

# Organometallic Chemistry and Homogeneous Catalysis

Dr. Alexey Zazybin

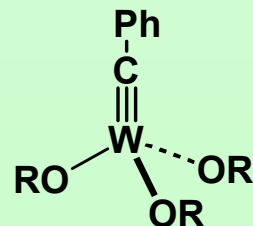
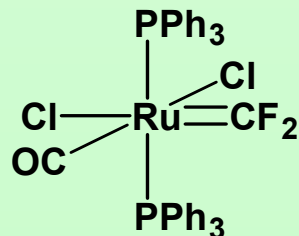
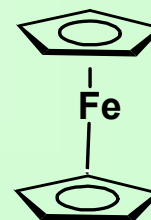
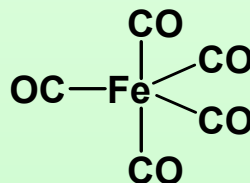
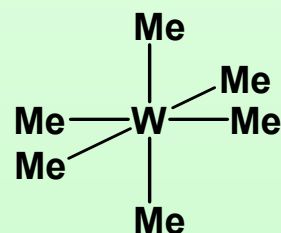
Lecture N1

Kashiwa Campus, October 9, 2009



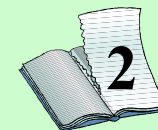
What compounds we can call organometallic compounds?

Compounds containing direct metal-carbon bonds:



MeLi  
PhMgBr

# Organometallic vs. Metal-organic

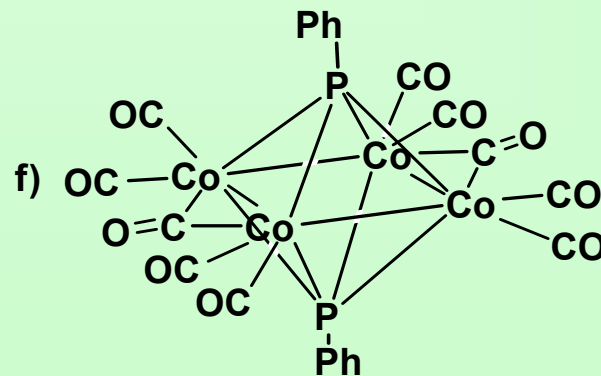
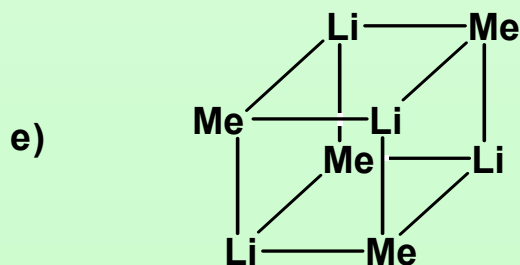
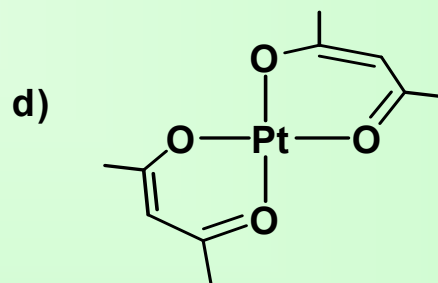
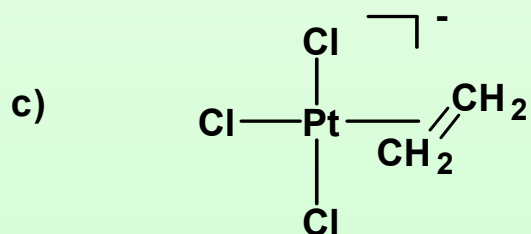
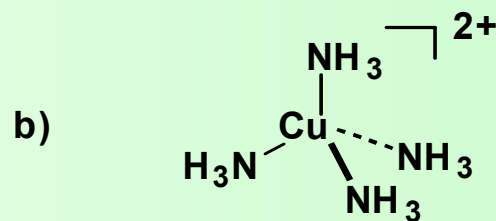
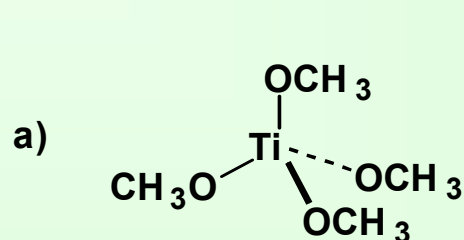


Organometallic compounds  
contain M-C bonds

Metal-organic compound  
e.g.  $\text{Ti}(\text{OMe})_4$

Coordination compounds  
e.g.  $[\text{Co}(\text{NH}_3)_6]^{3+}$

Which of the following compounds is (are) organometallic compound(s)?



# Why organometallic chemistry?



a) *From practical point of view:*

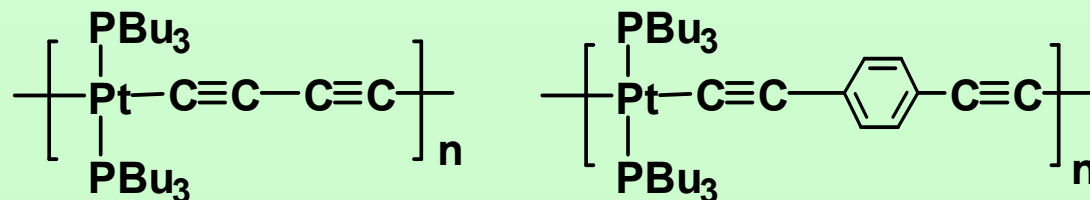
OMC are related to many industrial processes, especially **catalytic processes**, e.g.

→ *In production of fine chemicals*

→ *In production of chemicals in large-scale*

b) *Organometallic chemistry is related to **material science**, e.g. some organometallic compounds can be used to prepare solid materials:*

*Organometallic Polymers, e.g.*

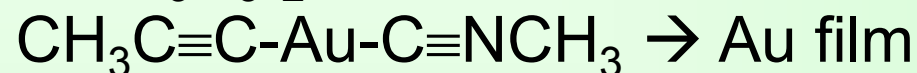
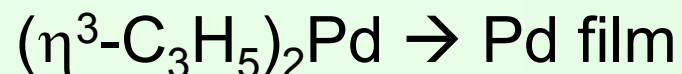


# Why organometallic chemistry?



c) *OMC are precursors to:*

- films for coating



-nanoparticles (applications in electronic, magnetic, or optical devices or in sensors)

d) *Main use in organic synthesis and (homogeneous) catalysis.*

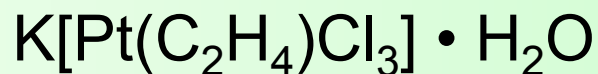
Using metals, you can make complicated organic structures that would be hard to make otherwise.

This is because, compared to "standard organic chemistry", metals display new and unusual reaction types.

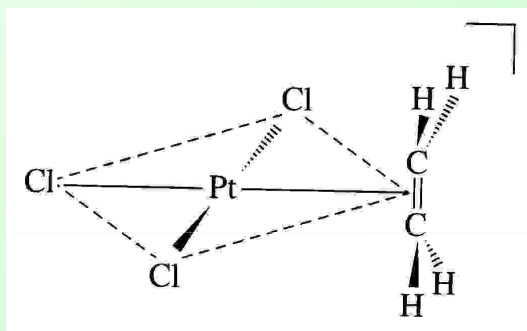


# History

1) Zeise's Salt synthesized in 1827



- Confirmed to have  $\text{H}_2\text{C}=\text{CH}_2$  as a ligand in 1868
- Structure not fully known until 1975



2)  $\text{Ni}(\text{CO})_4$  synthesized in 1890

3) Grignard Reagents ( $\text{XMgR}$ ) synthesized about 1900

Accidentally produced while trying to make other compounds

#### 4) Ferrocene synthesized in 1951

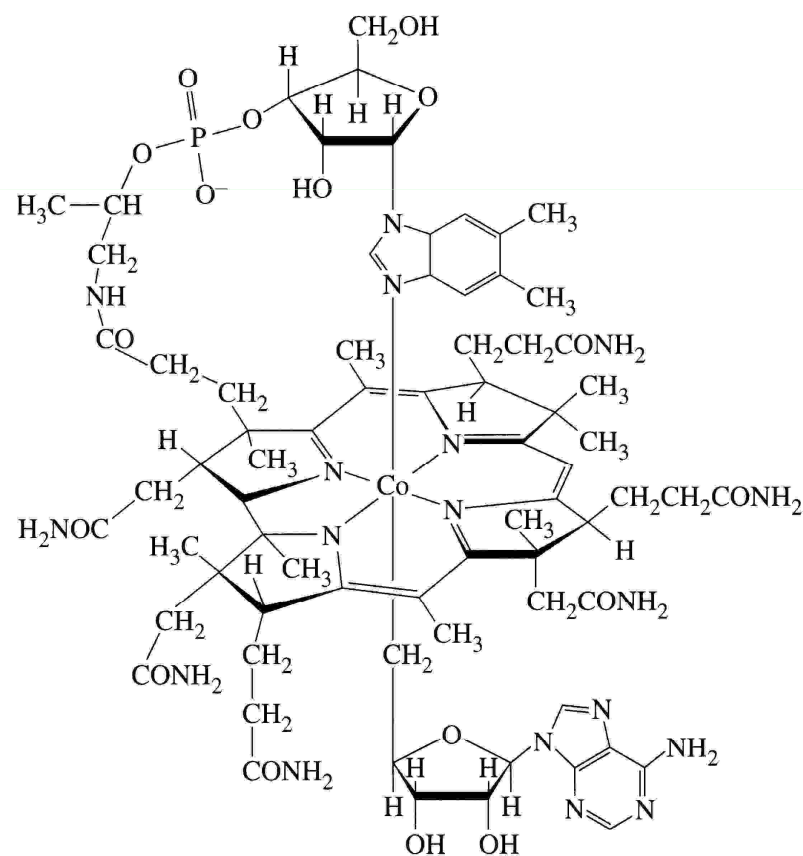
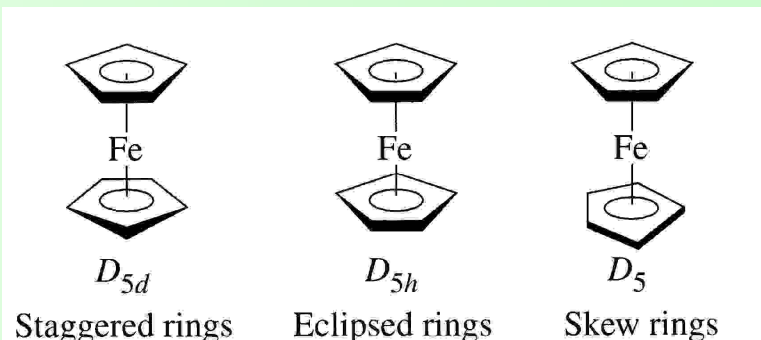
a) Modern Organometallic Chemistry begins with this discovery

b) Many new ligands and reactions produced ever since

#### 5) Organometallic Chemistry has really been around for millions of years

a) Naturally occurring Cobalimins contain Co—C bonds

b) Vitamin B<sub>12</sub>




# *Nobel-Prize Winners related to the area:*




K. Ziegler, G. Natta (1963)  
Ziegler-Natta catalyst: polymerization catalyst

E. O. Fisher, G. Wilkinson (1973)  
Organometallic sandwich compounds

The Nobel Prize in Chemistry 1973

 Ernst Otto Fischer  
Germany, Technical University,  
Munich

 Geoffrey Wilkinson  
UK, Imperial College, London

"for their pioneering work, performed independently, on the chemistry of the organometallics, so called sandwich compounds"

Transition metal organometallic chemistry

10








# *Nobel-Prize Winners related to the area:*

K. B. Sharpless, R. Noyori, W. S. Knowles (2001)  
Asymmetric catalysis

Y. Chauvin, R. H. Grubbs, R. R. Schrock (2005)  
Metathesis method in organic synthesis

**The Nobel Prize in Chemistry 2005**

Yves Chauvin  
Institut Français du Pétrole  
Rueil-Malmaison, France

Robert H. Grubbs  
California Institute of  
Technology  
Pasadena, CA, USA

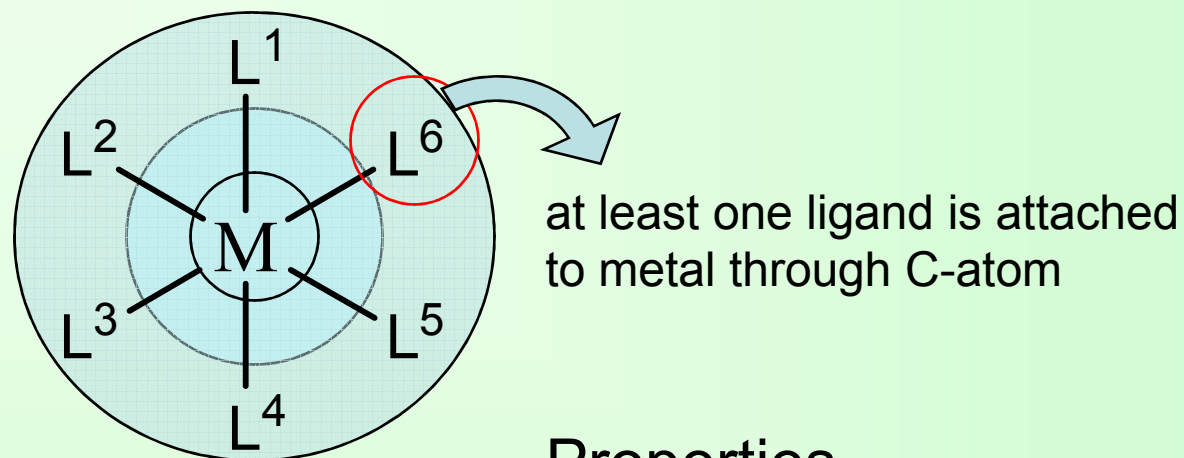
Richard R. Schrock  
MIT,  
Cambridge, MA, USA

"for the development of the  
metathesis method in organic  
synthesis"

**Catalysis, Organometallics**

10

# Structure of organometallic compounds



## Properties

- I. Nature of M
- II. Nature of L

II.a. Ligands with C-atom attached to M  
(CH<sub>3</sub>, aryls, alkenes, arenes, cyclopentadienyls)

II.b. Ligands with other atoms attached to metal (H, halogens, CO, phosphines)





# Early Transition Metals

## Groups 3,4

Strongly electrophilic and oxophilic

Few redox reactions (exception: Ti)

Nearly always  $< 18e$

Polar and very reactive M-C bonds  
(to alkyl and aryl)

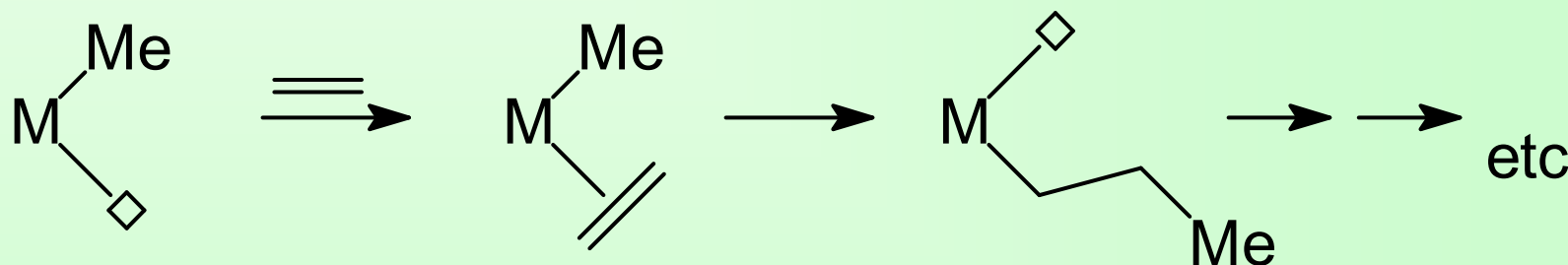
Few *d*-electrons:

- preference for "hard"  $\sigma$ -donors
- weak complexation of  $\pi$ -acceptors

# Early Transition Metals

## Groups 3,4

Typical catalysis: Polymerization





# "Middle" Transition Metals

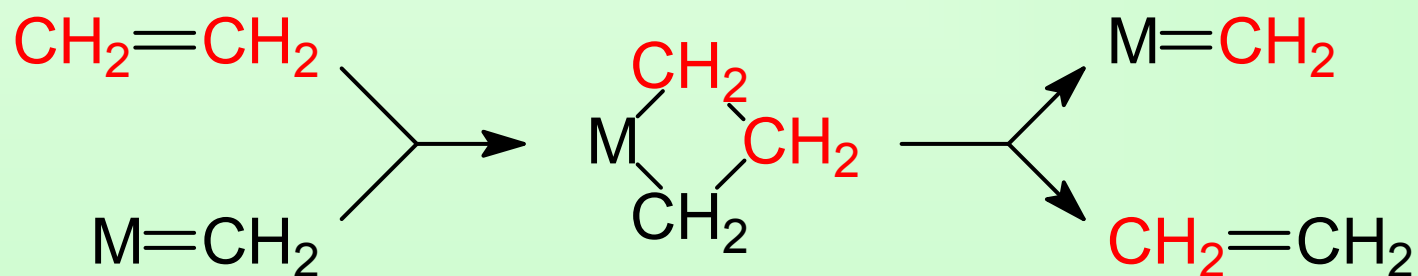
## Groups 5-7

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

# "Middle" Transition Metals

## Groups 5-7

Typical catalysis: Alkene and alkyne metathesis



# Late Transition Metals

## Groups 8 (and 9)

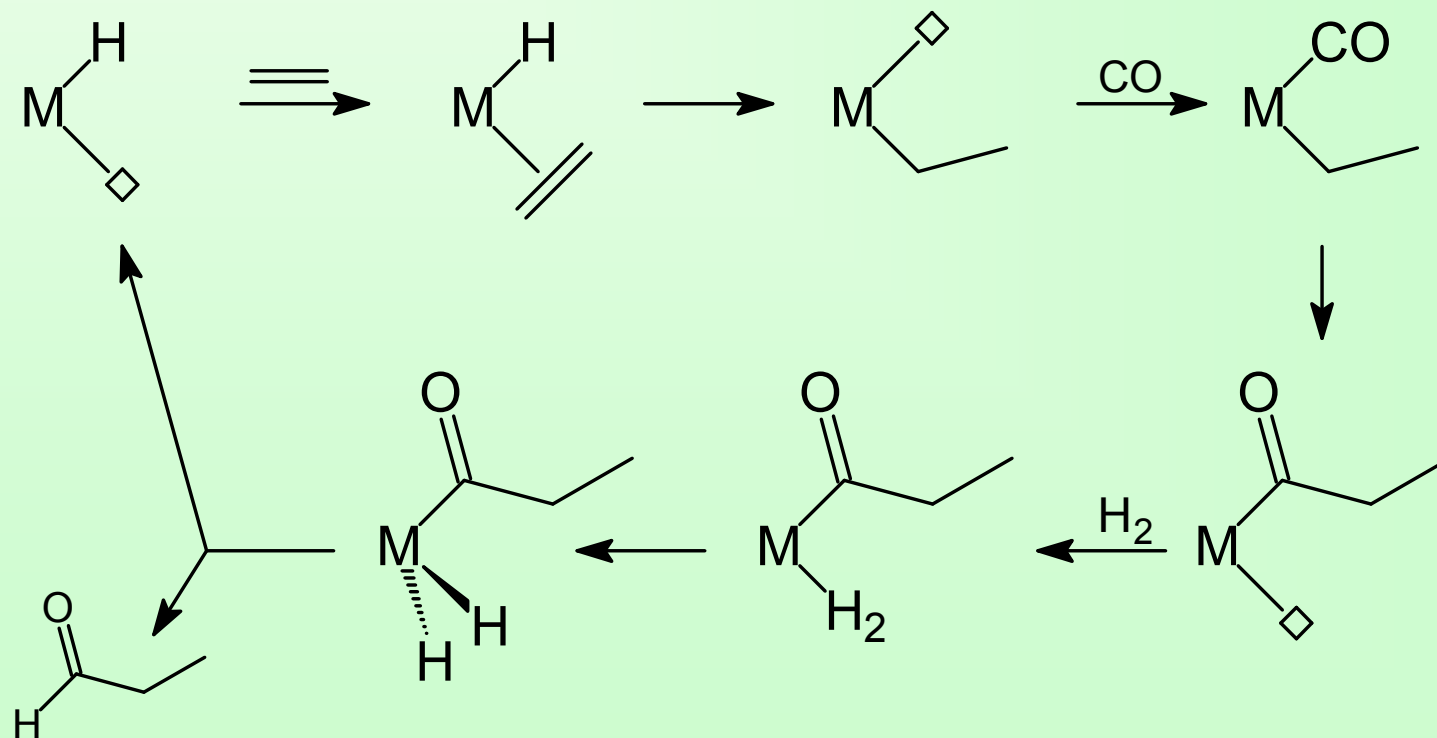
- Many accessible oxidation states
- Mostly 18e or 16e  
16e common for square-planar complexes
- Easy ligand association/dissociation
- Weak, not very reactive M-C bonds
- Even weaker, reactive M-O/M-N bonds
- Preference for  $\sigma$ -donor/weak  $\pi$ -acceptor ligands (phosphines)



# Late Transition Metals

## Groups 8 (and 9)

Typical catalysis: Hydroformylation



# Transition Metals

	H																	He
	Li	Be										B	C	N	O	F		Ne
	Na	Mg										Al	Si	P	S	Cl		Ar
1 <sup>st</sup> row	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
2 <sup>nd</sup> row	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
3 <sup>rd</sup> row	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	Fr	Ra	Ac															
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw	



## 1<sup>st</sup> row:

- often unpaired electrons
- different spin states (HS/LS) accessible
- highest oxidation states not very stable

## 2<sup>nd</sup>/3<sup>rd</sup> row:

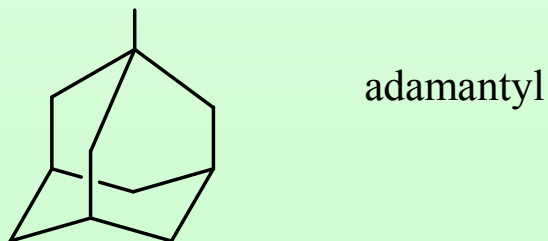
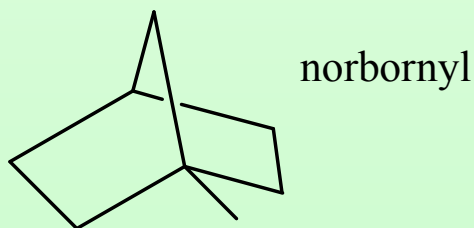
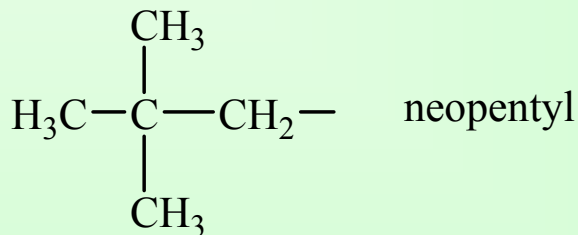
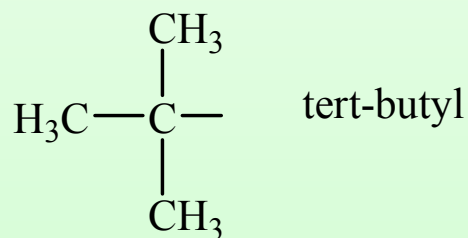
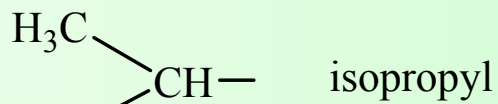
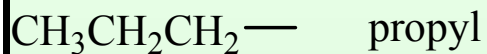
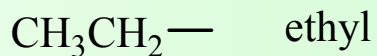
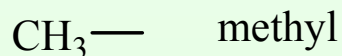
- nearly always "closed shell"
- highest oxidation states fairly stable
- 2<sup>nd</sup> row often more reactive than 3<sup>rd</sup>

## II.a. Ligands with C-atom attached to metal

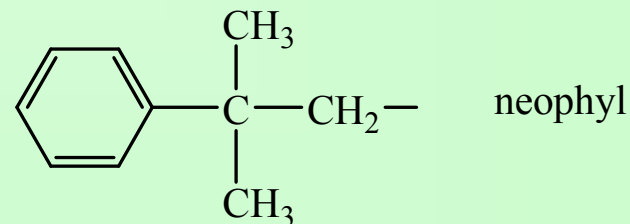
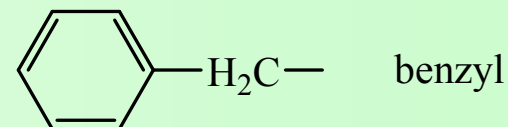
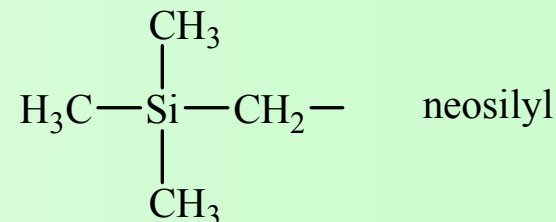


### Alkyl ligands

“pure” alkyls:



alkyls with other functional groups:



Nature of M-C bond: Electronegativity

C 2.5

M 0.9÷2.3

so, polarization is  $\text{M}^{\delta+}\text{—C}^{\delta-}$



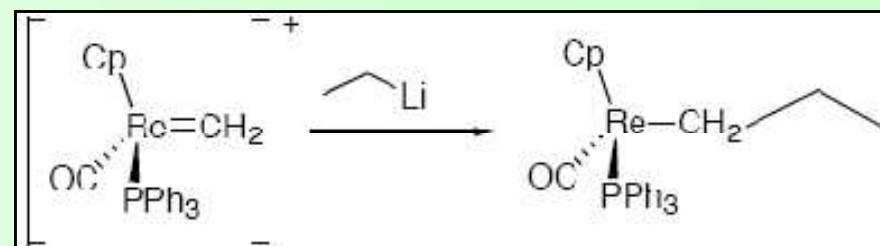
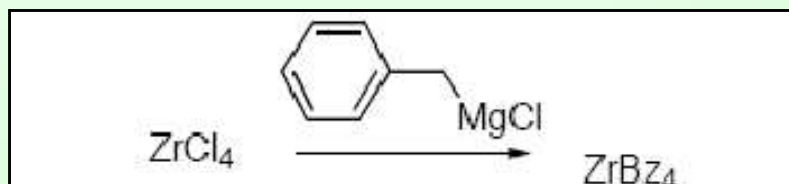
## II.a. Ligands with C-atom attached to metal

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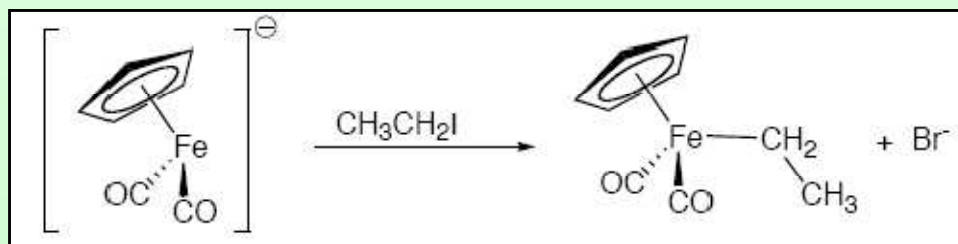
### Alkyl ligands

### Synthesis of Metal Alkyls

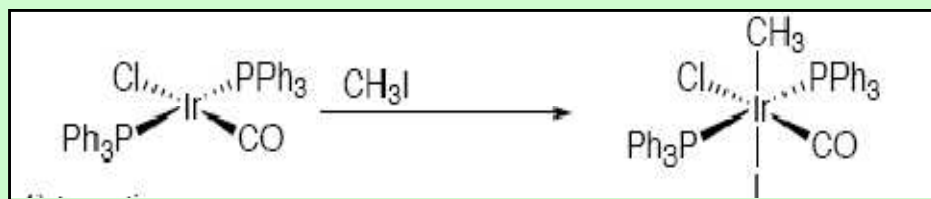
#### 1) Alkylation with a nucleophilic organometallic species



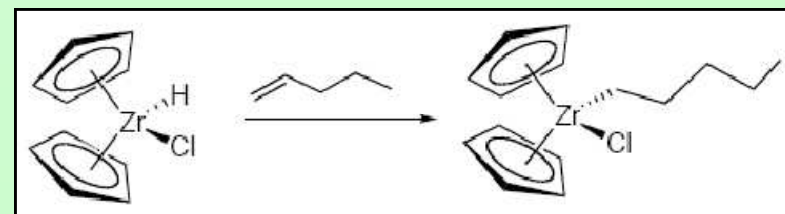
#### 2) Nucleophilic addition to an electrophilic alkyl



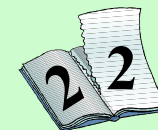
#### 3) Oxidative Addition



#### 4) Insertion



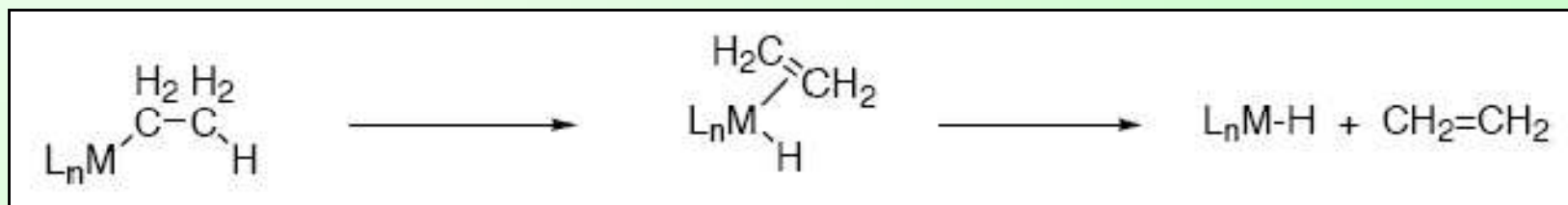
## II.a. Ligands with C-atom attached to metal



### Alkyl ligands

“Internal” stability of metal-alkyl compounds:

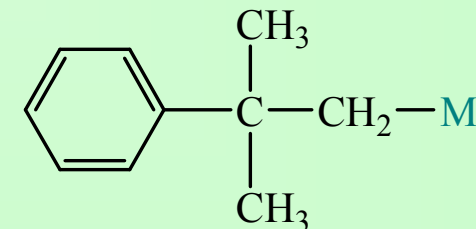
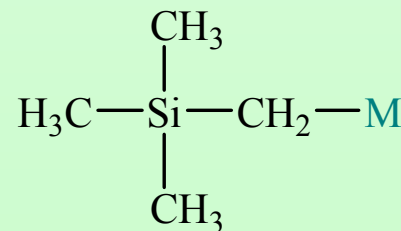
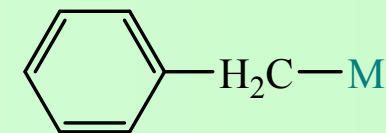
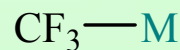
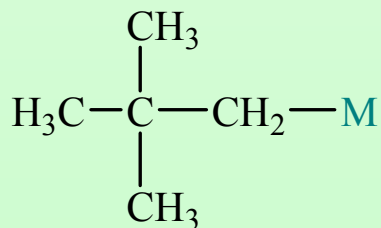
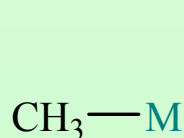
#### $\beta$ -hydride elimination



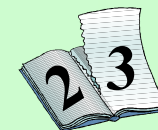
$\beta$ -Hydride elimination occurs for nearly all transition metal-alkyls that meet the following requirements:

1. The  $\beta$ -carbon must have hydrogen substituents

Do not have  $\beta$ -hydrogens:



## II.a. Ligands with C-atom attached to metal

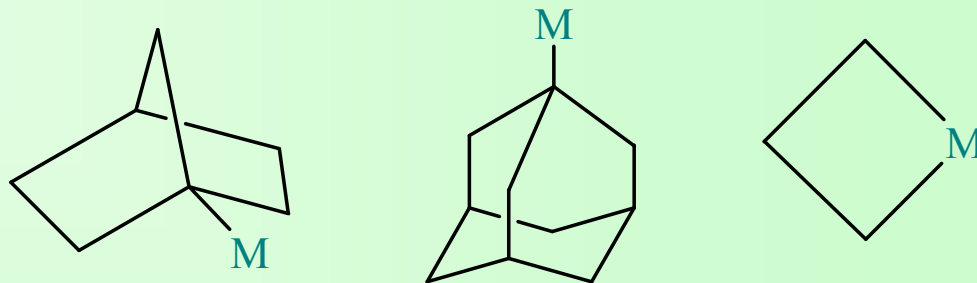


### Alkyl ligands

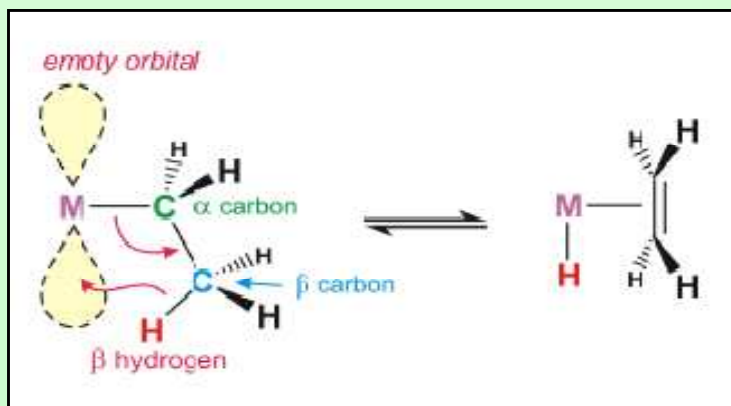
$\beta$ -Hydride elimination occurs for nearly all transition metal-alkyls that meet the following requirements:

2. The M-C-C-H unit can adopt a roughly syn-coplanar conformation that brings the  $\beta$ -hydrogen close to the metal center.

Can not adopt syn-coplanar conformation:



3. There is a vacant coordination site (orbital) *cis* to the alkyl substituent



## II.a. Ligands with C-atom attached to metal



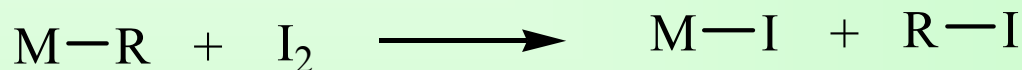
### Alkyl ligands

#### Stability of metal-alkyl compounds towards water, oxygen, etc.

Main group and early transition metal alkyls are very sensitive to water and oxygen.

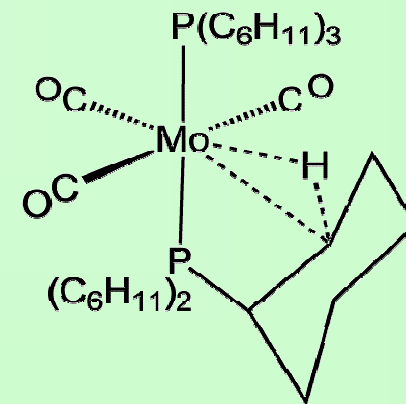
Late transition metal alkyls are more stable to water and oxygen.

Both main group and transition metal alkyls are unstable towards halogenes and solutions of halogenes:



#### Agostic interactions

The word **agostic** is derived from the Greek word for "to hold on to oneself". It most commonly refers to a C-H bond on a ligand that undergoes an interaction with the metal complex.

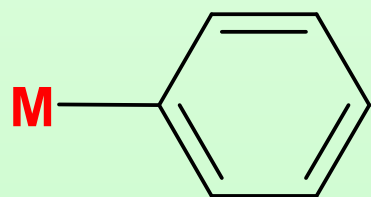




**Agostic interaction** is a term for the interaction of a coordinately-unsaturated Transition metal with a C-H bond, when the two electrons involved in the C-H bond enter the empty d-orbital of a transition metal, resulting in a **two electron three center bond**.

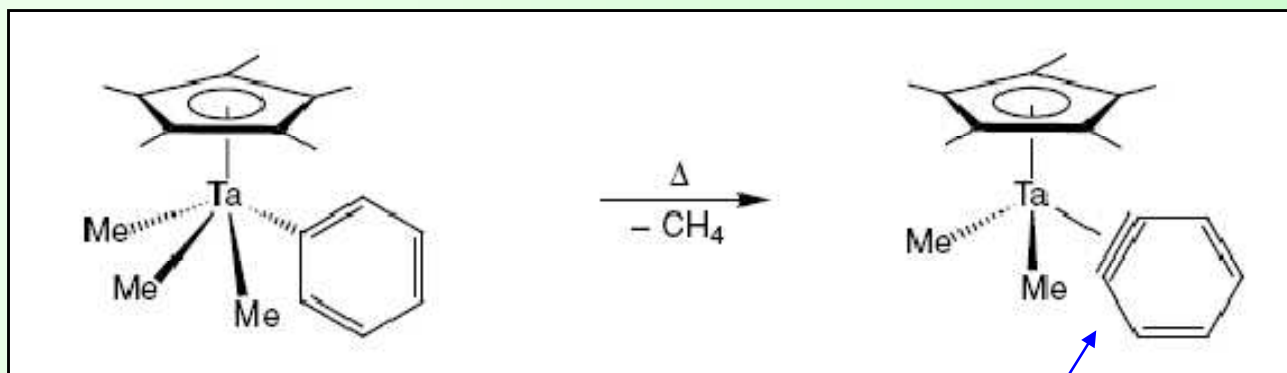
## II.a. Ligands with C-atom attached to metal

### Aryl ligands



Aryl ligands are relatively strong anionic two electron donors, essentially just like alkyls. Since they cannot easily  $\beta$ -hydride eliminate (formation of the **benzyne** intermediate is typically too unstable), metal aryl complexes

are usually relatively stable compared to alkyls with  $\beta$ -hydrogens. But “stable” is a relative term since transition metal aryl complexes are also quite air-sensitive and reactive.



Rare example of benzyne complex

Compare stability of alkyl and aryl ligands:

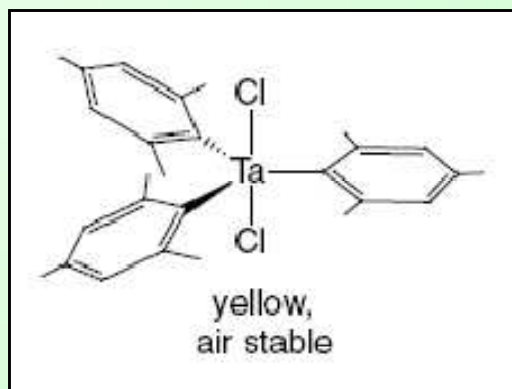
1)

Metal complex	Dissociation energy, kcal/mol
$\text{CH}_3\text{-Mn}(\text{CO})_5$	36
$\text{C}_6\text{H}_5\text{-Mn}(\text{CO})_5$	49

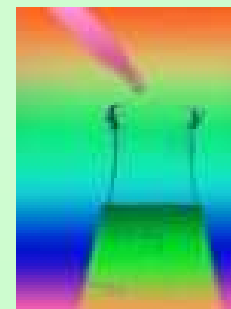
2)  $\text{TiPh}_4$  and  $\text{TiMe}_4$

$\text{TiPh}_4$  decomposes only above  $0^\circ\text{C}$ , whereas  $\text{TiMe}_4$  decomposes at  $-40^\circ\text{C}$ .

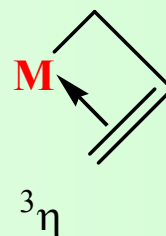
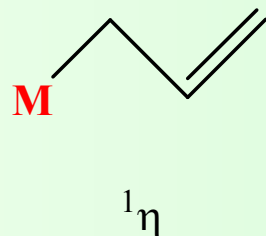
It is possible to obtain quite stable aryl complexes if the  $\beta$ -H-elimination reaction is blocked by replacing both *ortho* H  $\beta$ -atoms of the phenyl ligands by substituents. This condition is perfectly achieved in the mesityl ligand:



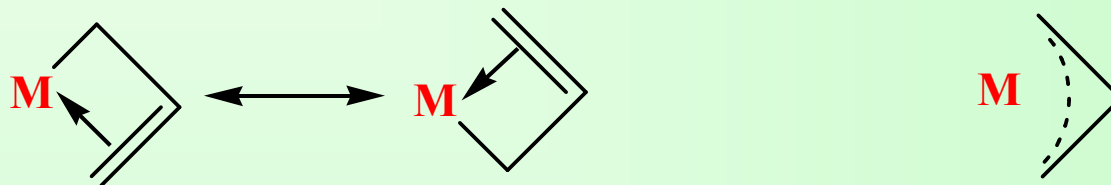
Aryls do have the potential for both  $\pi$ -donation and  $\pi$ -backbonding through the filled aryl  $\pi$ -orbitals and empty  $\pi^*$  antibonding orbitals. This can provide additional stability to a metal complex, depending on whether the metal needs additional electrons from the ligand or wants to dump excess electron density onto the ligand.



## Allyl ligands

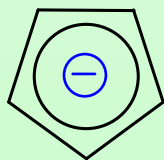


Allyl ligands can act both as  $^1\eta$  – ligand (similar to any other alkyl) and  $^3\eta$  – ligand (3-electron ligand). Usually 2 resonance forms can be drawn as hybrid:



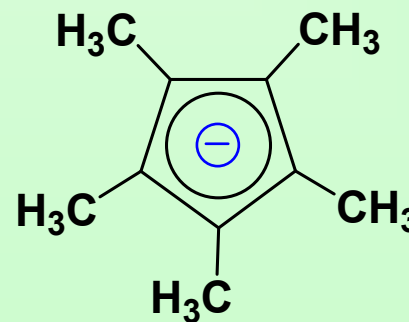
## Cyclopentadienyl ligands

KC<sub>5</sub>H<sub>5</sub>, 1901; Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>, Miller, 1951



*6e-  
strong  
donor*

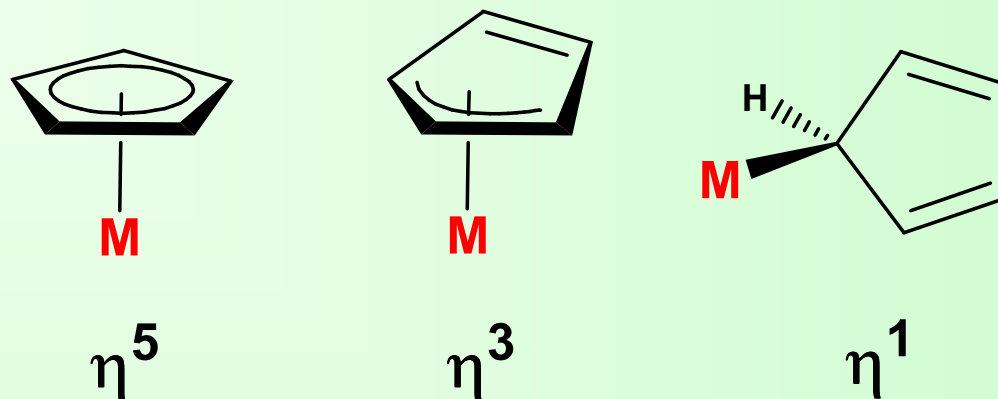
**Cp**



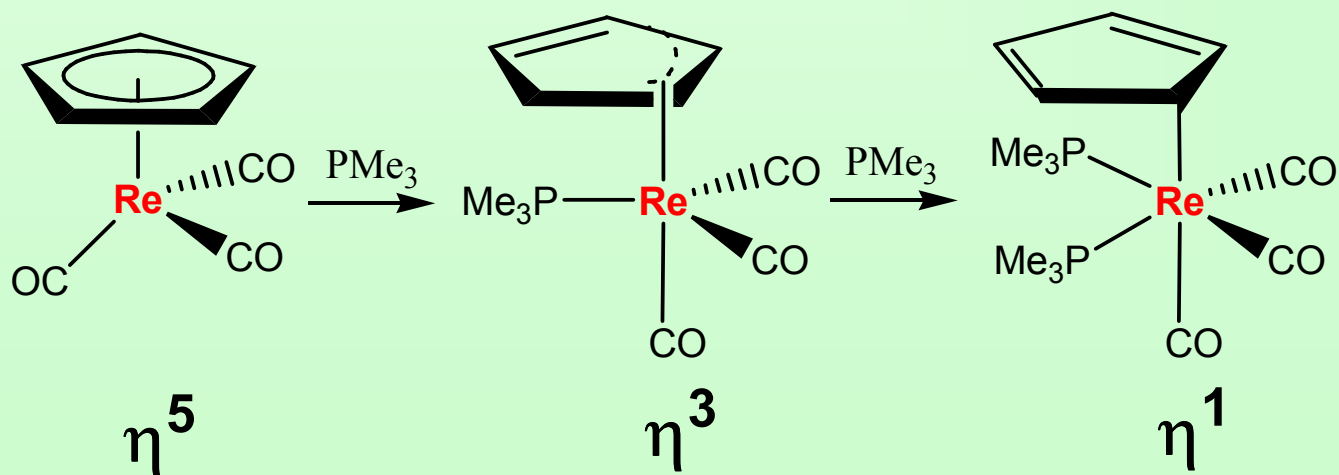
*6e- stronger donor  
bulky ligand*

**Cp\***

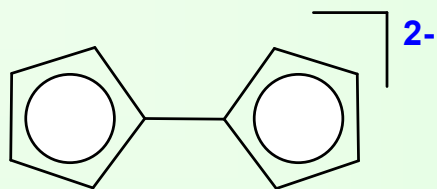
Cyclopentadienyl ligand that normally coordinates in an  $\eta^5$  mode as a  $6e^-$  donor, but it can adopt  $\eta^3$ - and  $\eta^1$ -coordination modes:



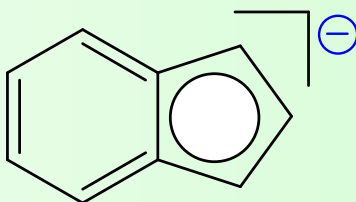
Different types of coordination can be seen within one range of complexes:



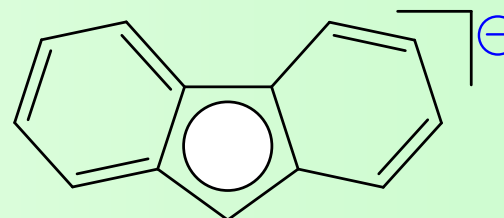
## Cp-variants:



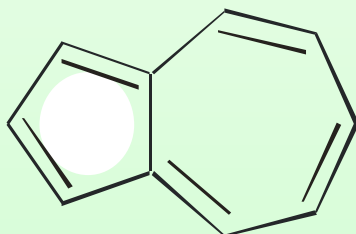
fulvalenediyl (2-)



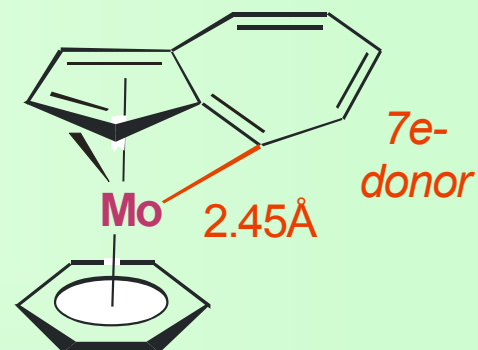
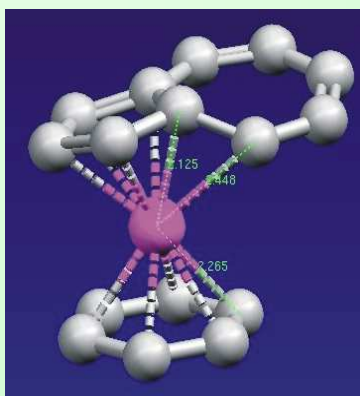
indenyl (-)



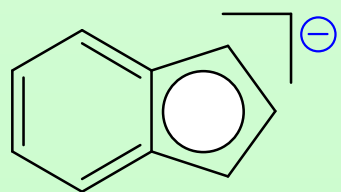
fluorenyl (-)



azulene

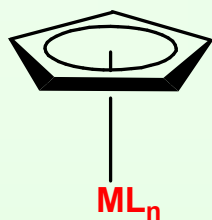


Behrens, *Angew. Chem.*, 1987

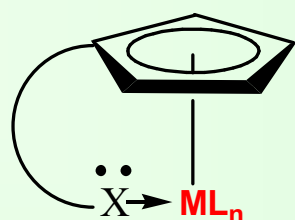


In compare to Cp, indenyl can more easy switch between  $^5\eta$  and  $^3\eta$  coordination mode. Indenyl is also a better  $\pi$ -acceptor than Cp

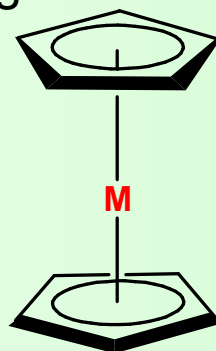
Complexes of the cyclopentadienyl ligand fall into 4 classes:



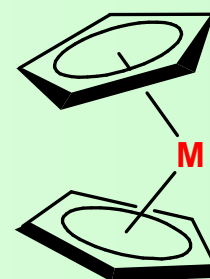
Half-sandwich



Scorpionate



Sandwich



Bent-metalloenes

Reactivity of ferrocene complex:

