CHAPTER 5

ORGANOMETALLIC CHEMISTRY

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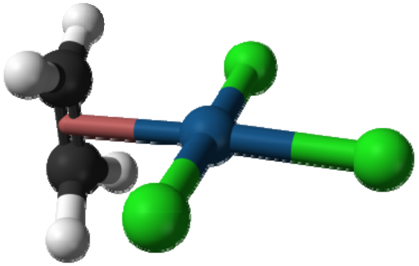
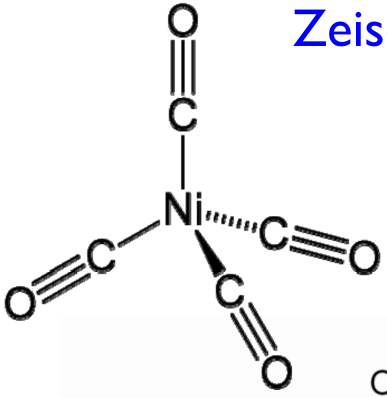
5-1 INTRODUCTION

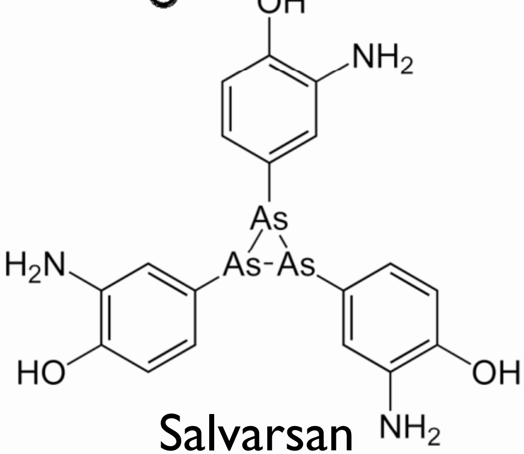
I. Organometallic chemistry timeline

- 1827 Zeise's salt is the first platinum-olefin complex: **$K[PtCl_3(C_2H_4)]\cdot H_2O$**
- 1863 C. Friedel & J. Crafts prepare organochlorosilanes
- 1890 L. Mond discovers **Nickel carbonyl**
- 1899 Introduction of **Grignard reaction**
- 1900 P. Sabatier works on hydrogenation organic compounds with metal catalysts. Hydrogenation of fats
- 1909 P. Ehrlich introduces Salvarsan for the treatment of syphilis(梅毒), an early arsenic based organometallic compound.



Zeise's salt





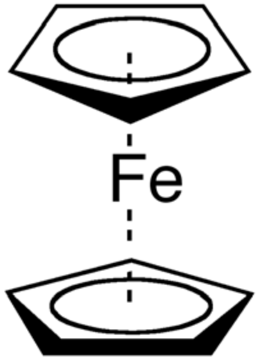
Salvarsan
撒尔佛散

- 1912 Nobel Prize: Victor Grignard and Paul Sabatier
- 1930 Henry Gilman works on lithium cuprates

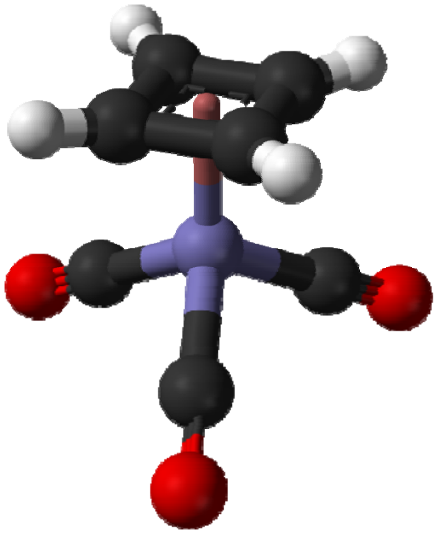
  $RX + 2Li \rightarrow RLi + LiX$

  $2RLi + CuI \rightarrow R_2CuLi + LiI$

  $(R_2CuLi + R'\text{-}X \rightarrow R\text{-}R' + RCu + LiX)$
- 1951 Ferrocene was discovered
- 1963 Nobel prize: *Ziegler-Natta catalyst*
- 1965 Discovery of cyclobutadieneiron tricarbonyl, $(C_4H_4)Fe(CO)_3$
- 1968 Heck reaction
- 1973 Nobel prize G. Wilkinson and E. O. Fischer on *sandwich compounds*
- 2005 Nobel prize Y. Chauvin, R. Grubbs, and R. Schrock: metal-catalyzed *alkene metathesis* (易位)
- 2010 Nobel prize Richard F. Heck, Ei-ichi Negishi, Akira Suzuki. "*for palladium-catalyzed cross couplings in organic synthesis*"



Ferrocene



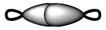
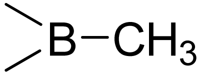
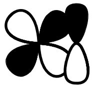
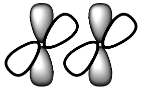
$(C_4H_4)Fe(CO)_3$

II. DEFINITION

Organometallic compounds (metal organyls, organometallics) are defined as materials which possess direct, more or less polar bonds **$M^{\delta+}$— $C^{\delta-}$** between metal and carbon atoms. In addition to the traditional metals, lanthanides, actinides, and semimetals, elements such as **boron**, **silicon**, **arsenic**, and **selenium** are considered to form organometallic compounds, e.g. organoborane compounds such as triethylborane (Et_3B).

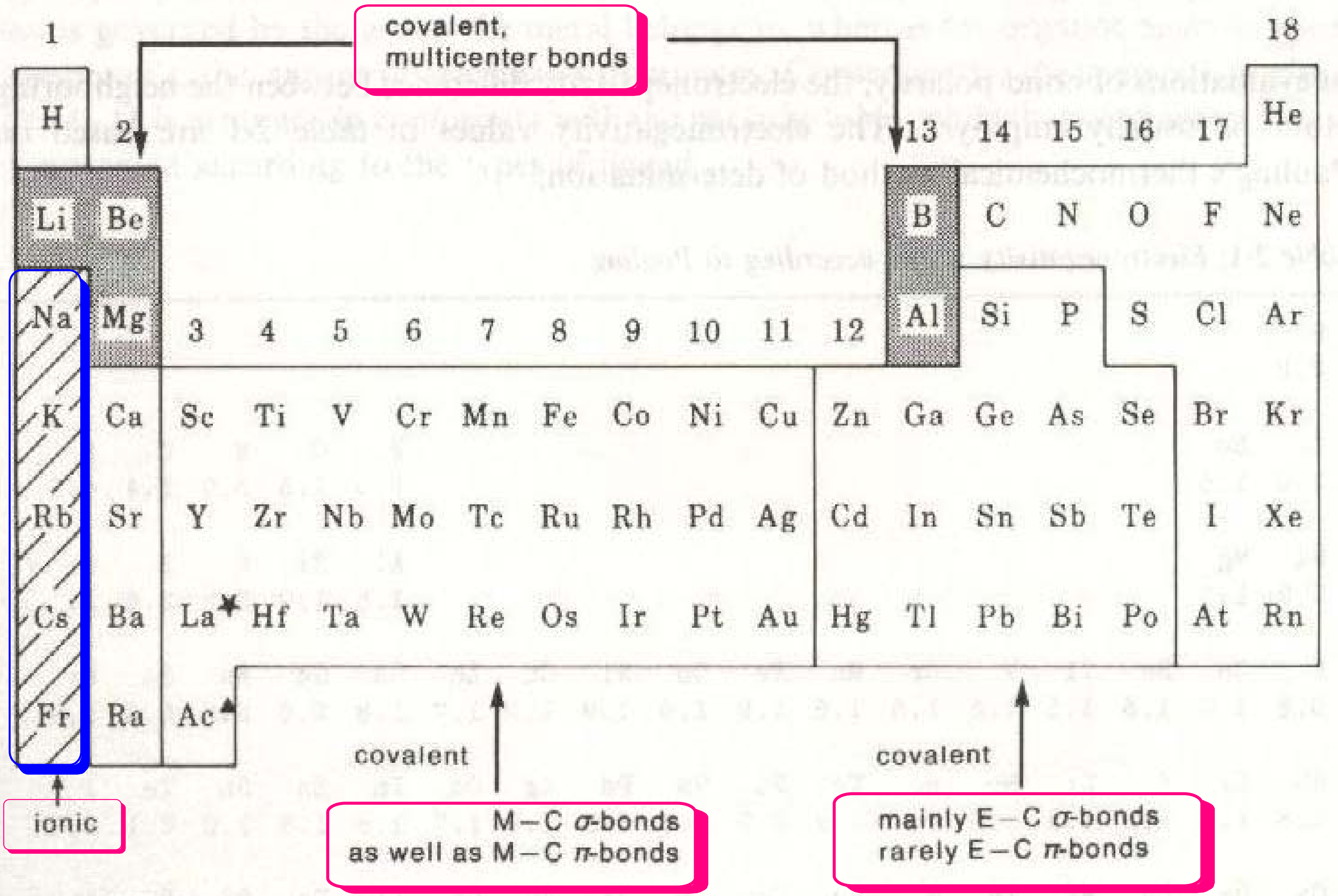
Organometallic chemistry is the study of organometallic compounds. Since many compounds without such bonds are chemically similar, an alternative may be compounds containing metal-element bonds of a largely covalent character. Organometallic chemistry combines aspects of inorganic chemistry and organic chemistry.

- Classification of organometallics based on the bond type: *σ*-, *π*-, *δ*-bond:

Overlap	Number of nodal planes including the bond axis	Bond Type	Example
	0	σ	
	1	π	$(CO)_5Cr{=}CR_2$
	2	δ	$[R_4Re{\equiv}ReR_4]^{2+}$

- In evaluations of bond polarity, the electronegativity difference between the neighboring atoms is usually employed.

- By way of generalization, it may be stated that the chemistry of main-group organometallics is governed by the group the metal belongs to, whereas for organotransition-metal compounds, the nature of the ligand dominates. 主族金属有机化合物的化学主要取定于金属本身的性质，而有机过渡金属化合物的性质则主要受其配体支配。



covalent, multicenter bonds

ionic

covalent

M – C σ-bonds
as well as M – C π-bonds

covalent

mainly E – C σ-bonds
rarely E – C π-bonds

★ Lanthanoids
▲ Actinoids

M – C bond predominantly ionic covalent

5-2 BASIC CONCEPTS

I. 18-Electron Rule

- The 18e rule: characterizing and predicting the stability of transition-metal complexes.

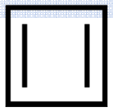
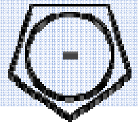
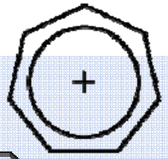
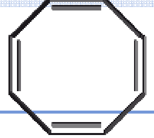
Valence shells of a M_T can accommodate **18** electrons: 2 in each of the five ***d*** orbitals (10 in total); 2 in each of the three ***p*** orbitals (6 in total); and 2 in the ***s*** orbital.

Combination of these atomic orbitals with ligand orbitals: **9** MOs which are either *metal-ligand bonding* or *non-bonding*. (There are also some higher energy *anti-bonding orbitals*). The complete filling of these nine lowest energy orbitals with electrons, whether those electrons originate from the metal or from any ligand, is the basis of the **18-electron rule**.

- **Thermodynamically stable transition-metal organometallics: the sum of the metal *d* electrons plus the electrons of conventionally regarded as being supplied by the ligands equals 18.**

W.B. Jensen. *J. Chem. Educ.* **2005**, *82*, 28

Table 1. Electrons donated by common fragments

Neutral	Positive	Negative	Ligands
1	0	2	H; X (F, Cl, Br, I); alkyl, aryl
2	–	–	CH_2=CH_2, CO, phosphane, etc.
3	2	4	π-ally, cyclopropenyl, NO
4	–	–	diolefin
4		6	Cyclobutdiene 
5	–	6	cyclopentadienyl 
6	–	–	Arene, triolefin
7	6	–	Tropylium ($C_7H_7^+$) 
8	–	10	cyclooctatetraene 

Examples:

- **$TiCl_4$** $3s^2 3p^6 3d^2 4s^2$

Neutral counting: **Ti** 4e, **Cl** 1e; 4+4(1) = 8 valence electrons

Ionic counting: **Ti^{4+}** 0e, **Cl^-** 2e; 0+4(2) = 8 valence electrons

Conclusion: Having only 8e (vs. 18 possible), we can anticipate that $TiCl_4$ will be a good Lewis acid. Indeed, it reacts (in some cases violently) with water, alcohols, ethers, amines.

- **$Fe(CO)_5$** $3s^2 3p^6 3d^6 4s^2$

Neutral counting: **Fe** 8e; **CO** 2e; 8 + 2(5) = 18 valence electrons

Conclusion: This is a special case, all fragments being neutral. Since this is an 18-electron complex, $Fe(CO)_5$ is a stable compound.

- **$Fe(C_5H_5)_2$, $FeCp_2$**

Neutral counting: **Fe** 8e, **C_5H_5** 5e: 8 + 2(5) = 18 electrons

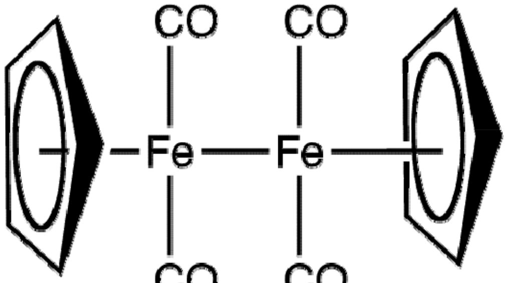
Ionic counting: **Fe^{2+}** 6e, **$C_5H_5^-$** 6e: 6 + 2(6) = 18 electrons

Conclusion: Ferrocene is expected to be a stable compound.

- **$[CpFe(CO)_2]_2$**

Neutral counting:

Cp 5 + Fe 8 + 2 CO 4 + Fe-Fe 1 = **18**



Counting electrons for just one iron center can be done by considering the other iron as contributing 1 electron to the count.

- **$CpFe(CH_3)(CO)_2$**

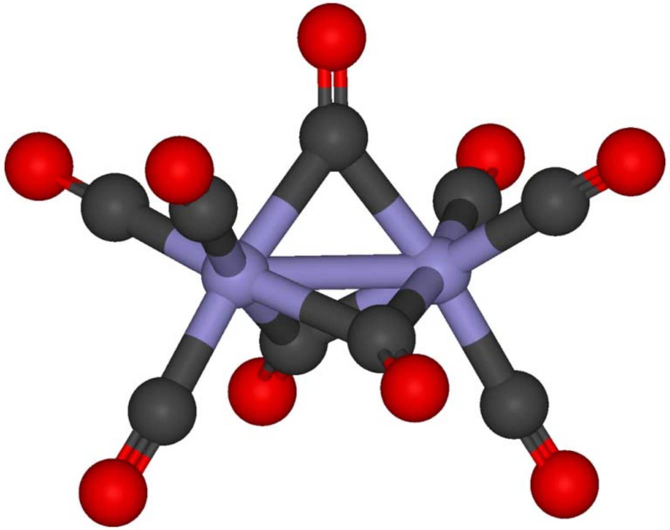
Neutral counting:

Cp 5 + Fe 8 + CH_3 1 + 2 CO 4 = **18**

- **$Fe_2(CO)_9$** 九羰基二铁

Neutral counting:

3 CO 6 + 3 μ-CO 3 + Fe 8 + Fe-Fe 1 = **18**



tri-μ-carbonyl-bis(tricarbonyliron)(*Fe-Fe*)

- **$Mn_2(CO)_5$**

NOTE:

i. These examples show the methods of electron counting, they are a *formalism*, and don't have anything to do with *real life* chemical transformations. Most of the 'fragments' mentioned above do not exist as such; they cannot be kept in a bottle. **These formalisms are only used to predict stabilities or properties of compounds!**

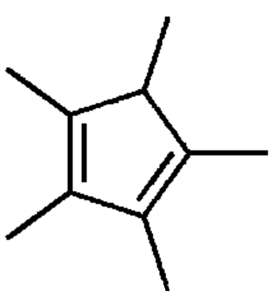
ii. The 18-electron rule is just that - a rule, not a law. Many M_T complexes do not follow this rule, and, furthermore, compounds which have fewer than 18 valence electrons tend to show enhanced reactivity. In fact, 18 electrons is often a recipe for non-reactivity in either a stoichiometric or catalytic sense.

iii. It is especially useful for organometallic complexes of the **Cr**, **Mn**, **Fe**, and **Co** triads, and applies to compounds such as ferrocene, iron pentacarbonyl, chromium carbonyl and nickel carbonyl.

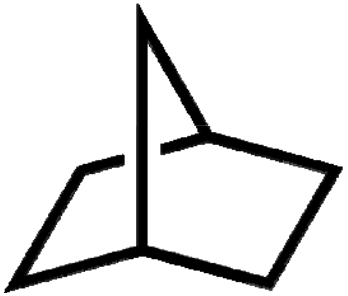
Violations to the 18-electron rule:

i. Bulky ligands

- $Ti(neopentyl)_4$ (8 VE)
- $Cp^*{}_2Ti(C_2H_4)$ (16 VE)
- $Cp^*Cr(CO)_3$ (17 VE)
- $Co(norbornyl)_4$ (11 VE)



Cp*



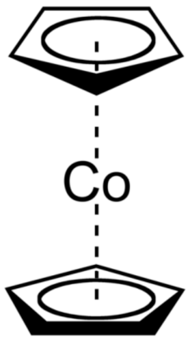
Norbornane
降莰烷

ii. High spin complexes

- $CrCl_3(THF)_3$ (15 VE) $3s^2 3p^6 3d^5 4s^1$
- $[Mn(H_2O)_6]^{2+}$ (17 VE)
- $[Cu(H_2O)_6]^{2+}$ (21 VE)

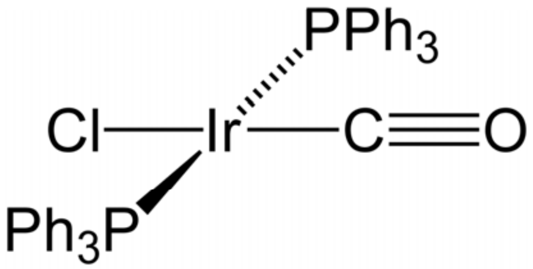
iii. Higher electron counts

- Cobaltocene (19 VE)
- Nicklocene (20 VE)



iv. 'Inaccessible' high energy orbitals

- CuCl(CO) (14 VE)
- Vaska's compound: $[IrCl(CO)(PPh_3)_2]$ (16 VE)



II. π-Backbonding

π-Backbonding (π-backdonation): electrons move from an atomic orbital on one atom to a π* anti-bonding orbital on another atom or ligand, in the process relieving the metal of excess negative charge. π-反馈键

Examples:

$Ni(CO)_4$, Zeise's salt

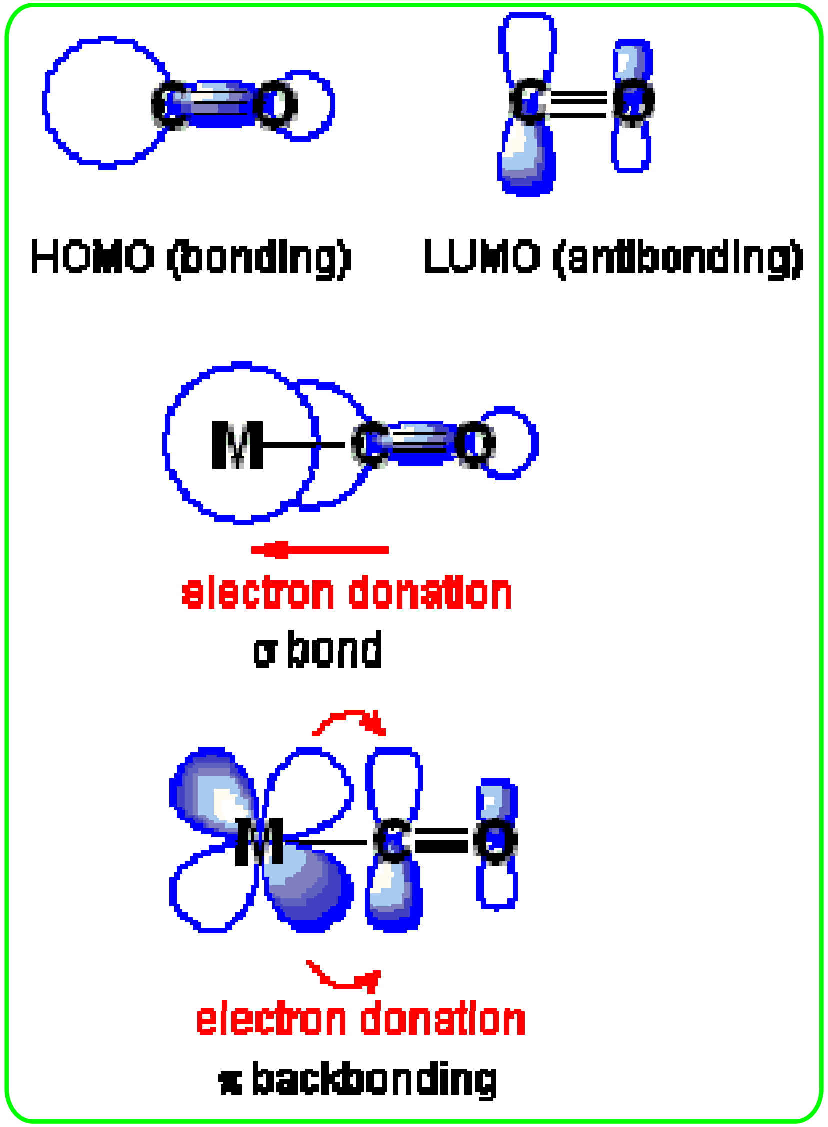


FIG.1. Top: the HOMO and LUMO of CO. Middle: a sigma bonding orbital in which CO donates electrons to a metals center from its HOMO. Bottom: the metal center donates electron through a *d* orbital to CO's LUMO.

