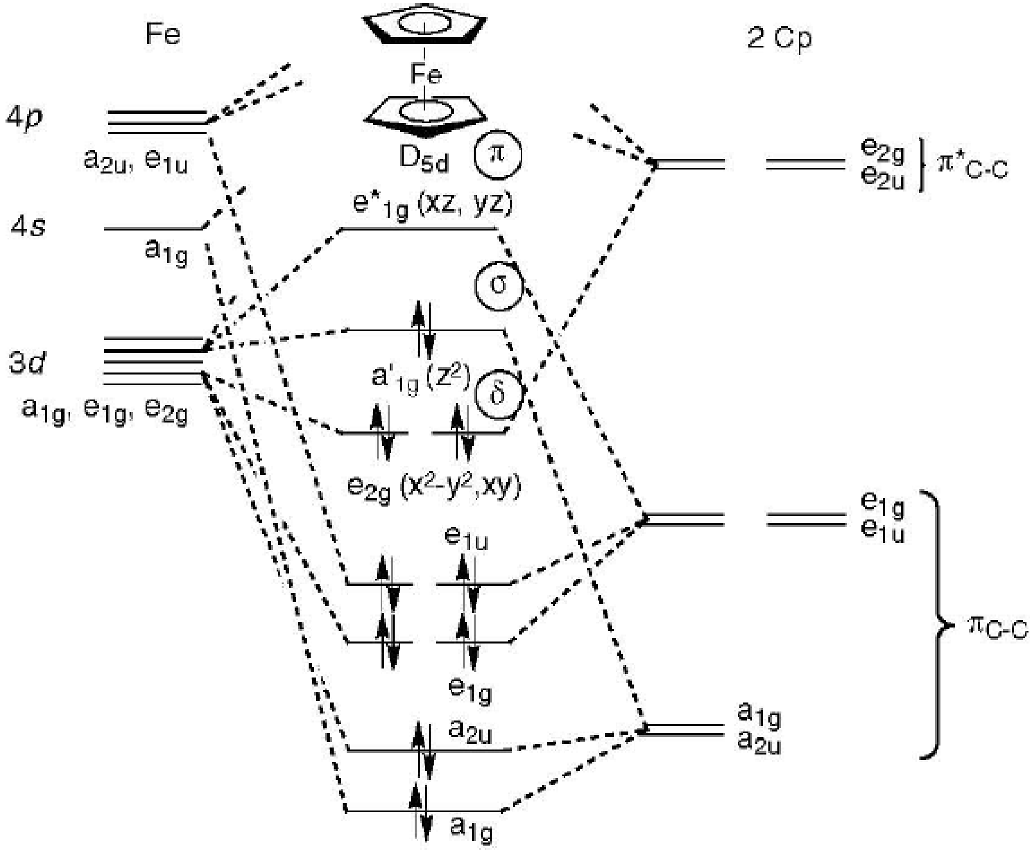

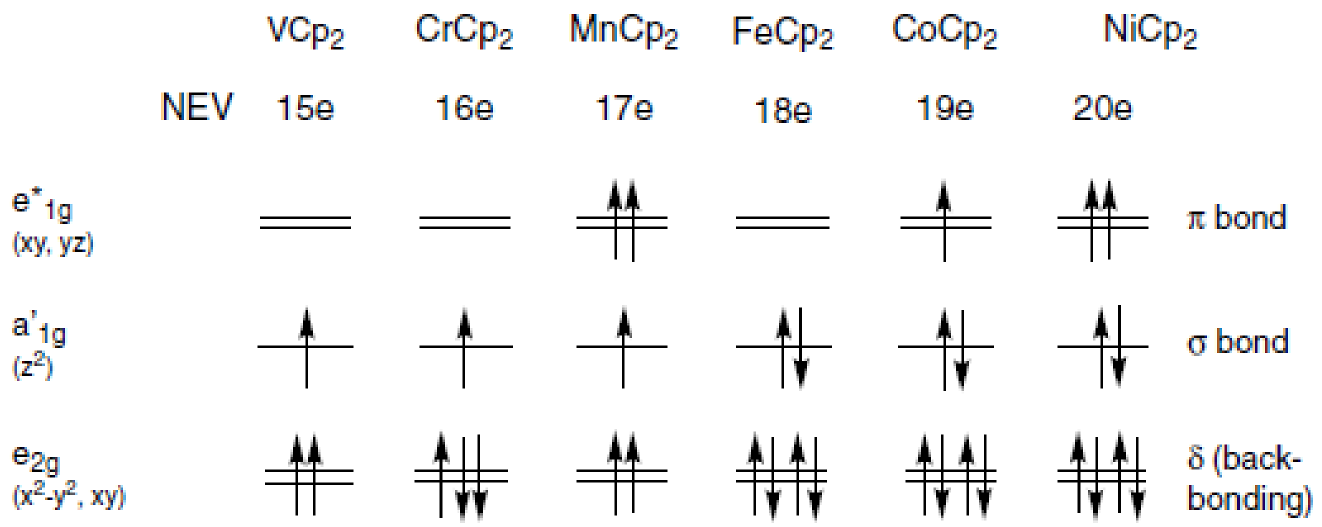

	VCp_2	$CrCp_2$	$MnCp_2$	$FeCp_2$	$CoCp_2$	$NiCp_2$
NEV	15e	16e	17e	18e	19e	20e
unpaired electrons (n)	3	2	5	0	1	2
$\sqrt{n(n+2)}$	3.87	2.83	5.92	0	1.73	2.93
$\mu(\mu_B)$ exper.	3.84	3.20	5.81	0	1.76	2.86
color	purple	scarlet	brown	orange	purple	green

Electronic structure (see the MO diagram of ferrocene), theoretical magnetic moment ($\mu = \sqrt{n(n+2)}\,\mu_B$), n being the number of unpaired electrons, experimental magnetic moment in μ_B = Bohr magnetons, and color of neutral metallocenes MCp_2.

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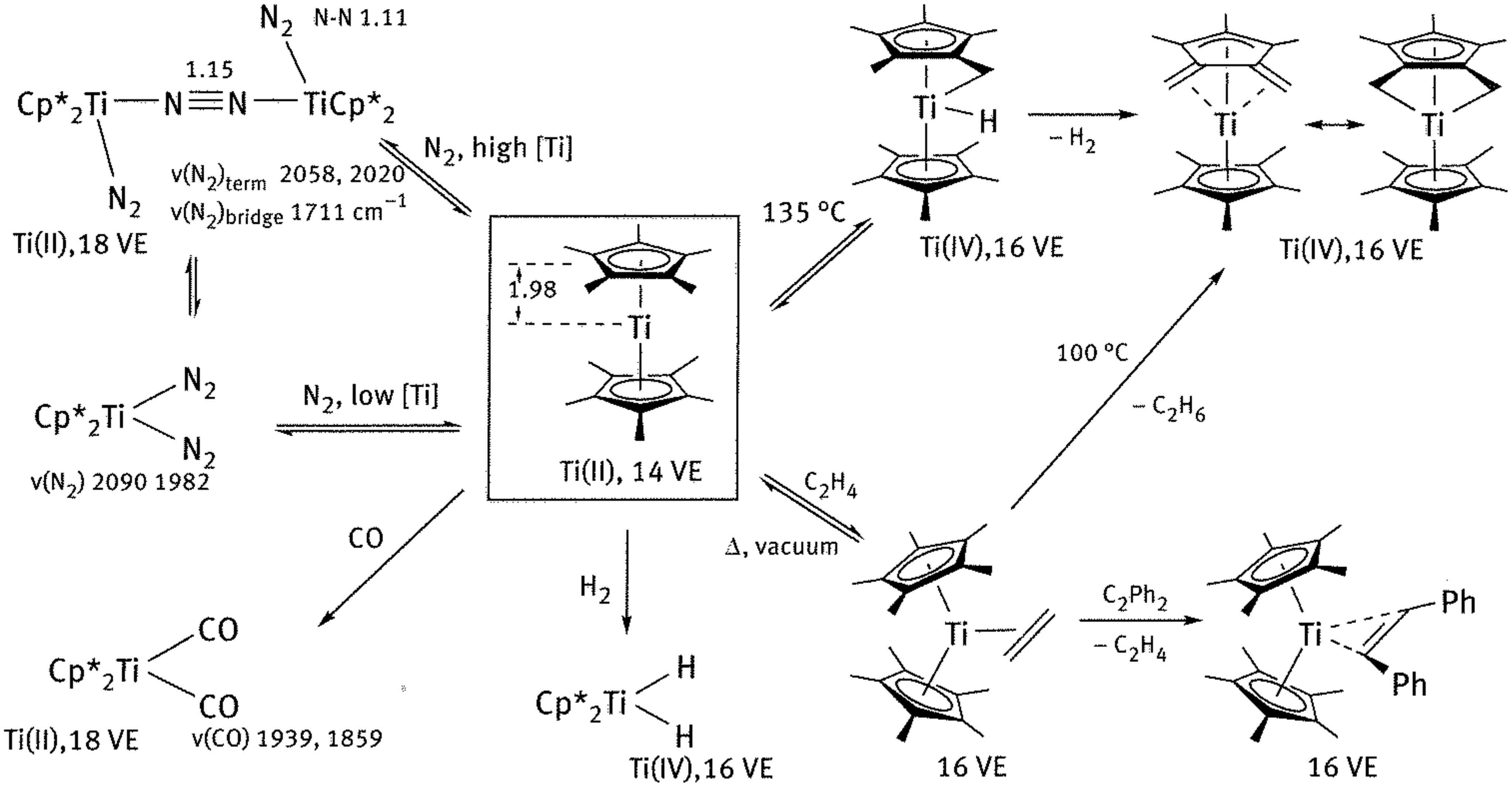
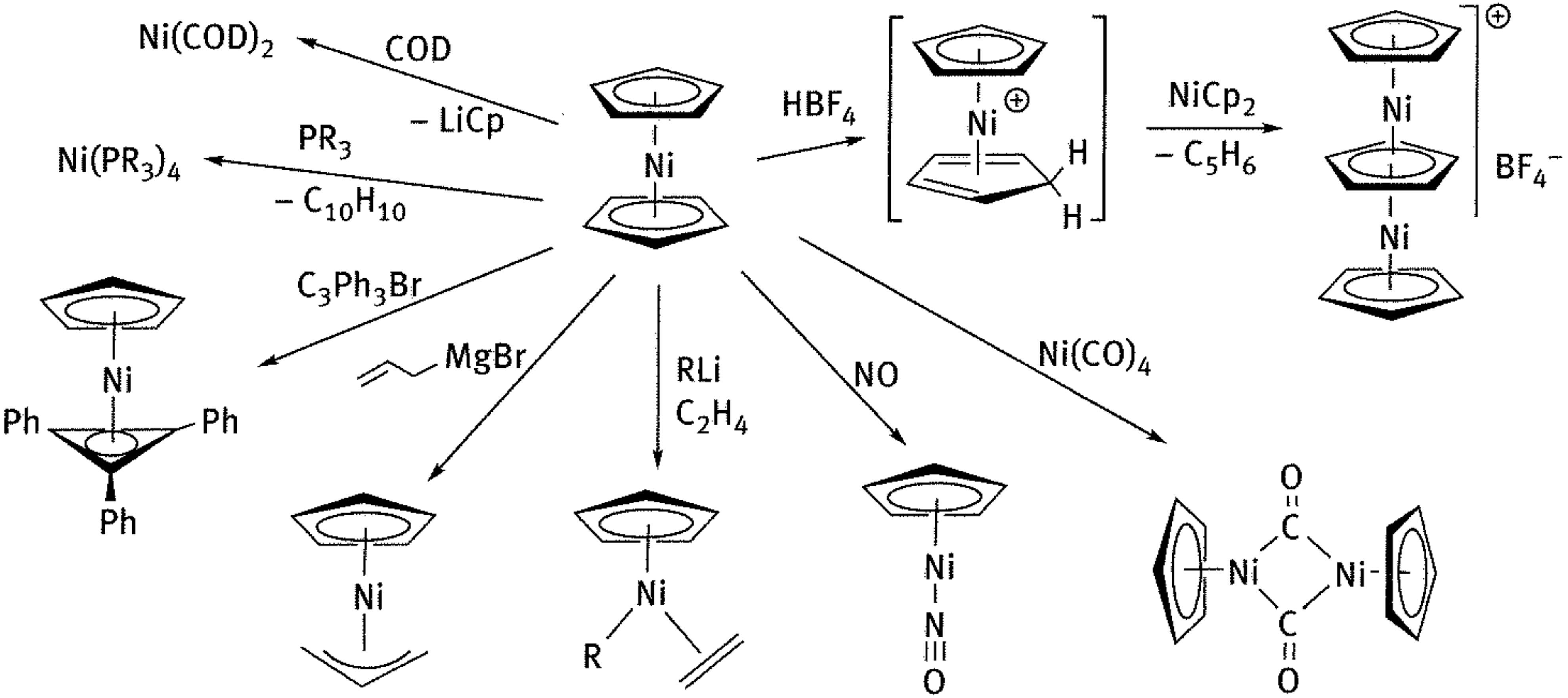
Other metallocenes

- $(\eta^5\text{-}C_5H_5)_2V$ (violet solid), $(\eta^5\text{-}C_5H_5)_2Cr$ (red solid), $(\eta^5\text{-}C_5H_5)_2Co$ (black solid) are air-sensitive & $(\eta^5\text{-}C_5H_5)_2Ni$ (green solid). Except, $(\eta^5\text{-}C_5H_5)_2Fe$ all are paramagnetic.
- $(\eta^5\text{-}C_5H_5)_2Mn$ (brown solid) unlike others is dimorphic; the room-temperature form is polymeric while the high-temperature form is structurally related to ferrocene.
- In typical metallocene compounds $(\eta^5\text{-}C_5Me_5)_2M$, all of the C-C bonds are equal and the rings are parallel. However, tilting is also observed in some metallocenes.
- There are also some compounds with one as well as more than two Cp rings.

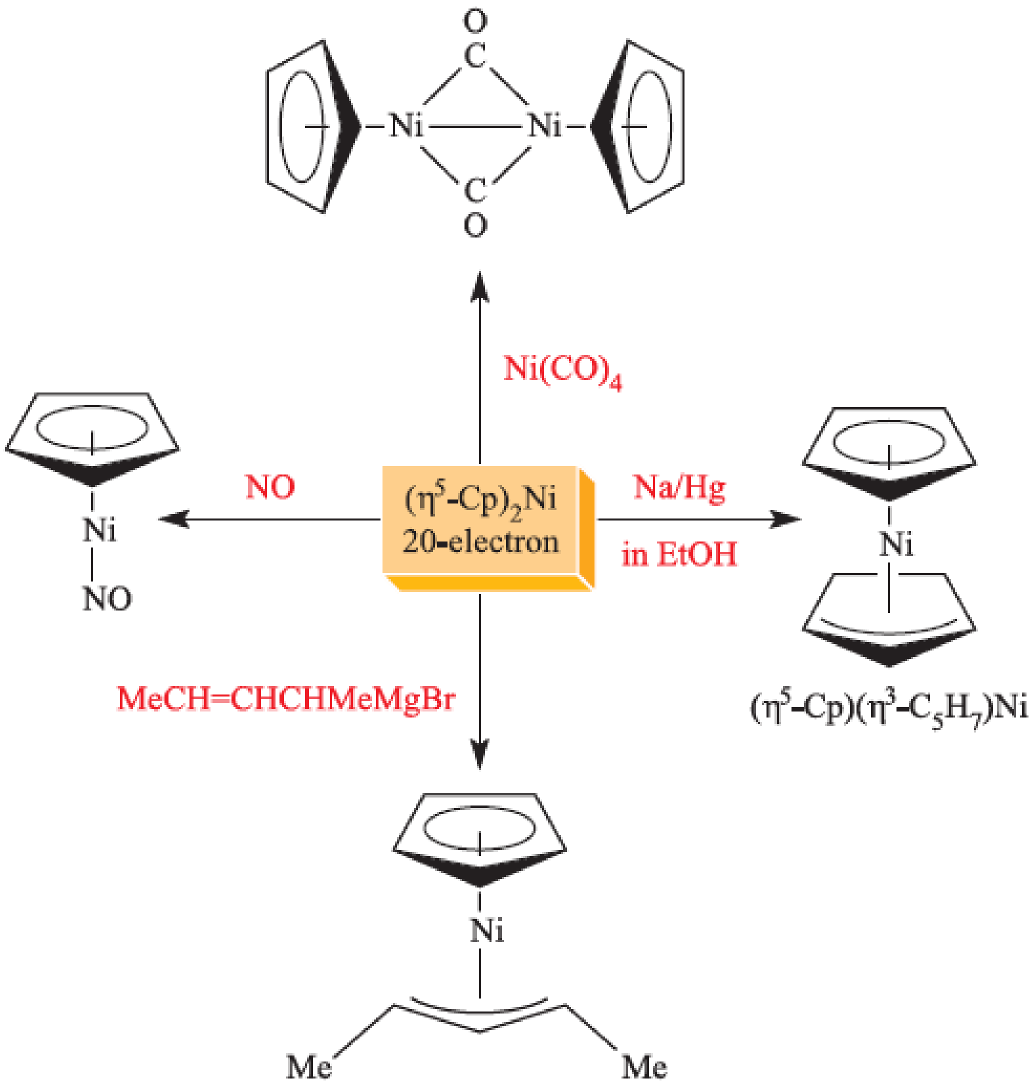
Reactions of titanocene



Reactions of nickelocene



- ➢ The 19-e $(\eta^5\text{-Cp})_2Co$ is readily oxidized to the 18-e $(\eta^5\text{-Cp})_2Co^+$, air stable yellow salts.
- ➢ Nickelocene is a 20-e complex and forms 18-e complexes, bears eclipsed Cp ring



Selected reactions of nickelocene, $(\eta^5\text{-Cp})_2Ni$.

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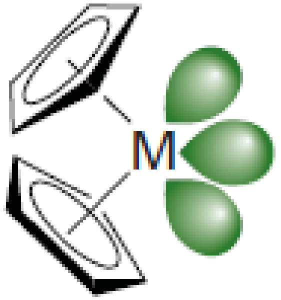
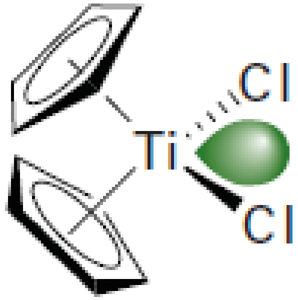
Bent metallocene

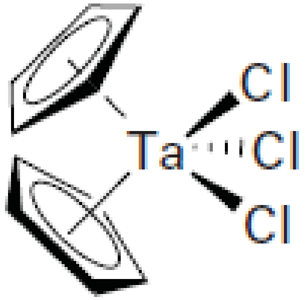
- Bent sandwich complexes contain two Cp ligands and one or more X or L-type ligands.
- Three metal atom orbitals project towards the open face of the bent Cp_2M fragment.
- The metal atom often satisfies its electron deficiency when the electron count is less than 18 by interaction with lone pairs or agostic CH groups on the ligands
- Bent sandwich compounds play a major role in the organometallic chemistry of the early and middle d-block elements such as , and examples include $[Ti(\eta^5\text{-}Cp)_2Cl_2]$, $[Re(\eta^5\text{-}Cp)_2Cl]$, $[W(\eta^5\text{-}Cp)_2(H)_2]$, and $[Nb(\eta^5\text{-}Cp)_2Cl_3]$.
- Bent sandwiches occur with a variety of electron counts and stereochemistry.



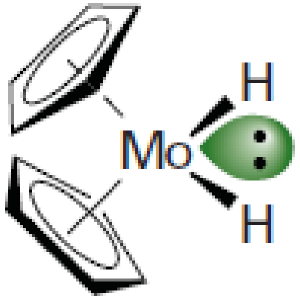
General form



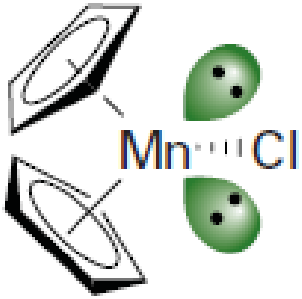
16-electron



18-electron



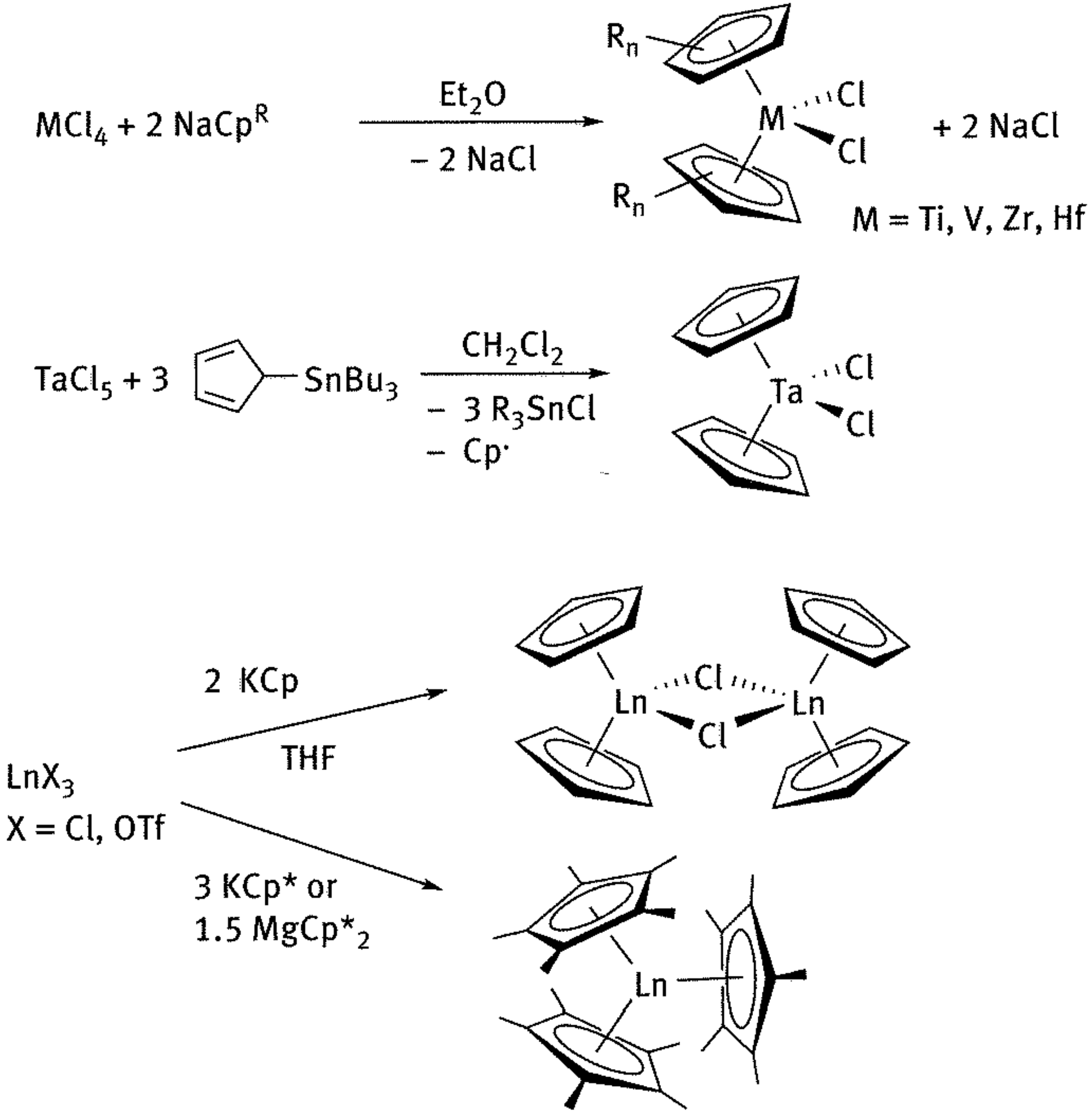
18-electron

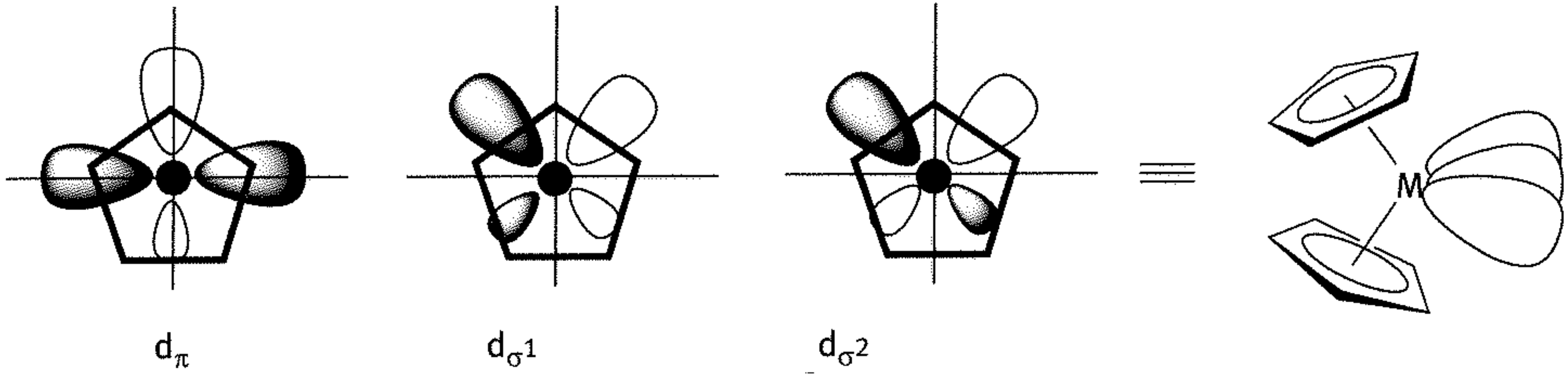


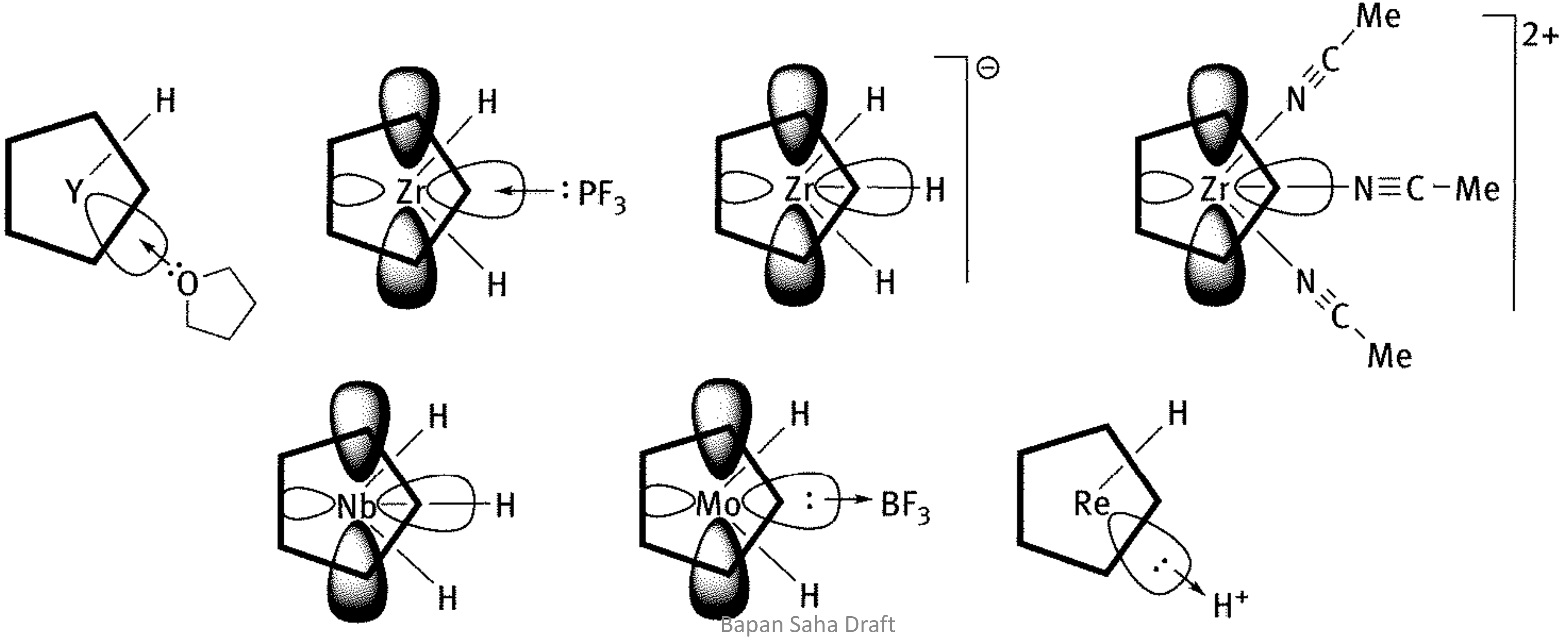
18-electron

Synthesis of bent metallocenes

- The most important synthetic route is the reaction of early transition metal halide, for example MX_4 (M= Ti, Zr, Hf, V) with NaCp or LiCp derivatives in 1:2 molar ratio to give Cp_2MX_2 complexes
- The analogous reaction of the heavier Gr V metal halides would expected to give M(V) complexes Cp_2MX_3 (M = Nb, Ta)
- Lanthanide halides give compounds of the types Cp_2LnX and $LnCp_3$, depending on the stoichiometry.
- Cp_2LnX complexes are halide-bridged dimers







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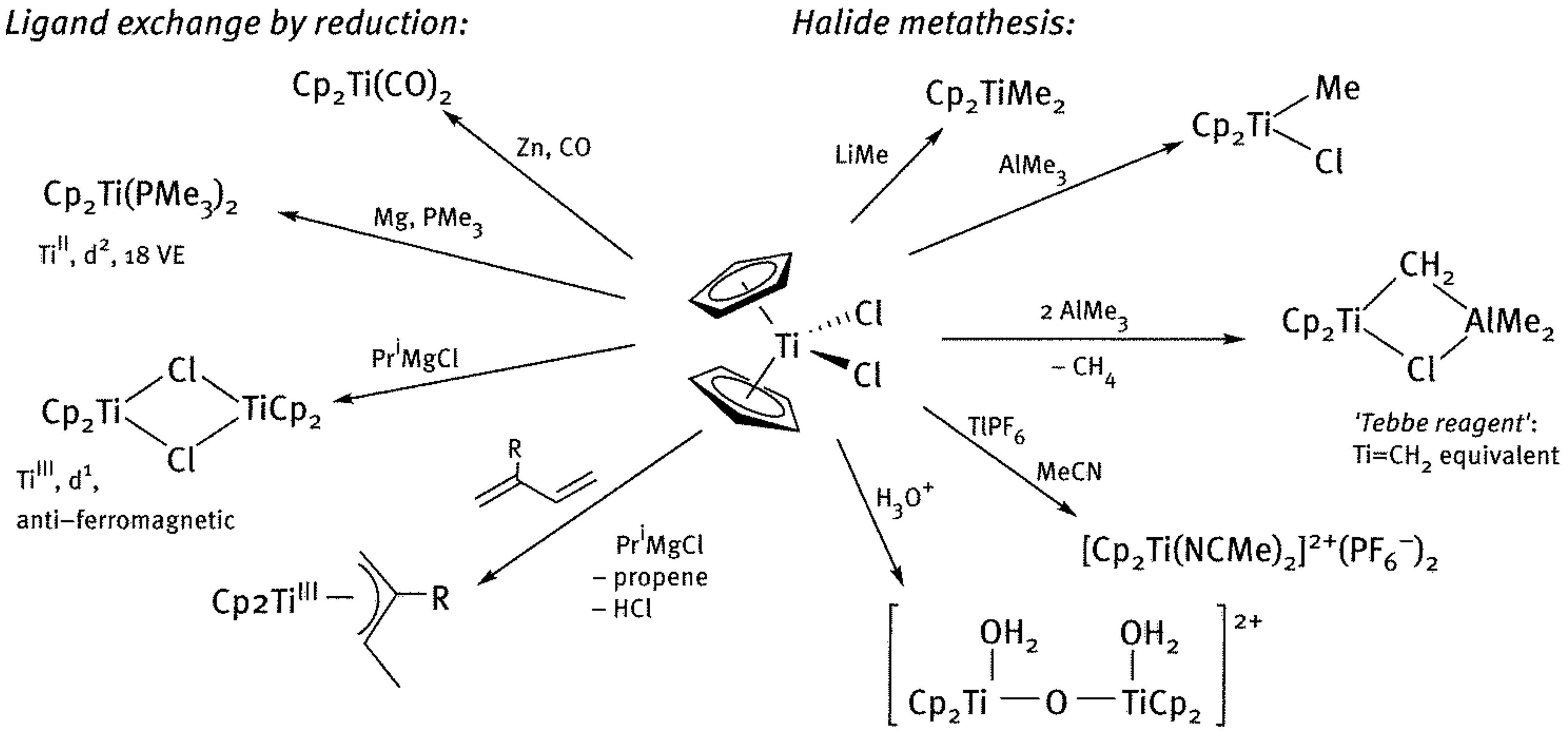
Reactivity of bent metallocenes

- The most important reaction in terms of synthetic utility and catalytic applications is the exchange of halide ligands by alkyls



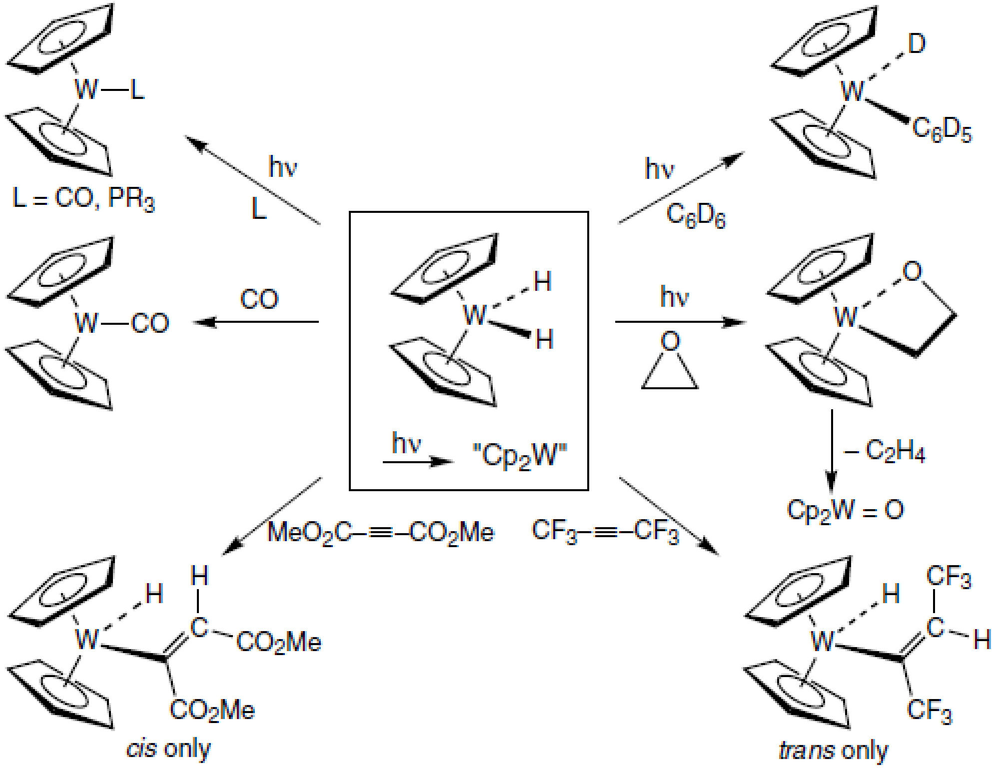
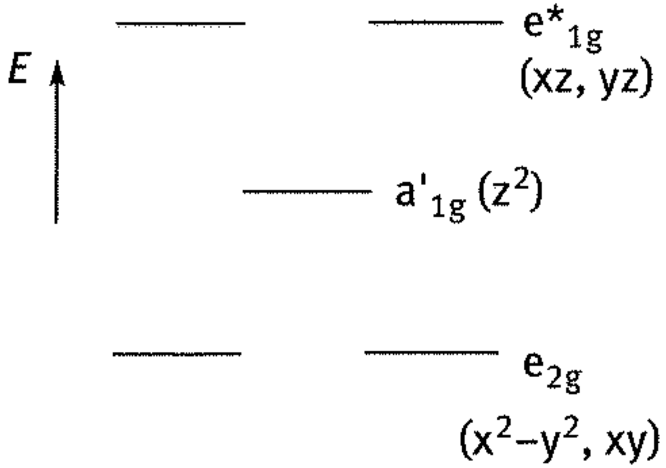
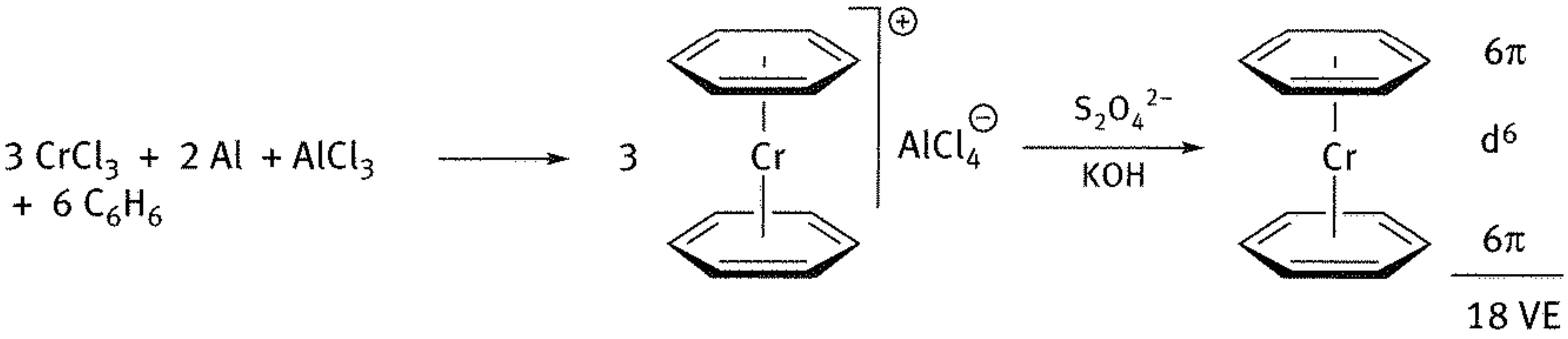

W—L
L = CO, PR$_3$
hν
L
W—CO
CO
W
H
H
hν
"Cp$_2$W"
hν
C$_6$D$_6$
D
W
C$_6$D$_5$
hν
O
W
O
– C$_2$H$_4$
Cp$_2$W = O
MeO$_2$C–≡–CO$_2$Me
CF$_3$–≡–CF$_3$
W
H
H
C
CO$_2$Me
CO$_2$Me
cis only
W
H
CF$_3$
C
H
CF$_3$
trans only

Table 2.8.1.2 Electron configuration and magnetic properties of metallocenes.

Partial qualitative MO diagram for MCp_2		d-level occupancy	VE count	Unpaired electrons	μ_{eff}, spin-only value	Found [Bohr magnetons]
	Cp_2V	$(e_{2g})^2(a'_{1g})^1$	15	3	3.87	3.84
	Cp_2Cr	$(e_{2g})^3(a'_{1g})^1$	16	2	2.83	3.20
	Cp_2Fe^+	$(e_{2g})^3(a'_{1g})^2$	17	1	1.73	2.34
	Cp_2Mn	$(e_{2g})^2(a'_{1g})^2(e^*_{1g})^2$	17	5	5.92	5.81
	Cp_2Co	$(e_{2g})^4(a'_{1g})^2(e^*_{1g})^1$	19	1	1.73	1.76
	Cp_2Ni	$(e_{2g})^4(a'_{1g})^2(e^*_{1g})^2$	20	2	2.83	2.86

Metal arenes

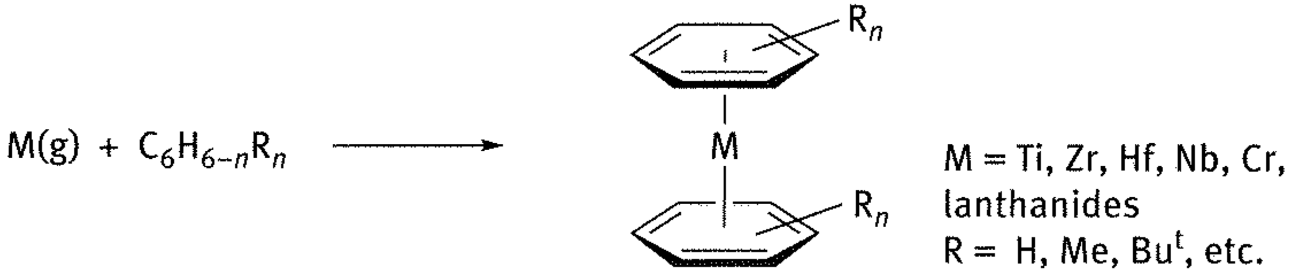
- Arenes such as benzene and toluene can act as 6-electron donors (can form π-complexes, closely related to Cp complexes
- The arene ring can be considered to occupy three coordination sites
- The C-C bonds in arene complexes are slightly elongated, indicative of back bonding contribution
- Classical example if bis(benzene) chromium.
- First prepared by E. O. Fischer in 1950s by reduction of $CrCl_3$ with Al/$AlCl_3$ in benzene (Fischer-Hafner synthesis)



C-C bond length 142 pm

- Arene ring can bridge two metal to give triple=decker structure, with more than two metals give multidecker

- Alternatively, arene complexes can be made by co-condensation of metal and arene vapors, substituted bis(arene) complexes are primarily isolated (particularly 1,3,5-$R_3C_3H_3$).
- Stability of the arene complexes increases with degree of substitution



- Group 6 (M = Cr, Mo, W) metals form air-sensitive 18-electron complexes η^6-$(C_6H_6)_2M$. In the solid state, the two benzene rings in η^6-$(C_6H_6)_2Cr$ are eclipsed.
- The bonding results from the interaction between the π-MOs of the ligands and 3d metal orbitals (occupied ligand π-MOs-as donors and vacant MOs - as acceptors).
- Many bis(arene) complexes deviate from 18 e rule and are paramagnetic

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Complex	Electron count	Unpaired electrons	Comments
$Ti(C_6H_6)_2$	16	0	
$[V(C_6H_3Me_3)_2]^+$	16	0	
$[Ti(C_6H_5Ph)_2]^-$	17	1	
$V(C_6H_6)_2$	17	1	
$[V(C_6H_6)_2]^-$	18	0	
$Cr(C_6H_6)_2$	18	0	
$[Fe(C_6Me_6)_2]^{2+}$	18	0	orange, very stable
$[Fe(C_6Me_6)_2]^+$	19	1	deep purple
$[Co(C_6Me_6)_2]^{2+}$	19	1	
$Fe(C_6Me_6)_2$	20	0	probably η^6,η^4
$[Co(C_6Me_6)_2]^+$	20	2	yellow, η^6,η^6
$[Ni(C_6Me_6)_2]^{2+}$	20	2	red-brown

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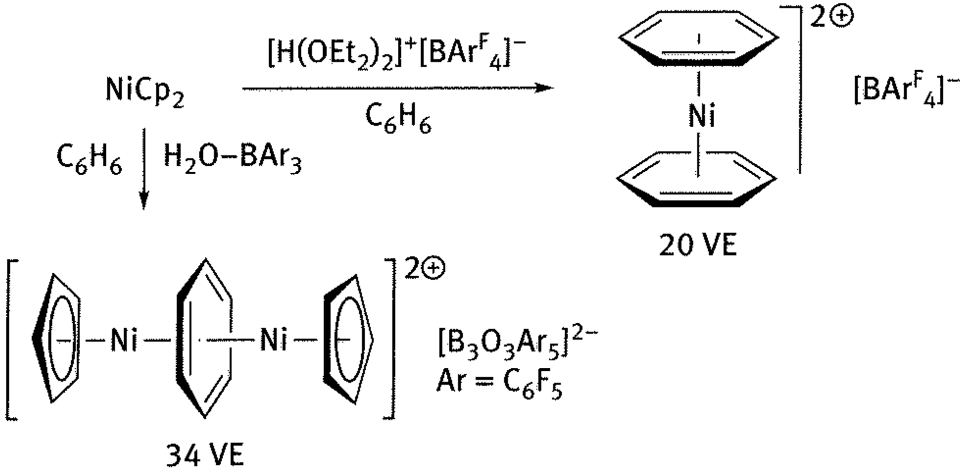
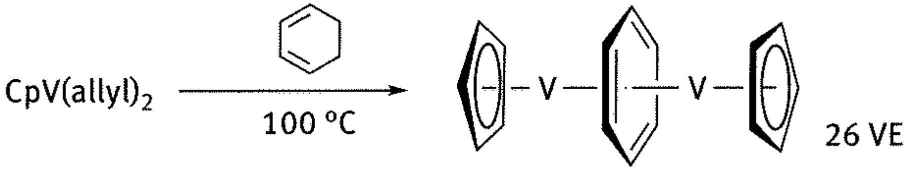
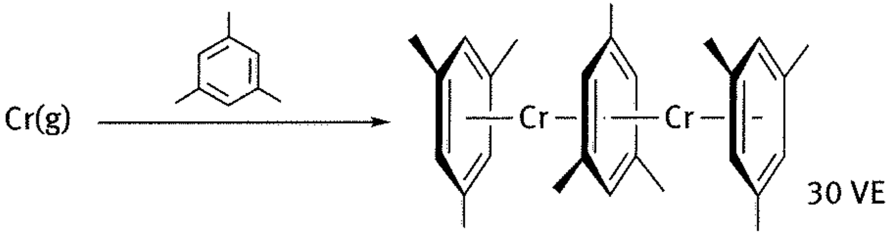
- Arene complexes can be made from Cp complexes by ligand exchange. The arene ring can bridge two metals to give triple decker structures







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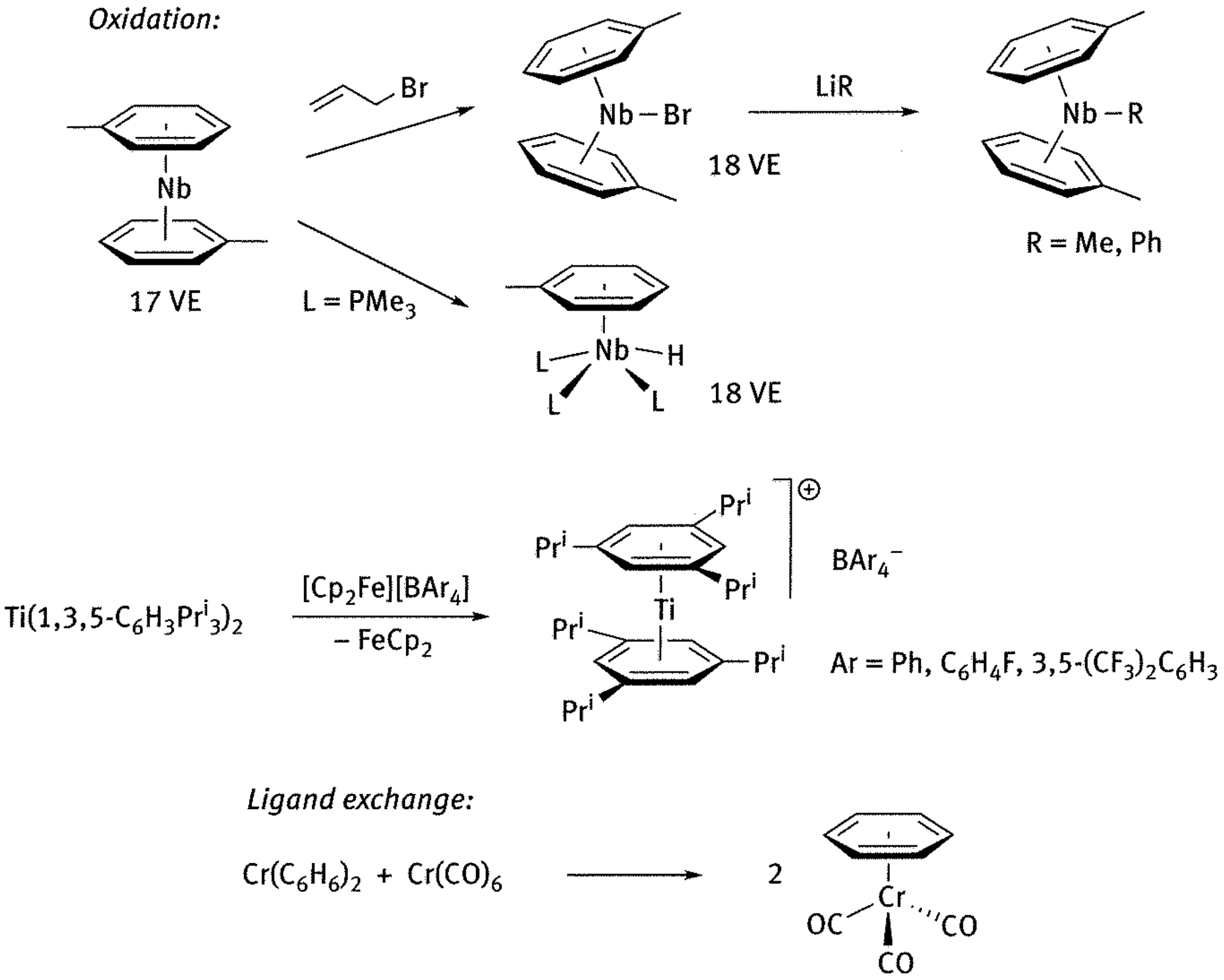
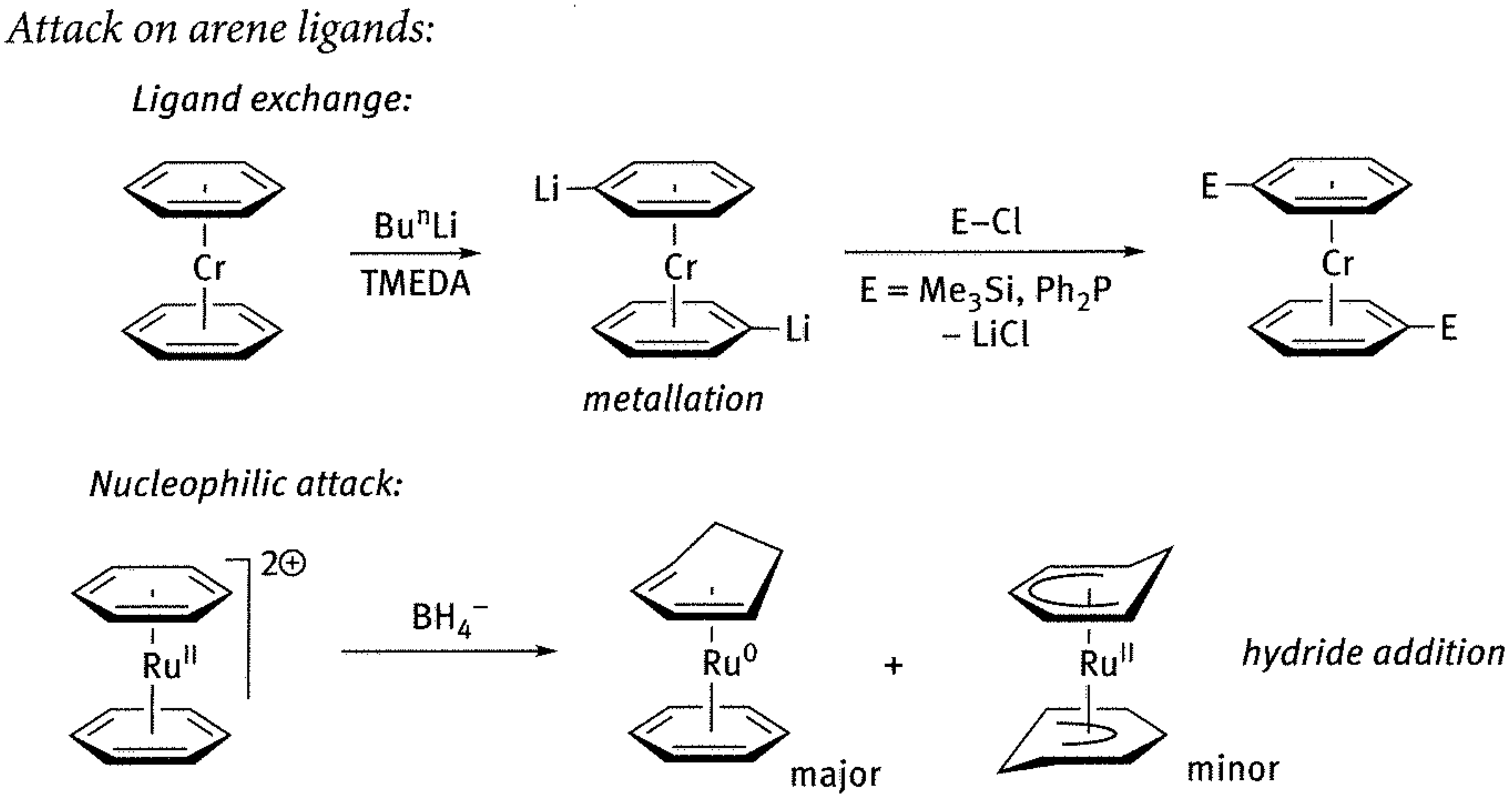
Reactivity of bis(arene) complexes

- Arene complexes undergo reactions

1. on the metal, by oxidation and reduction
2. by ligand substitution
3. on the arene ligand, by metalation and nucleophilic attack

- Reactions of the metals and ligand substitution is shown by redox reaction of Nb(η^6-toluene)
- Low valent arene complexes are easily oxidized (reaction of Ti($C_6H_3Pr_3^i$)$_2$ with 1e oxidant Fe(Cp)$_2^+$ to give Ti(I) - 15 e paramagnetic species
- Reaction of Cr(ben)$_2$ and Cr(CO)$_6$ leads to ligand exchange





- The lithiated derivative η^6-$(C_6H_5Li)_2Cr$ can be prepared by reaction of η^6-$(C_6H_6)_2Cr$ with n-BuLi and is a precursor to other derivatives.
- $Cr(ben)_2$ can be surprisingly, is easily oxidized by I_2 to the 17-electron, air-stable yellow η^6-$(C_6H_6)_2Cr^+$.

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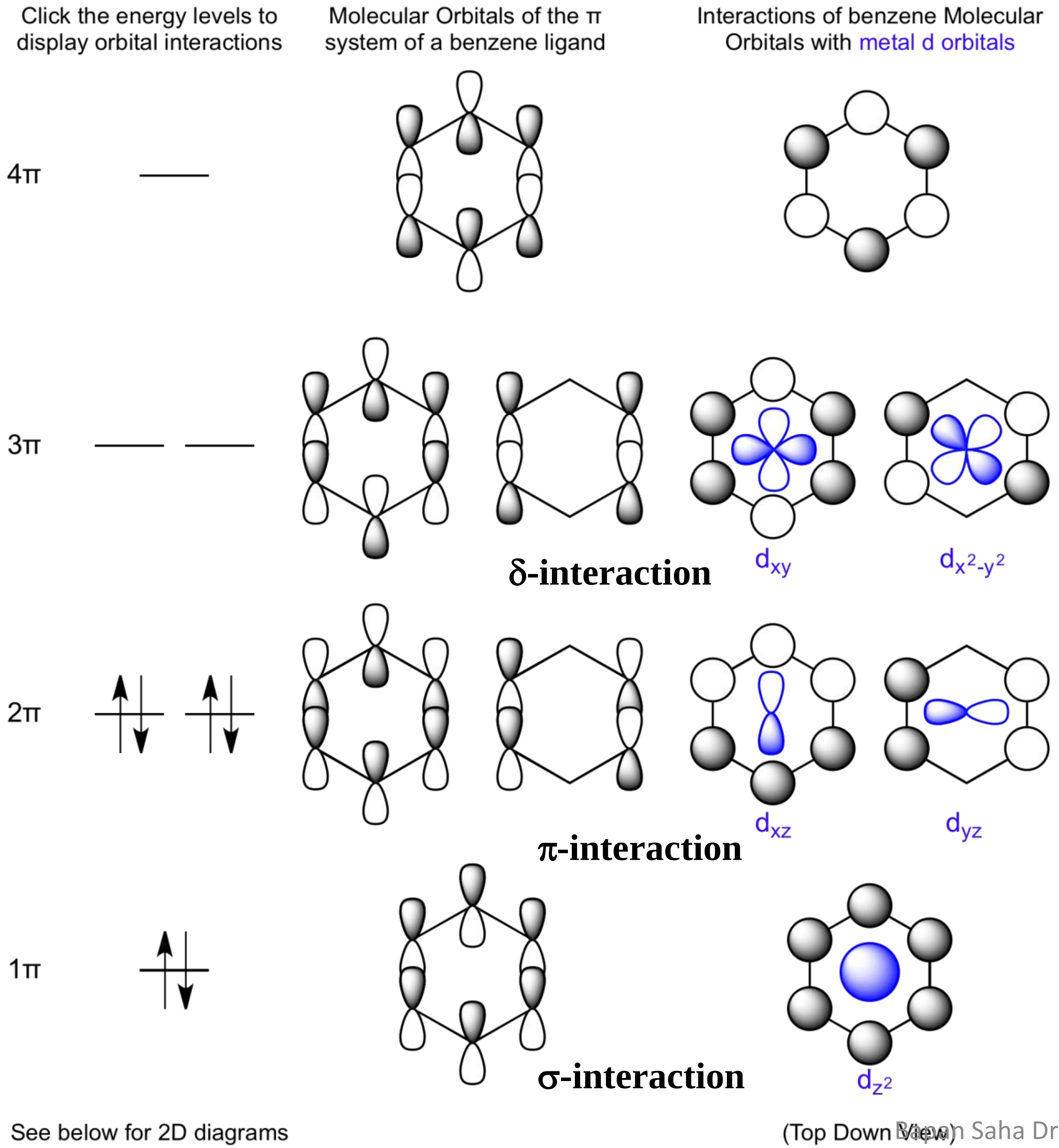
Bonding in Chromocene

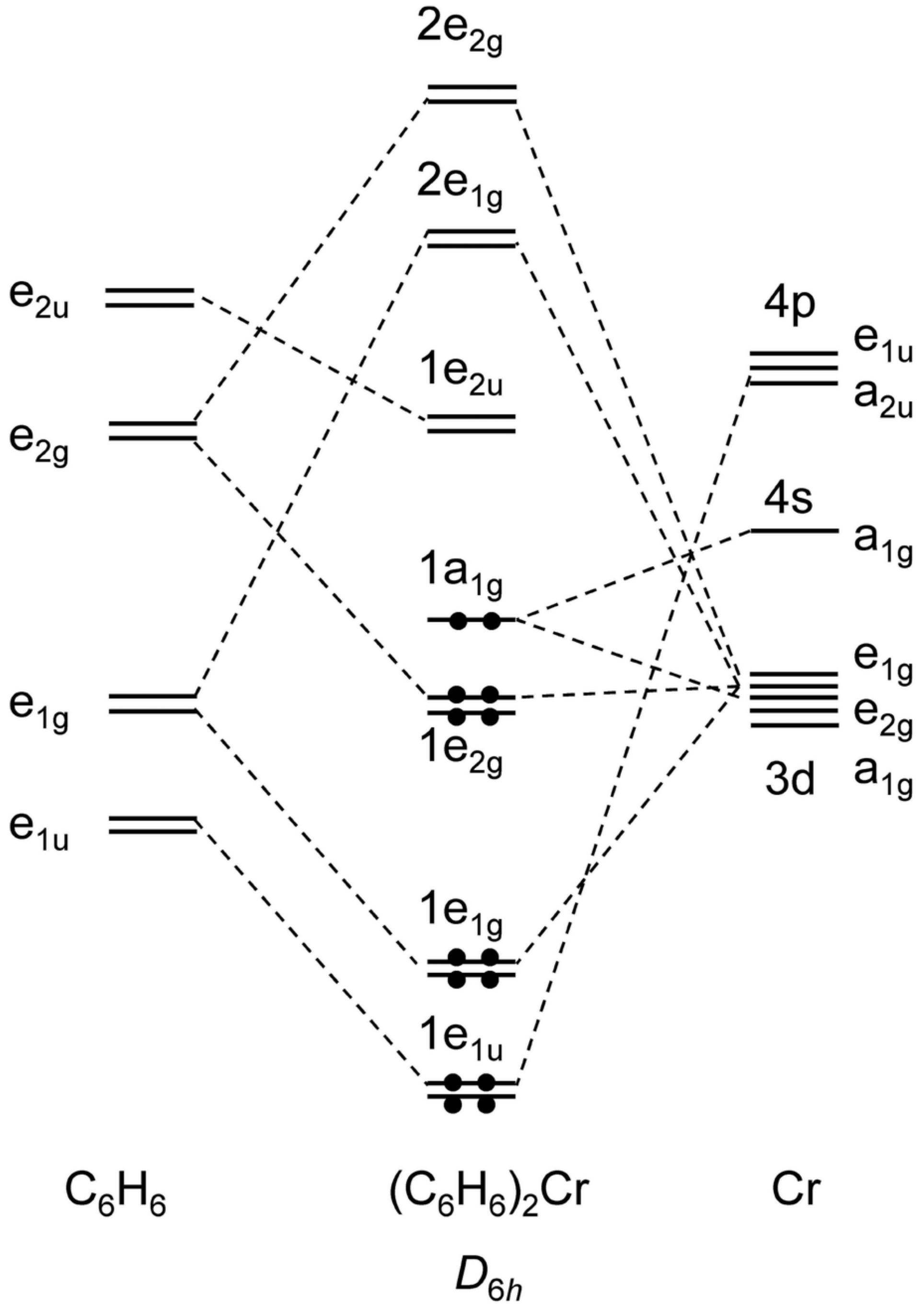
- C_6H_6 (each double bond behaves as ligand) behaves as a tridentate η^6-ligand.
- Bis(η^6-benzene)chromium, η^6-$(C_6H_6)_2Cr$ is considered to be made up of six coordinated double bonds, each donating two electrons, bound to a d^6 metal atom, giving a total of 18 valence electrons.
- C_6H_6 has three bonding and three antibonding orbitals π-bonding MOs
- The strongest interaction is a σ-interaction occurs between the most strongly bonding a_1 benzene MO and the d_{z2} orbital of the metal atom
- π-bonds are possible between the two other bonding benzene MOs (e_1) and the d_{zx} and d_{yz} orbitals.
- Back bonding from the metal to the C_6H_6 is possible as a δ-interaction between the d_{x2-y2} and d_{xy} orbitals and the empty antibonding e_2 orbitals of C_6H_6.
- η^6-Arenes are neutral ligands that donate six electrons and normally take up three coordination sites at a metal.



δ-interaction

π-interaction

σ-interaction



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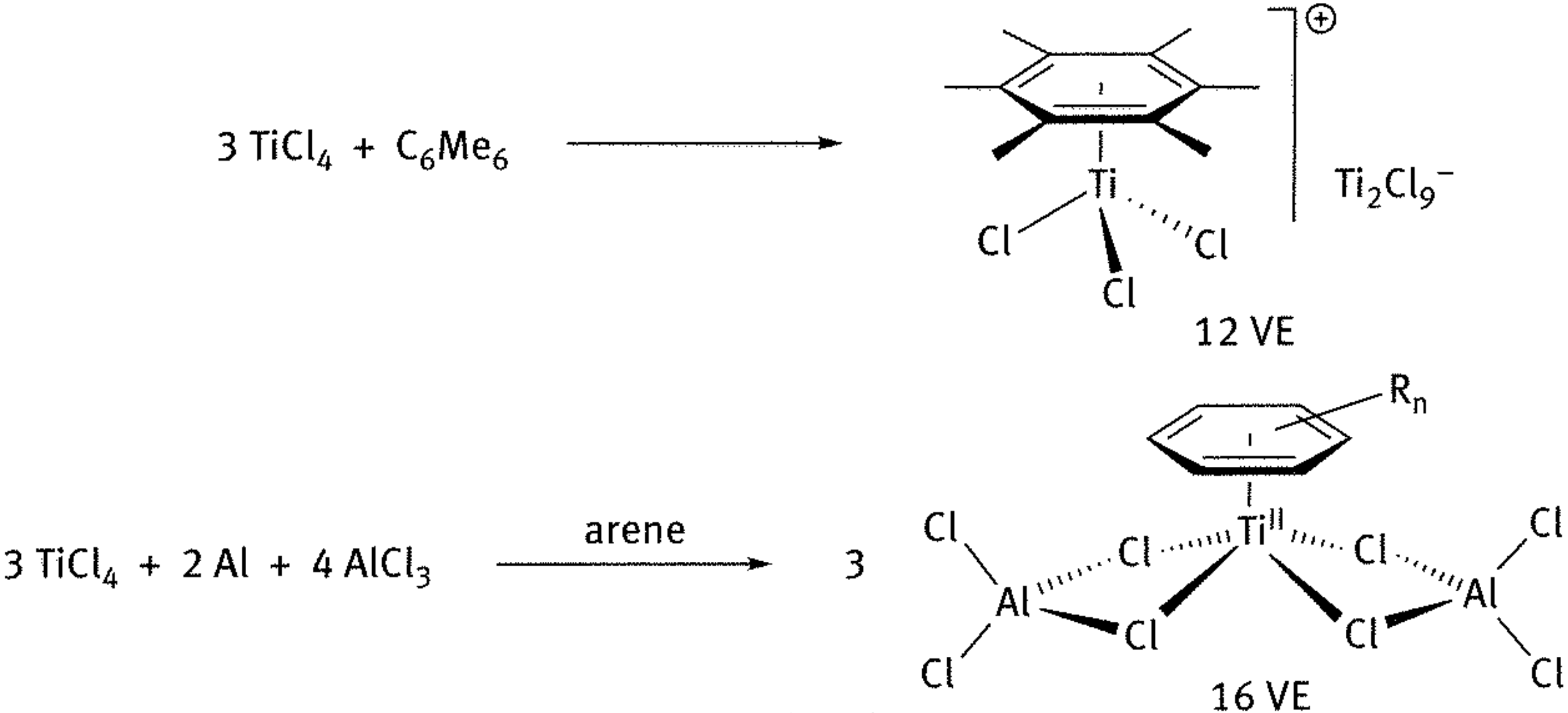
	$Ti(C_6H_6)_2$	$V(C_6H_6)_2$	$Cr(C_6Me_6)_2$	$Fe(C_6Me_6)_2$
NEV	16e	17e	18e	20e
e^*_{1g} (xy, yz)	— —	— —	— —	↑ ↑
a'_{1g} (z^2)	—	↑	↑↓	↑↓
e_{1g} (x^2-y^2, xy)	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
unpaired electrons (n)	0	1	0	2
$\sqrt{n(n+2)}$	0	1.73	0	2.83
exp. $\mu(\mu_B)$	0	1.68	0	3.08
color	red	dark red	brown	pink

Electronic structure (see the MO diagram of [$Cr(\eta^6$-$C_6H_6)_2$] above), theoretical ($\mu = \sqrt{n(n+2)}\ \mu_B$) and experimental ($\mu$ in Bohr magnetons) magnetic moment and color of the neutral metal-bis-arene sandwich complexes

Arene half sandwiches: Piano stool compounds

- These exists in combination with X-type ligands, as (arene)metal halide, and with L-type ligands, particularly (arene) metal carbonyl complexes
- Early transition metal halides posses sufficient Lewis acidity to form π-complexes with arene.
- Arene complexes of low valent transition metal halides are also known, often stabilized by AlX_3



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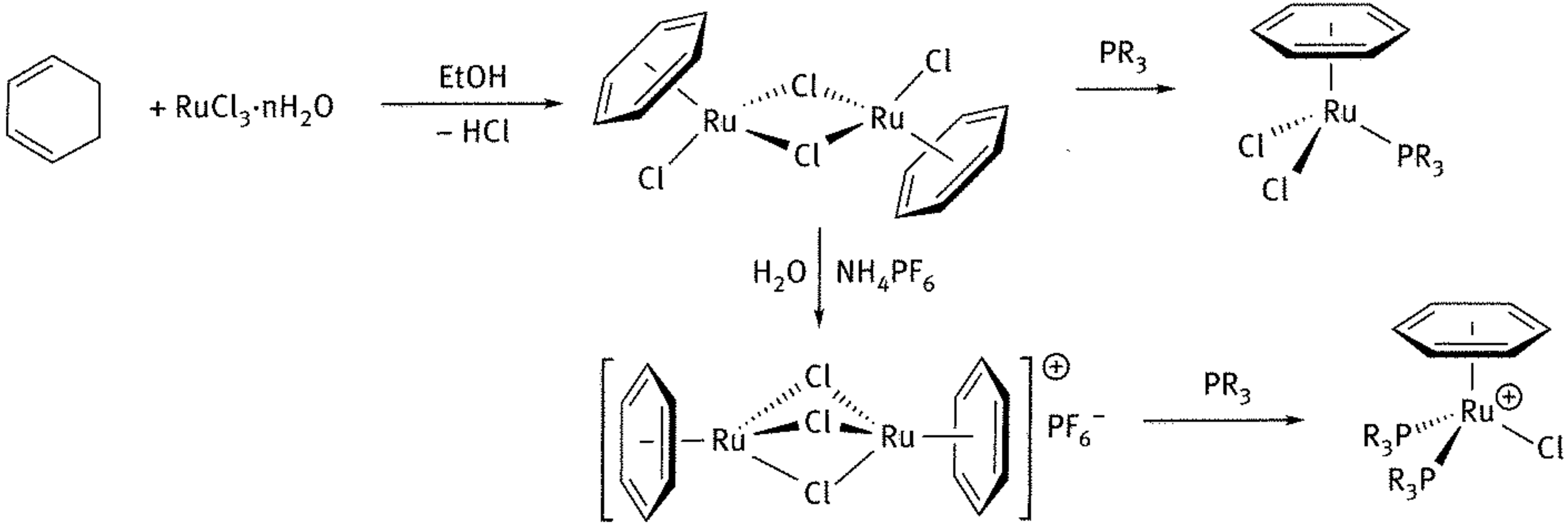
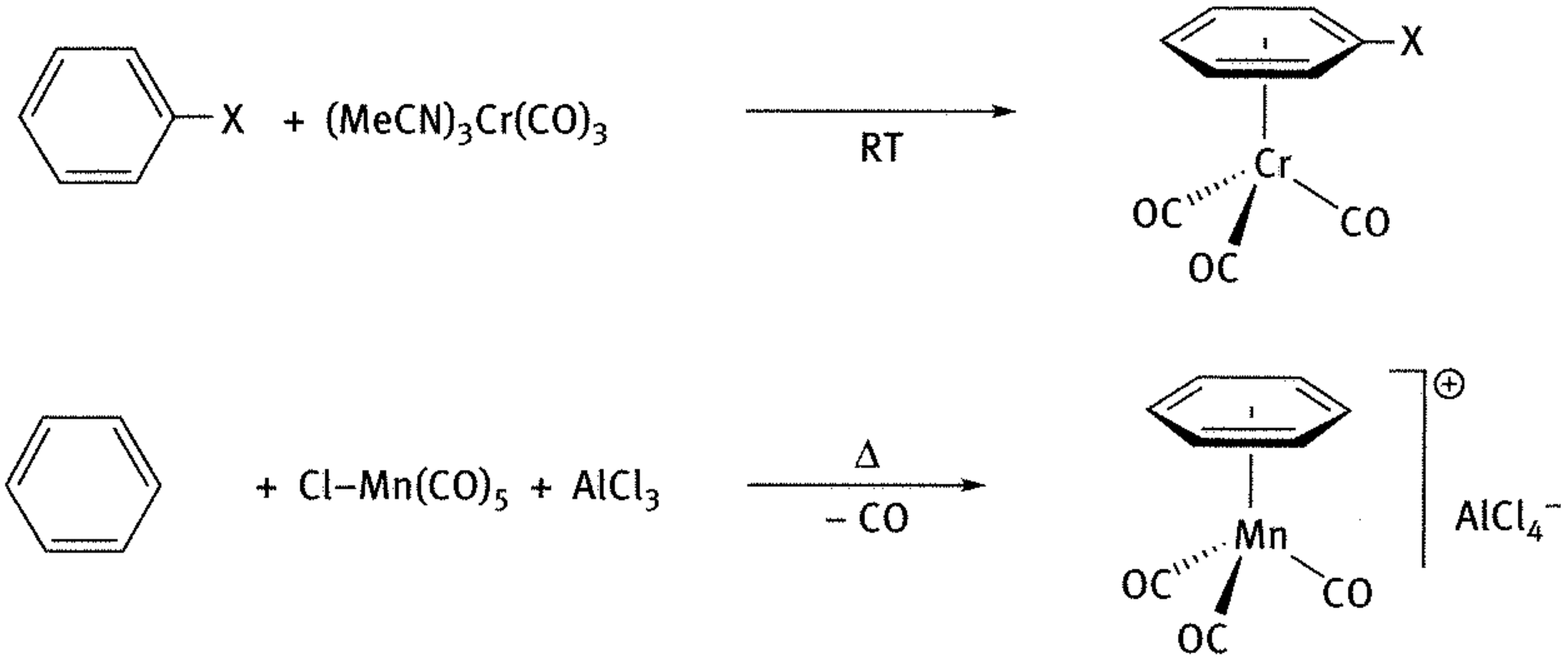
- Arene complexes of noble metals may be prepared by dehydrohalogenation of dienes which act as reducing agents, reduce Ru(III) to Ru(II), leading to important class of (arene)$RuCl_2L$ complexes (even used in cancer treatment).



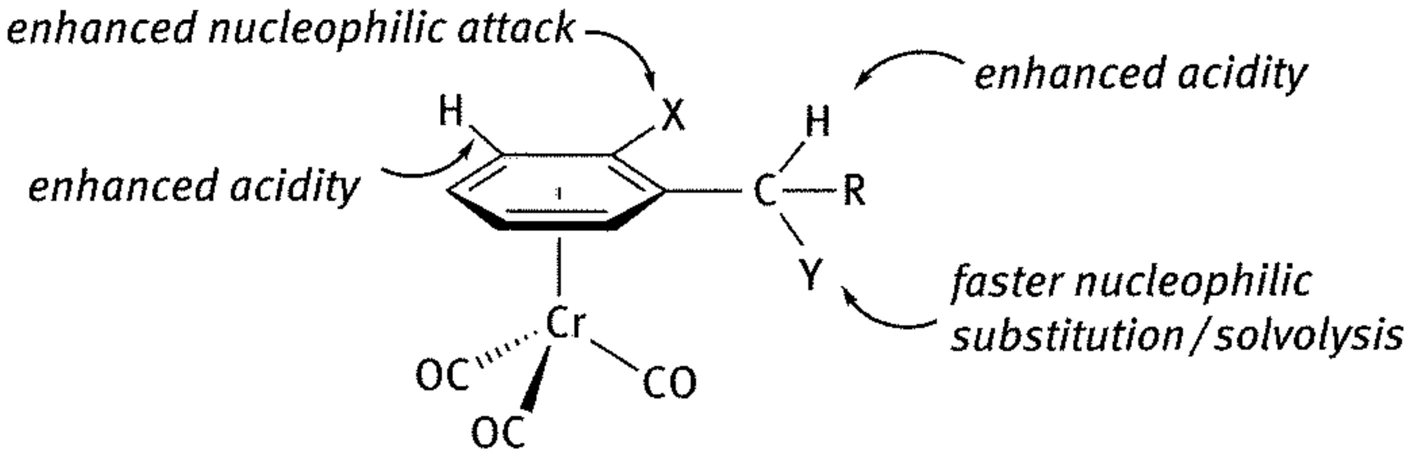
- The coordination of $M(CO)_n$ fragment activates the arene ligands. Common synthetic approaches are ligand substitution and abstraction of halides from metal carbonyl halides with $AlCl_3$



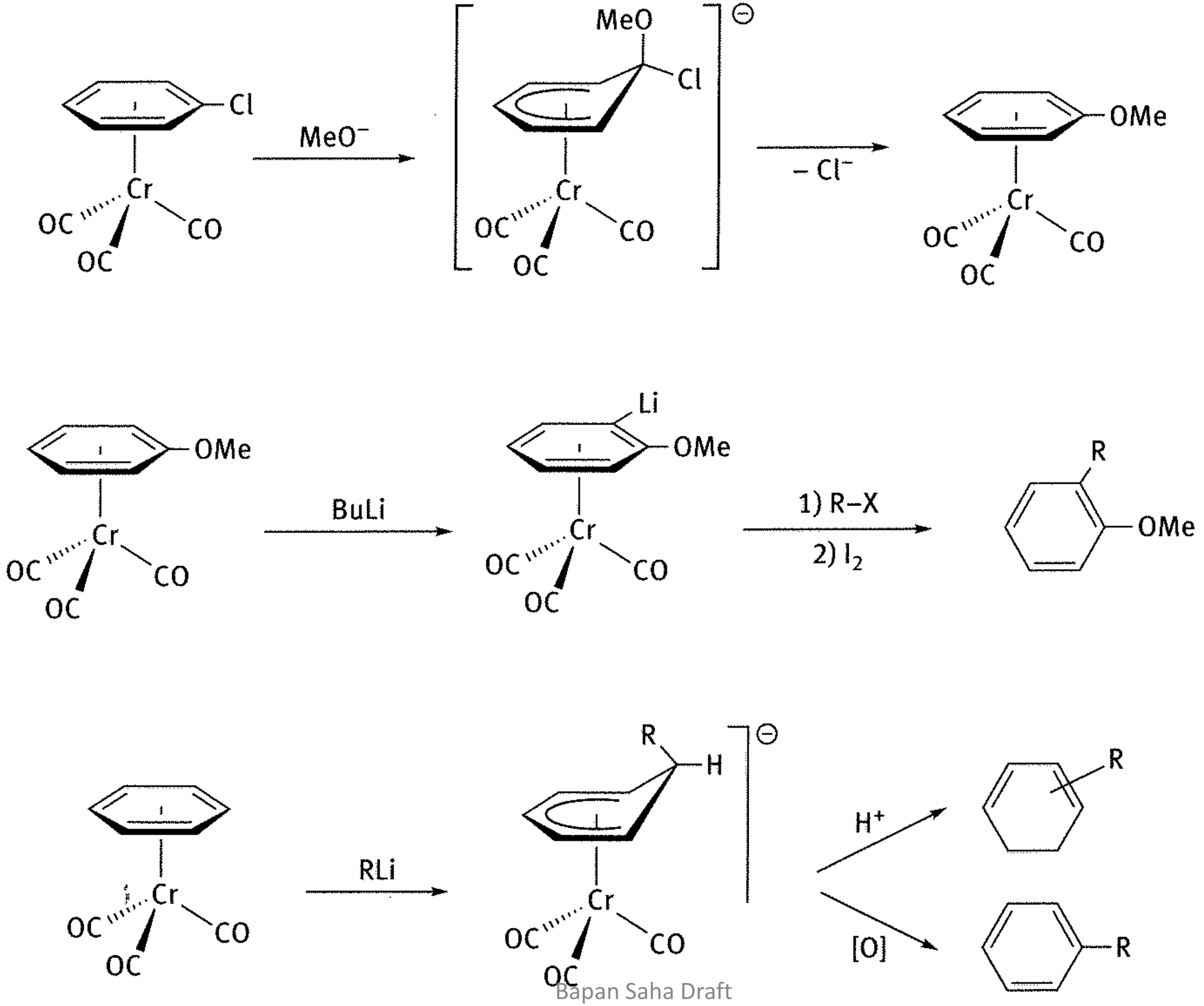
Reactivity of mono arene carbonyl complexes

- Arene chromium tricarbonyl complexes possess very varied reactivity
- The coordinated arene shows enhanced susceptibility towards nucleophilic attack
- Cr(CO)3 fragment also increases the C-H acidity, making more facile metalation

Effects of $Cr(CO)_3$ coordination:



- These properties are explored in several ways



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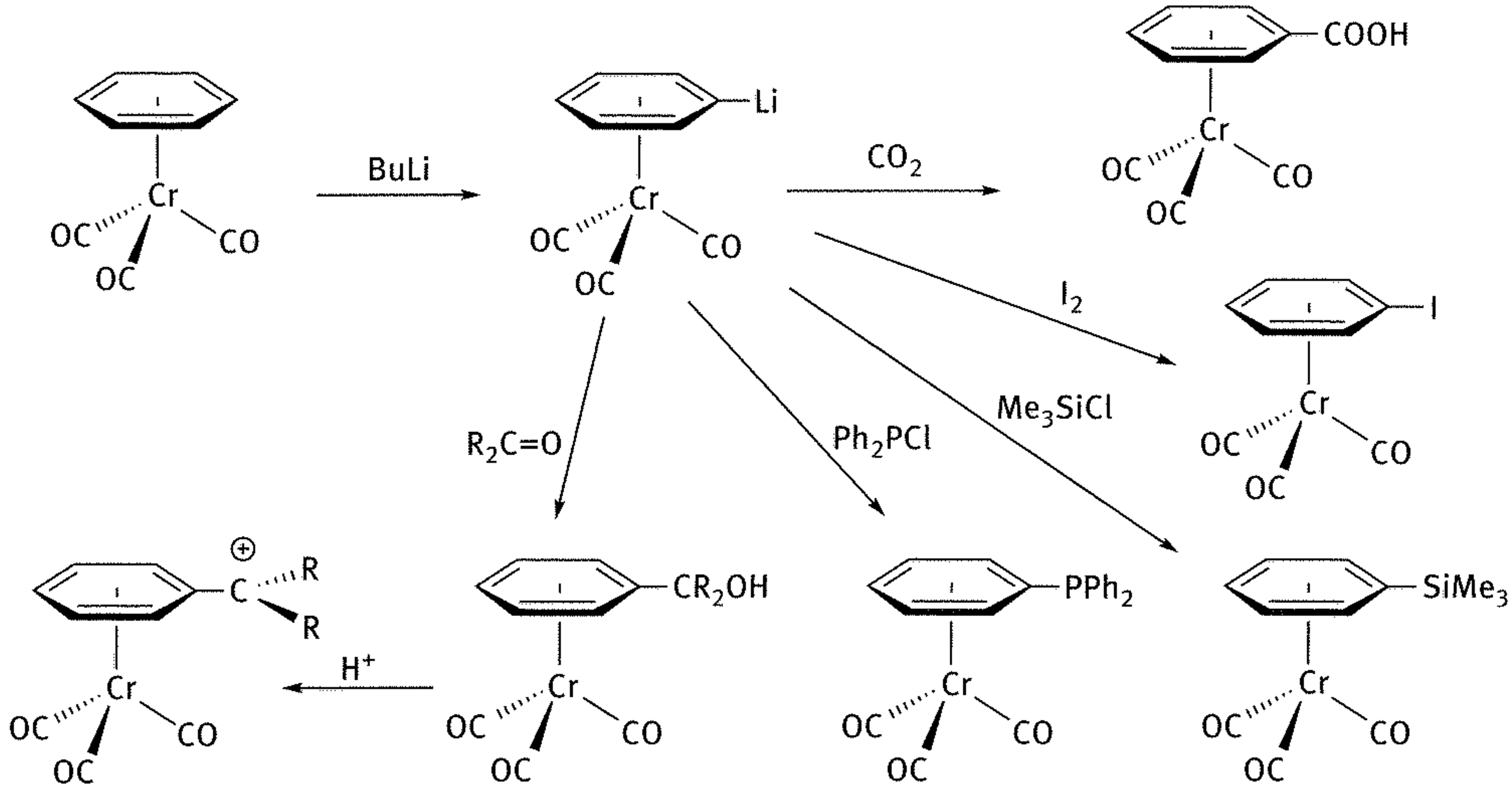
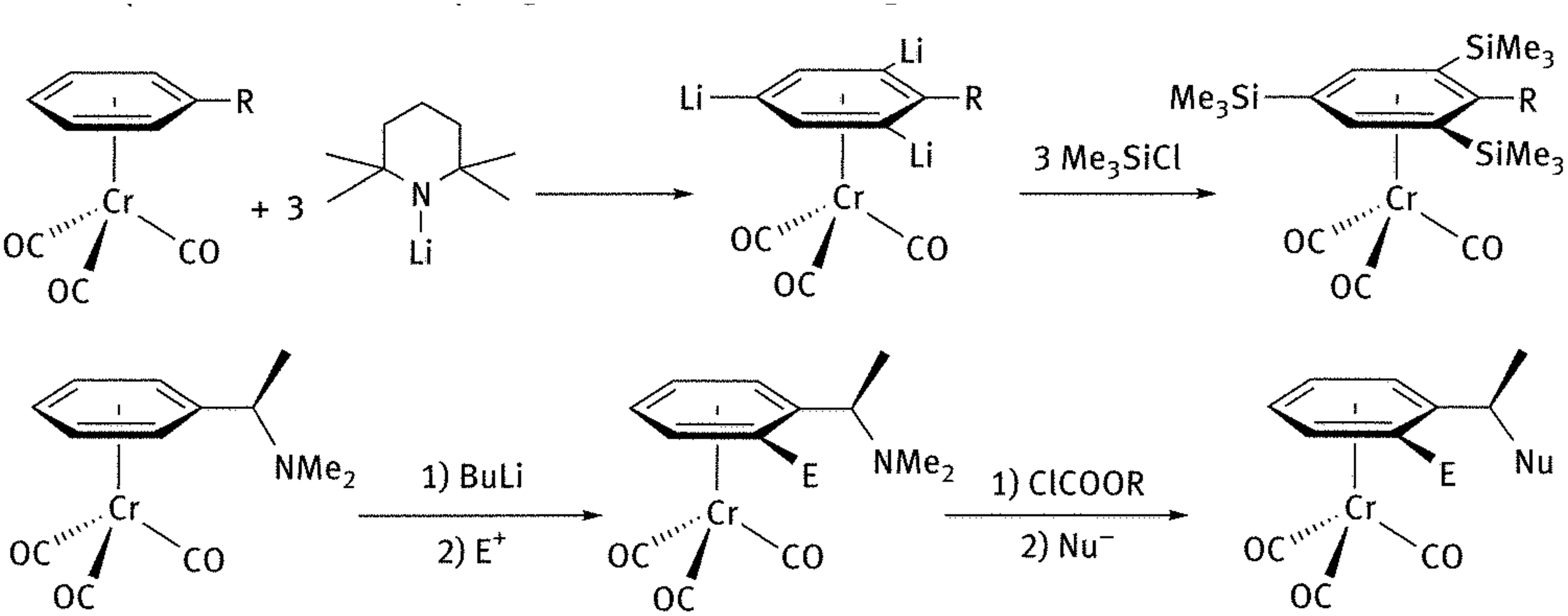


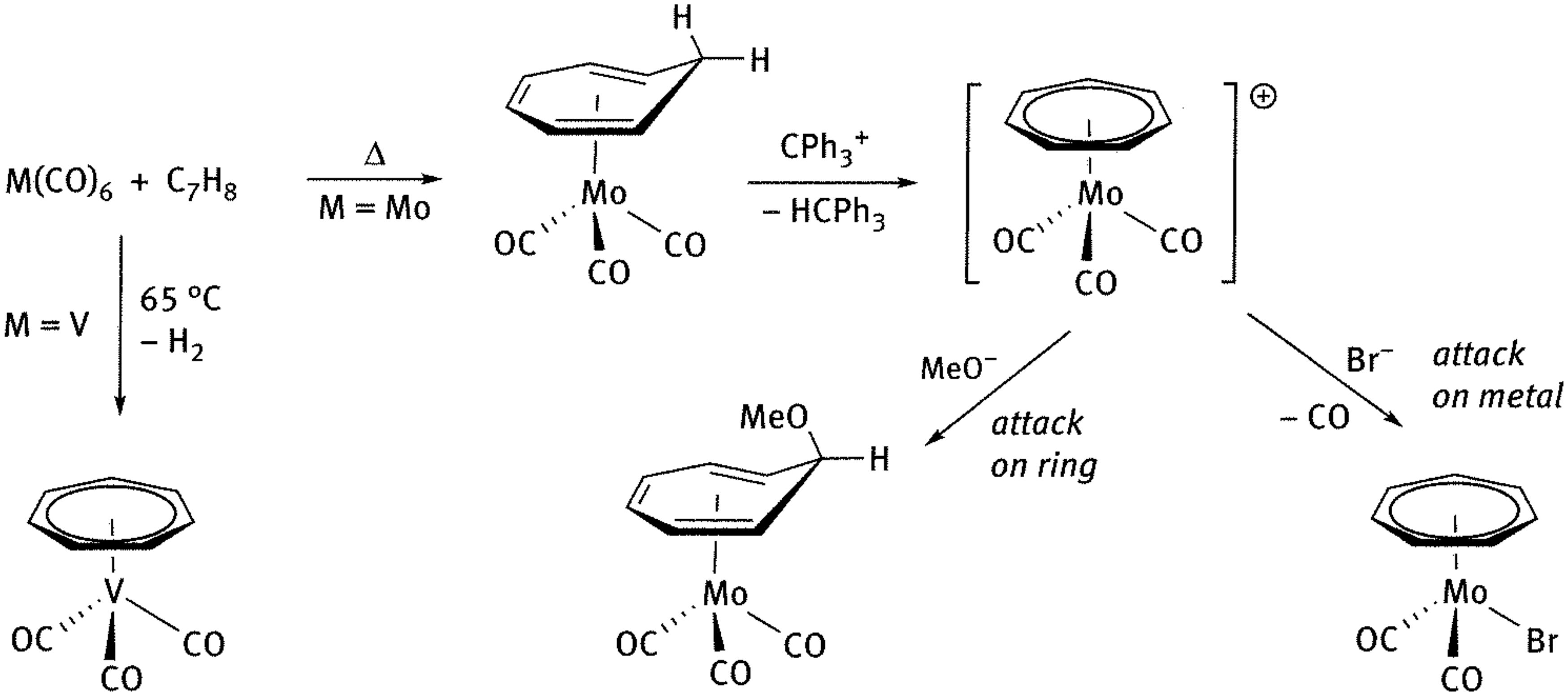
stabilized carbocation

- Multiple metalation are also possible, as are chiral substitutions on the ring (planar chiral system) and in benzylic positions



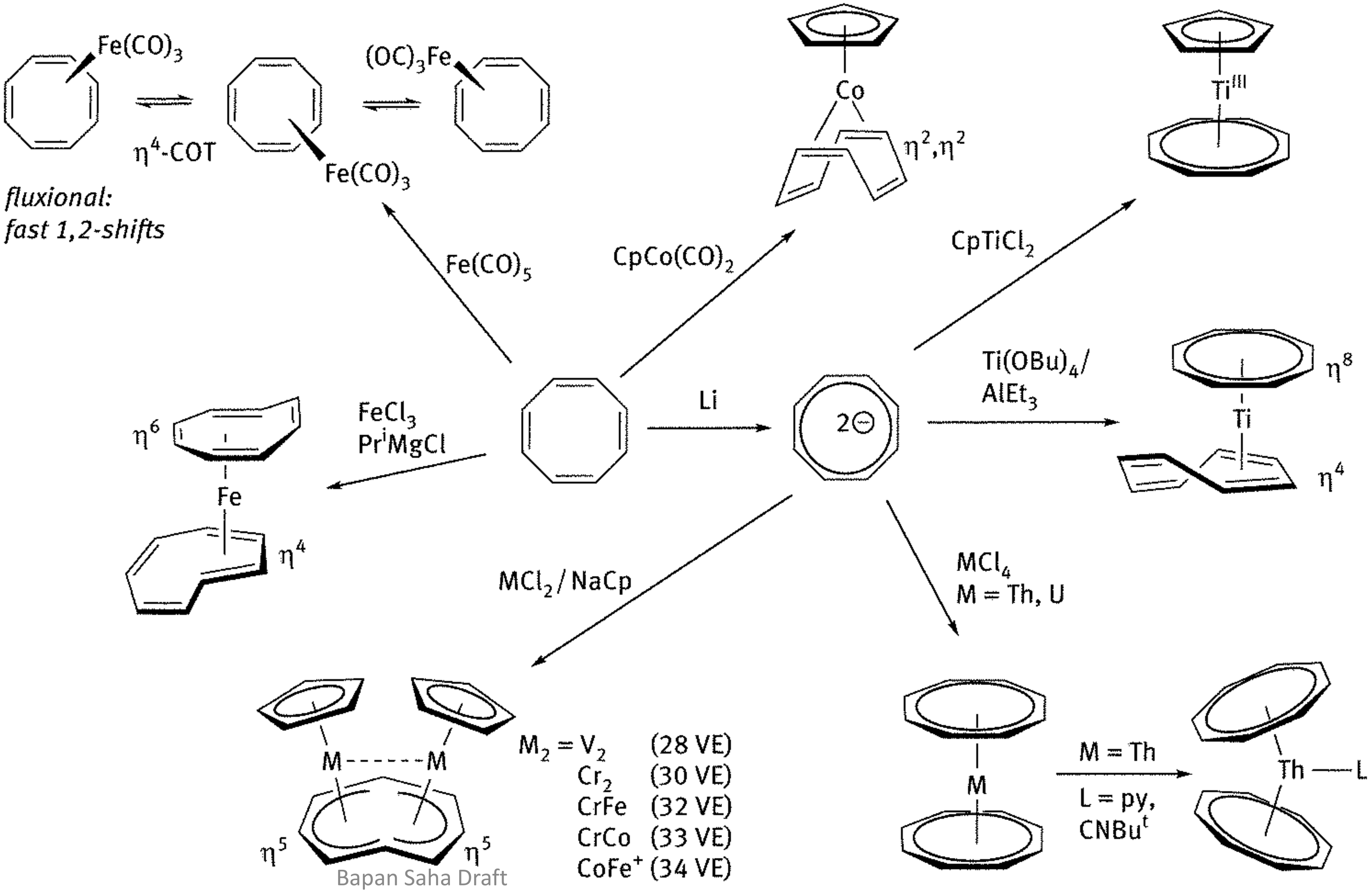
π-C_7H_7 complexes

- The cycloheptatrienyl ring can be regarded as the 6π-tropylium cation or as 10-π trianion depending upon the nature of coordinated metal ions
- The precursor of cycloheptatrienyl complex, [η^6-$C_7H_8M(CO)_3$] (M = Cr, Mo, W) undergoes hydride abstraction giving [η^6-$C_7H_7M(CO)_3$]$^+$, susceptible to nucleophilic attack.



π-C_8H_8 complexes

- COT is a versatile ligand, can bind metals as the non planar, antiaromatic neutral tetraene or as the planar 10π COT^{2-} anion
- Only one or two double bonds of COT are also known to coordinate to a metal centre
- Large size of the C8 ring indicates its ability to bridge across two metal centres, giving binuclear compounds



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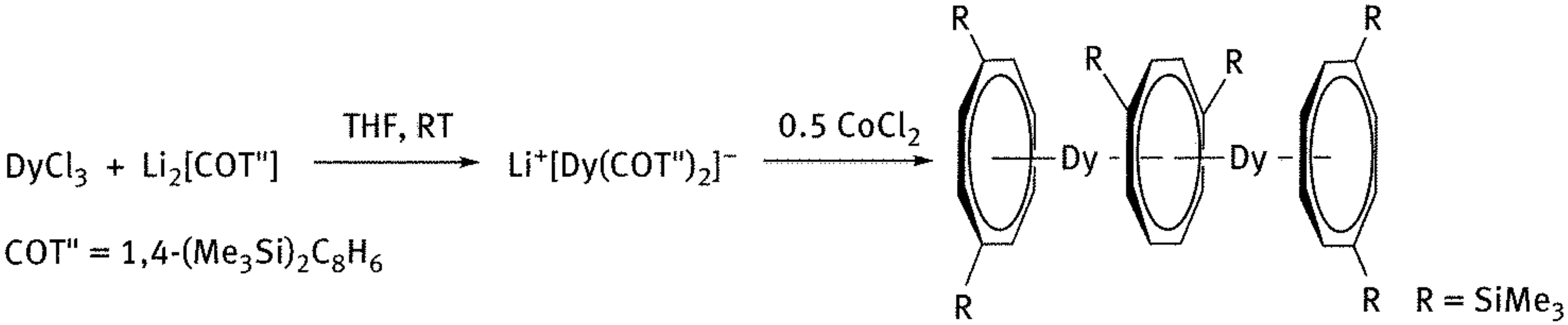
- Binuclear compounds $(CpM)_2(\mu\text{-}C_8H_8)$ have been described as twinnocenes and on the basis of 18e rule M-M multiple bonds have been postulated
- Large ions such as Ln and Ac, form COT sandwich complexes, Uranocene U(COT)2 is the best known
- It has structural similarity with metallocenes and the possible involvement of f-orbitals in bonding
- It is stable in water and its bonding is more covalent (participation of 6d and 5f orbitals)
- COT complexes of lanthanides have been extensively studied as single molecule magnet (SMM)



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