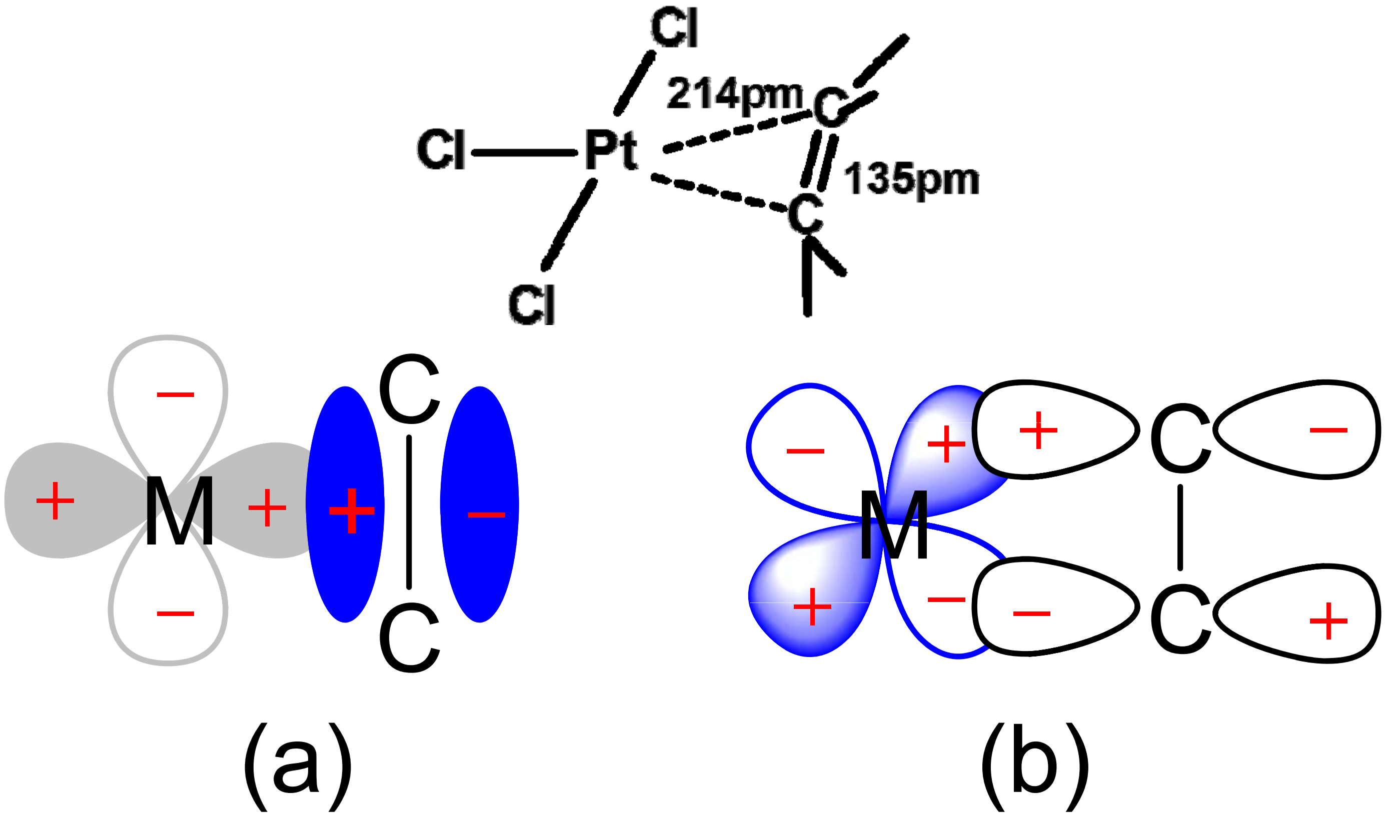
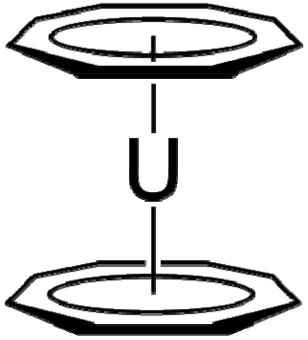


FIG.2. Orbital overlap scheme for the formation of a π-type interaction between an olefin and a transition metal: (a) overlap of one lobe of a $d_{x2\text{-}y2}$ orbital from the metal and a π-bonding orbital of the olefin; (b) use of the π-antibonding orbital of the olefin.

III. Hapticity 哈普托数

The term hapticity is used to describe how a group of *contiguous* atoms of a ligand are coordinated to a central atom. Hapticity of a ligand is indicated by the Greek character 'eta', η.

η^n: n = the number of contiguous atoms of the ligand that are bound to the metal.



☞ The term is usually employed to describe ligands containing extended π-systems or where agostic bonding is not obvious from the formula.

- **Ferrocene:** bis(η^5-cyclopentadienyl)iron
- **Zeise's salt:** $K[PtCl_3(\eta^2\text{-}C_2H_4)]\cdot H_2O$
- **Uranocene:** bis(η^8-1,3,5,7-cyclooctatetraene)uranium
- $W(CO)_3(PPr^i_3)_2(\eta^2\text{-}H_2)$
- $IrCl(CO)[P(C_6H_5)_3]_2(\eta^2\text{-}O_2)$

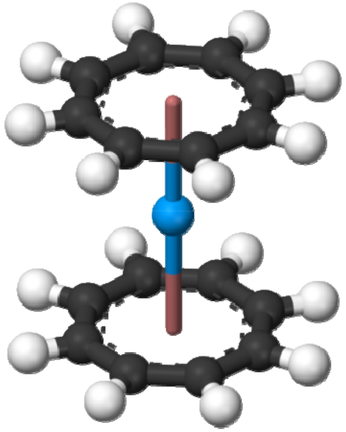
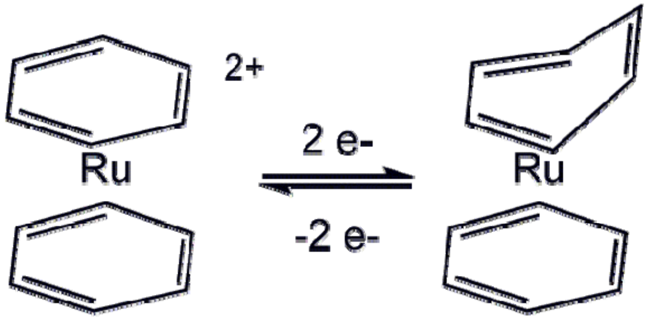


TABLE 2. Electrons donated by "π-ligands" vs. hapticity

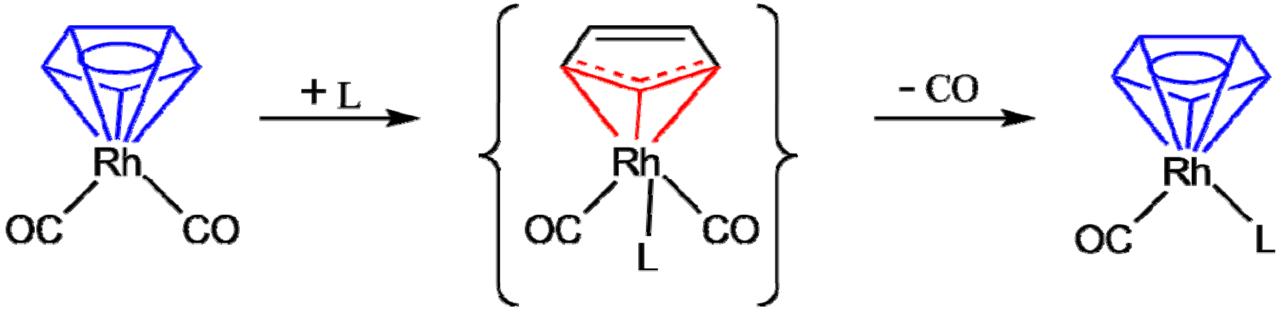
Ligand	Electrons contributed (neutral counting)	Electrons contributed (ionic counting)
η^1-Allyl	1	2
η^3-Allyl, cyclopropeny	3	4
η^3-Allenyl	3	4
η^2-Butadiene	2	2
η^4-Butadiene	4	4
η^1-cyclopentadienyl	1	2
η^5-cyclopentadienyl cyclohexadienyl	5	6
η^2-Benzene	2	2
η^6-Benzene	6	6
η^7-Cycloheptatrienyl	7	6
η^8-Cyclooctatetraenyl	8	10

Changes in hapticity

The hapticity of a ligand can change in the course of a reaction.



$[Ru(\eta^6\text{-}C_6H_6)_2]^{2+}$ $Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_6)$



The η^5-cyclopentadienyl changes to an η^3-cyclopentadienyl, giving room on the metal for an extra 2-electron donating ligand 'L'.

➢ **Hapticity vs. denticity** 哈普托数 *vs* 齿合度

Polydentate ligands coordinate via multiple coordination sites within the ligand. **Denticity** refers to the number of atoms in a single ligand that bind to a central atom in a coordination complex.

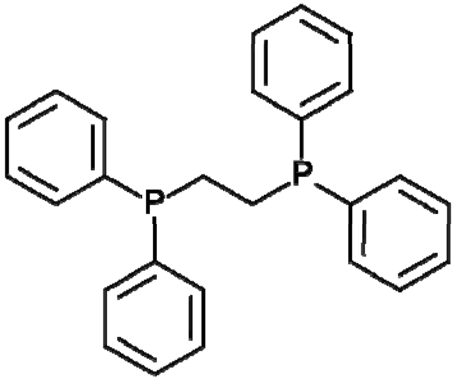
Examples:

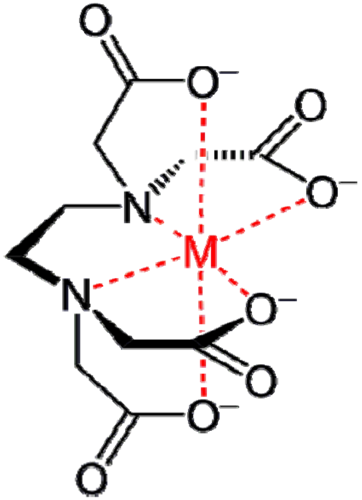
☞ 1,2-bis(diphenylphosphino)ethane, $(Ph_2PCH_2CH_2PPh_2)$

dichloro[ethane-1,2-diylbis(diphenylphosphane)-κ^2 P]nickel(II)

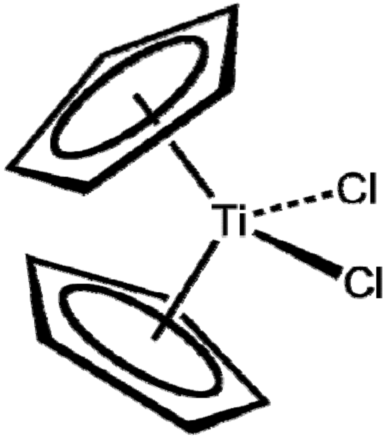
☞ titanocene dichloride: (Cp_2TiCl_2)

dicholorobis(η^5-2,4-cyclopentadien-1-yl)titanium





Metal-EDTA **chelate**

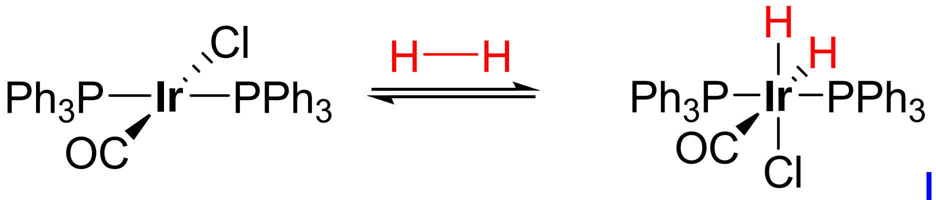


5-3 IMPORTANT TYPES OF REACTIONS

I. Oxidative addition/Reductive elimination

- In oxidative addition, a metal complex with vacant coordination sites and a relatively low oxidation state is oxidized by the insertion of the metal into a covalent bond (X—Y).
- Both the formal oxidation state of the metal and the electron count of the complex increase by two.
- Oxidative additions can occur with the insertion of a metal into many different covalent bonds, they are most commonly seen with H–H and C_{sp3}–halogen bonds.

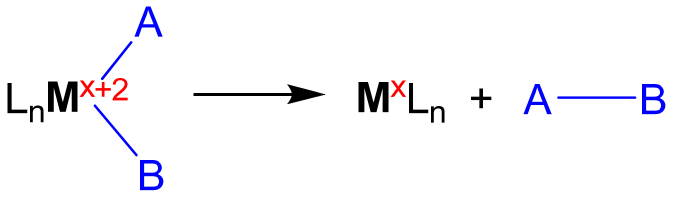
Vaska's complex:



	Ir(I)	Ir(III)
VE	16	18
CN	4	6

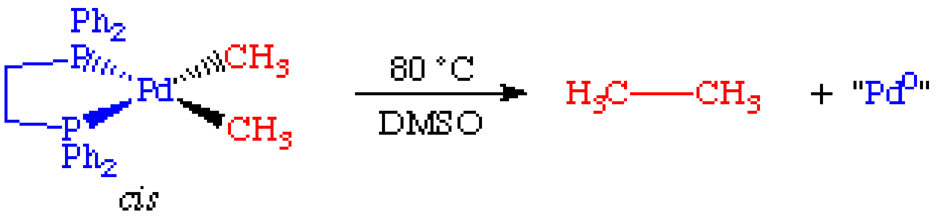
IR:	CO cm^{-1}
Vaska's complex:	1967
Vaska's + I_2:	2067

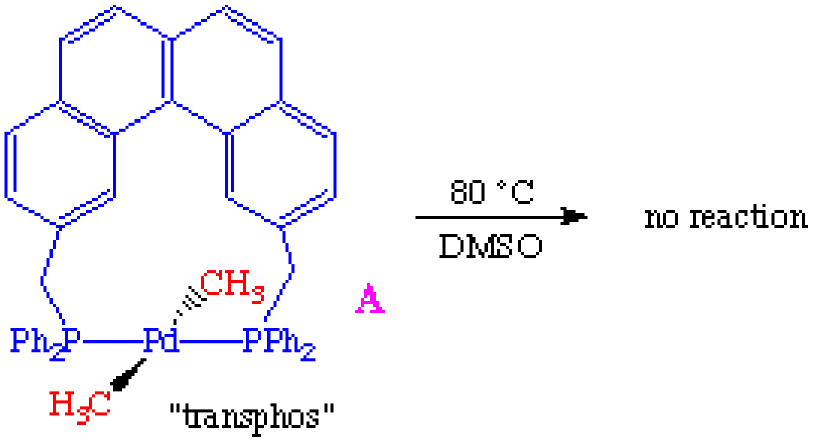
A **reductive elimination** involves the elimination or expulsion of a molecule from a transition metal complex. In the process of this elimination, the metal center is reduced by two electrons.



$$L_nM^{x+2}{<}^{A}_{B} \longrightarrow M^{x}L_n + A{-}B$$

$$L_nAM^{x+1}{-}M^{x+1}L_nB \longrightarrow L_nM^{x}{-}M^{x}L_n + A{-}B$$





- The groups being eliminated must be in a mutually *cis* orientation.
- A series of reactions involving an oxidative addition, a rearrangement and then a reductive elimination form the basis for a variety of industrially important catalytic cycles.

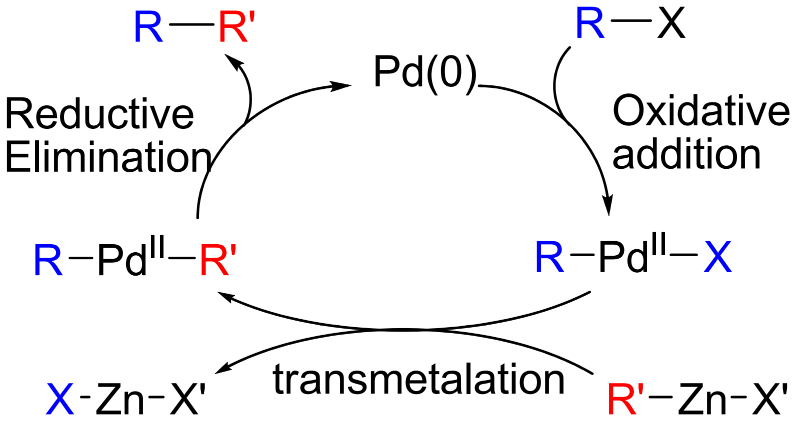
II. Transmetalation

➢ Transmetalation is a general chemical reaction type describing the exchange of ligands between two metal centers. The metal centers need not be the same. The ligands R and R' can be organic or inorganic.

$$\mathrm{M{-}R} + \mathrm{M'{-}R'} \longrightarrow \mathrm{M{-}R'} + \mathrm{M'{-}R}$$

☞ Transmetalation is important in the synthesis of various organometallic compounds. This reaction type also appears frequently in the catalytic cycle of various metal catalyzed organic reactions.

Negishi coupling: $\mathrm{R{-}X} + \mathrm{R'{-}Zn{-}X'} \xrightarrow{\mathrm{PdL_n}} \mathrm{R{-}R'}$



R—R'

Pd(0)

R—X

Reductive Elimination

Oxidative addition

$\mathrm{R{-}Pd^{II}{-}R'}$

$\mathrm{R{-}Pd^{II}{-}X}$

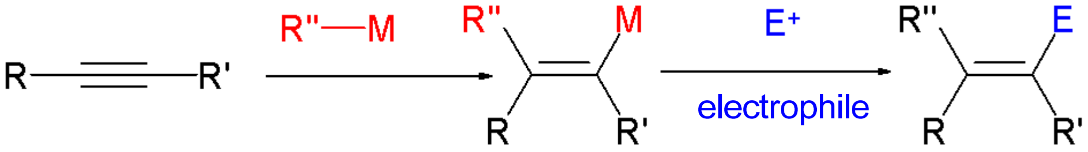
X-Zn-X'

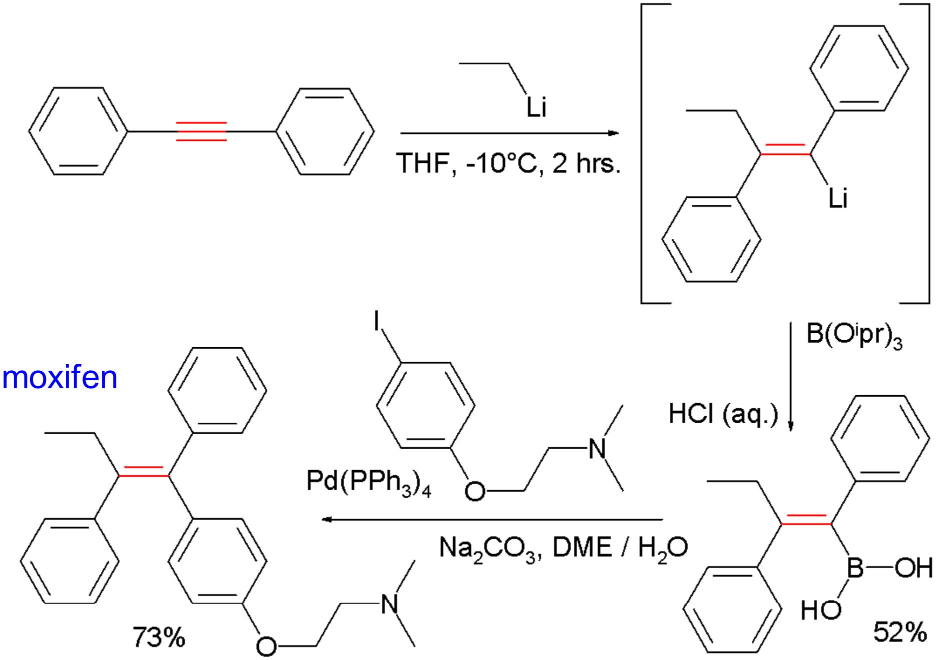
transmetalation

R'-Zn-X'

III. Carbometalation

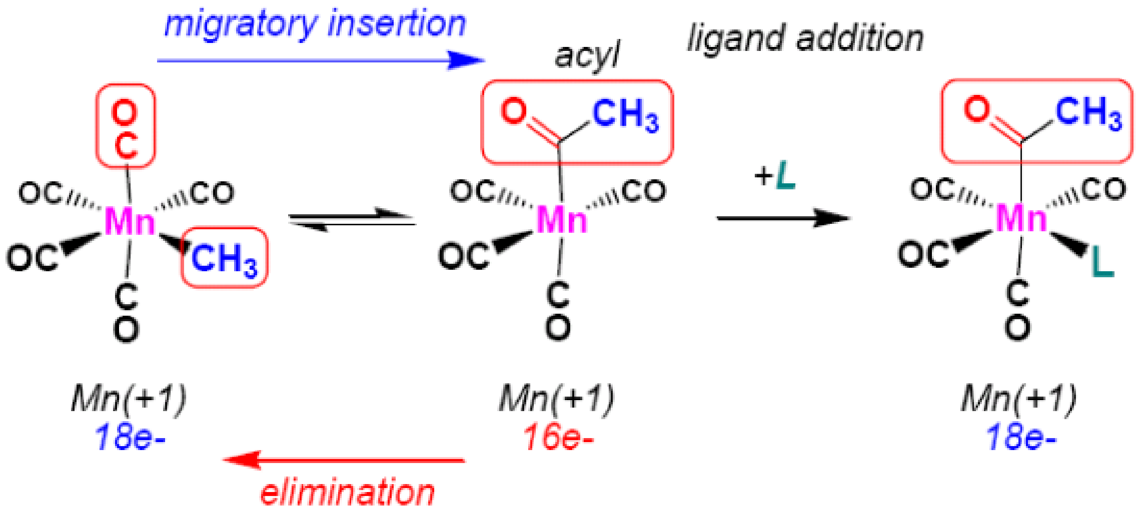
- Carbometalation is an reaction involving the nucleophilic addition to alkenes and alkynes of a diverse range of organometallic reagents such as organolithium compounds, organocopper compounds and Grignard reagents according to the following general alkyne scheme:





IV. Migratory insertion

A migratory insertion reaction is when a cisoidal anionic and neutral ligand on a metal complex couple together to generate a new coordinated anionic ligand. This new anionic ligand is composed of the original neutral and anionic ligands now bonded to one another.



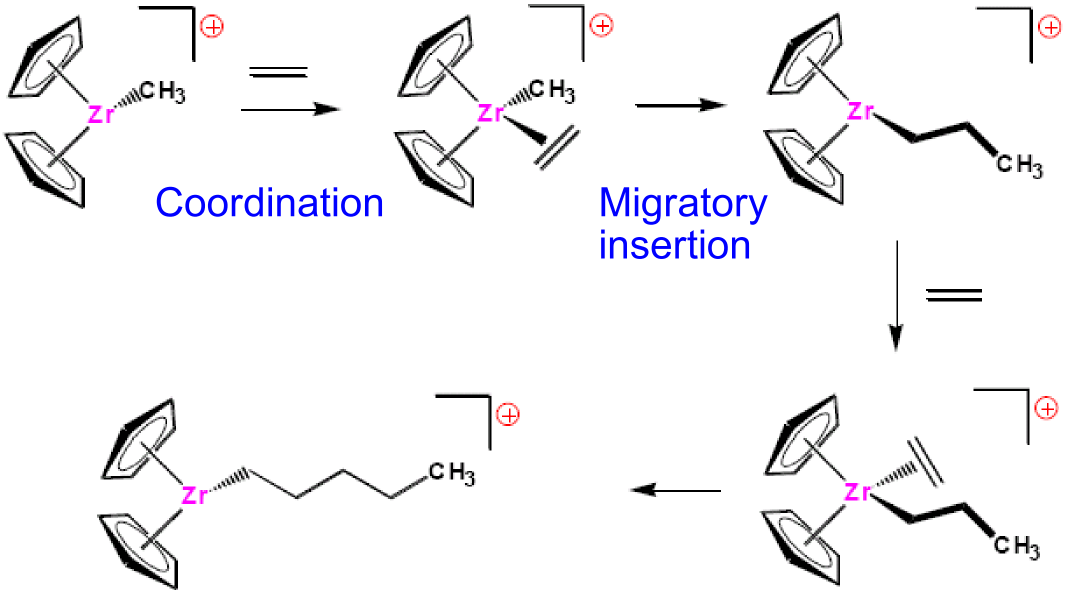
Anionic: **H^-, R^- (alkyl)**,
Ar^-(aryl), acyl$^-$, O^{2-} (oxo)

Neutral: **CO, alkenes**,
alkynes, carbenes

- No change in formal oxidation state (exception: alkylidenes).
- The two groups that react must be cisoidal to one another.
- A vacant coordination site is generated by the migratory insertion.
- Migratory insertions are favored on more electron-deficient metal centers.

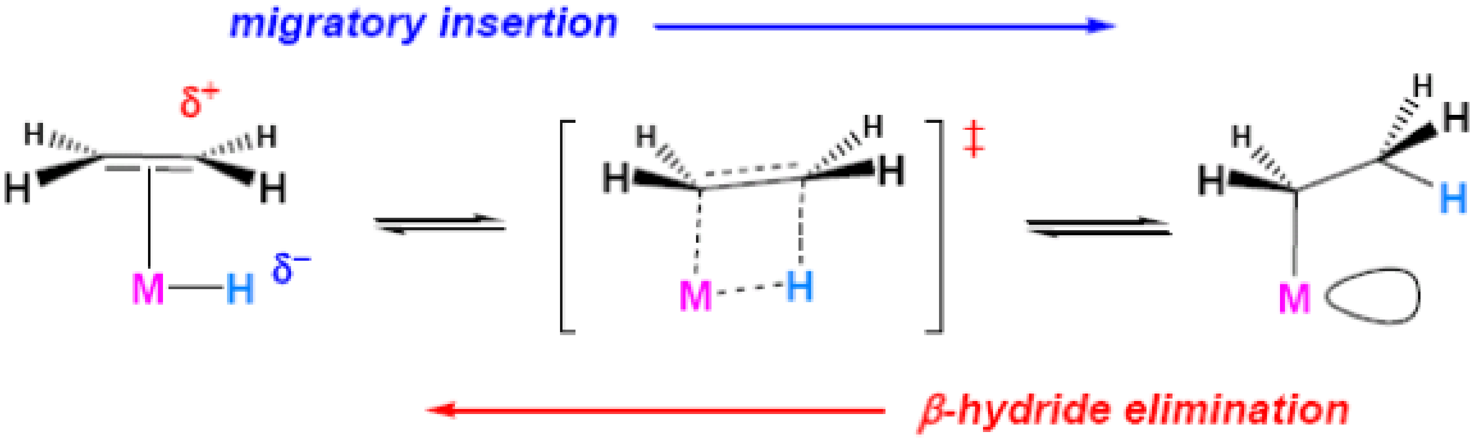
➢ Alkene Migratory Insertions.

Alkene and hydride/alkyl migratory insertion is the basis for almost all transition metal-based polymerization catalysts.



A polymerization is just many, many migratory insertions of an alkene and alkyl (the growing polymer chain) interspaced with alkene ligand addition reactions.

- An alkene and a hydride usually react via a migration of the hydride to the coordinated alkene ligand:

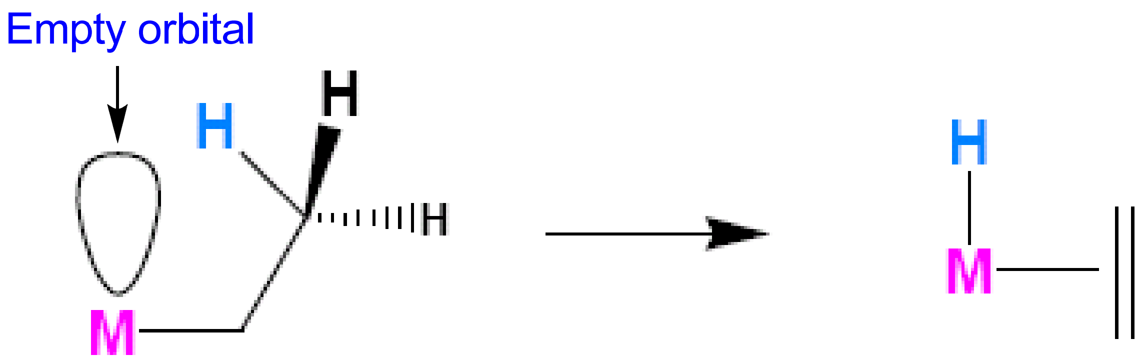


The backwards reaction, of course, is a β-hydride elimination and is usually quite favorable if there is an empty orbital *cis* to the alkyl ligand. Thus, the general importance of having a trapping ligand to coordinate to the empty orbital generated from the migratory insertion.

V. β-Hydride elimination

Elimination reactions are just the reverse of migratory insertion reactions.

- β-Hydride elimination is a reaction in which an alkyl group bonded to a metal centre is converted into the corresponding metal-bonded hydride and an alkene.



The key points to remember are:

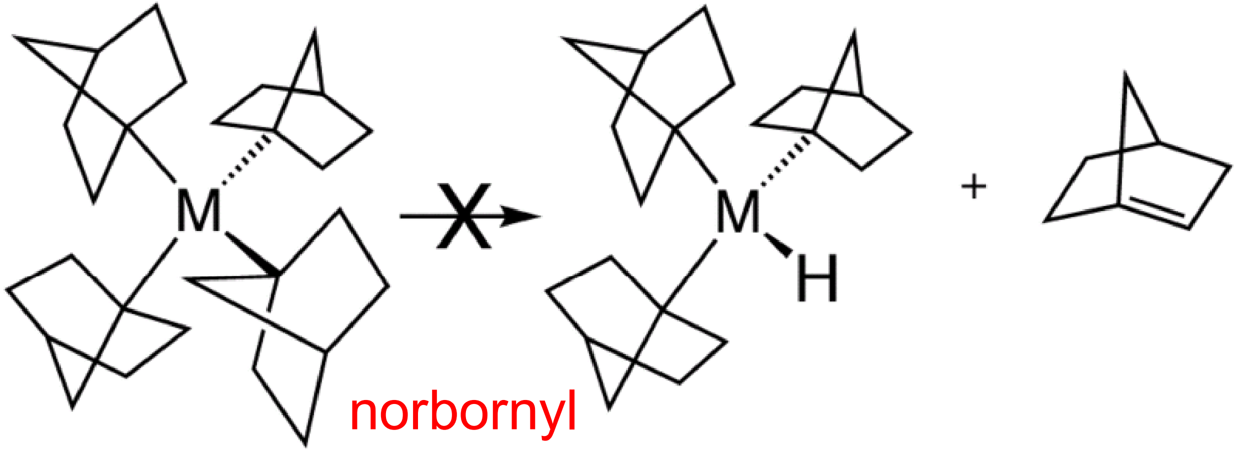
i. No change in formal oxidation state (exception: alkylidenes).

ii. A vacant orbital is cisoidal to the group to do an elimination reaction on. Alternatively, a cisoidal labile ligand that can easily dissociate to open up an empty orbital.

- Avoiding β-hydride elimination:

i. to employ an alkyl ligand that lacks a β-hydrogen (methyl or neopentyl).

ii. It is also inhibited when the reaction would produce a strained alkene.



iii. The beta position may be blocked by non-hydrogen atoms.

iv. If the metal center does not have empty coordination sites, for example, by the complex already having 18 electron configuration, β-hydride elimination is not possible as well.

5-4 MAIN-GROUP ORGANOMETALLICS

I. PREPARATION

- Direct Synthesis

$$Li + C_4H_4Br \longrightarrow C_4H_9Li + LiBr$$

$$Mg + C_6H_5Br \longrightarrow C_6H_5MgBr$$

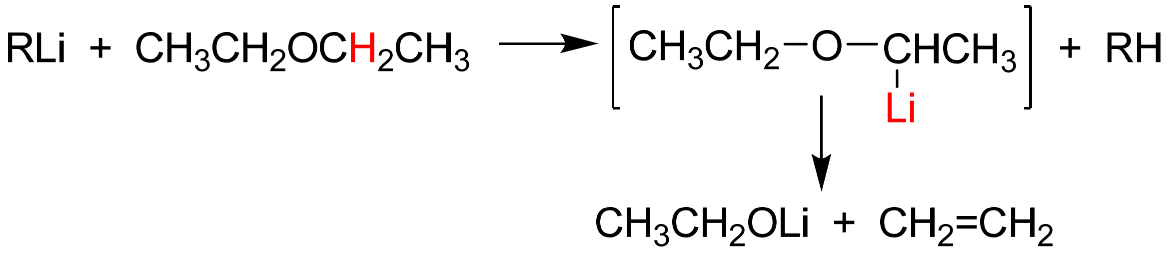
Mixed metal synthesis:

$$2\ Na + Hg + 2\ CH_3Br \longrightarrow (CH_3)_2Hg + 2\ NaBr$$

$$4\ Na/Pb + 4\ C_2H_5Cl \longrightarrow (C_2H_5)_4Pb + 3\ Pb + 4\ NaCl$$

$\triangle H_f^\circ(NaX)$ boosts the driving force.

Side reactions:



$$RLi + CH_3CH_2OCH_2CH_3 \longrightarrow \left[CH_3CH_2{-}O{-}\underset{Li}{C}HCH_3\right] + RH$$

$$\downarrow$$

$$CH_3CH_2OLi + CH_2{=}CH_2$$

Transmetallation

$$\boxed{\mathrm{Zn} + (\mathrm{CH_3})_2\mathrm{Hg} \longrightarrow (\mathrm{CH_3})_2\mathrm{Zn} + \mathrm{Hg}}$$

$$\Delta H = -35\ \mathrm{kJ/mol}$$

This general method may be applied to M = Li ~ Cs, Be ~ Ba, Al, Ga, Sn, Pb, Bi, Se, Te, Zn, Cd.

Metal exchange

$$4\ \mathrm{PhLi} + (\mathrm{CH_2{=}CH})_4\mathrm{Sn} \longrightarrow 4\ (\mathrm{CH_2{=}CH})\mathrm{Li} + \mathrm{Ph_4Sn}\downarrow$$

This method is useful for making certain organolithium compounds from derivatives of less electropositive metals.

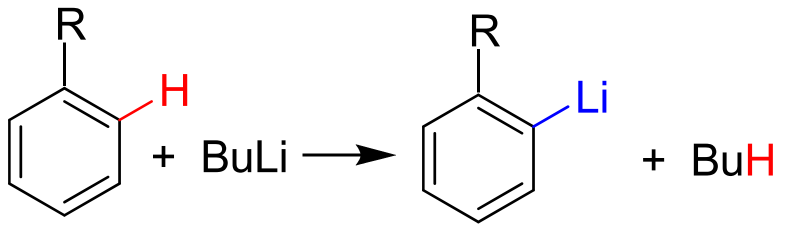
Metal Halogen Exchange

$$n\text{-}\mathrm{BuLi} + \mathrm{PhX} \longrightarrow n\text{-}\mathrm{BuX} + \mathrm{PhLi}$$

Acidity: $n\text{-}\mathrm{Bu{-}H} < \mathrm{Ph{-}H}$

Metallation of C–H acids

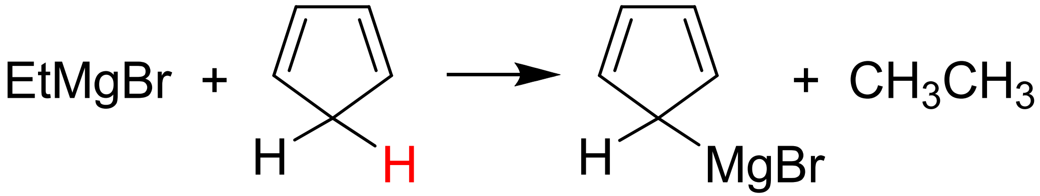
Metallation (replacement of H by M) are acid/base equilibrium. The arenes with their higher acidities are appropriate substrates and the method is particularly valuable for the preparation of aryllithium compounds.

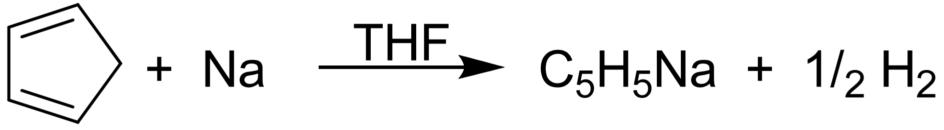


R = MeO, Me_2N, $CONMe_2$, SO_2Me, etc.

$$PhNa + PhCH_3 \rightleftharpoons PhH + PhCH_2Na$$

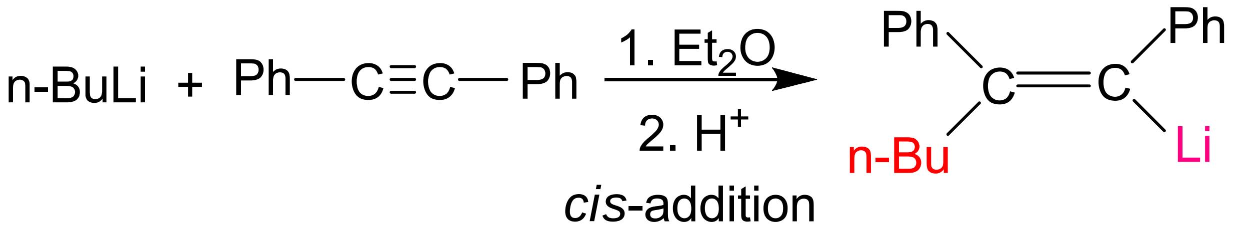
$$EtMgBr + RC{\equiv}CH \longrightarrow RC{\equiv}CMgBr + CH_3CH_3$$





Carbometallation and Hydrometallation

Carbometallation

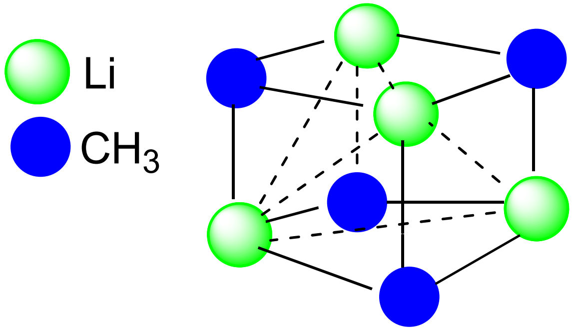


Hydroalumination

$$(C_2H_5)_2Al{-}H + H_2C{=}CH_2 \longrightarrow (C_2H_5)_2Al{-}CH_2CH_3$$

II. Organolithium reagents

- ➢ Organolithium reagents can be aggregated, with lithium coordinating to more than one carbon atom and carbon coordinating to more than one lithium atom.

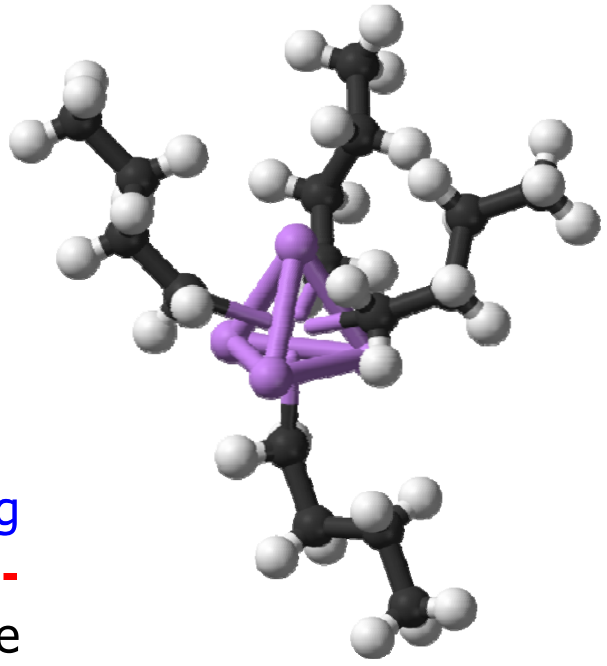


d (Li—C) = 2.31 Å
d (Li—Li) = 2.56 Å
d (C—C) = 3.68
Li−C−Li 68°

Schematic drawing of the unit $(LiCH_3)_4$

Solid methyllithium: cubic body-centered packing of **$(LiCH_3)_4$** units, the latter consisting of **Li_4-tetrahedron** with methyl groups capping the triangular faces. 立方体心堆积

☞ In the aggregates $(LiR)_n$, the "electron deficiency" is compensated for by the formation of multicenter bonds.



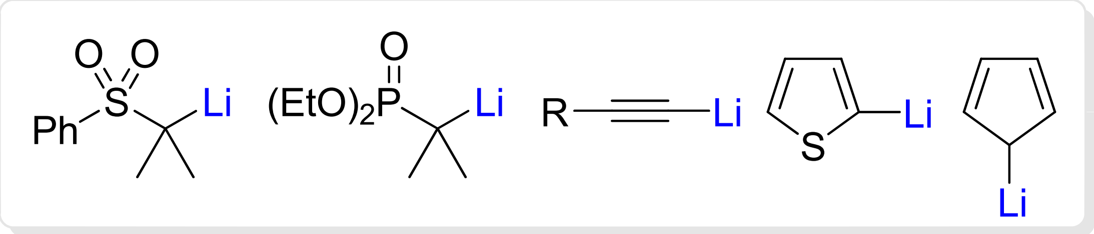
n-Butyllithium

☞ Three general factors affect aggregation: the electrostatic interaction between opposite charges, the coordination sphere of lithium (solvent molecules or Lewis base) and the steric hindrance of the hydrocarbon part.

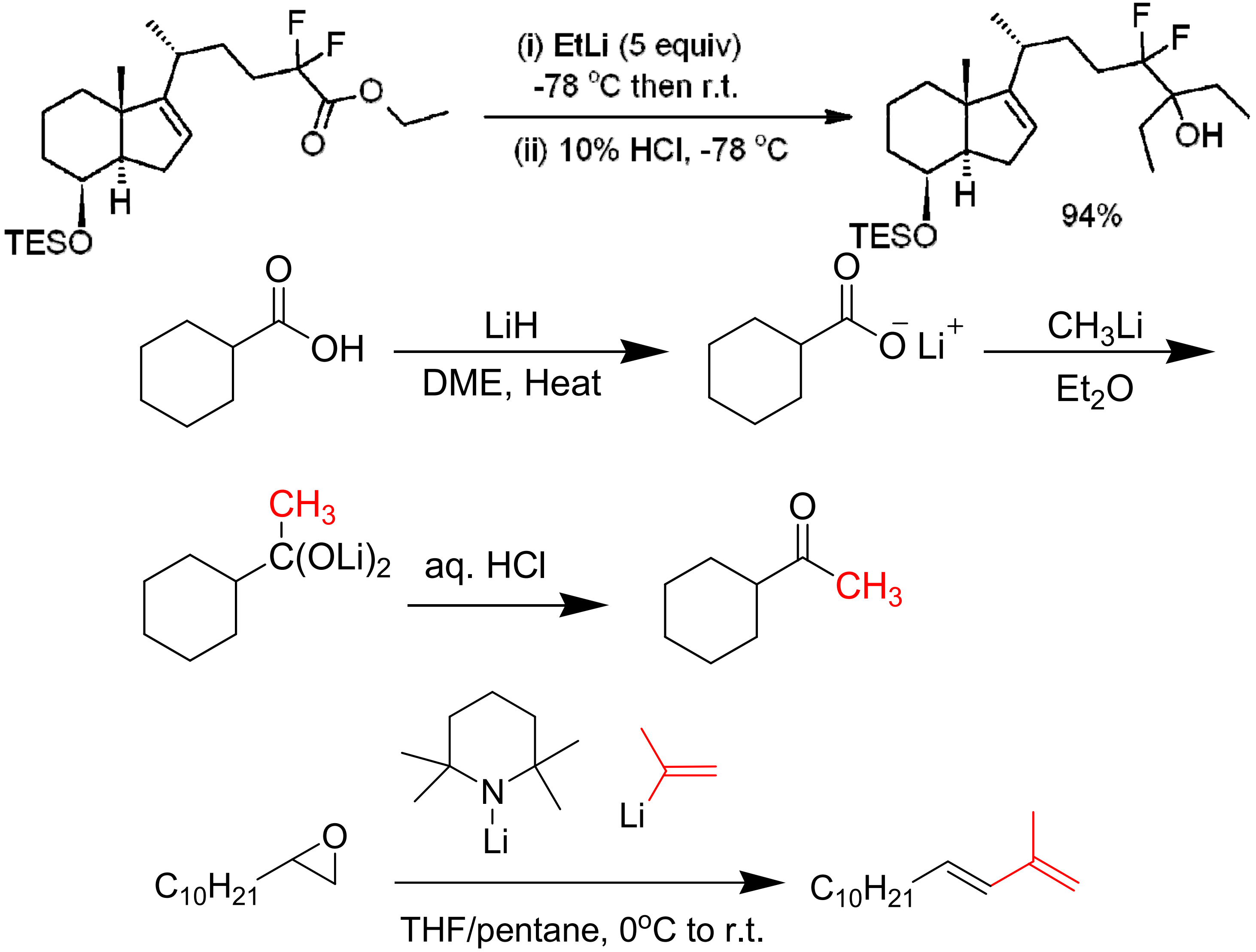
LiR	Solvent	Aggregation
$LiCH_3$	hydrocarbon	Hexamer (Li_6 octahedron)
	THF, Et_2O	Tetramer (Li_4 tetrahedron)
	$Me_2NCH_2CH_2NMe_2$	monomer
n-BuLi	cyclohexane	hexamer
	Et_2O	tetramer
t-BuLi	hydrocarbon	tetramer
PhLi	THF, Et_2O	dimer
$PhCH_2Li$	THF, Et_2O	monomer
C_3H_5Li (allyl)	THF	monomer

➢ REACTIONS

- Metalation or Li/H exchange reaction: The metalation reaction is an important synthetic method for the preparation of many organolithium compounds.



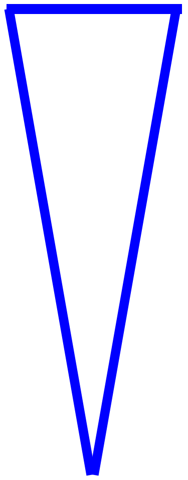
- Reaction with ketones and aldehydes to alcohols.
- Reaction with carboxylic acid salts and acid chlorides to the corresponding ketone.
- Reaction with oximes to the corresponding amines. (肟)
- Reaction with isonitriles to the corresponding lithium aldimine (醛亚胺). Subsequent hydrolysis effectively converts the organolithium compound to its aldehyde.
- Reaction with certain epoxides to the corresponding alkenes.



Organic Syntheses, Vol. 85, p1 (2008)

III. Organomagnesium and Organozinc

➢ In many ways the chemistry of group 2 elements (the alkaline earth metals) mimics that of group 12 elements because both groups have filled s shells for valence electrons.



Group 2

Ba
Sr
Ca
Mg
Be

Group 12

Zn
Cd
Hg

Electropositive character of the metal

and

reactivity of organometallics in heterolytic reactions

decreases

Among the organometallic compounds of groups 2 and 12, organomagnesium compounds are of prime importance because of their application in organic synthesis. Organomagnesium compounds combine in a unique way high reactivity and ease access.

Grignard reagent

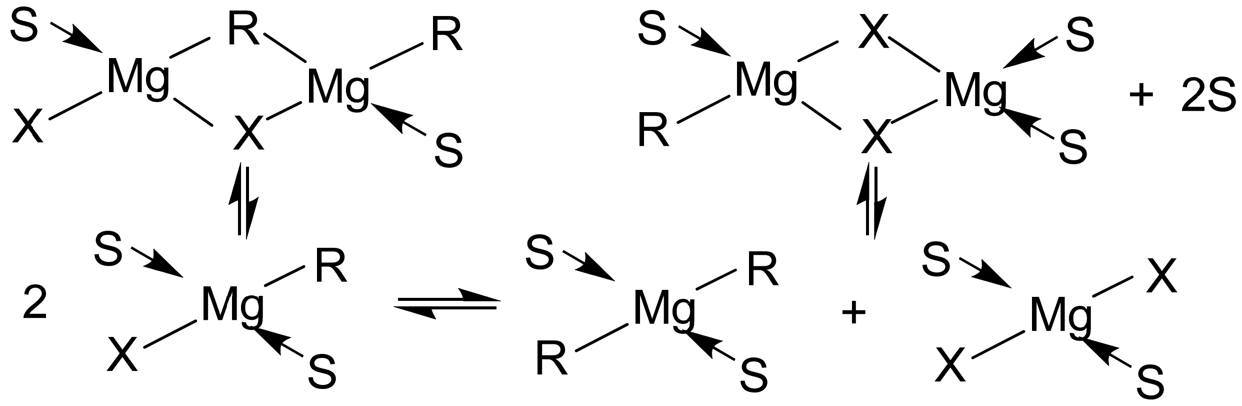
- Grignard reagents are formed via the action of an alkyl or aryl halide on magnesium metal. Typical solvents are Et_2O and THF. The reaction proceeds through single electron transfer..

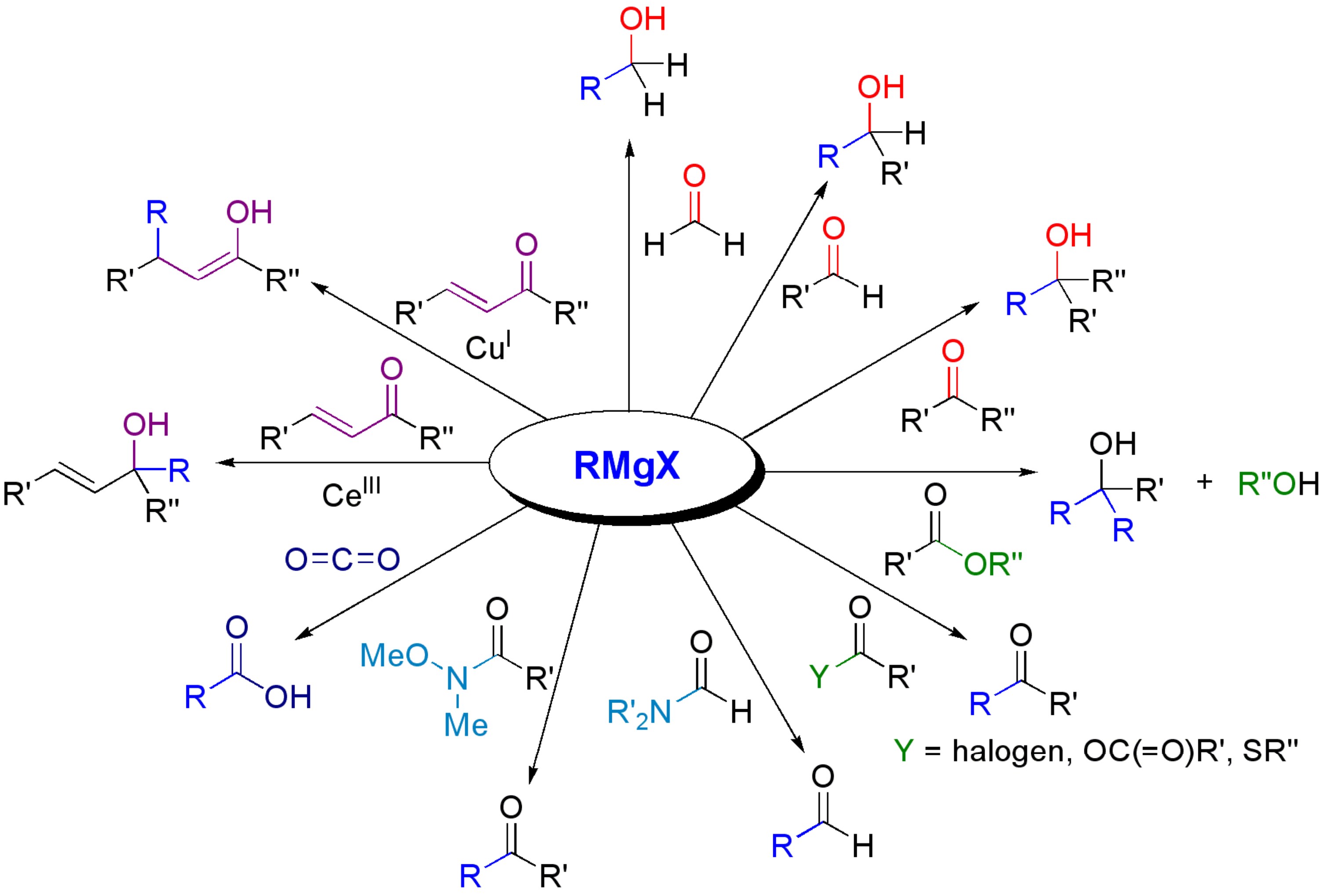
$$Mg + RX \xrightarrow{Et_2O} RMgX(Et_2O)_n \qquad X = Br, I$$

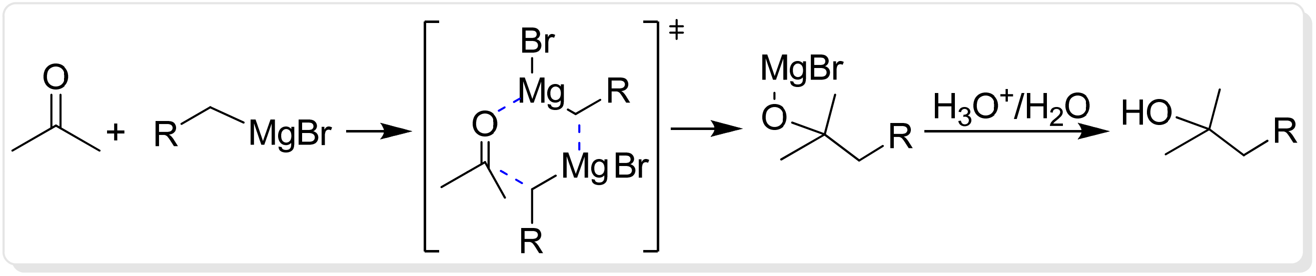
☞ The addition of I_2 activates the Mg surface; MgI_2 thus formed, binds the last traces of water in the reaction mixture.

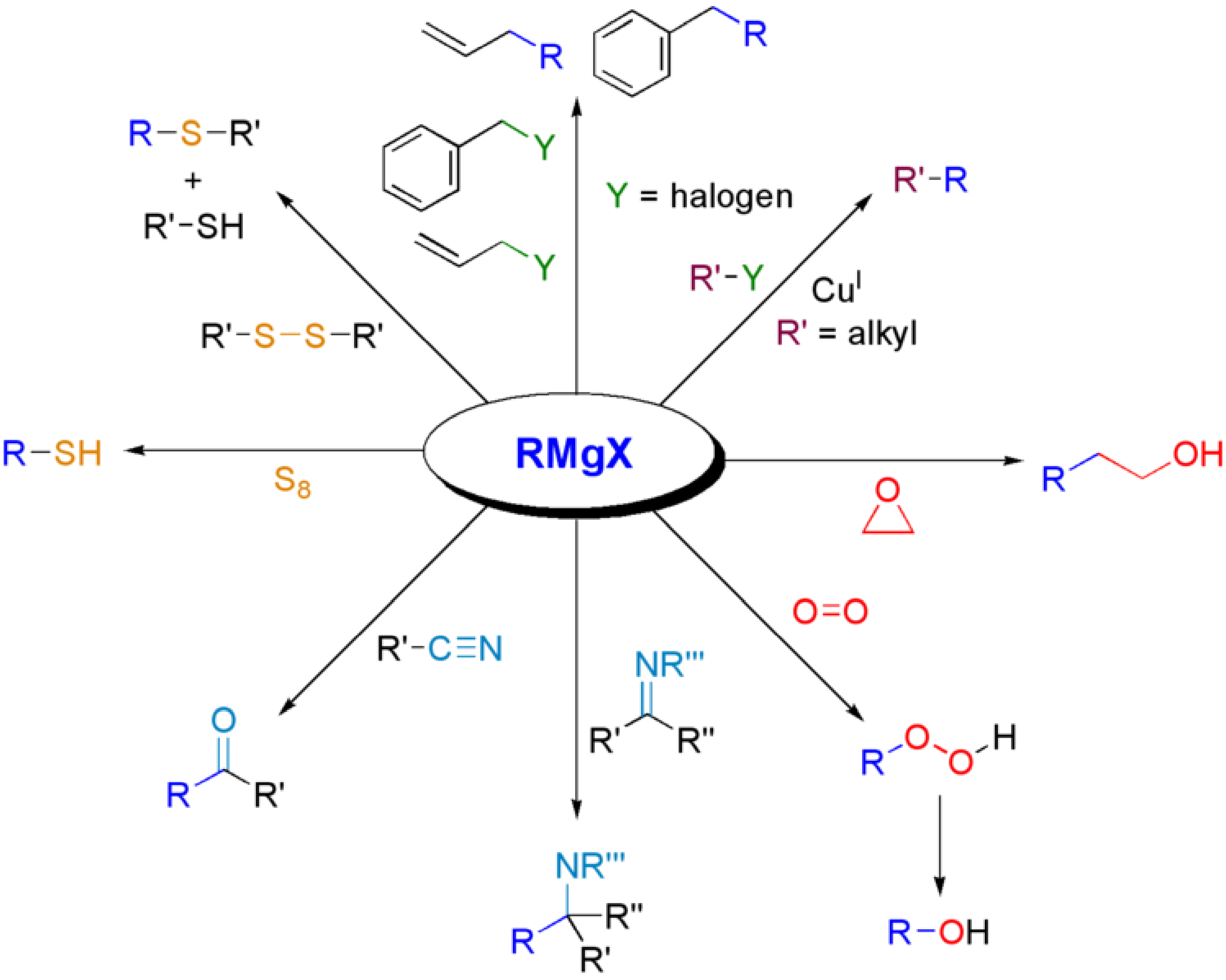
☞ Schlenk equilibrium, Grignard reagents form varying amounts of diorganomagnesium compounds (R = organic group, X = halide):

$$2\ RMgX \rightleftharpoons R_2Mg + MgX_2$$

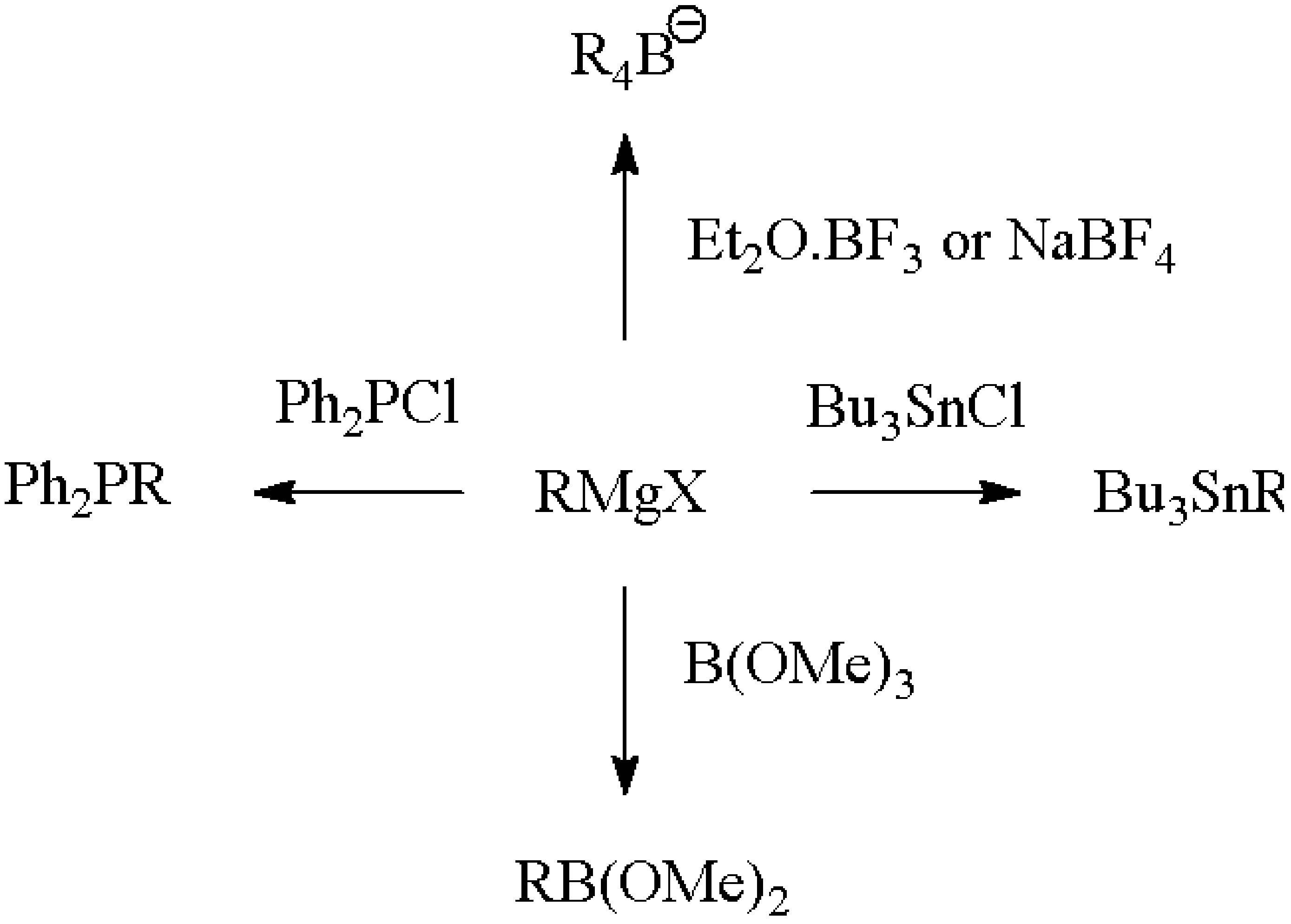



RMgX
Cu^I
Ce^III
O=C=O
R'₂N
MeO
Y = halogen, OC(=O)R', SR''
+ R''OH


MgBr
‡
H₃O⁺/H₂O
HO


RMgX
Y = halogen
R'–Y
Cu^I
R' = alkyl
R'–R
R'–S–S–R'
R–S–R'
+
R'–SH
S$_8$
R–SH
R–OH
O=O
R'–C≡N
NR'''
R'
R''
R

- Also the Grignard reagent is very useful for forming carbon-heteroatom bonds.



$R_4B^{\ominus}$

$Et_2O.BF_3$ or $NaBF_4$

Ph_2PCl

Bu_3SnCl

Ph_2PR

$RMgX$

Bu_3SnR

$B(OMe)_3$

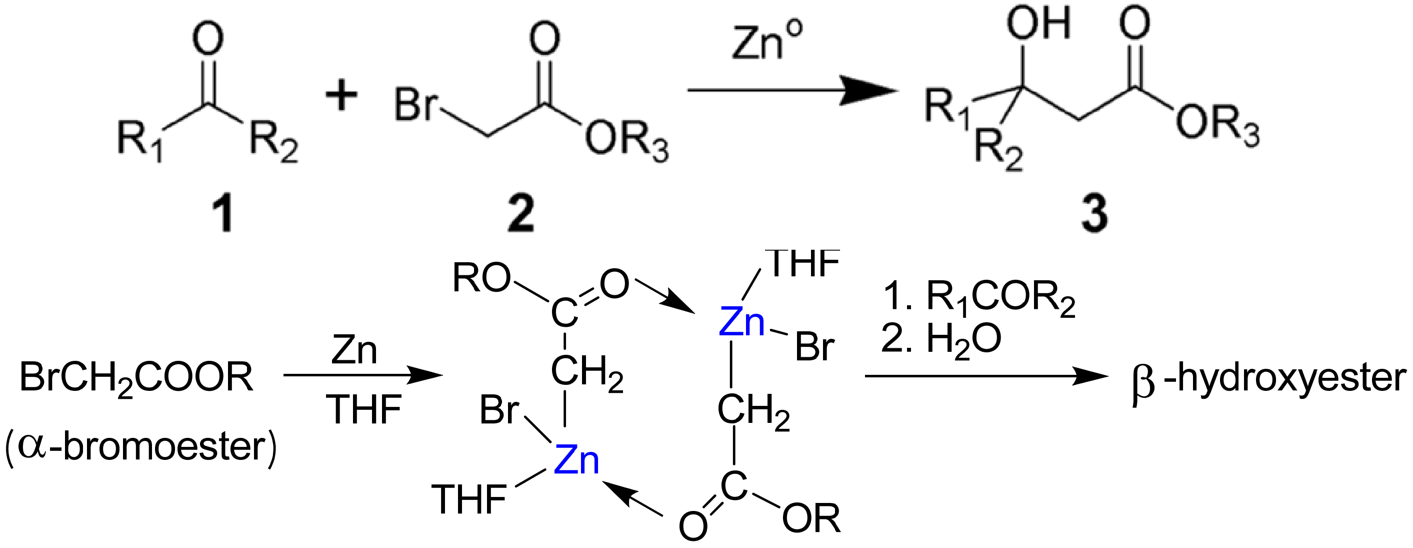
$RB(OMe)_2$

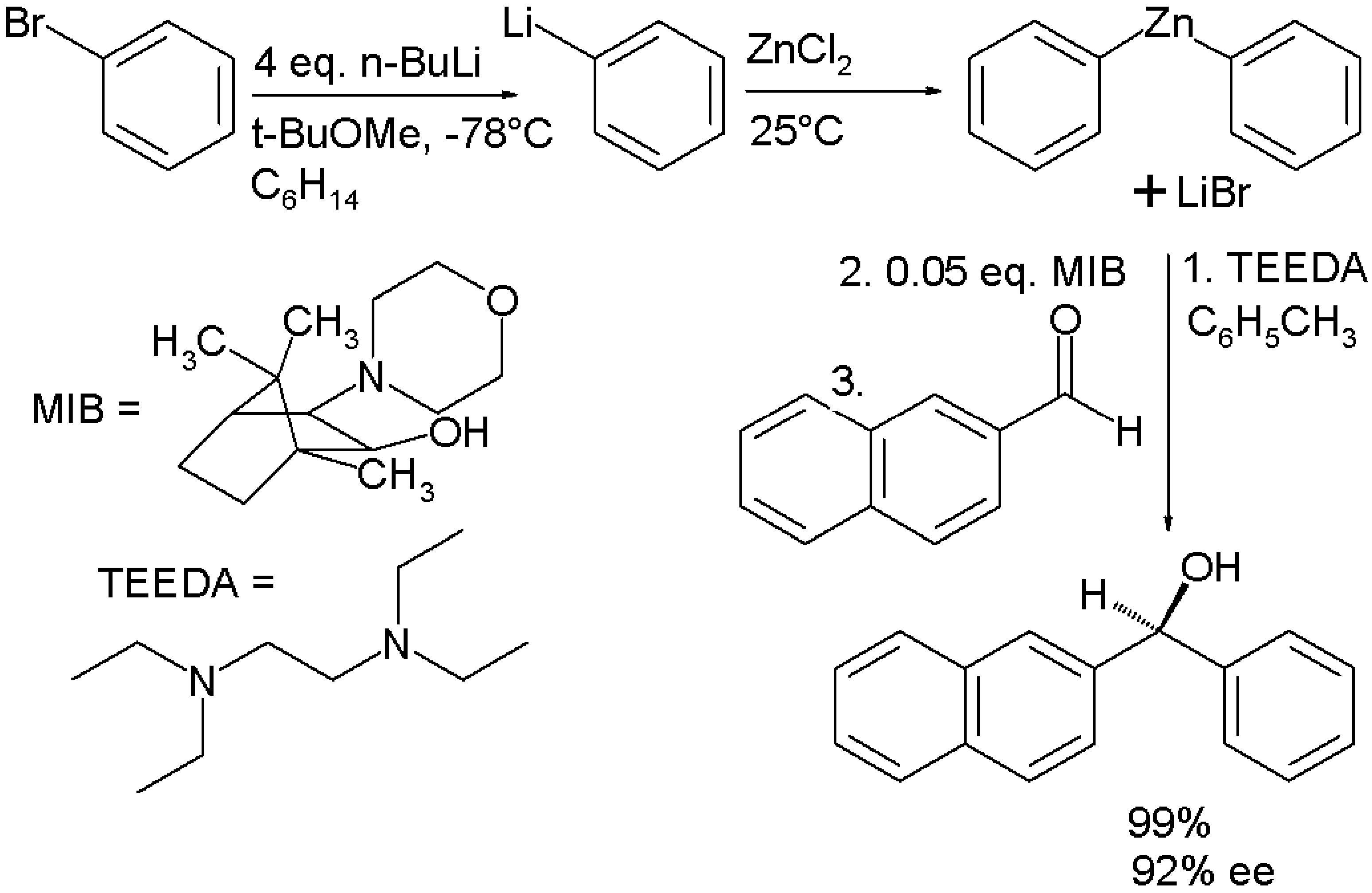
ORGANOZINC COMPOUND

Several general methods:

- Oxidative addition. The original Et_2Zn synthesis by Frankland was an oxidative addition of C_5H_2I to Zn metal with hydrogen gas as a "protective" blanket.
- Halogen zinc exchange. Two main halogen zinc exchange reactions are *iodine zinc exchange* and *boron zinc exchange*.
- Transmetalation. In a typical transmetalation, diphenylmercury reacts with zinc metal to Ph_2Zn and metallic Hg in Et_2O.

Reformatsky reaction




Br
4 eq. n-BuLi
t-BuOMe, -78°C
C_6H_{14}
Li
$ZnCl_2$
25°C
Zn
+ LiBr
1. TEEDA
$C_6H_5CH_3$
2. 0.05 eq. MIB
3.
O
H
H
OH
99%
92% ee
MIB =
H_3C
CH_3
N
O
OH
CH_3
TEEDA =
N
N

IV. ORGANOMETALLICS OF THE BORON GROUP

A. Organoboron Compounds

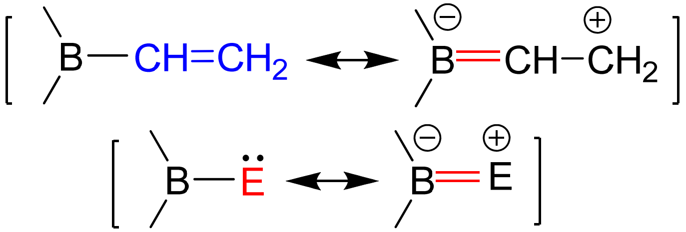
Organoborane or organoboron compounds are organic derivatives of BH_3, for example trialkyl boranes. Organoboron compounds are important reagents in organic chemistry enabling many chemical transformations, the most important one called hydroboration.

$$Et_2O{\cdot}BF_3 + 3RMgX \longrightarrow R_3B + 3MgXF + Et_2O$$

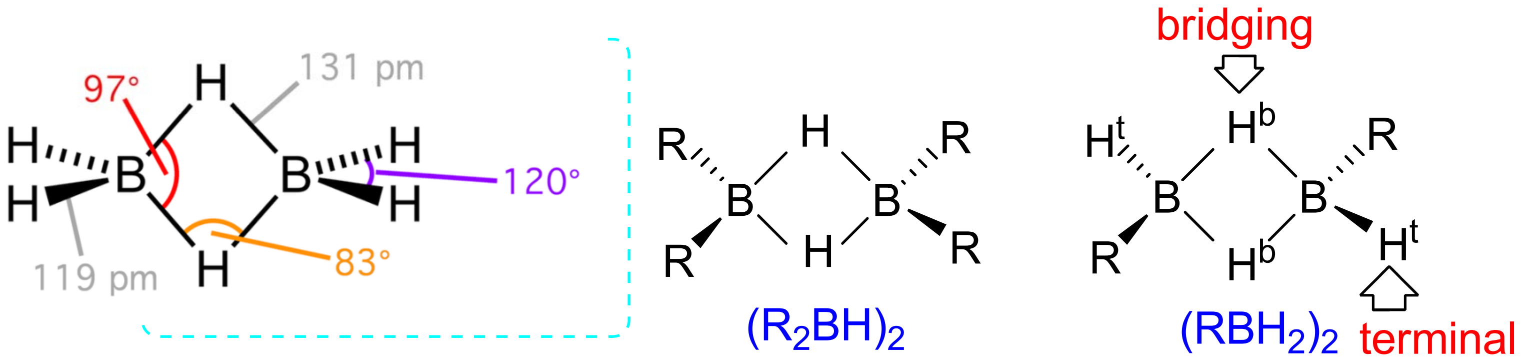
(R = alkyl, aryl)

$$HB\langle + RCH{=}CH_2 \xrightarrow{\text{Hydroboration}} RCH_2{-}CH_2B\langle$$

- Characteristics:
- C–B bond, low polarity (electronegativity C 2.55, B 2.04)
- Electron-rich groups like vinyl or phenyl provide the C–B bond with partial double bond character.

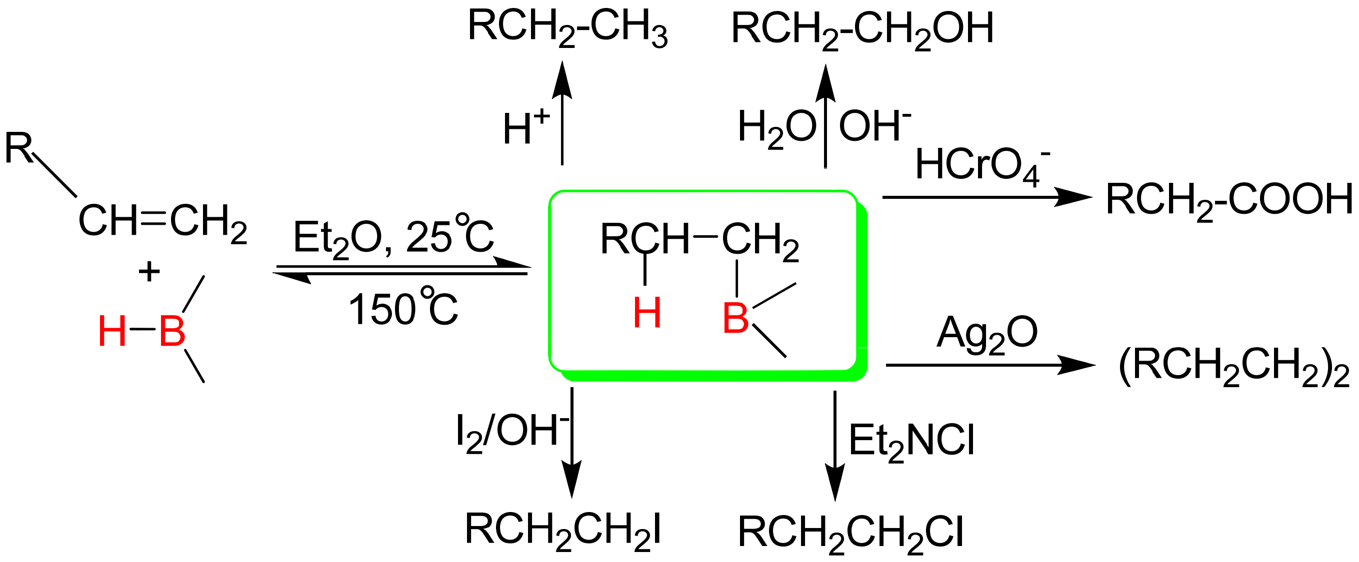


- **Organoboron hydrides** R_2BH and RBH_2 form dimers which always display **hydride bridges** rather than alkyl bridges:



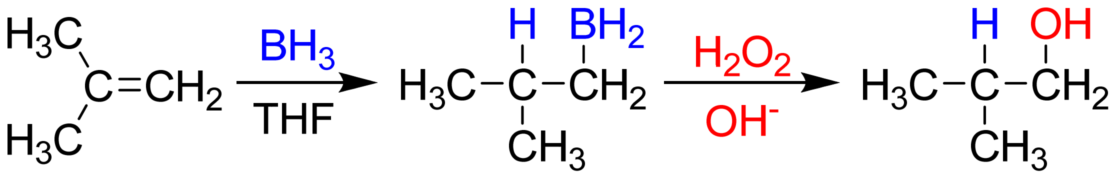
	Stretching frequency	Intensity
$\nu(\mathrm{B}{-}\mathrm{H^b}{-}\mathrm{B})$ symm.	1500-1600 $\mathrm{cm^{-1}}$	strong
$\nu(\mathrm{B}{-}\mathrm{H^b}{-}\mathrm{B})$ asymm.	1850	medium
$\nu(\mathrm{B}{-}\mathrm{H^t})$	2500-2600	

- **Hydroboration-oxidation reaction**. One of the most versatile methods in organic synthesis is hydroboration. Herein, rather than the resulting organoboranes themselves, the products of their subsequent reactions are important:

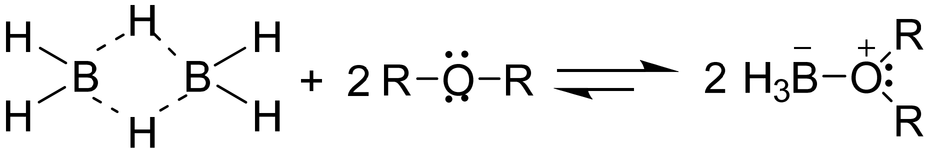


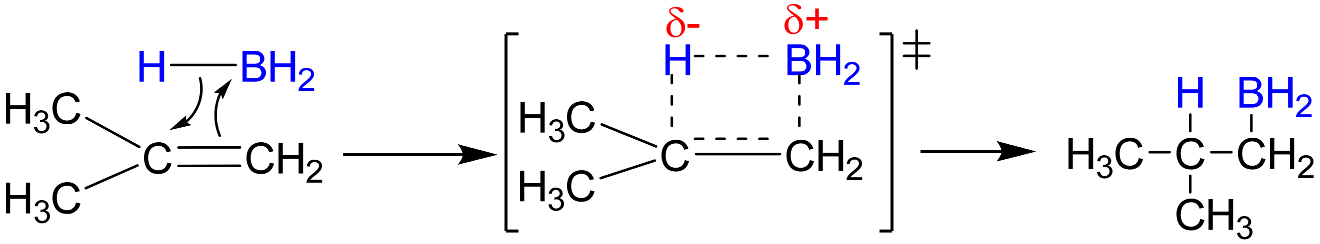
☞ Regioselective — anti-Markovnikov addition, the hydrogen adds to the most-substituted carbon. The reason is that boron is less electronegative than hydrogen.

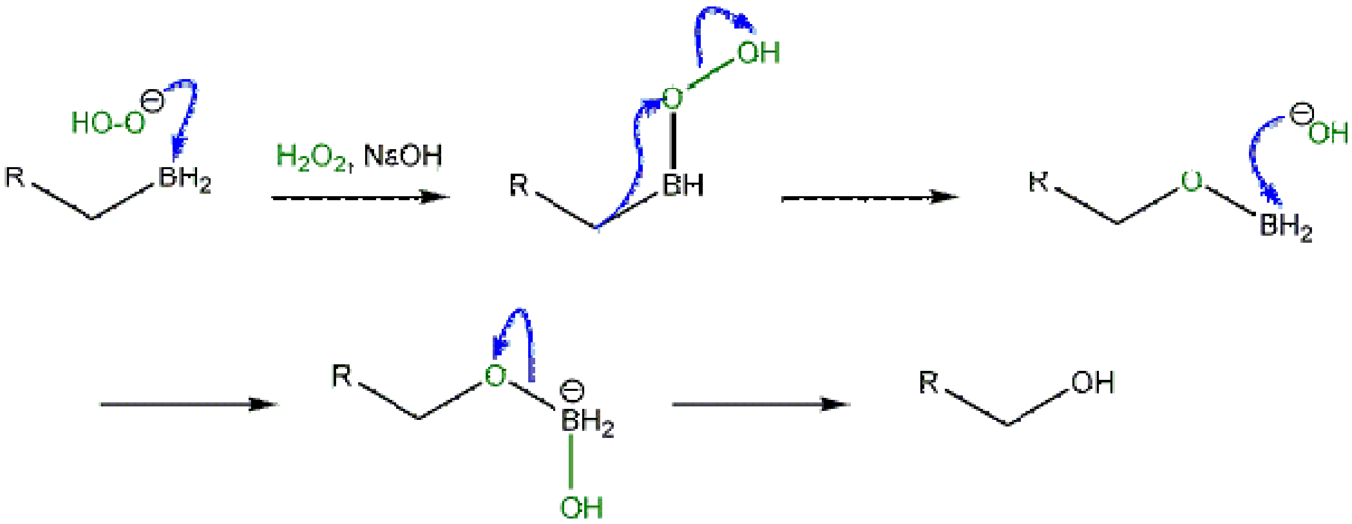
☞ Stereospecificity — addition in a *syn* mode, that is on the same face of the alkene.


BH3
THF
H2O2
OH-

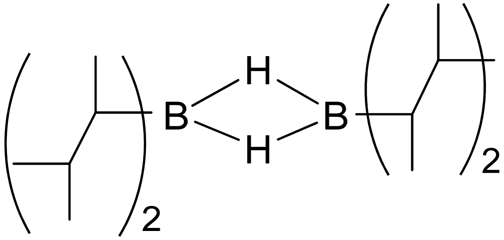
Mechanism:


diborane
ether
borane-ether complex

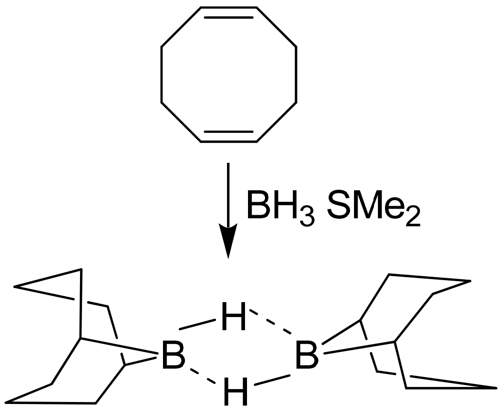



H2O2, NaOH

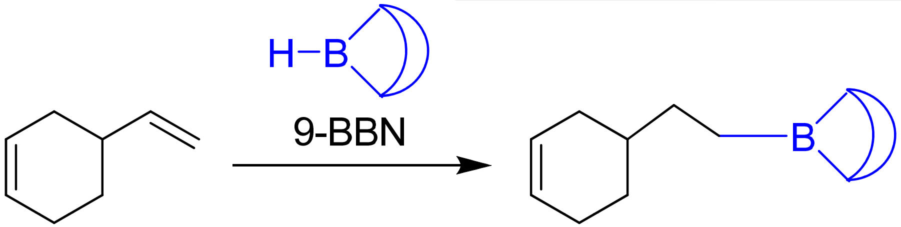
☞ The so called anti-Markovnikov addition is most pronounced when the boron compound has very bulky substituents. Thus, bis-(1,2-dimethylpropyl)borane (“disiamylborane”) adds to 1-pentene, leaving 2-pentene, unaffected (selectivity > 99%).



disiamylborane

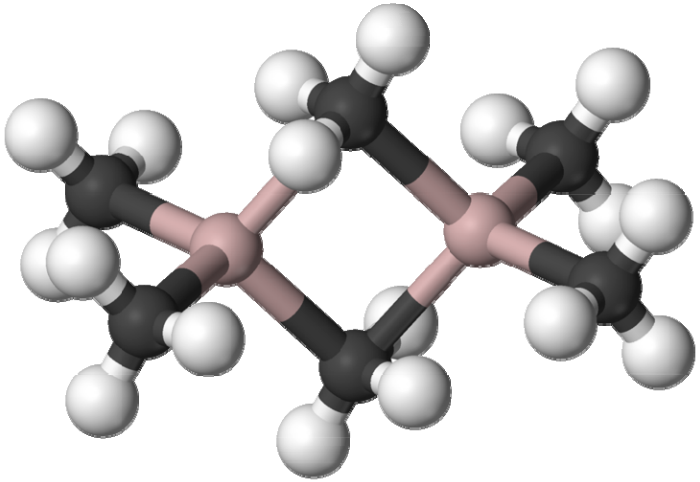


Bis-(9-borabicyclo[3.3.1]nonane)
9-BBN



B. Organoaluminum Compounds

The chemistry of organoaluminium compounds can be understood in terms of the dynamic nature of the C−Al bond and the high Lewis_acidity of the monomeric species.



Al_2Me_6 exists as a dimer. the metalloids are connected by a 3-center-2-electron bond as with diborane.

^1H NMR: At −25°C the 1H NMR of Me_6Al_2 comprises two signals in 1:2 ratio, as expected from the solid state structure. At 20°C, only one signal is observed because exchange of terminal and bridging methyls is too fast to be resolved by NMR.

- **Laboratory preparation**

- Metathesis with RLi or RMgX

$$AlCl_3 + 3\ BuLi \rightarrow Bu_3Al + 3\ LiCl$$

- Transmetalation

$$2\ Al + 3\ HgPh_2 \rightarrow 2\ AlPh_3 + 3\ Hg$$

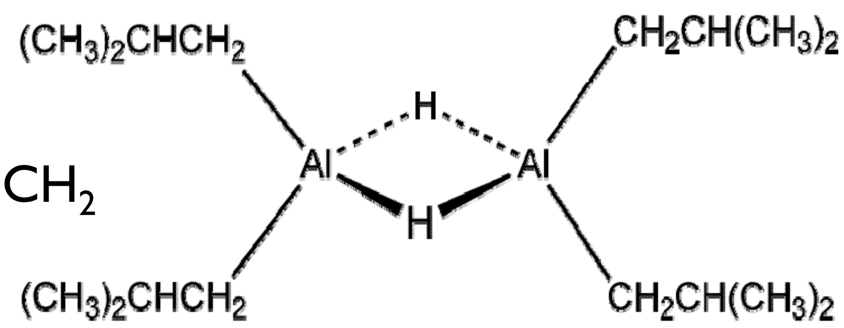
- Industrially, simple aluminium alkyls (Me, Et) can be prepared by a direct process:

$$4\ Al + 6MeCl \rightarrow 2\ Me_3Al_2Cl_3 \rightarrow Me_4Al_2Cl_2 + Me_2Al_2Cl_4 \rightarrow Me_4Al_2Cl\ (l) + 2\ Na[MeAlCl_3]\ (s) \rightarrow \mathbf{Me_3Al} + Al + 6\ NaCl$$

- Diisobutylaluminium hydride is Prepared by β-hydride elimination:

$$(i\text{-}Bu_3Al)_2 \rightarrow (i\text{-}Bu_2AlH)_2 + 2(CH_3)_2C{=}CH_2$$

DIBAl-H

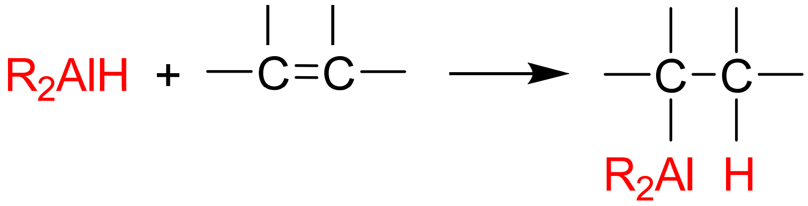


➢ Reactions

- Organoaluminium compounds are hard Lewis acids and readily form adducts with bases such as pyridine, THF and amines.
- Reaction with protonic reagents:

$$AlR'_3 + ROH \rightarrow (R'_2Al{-}OR)_n + R'H$$

- Hydroalumination of C=C double bonds

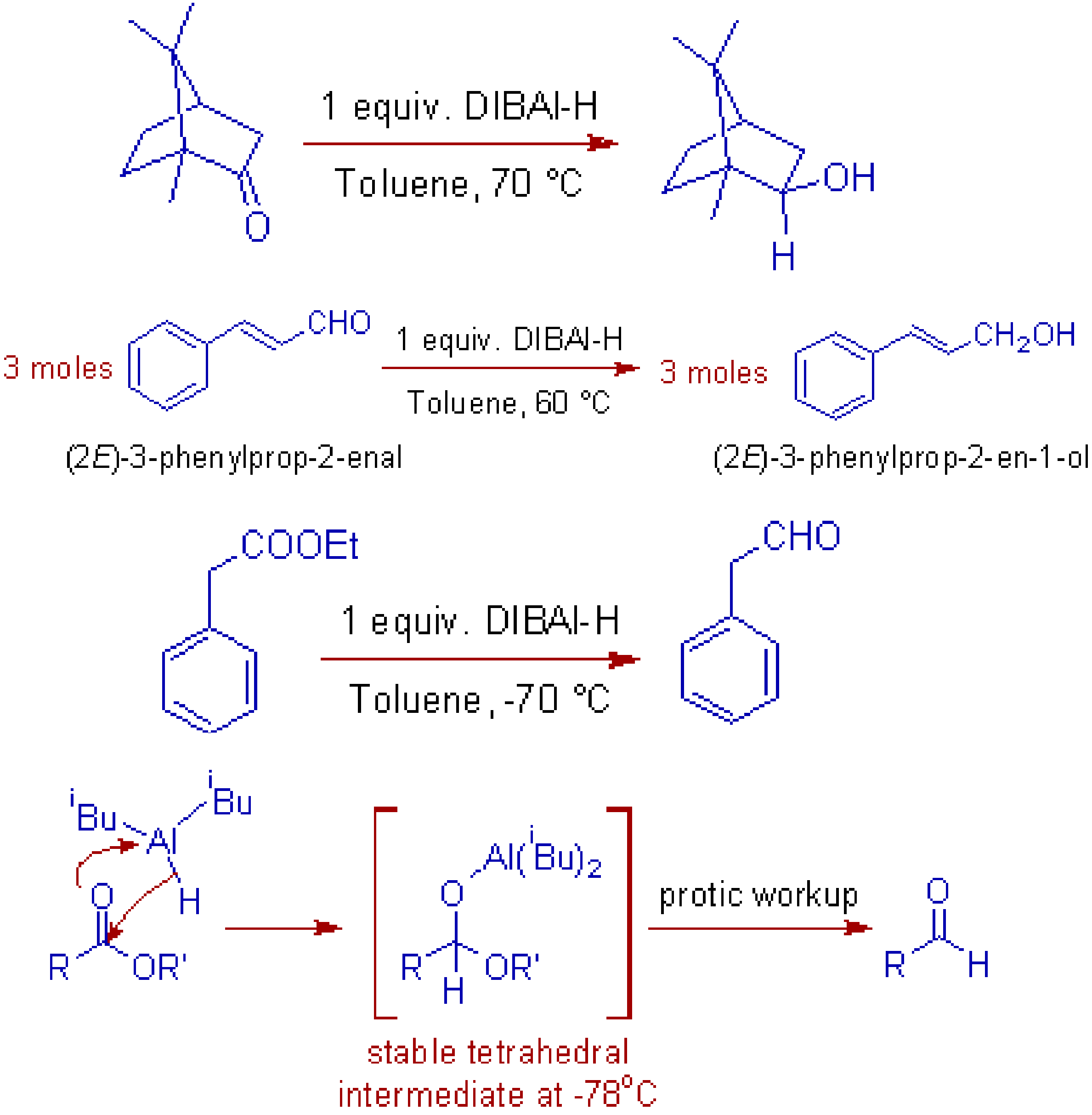


$$R_2AlH + {-}\overset{|}{C}{=}\overset{|}{C}{-} \longrightarrow {-}\underset{\underset{R_2Al}{|}}{\overset{|}{C}}{-}\underset{\underset{H}{|}}{\overset{|}{C}}{-}$$

☞ Readiness: $RCH{=}CHR < R_2C{=}CH_2 < RCH{=}CH_2 < CH_2{=}CH_2$

☞ Stereosepecity (*cis*) and regioselectivity (anti-Markvonikov).

$H{-}AlR'_2$	$RCH{=}CH_2$	$PhCH{=}CH_2$
anti-Markvonikov	97	75
Markvonikov	3	25


O
1 equiv. DIBAl-H
Toluene, 70 °C
OH
H
3 moles
CHO
1 equiv. DIBAl-H
Toluene, 60 °C
3 moles
CH2OH
(2E)-3-phenylprop-2-enal
(2E)-3-phenylprop-2-en-1-ol
COOEt
1 equiv. DIBAl-H
Toluene, -70 °C
CHO
iBu
iBu
Al
H
O
R
OR'
O
Al(iBu)2
R
OR'
H
protic workup
O
R
H
stable tetrahedral
intermediate at -78°C

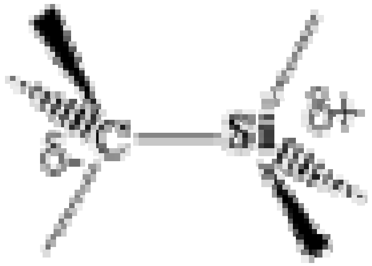
V. ORGANOSILICON

Organosilicon compounds are organic compounds containing carbon silicon bonds.

- Like carbon, the organically bound silicon is tetravalent and tetrahedral.

  C—Si 1.86 Å, 318 kJ/mol; electronegativity: Si 1.90, C 2.55

- **Preparation**



Direct process $2\,RCl + Si/Cu \xrightarrow{\Delta T} R_2SiCl_2 + \ldots$

(R=alkyl, aryl)

Metathesis reactions

$$SiCl_4 + 4\,RLi \longrightarrow R_4Si + 4\,LiCl$$

$$R_3SiCl + R'MgX \longrightarrow R_3R'Si + MgXCl$$

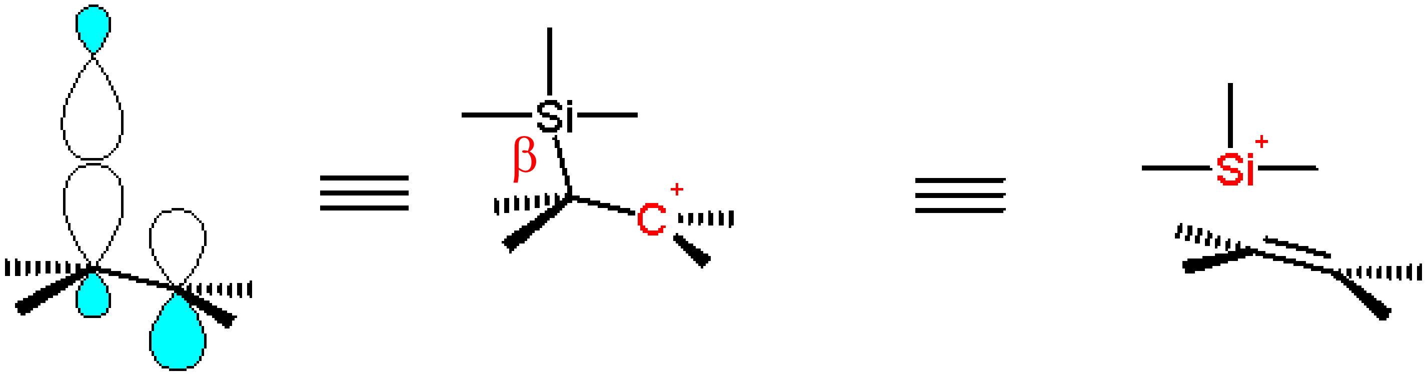
$$2\,R_2SiCl_2 + LiAlH_4 \longrightarrow 2\,R_2SiH_2 + LiCl + AlCl_3$$

Hydrosilation $HSiCl_3 + R{-}CH{=}CH_2 \longrightarrow RCH_2CH_2SiCl_3$

➢ Property and Reactions

☞ The trimethylsilyl cation, Me_3Si^+, departs from a carbon atom more readily than does a proton.

☞ Beta-silicon effect: The beta-silicon effect also called silicon hyperconjugation is a special type of hyperconjugation and describes the stabilizing effect of a silicon atom placed in a position once removed (β) from a carbocation.

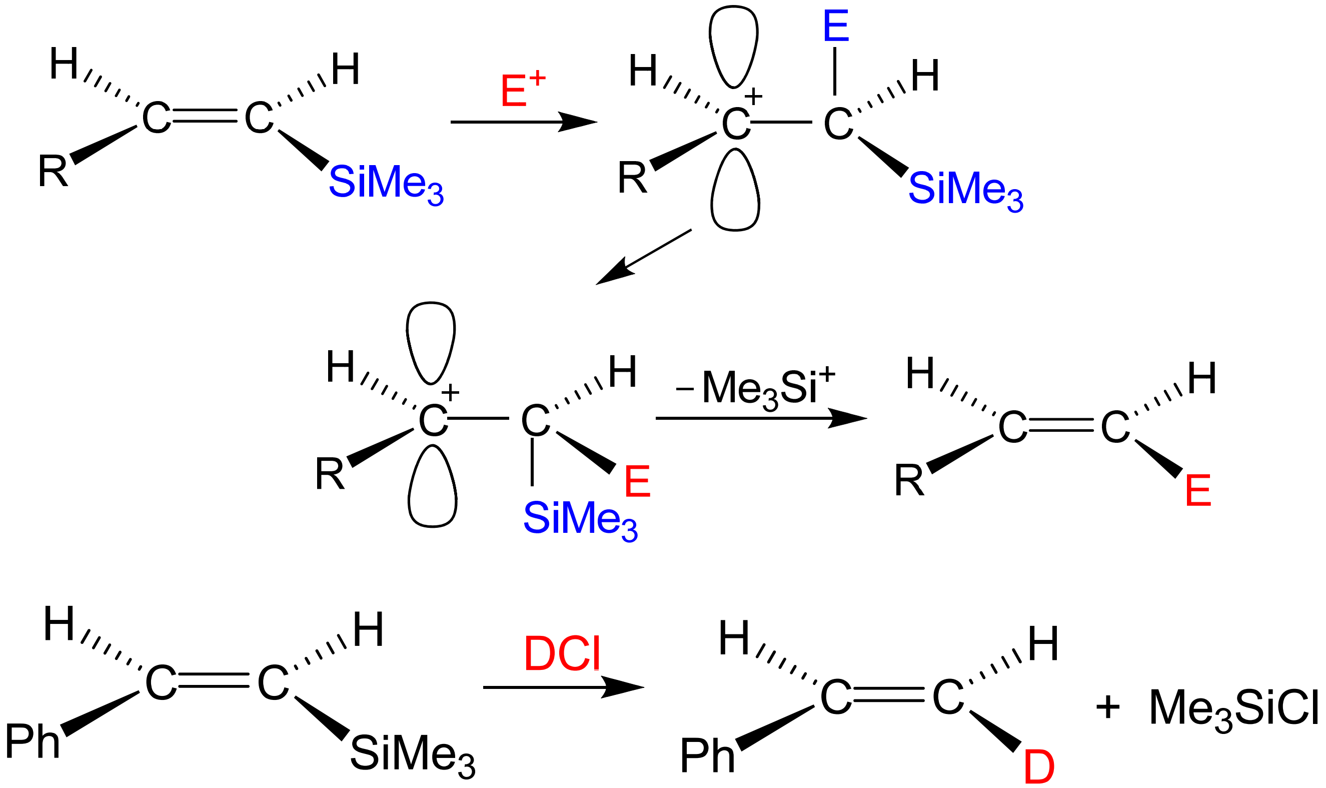


I

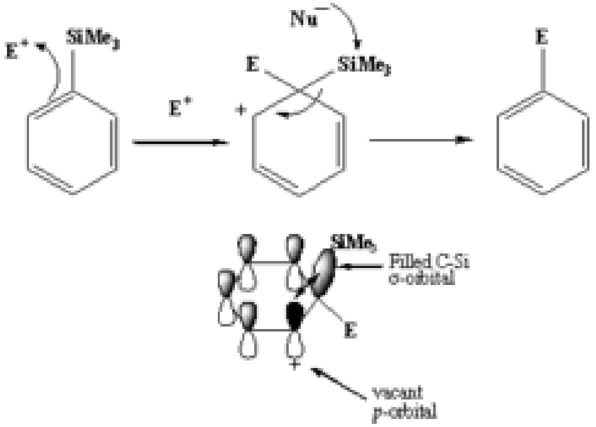
II

III

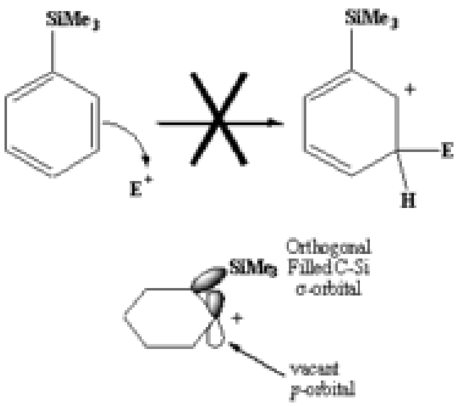
These two properties are manifest in reactions of vinylsilanes. Thus, many electrophiles give substitution rather addition, the silicon being eliminated as a cation and the configuration at the double bond is retained.

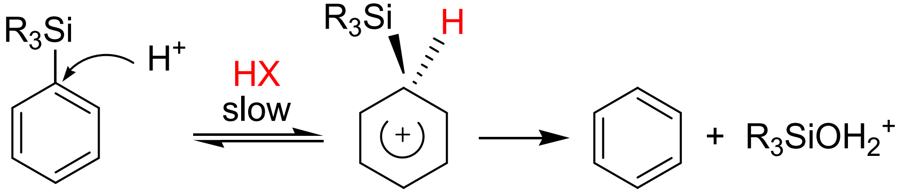


(100 per cent retention of configuration)

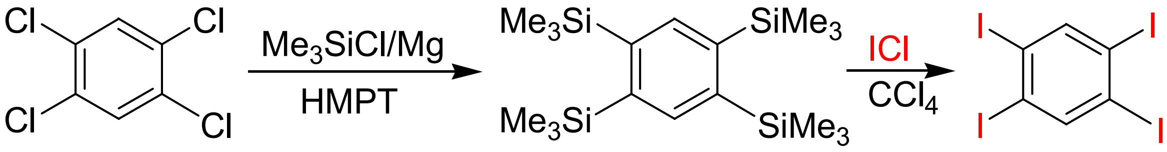


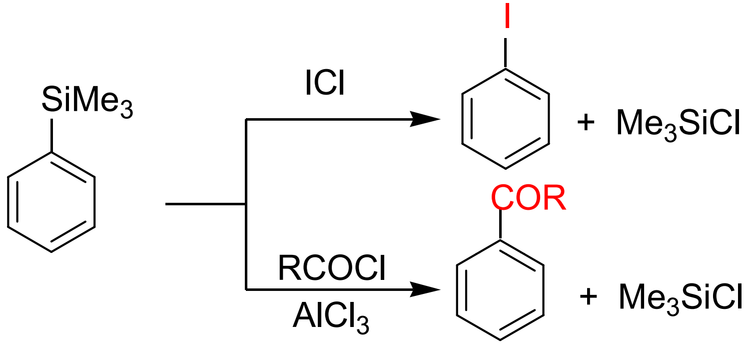
not:





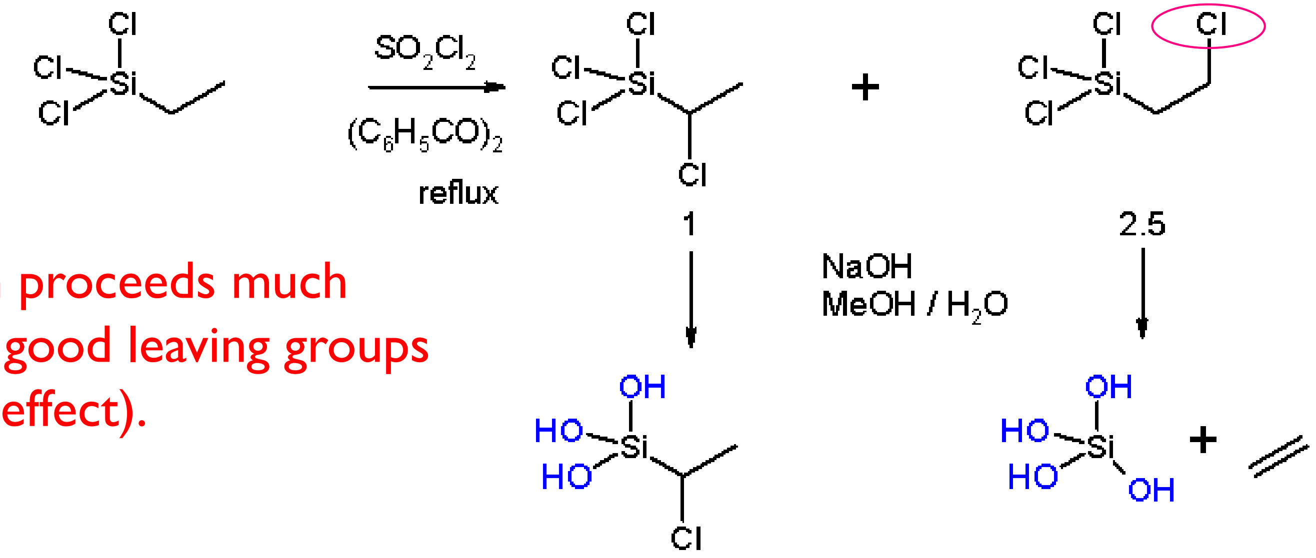
HX = CF_3CO_2H, R_fSO_3H





- The readiness to undergo heterolytic Si-C bond cleavage (desilyation):

Type:	**(I)**	**>**	**(II)**	**>**	**(III)**	**>**	**(iV)**
	Si—C(aryl)		Si—C(aryl)		Si—C(alkyl)		Si—C(alkyl)
	↑		↑		↑		↑
attacking species:	El		Nu		El		Nu



The desilyation proceeds much more rapidly if good leaving groups are present (β-effect).

Alsol®:

$(PhCH_2O)_2MeSiCH_2CH_2Cl$

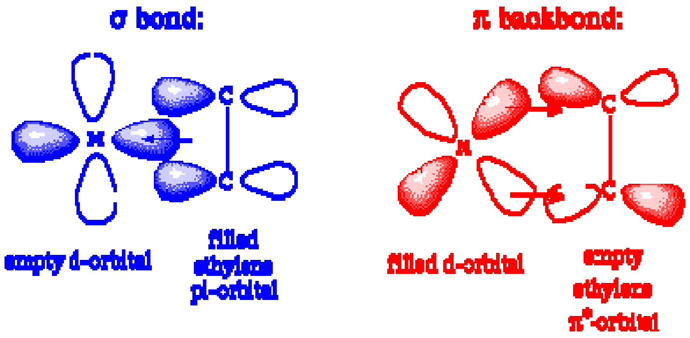
5-5 ORGANOMETALLICS OF THE TRANSITION ELEMENTS

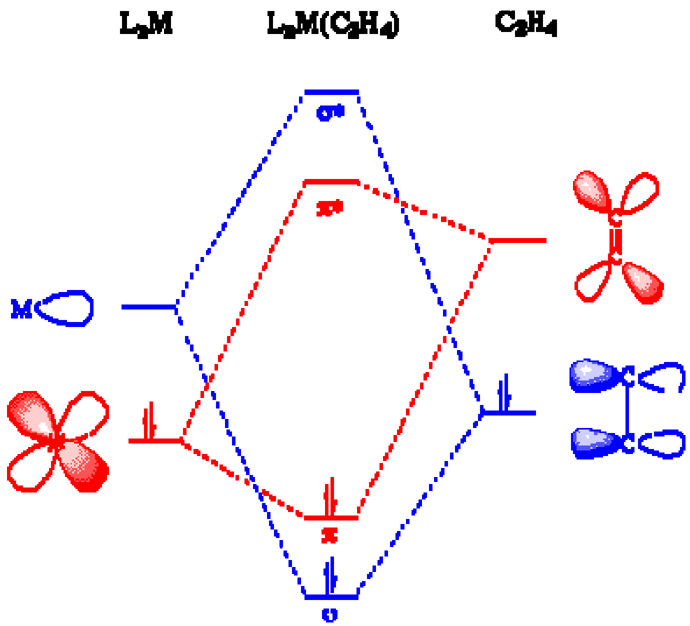
The full variety of organometallic chemistry presents itself in the realm of transition metals. Contributing factors include:

- For transition metals, the *(n-1)d*, *ns* and *np* orbitals must all be regarded as regular valence orbitals.
- Partial occupation of these orbitals gives transition metals both electron-donor and electron-acceptor properties (σ-donor/π-acceptor synergism).
- Various forms of metal-metal multiple bonding with or without additional bridging ligands.
- The ability to change the coordination number together with the lability of metal-carbon σ-bonds offers possibilities for organometallic catalysis.

I. ALKENE COMPLEXES

- **Bonding and Structure:** Dewar-Chatt-Duncanson model.



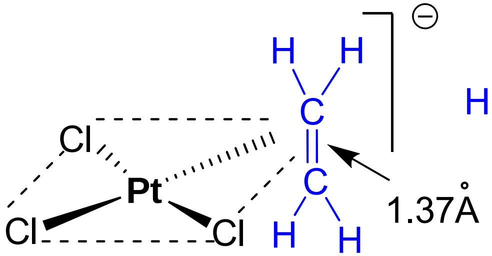


i. A synergistic bonding situation: the greater the σ-donation to the metal, the greater the π-backbonding.

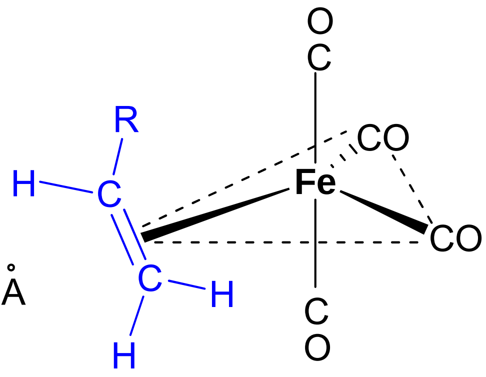
ii. The greater the electron density back-donated into the π* orbital on the alkene, the greater the reduction in the C=C bond order.

iii. Electronic factors: $CF_2=CF_2$ will bind more tightly than ethylene to a low valent metal complex.

iv. Steric factors: The stability of substituted alkene complexes is less than that of ethylene-complex.



$K[PtCl_3(C_2H_4)]{\cdot}H_2O$
(Zeise's salt)



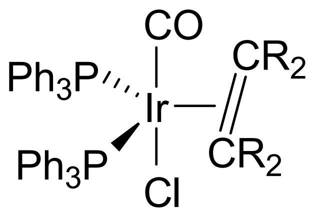
$CH_2{=}CHCNFe(CO)_4$
$C_2H_4Fe(CO)_4$

free C=C 1.34Å

$$K_2[PtCl_4] + C_2H_4 \xrightarrow[\text{60 bar}]{\text{dilute HCl}} K[C_2H_4PtCl_3]H_2O + KCl$$

Coordinatively unsaturated complexes can add olefinic ligands without replacement of another group.

$IrCl(CO)(PPh_3)_2 + R_2C{=}CR_2 \rightleftharpoons$



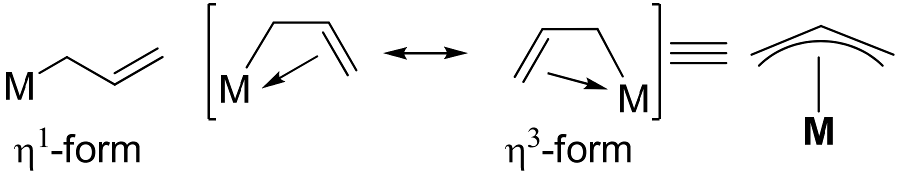
16 VE

18 VE

- **Reaction.** The bonding of an alkene to a transition metal can activate the ligand to electrophilic or nucleophilic attack depending on the nature and charge of the metal center.

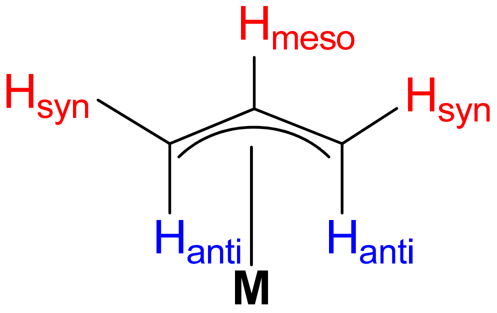
II. ALLYL COMPLEXES

- Bonding and Structure. Allyl ligands are ambidentate ligands that can bind in both a *monohapto* and *trihapto* form.



C–C: 1.35 ~1.40Å

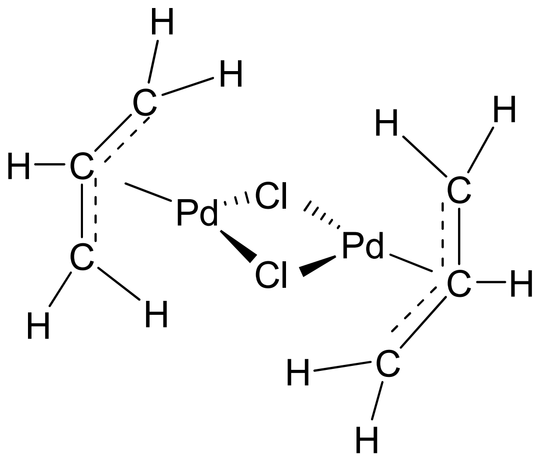
C–C–C : 120°



^1H NMR: H_{anti} 1 ~ 3 ppm, H_{syn} 2~5 ppm, H_{meso} 4 ~ 6.5 ppm.

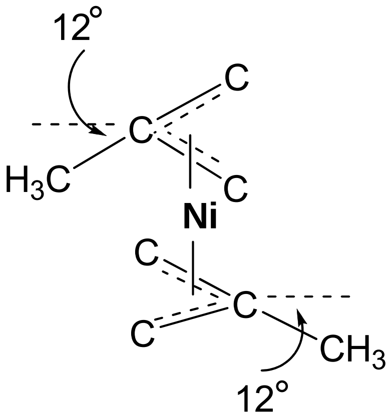
^{13}C NMR: terminal 80 ~ 90 ppm, central 110~130 ppm

H_{meso} and H_{syn} are bent towards the metal (7 and 13 degrees from planar) while H_{anti} is bent 31 degrees away. In η^3-allyl-NiCl, the Ni-C_1 and Ni-C_3 distances are approximately 2.03 Å and Ni-C_2 is 1.98 Å.



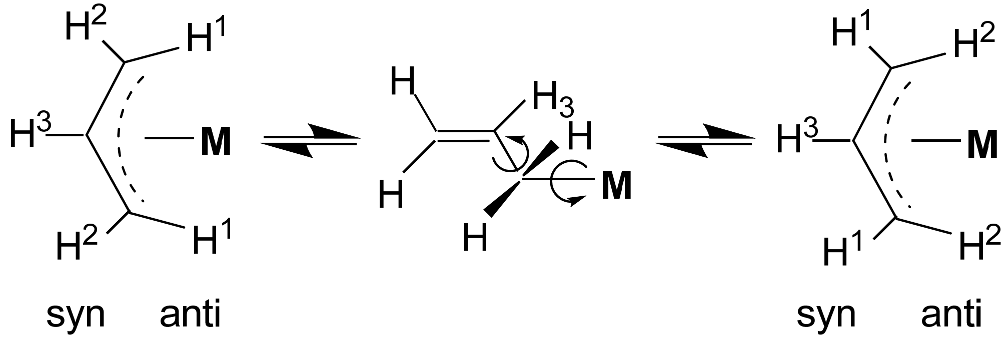
both C-C distances: 1.38 Å
C-C--C angle: 120°
Pd-C distances: 2.11Å
C-C-C plane with Pd_2Cl_2 plane: 111°

η^3-Allylpalladium Chloride Dimer



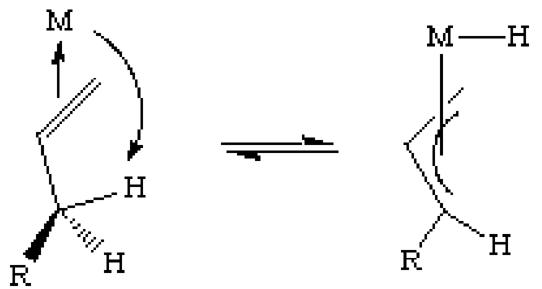
C-C distance: 1.41°
C-C-C angle: 119°
C_c-Ni: 1.98 Å
C_t-Ni: 2.02 Å

Bis(methylallyl)nickel



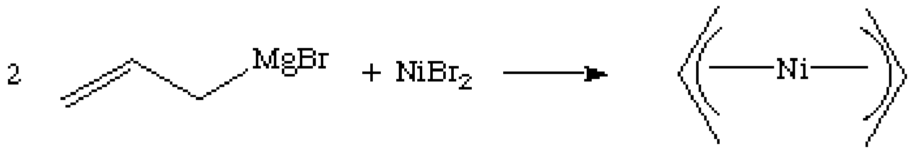
- In the ^1H NMR spectra of allyl complexes, *syn*- and *anti*-protons of the terminal CH_2 groups are generally nonequivalent.

- **Synthesis:** Most syntheses of *trihapto* allyl complexes involve the synthesis of a *monohapto* complex which then displaces a ligand to give the trihapto form.



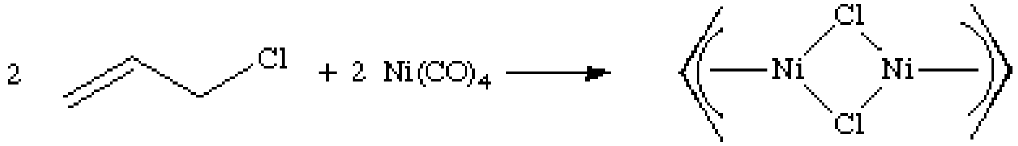
(1)

via hydrogen attack on the metal



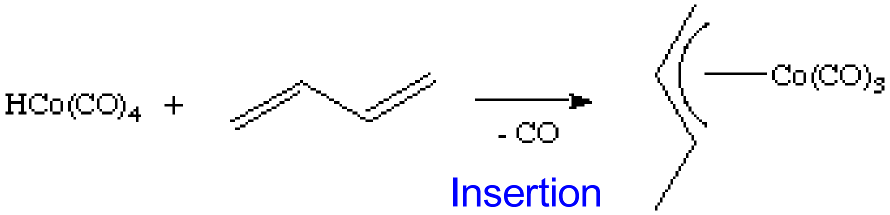
(2)

Nucleophilic or electrophilic substitution



(3)

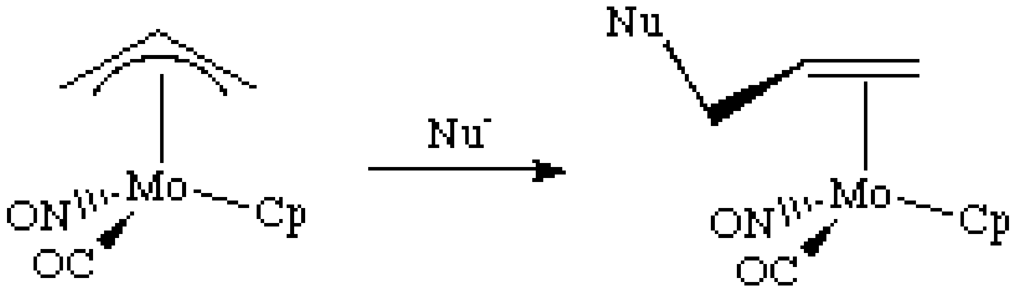
Oxidative addition



(4)

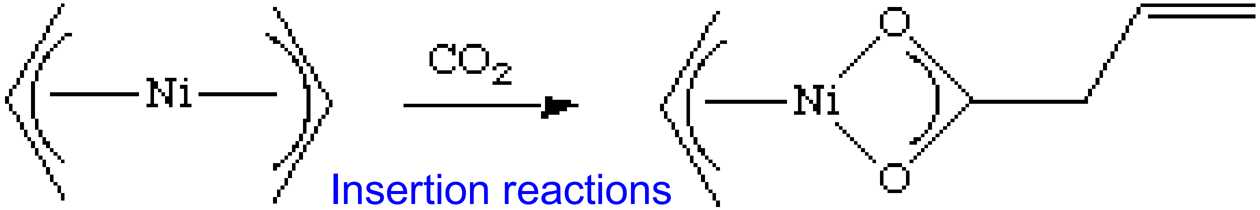
Insertion

Reactions:



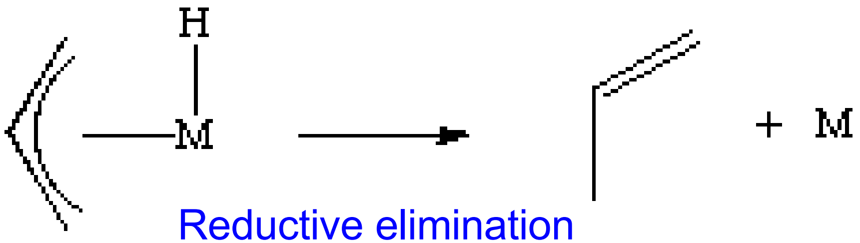
With nucleophiles, stereoselective

(5)



Insertion reactions

(6)



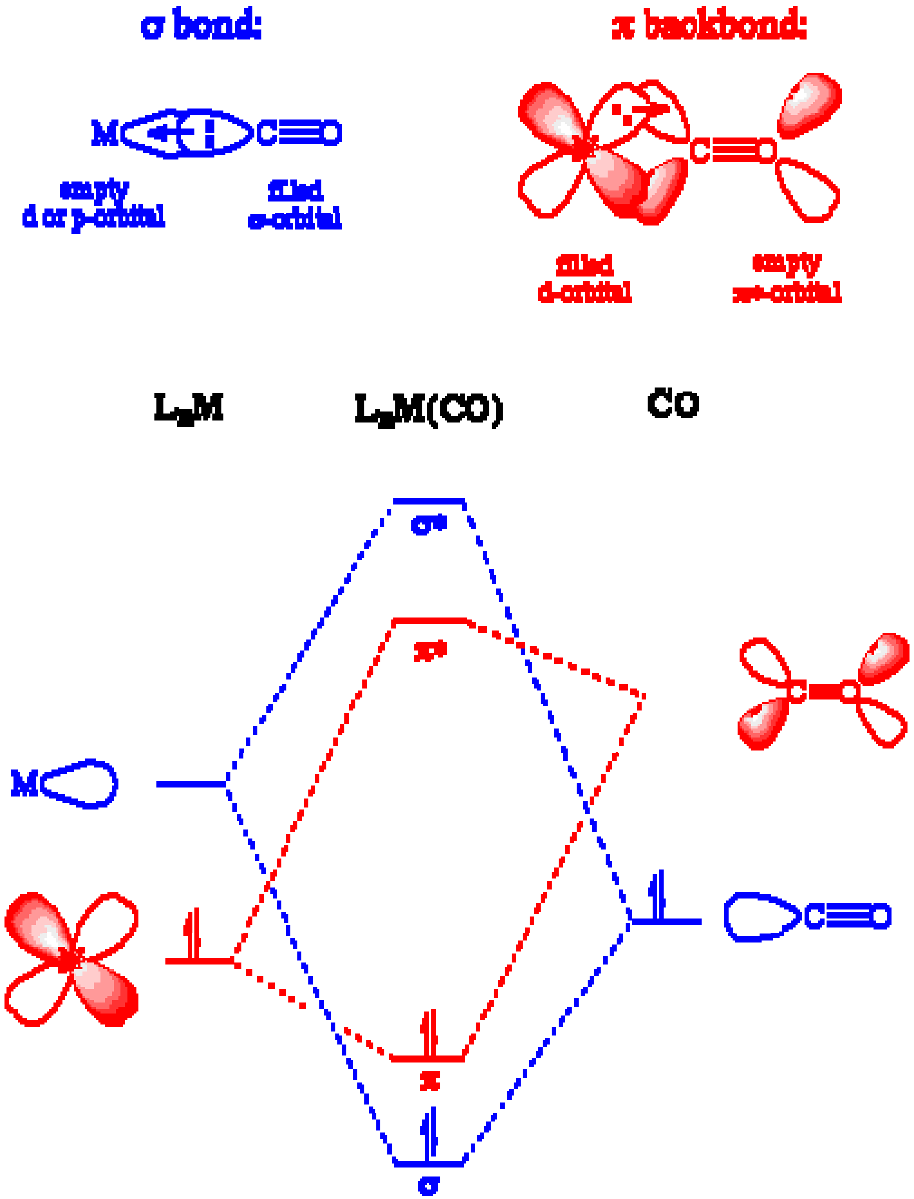
Reductive elimination

(7)

III. CARBONYL COMPLEXES

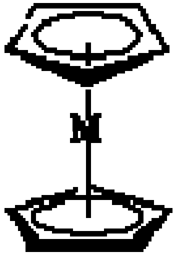
- Carbonyl complexes are compounds that contain carbon monoxide as a coordinated ligand.
- This bonding are synergistic. The more sigma donation by the carbonyl (or other sigma-donors on the metal center), the stronger the π-backbonding interaction.

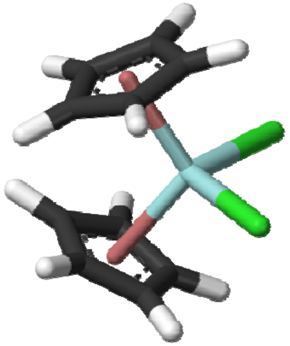
Free C≡O
d_{CO} = 1.128 A
ν_{CO} = 2143 cm^{-1}
$Ni(CO)_4$ ν_{CO} 2057 cm^{-1}
$CO(CO)_4^-$ ν_{CO} 1886 cm^{-1}

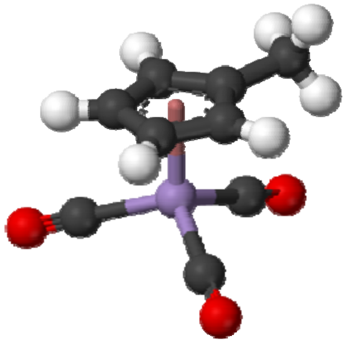


IV. METALLOCENE

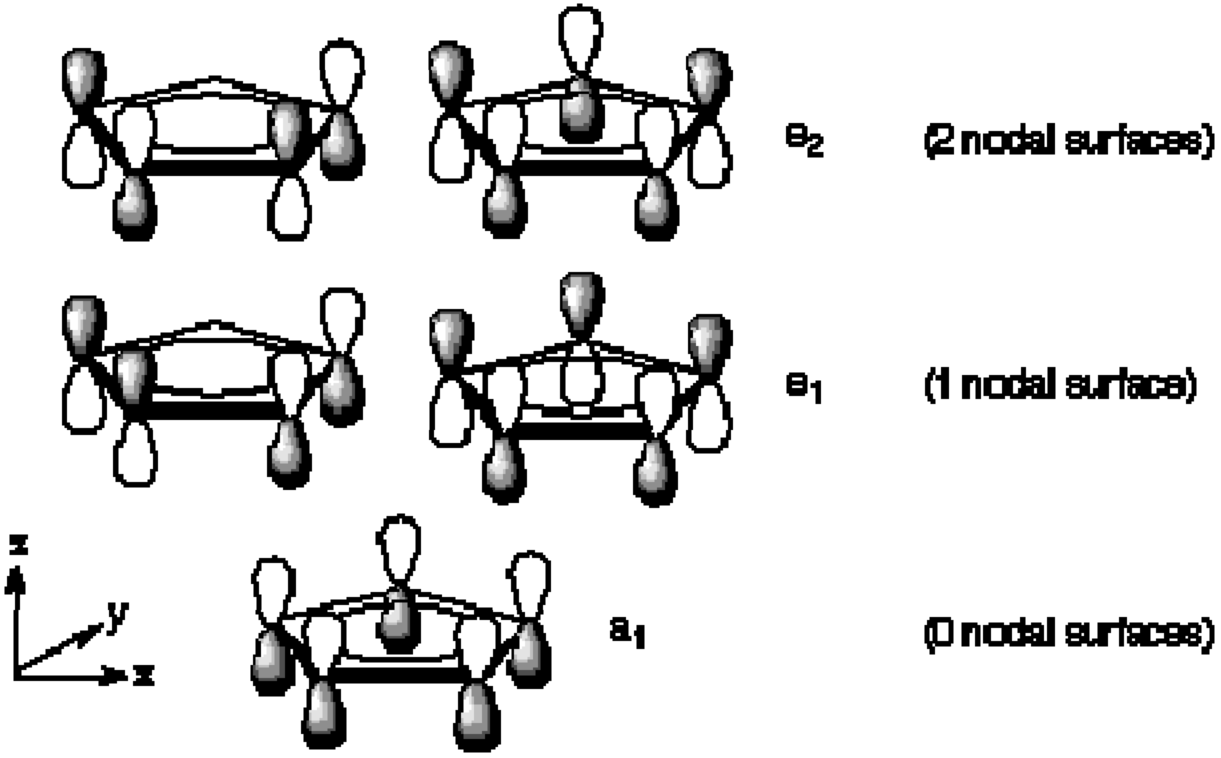
- A **metallocene** is a compound with the general formula $(C_5H_5)_2M$ consisting of two cyclopentadienyl anions (Cp, which is $C_5H_5^-$) bound to a metal center (M) in the oxidation state II. Bis(cyclopentadienyl) complexes are sometimes called "sandwich compounds”. Some metallocene derivatives, such as Cp_2TiCl_2, have their Cp rings tilted with respect to each other and are called "bent metallocenes", while complexes with only one Cp ligand have been colorfully described as having "half sandwich" and "3-legged piano stool" geometries, e.g., *methylcyclopentadienyl manganese tricarbonyl*.







- **Bonding of Cp-ligands**: Cp-ligands are generally bound via all 5 carbon atoms to a metal centre (η^5-coordination, π-complexes). In rare cases, the Cp unit can bond through three carbon atoms, like in $[(\eta^3\text{-Cp})\text{WCp(CO)}_2]$; or through one carbon atom, as in $[(\eta^1\text{-Cp})\text{FeCp(CO)}_2]$.



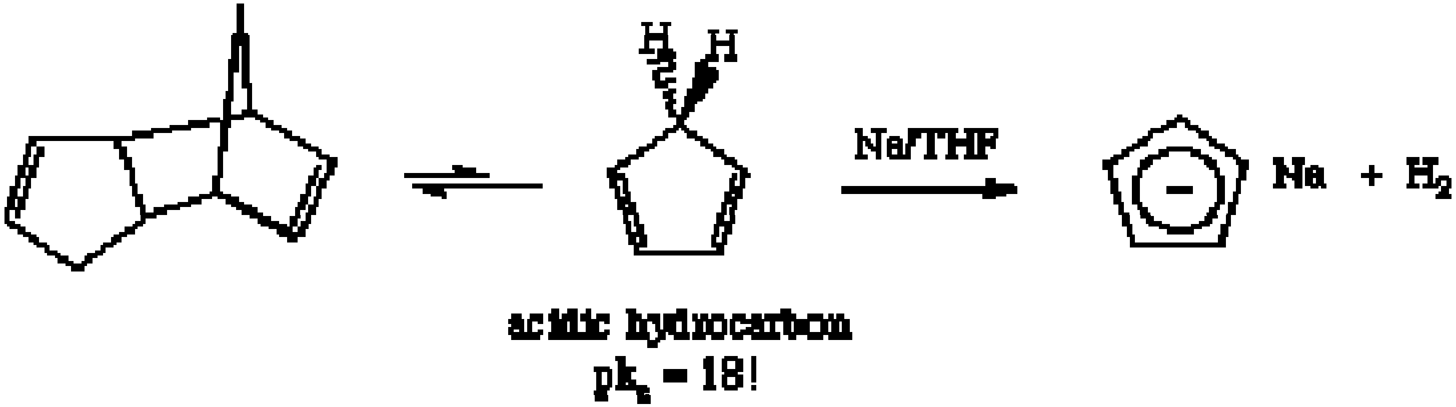
the five MO's of a Cp ligand

- Spectroscopic features

^{1}H NMR: Cp rings appear as singles in the range of 4.0 to 5.5 ppm. Cp* ligand typically appear at 1-2 ppm

^{13}C NMR: the carbons of CP are also equivalent, 80-95 ppm; Cp* 20-30 ppm.

- Synthesis of Cp Complexes



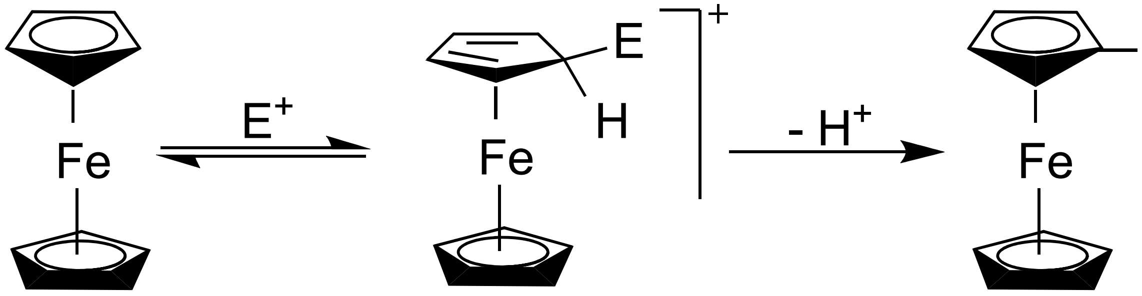
$$NaCp + L_nMX \longrightarrow CpML_n + NaX$$

Property and Reactions:

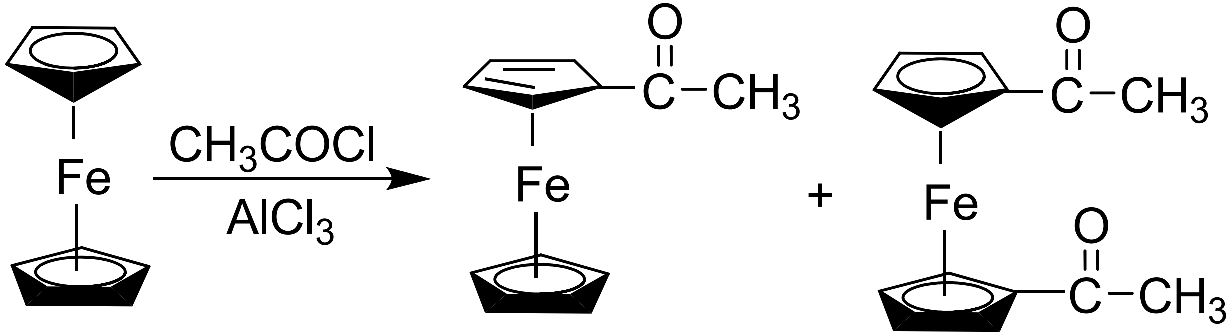
$C_5H_5FeC_5H_4NH_2$: a stronger base than aniline

$C_5H_5FeC_5H_4COOH$: a weaker acid than benzoic acid

The ferrocenyl group therefore acts as an electron donor.

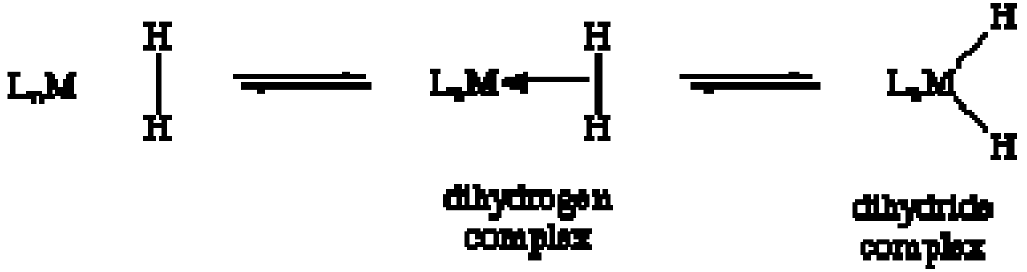


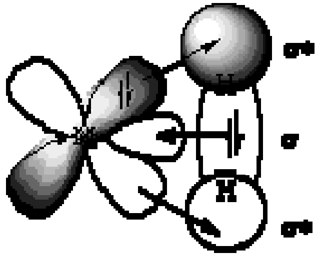
3x10^6 times faster than benzene.

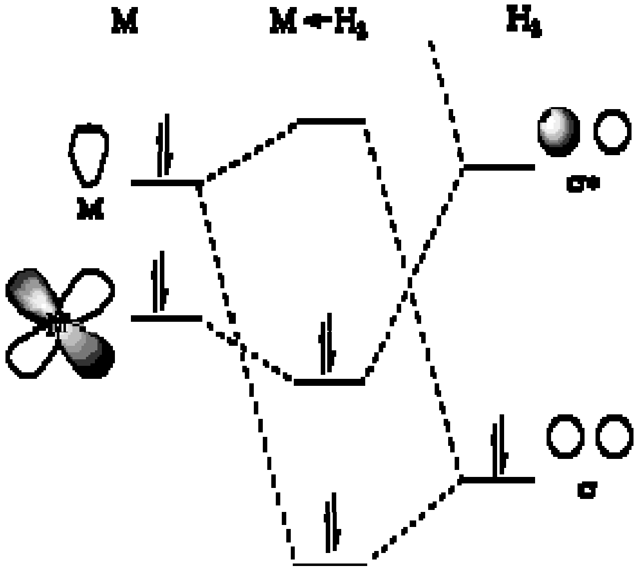


V. DIHYDROGEN COMPLEXES

- **Dihydrogen complexes** are transition metal species in which a molecule of molecular hydrogen acts as a two electron sigma donor to the metal center.

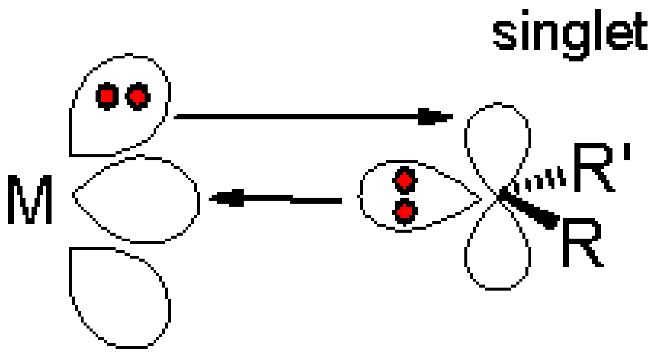






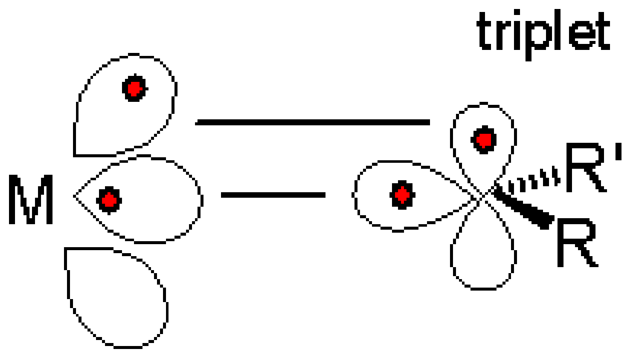
VI. TRANSITION METAL CARBENE COMPLEX

- A transition metal carbene complex is an organometallic compound featuring a divalent organic ligand. The divalent organic ligand coordinated to the metal center is called a carbene.
- Described often as **$M{=}CR_2$**, they represent a class of organic ligands intermediate between alkyls ($-CR_3$) and carbynes ($\equiv CR$).



Fischer

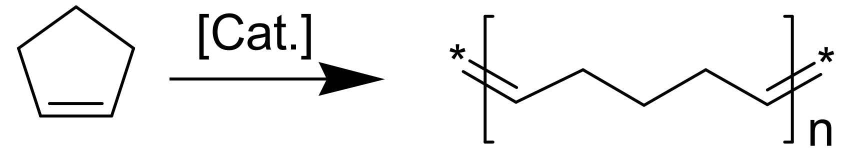
Fischer carbenes can be likened to ketones, with the carbene carbon being electrophilic.



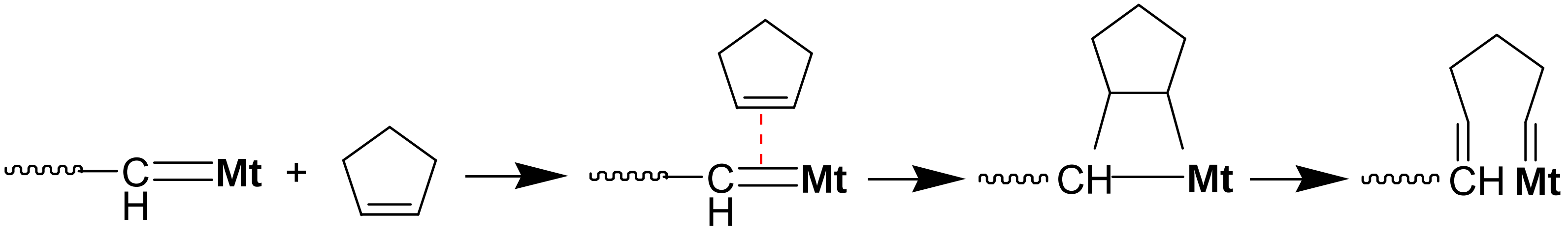
Schrock

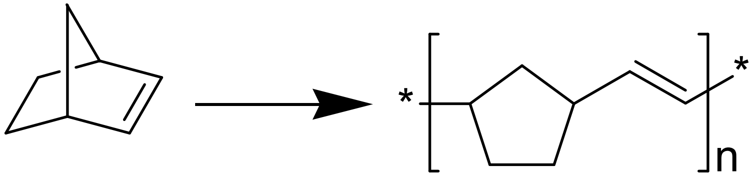
Schrock carbenes do not have π-accepting ligands. These complexes are nucleophilic.

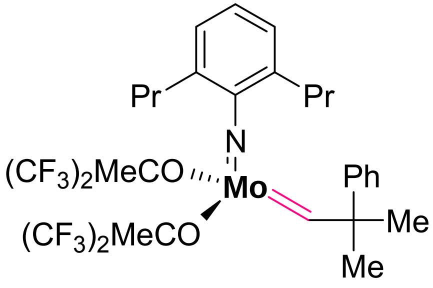
Metathesis polymerization

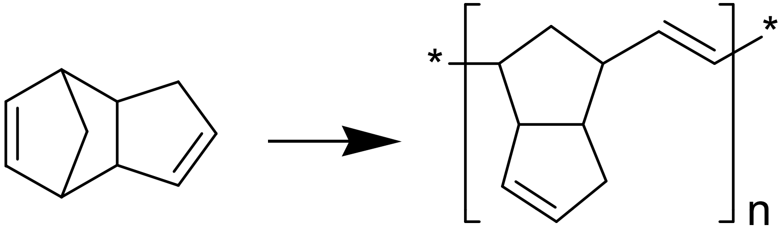


[cat.] = Mo(=CHBu^t(NAr)(OR)$_2$









5-6 ORGANOMETALLIC CATALYSIS

pro memorial: *A catalyst accelerates the rate of a thermodynamiclly feasible reaction by opening a lower activation energy pathway. If alternative routes exist, a catalyst can enhance product selectivity by accelerating just one of the competing reaction sequences.*

I. Mode of Action of Transition-Metal Complexes in Catalysis

◆ The coordination of the reaction partners to a transition metal brings them into close proximity, thus promoting the reaction.

◆ Through coordination to a transition metal, a reaction partner can become activated for subsequent reactions.

◆ The coordination of an organic substrate to a transition metal can facilitate nucleophilic attack.

Catalytically active systems therefore must possess vacant coordination sites or be able to generate them in a primary dissociation step.

➢ Heterogeneous Catalysis

The vacant coordination site is located at a phase boundary (solid/liquid, solid/gas), i.e., only the surface atoms are catalytically active.
Advantage: the easy recovery of the catalyst;
Disadvantage: low specificity, relatively high reaction temperatures and difficulties in the mechanistic study.

➢ Homogeneous Catalysis

The catalyst can be tailor-made by ligand variation and is obtained reproducibly. high specificity, the catalysis can often be carried out at low temperatures. Ideally, the catalyst complex is stable in more than one coordination number and, through fine-tuning of chemical bond strength (variation of the ligands), capable of holding a substrate molecule selectively but not too tightly.

◆ The most important homogeneous catalysis: the "late transition metals" complexes Ru, Co, Rh, Ni, Pd and Pt (M d^8, d^{10}).

II. Catalytic Reactions and the 16/18 VE Rule

Elementary organometallic reactions:

(1) Lewis-acid ligand dissociation/association

$$CpRh(C_2H_4)_2SO_2 \rightleftharpoons CpRh(C_2H_4)_2 + SO_2$$

(2) Lewis-base ligand dissociation/association

$$NiL_4 \rightleftharpoons NiL_3 + L$$

(3) Oxidative addition/reductive elimination

$$Ir^{I}Cl(CO)L_2 + H_2 \rightleftharpoons H_2Ir^{III}Cl(CO)L_2$$

(4) Migratory insertion/extrusion

$$MeMn(CO)_5 \rightleftharpoons MeCOMn(CO)_4$$

(5) Oxidative coupling/reductive decoupling

$$(C_2F_4)_2Fe^{0}(CO)_3 \rightleftharpoons (CF_2)_4Fe^{II}(CO)_3$$

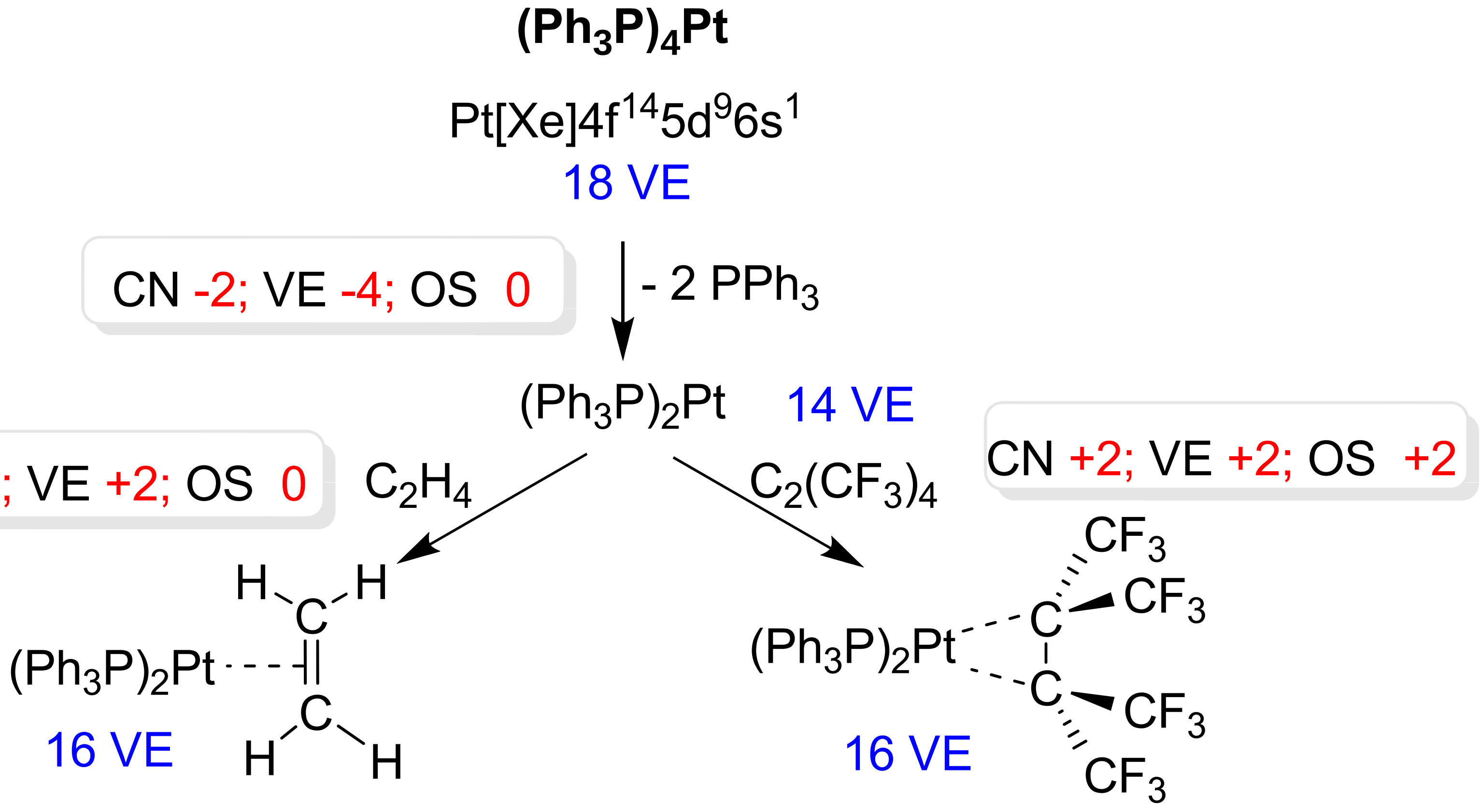
Characteristic variables

ΔCN	ΔVE	ΔOS	reaction
–1/+1	0	0	(1)
–1/+1	–2/+2	0	(2)
+2/–2	+2/–2	+2/–2	(3)
–1/+1	–2/+2	0	(4)
0	–2/+2	+2/–2	(5)

ΔVE: Change in the number of valence electrons at the central metal

ΔOS: Change in the oxidation state of the metal (usual convention: –hydride, -alkyl, -allyl, and –pentadienyl are regarded as anions)

ΔCN: Change in the coordination number



$Pt^{0}(d^{10})$ *π-complex*
Lewis-base ligand association

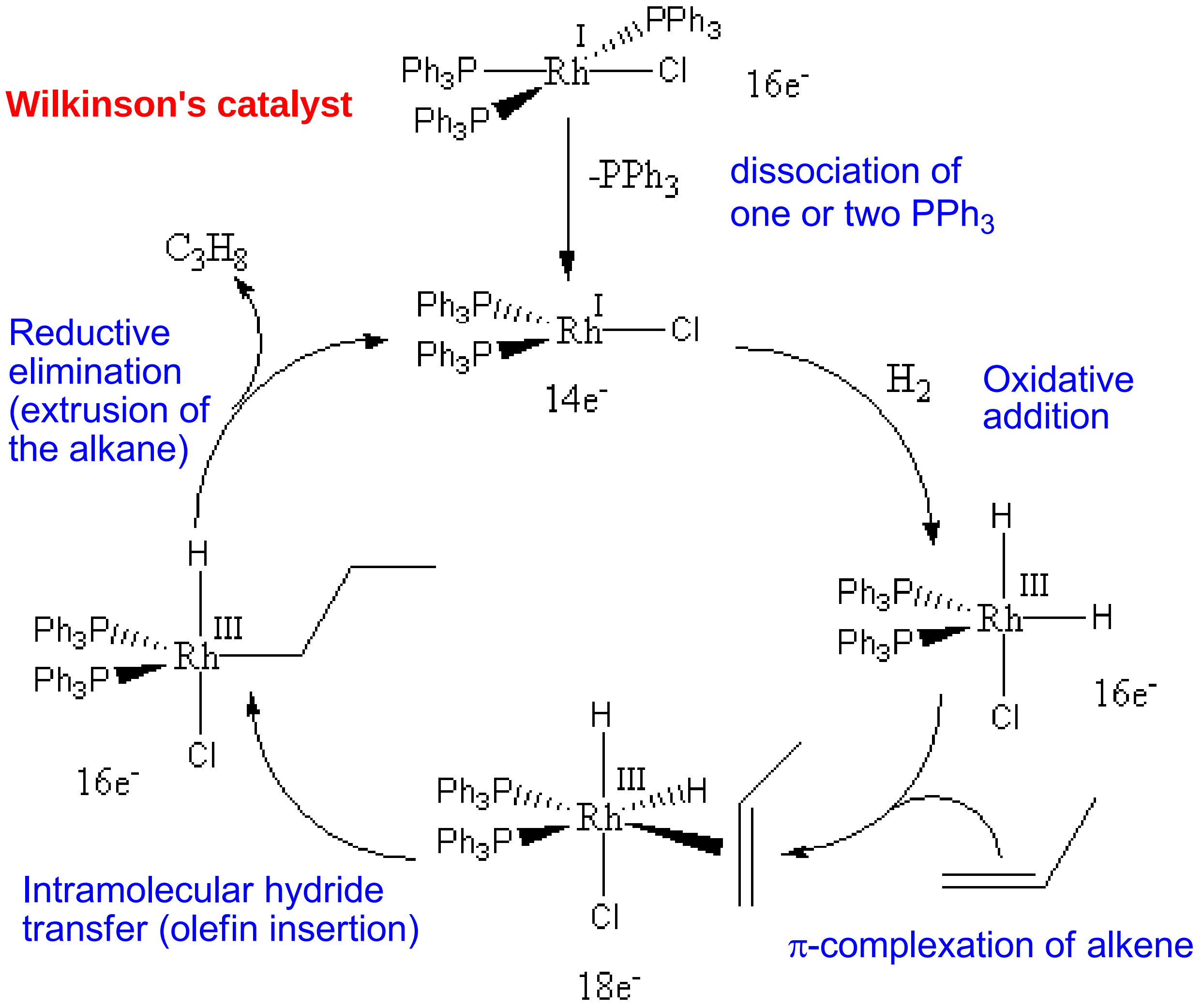
Pt^{II} (d^{8}) *σ-complex*
oxidative addition

- The formulation of a possible reaction mechanism for an organometallic catalysis is assisted by the 16/18 VE rule.

Elementary reaction step	Expected for complexes
Lewis-acid ligand dissociation	16, 18 VE
Lewis-acid ligand association	
Lewis-base dissociation	18 VE
Reductive elimination	
Migratory insertion	
Oxidative coupling	16 VE
Lewis-base association	
Oxidative addition	
Extrusion	
Reductive decoupling	

- It should be stressed that the 16/18 VE criterion in increasing regarded as an undue restraint.
- The actual catalyst of a reaction is not always known. The catalyst often refers to the “precatalyst”, Usually a well-known substance like $(PPh_3)_3RhCl$, which reacts with H_2, CO or other substrates in solution to generate the active catalyst.

III. EXAMPLES OF CATALYTIC APPLICATIONS



Wilkinson's catalyst

dissociation of one or two PPh$_3$

Oxidative addition

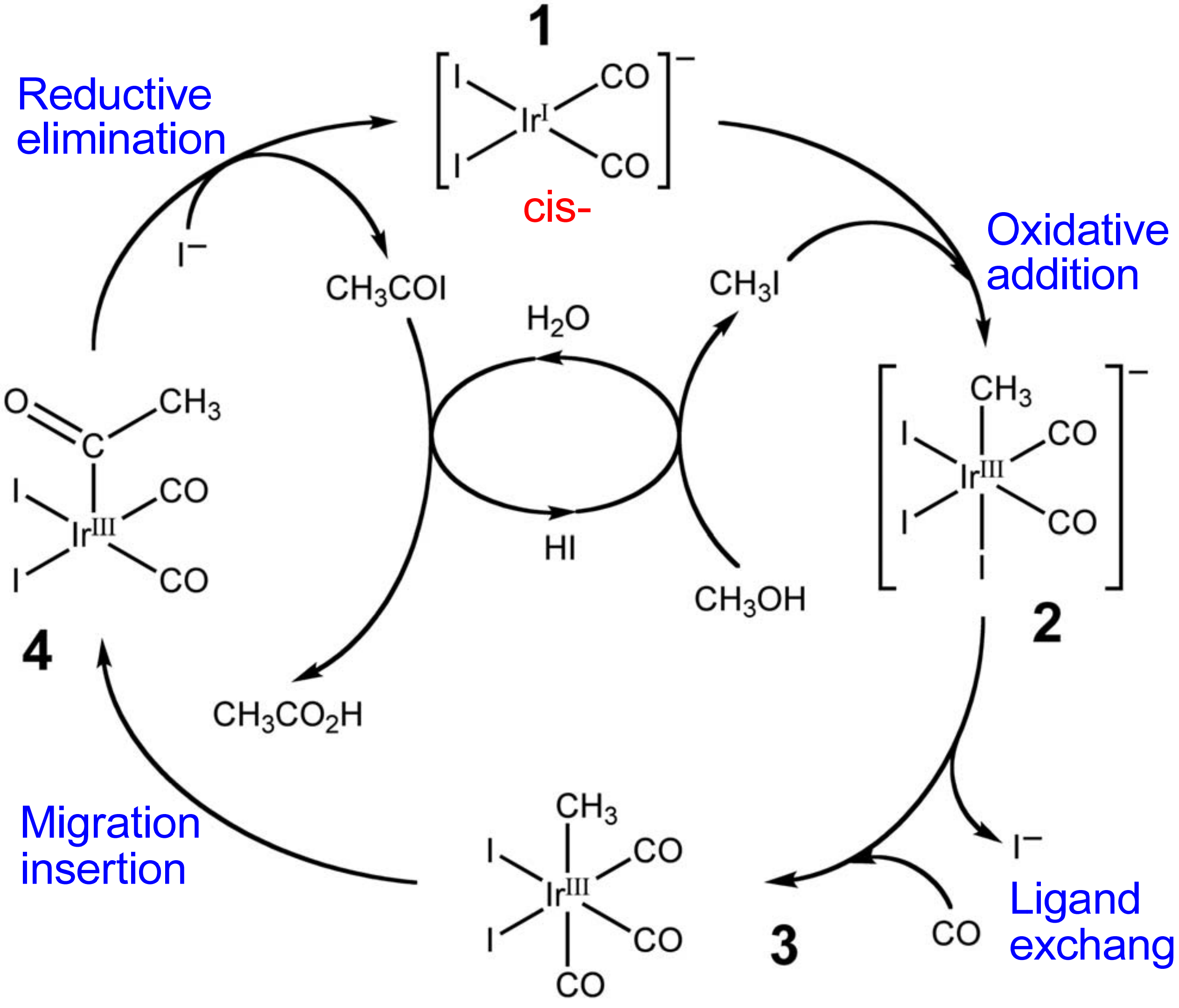
π-complexation of alkene

Intramolecular hydride transfer (olefin insertion)

Reductive elimination (extrusion of the alkane)

Catalytic hydrogenation of propylene

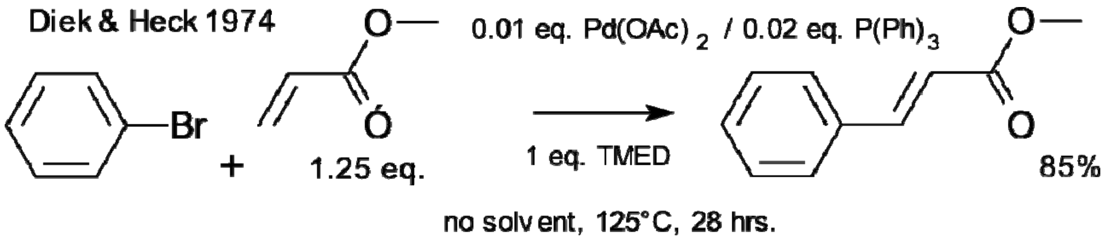
- The Cativa processes

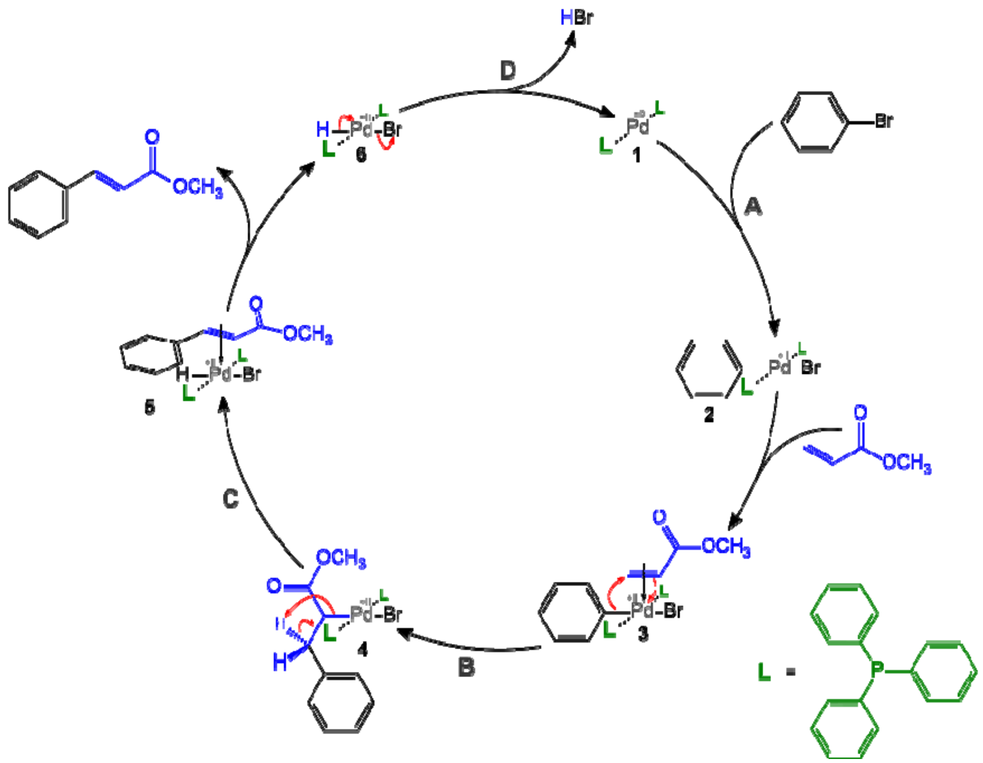


Palladium-catalyzed coupling reactions

In 2010, the Nobel Prize in Chemistry was awarded to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki for their work on palladium-catalyzed cross couplings in organic synthesis.

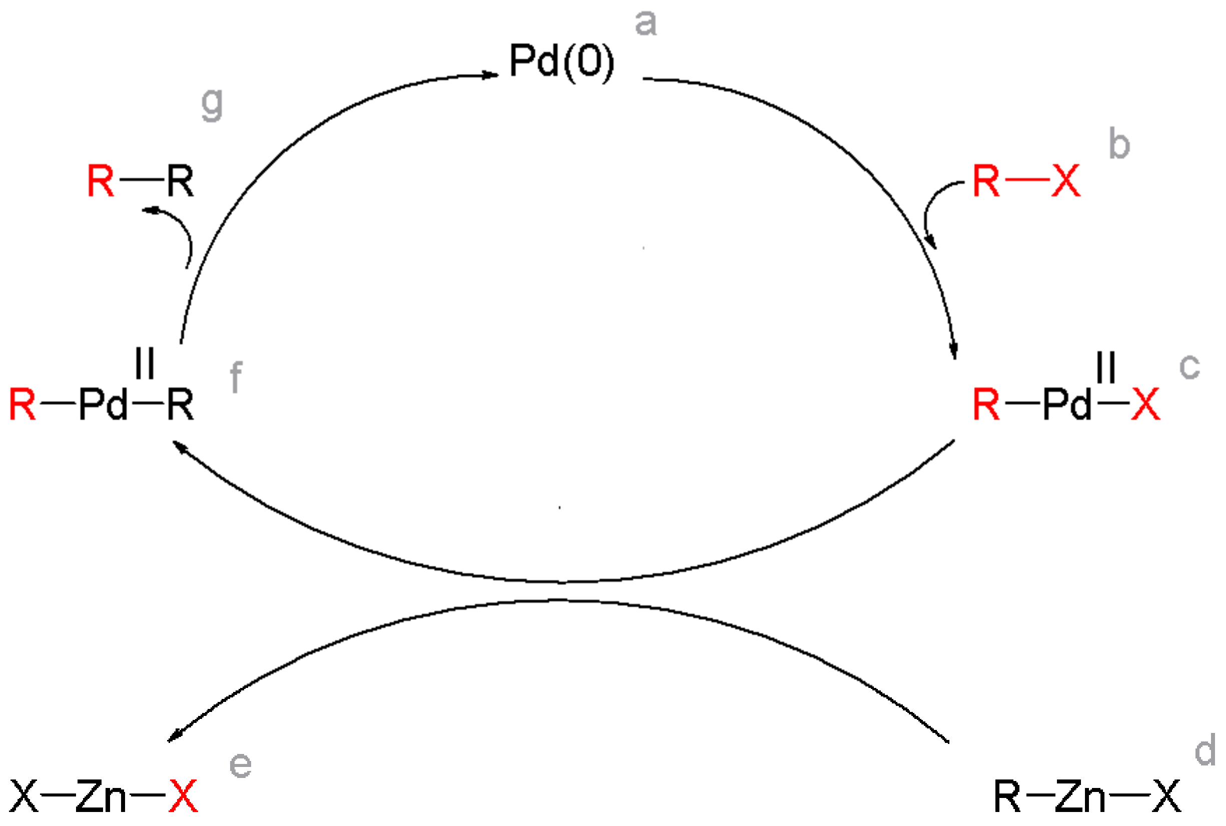
Heck reaction





Negishi coupling

$$R{-}X + R'{-}Zn{-}X' \xrightarrow{ML_n} R{-}R'$$



Pd(0) a

$R{-}X$ b

$R{-}Pd^{II}{-}X$ c

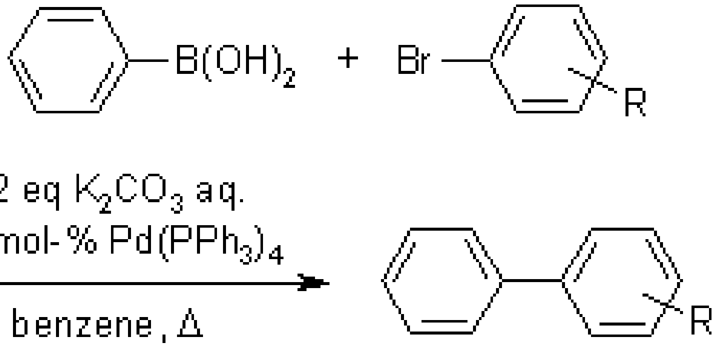
$R{-}Zn{-}X$ d

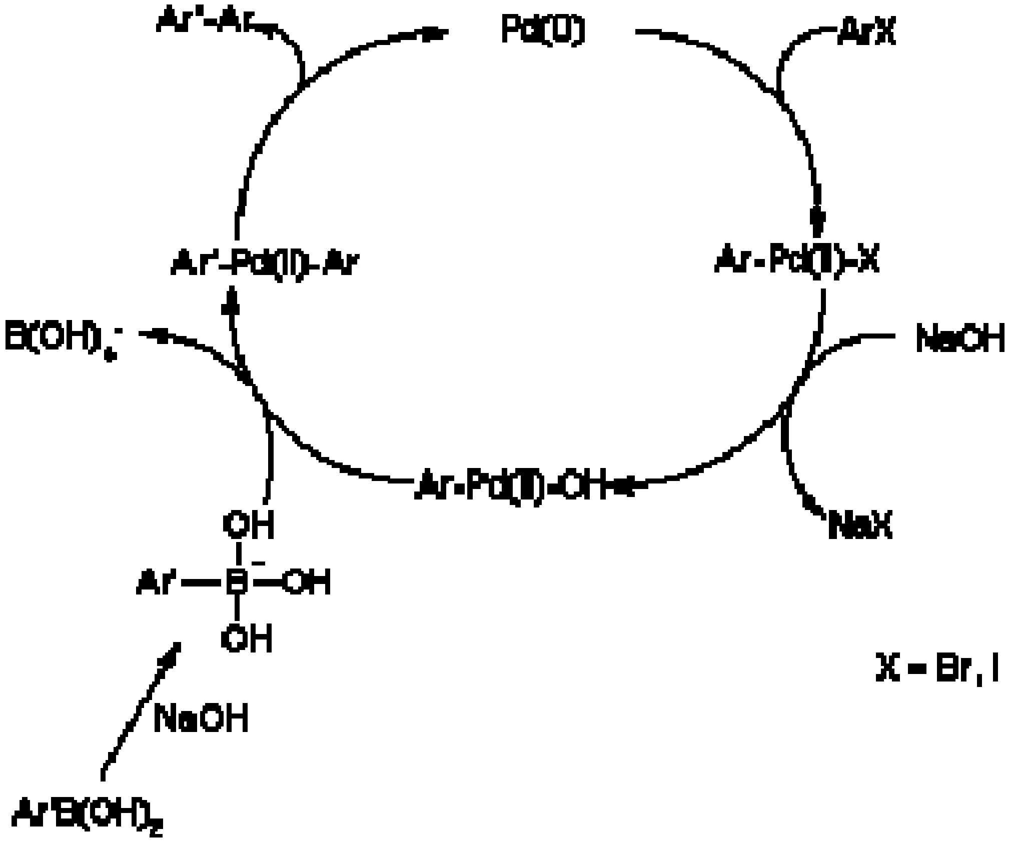
$X{-}Zn{-}X$ e

$R{-}Pd^{II}{-}R$ f

$R{-}R$ g

Suzuki Coupling





An example is the Sonogashira reaction: