

# Organometallics

Submitted by:  
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# ORGANOMETALLIC CHEMISTRY

1. Introduction (types and rationale)
2. Molecular orbital (bonding) of CO, arrangement “in space” or ligand types (hapticity)
3. 16 and 18 electron rule (learning to count)
4. Synthesis, steric effects and reactivity - Wilkinsons catalyst (part 1)
5. Characterisation IR nmr *etc.*
6. Applications (oxidative addition b elimination)

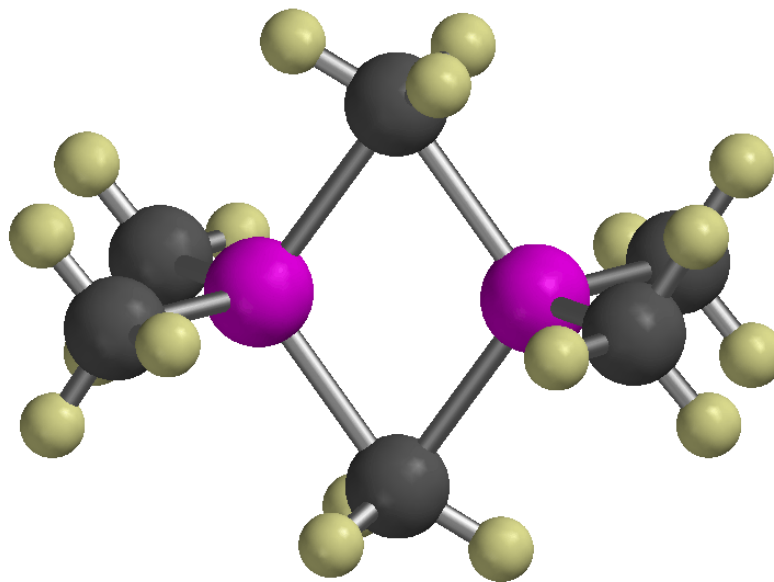
# What is organometallic chemistry?

*Chemistry:* structures, bonding and properties of molecules.

*Organometallic compounds:* containing direct *metal-carbon* bonds.

*Either s or p bonds can occur*

Main group:



❖ Structures

↻ s bonds and  $3c-2e$  (or even  $4c-2e$ ) bonds

↻ Chem 210

❖ Synthesis

↻ the first M-C bond

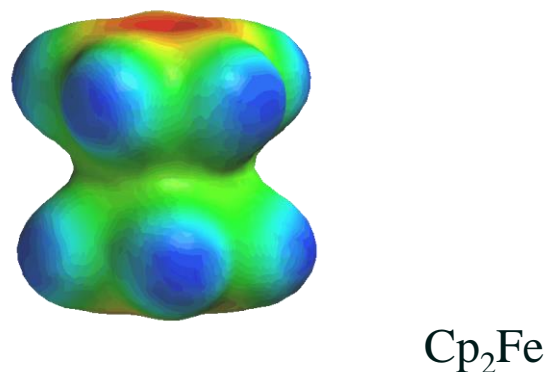
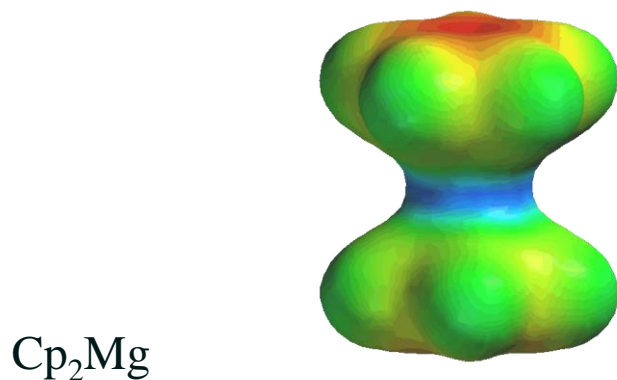
❖ Reactivity

↻ nucleophilic and basic

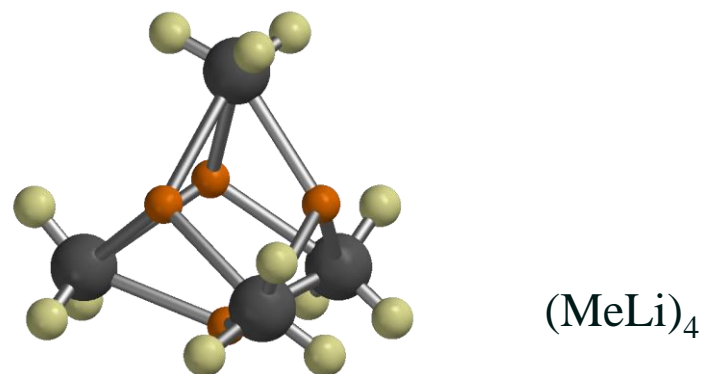
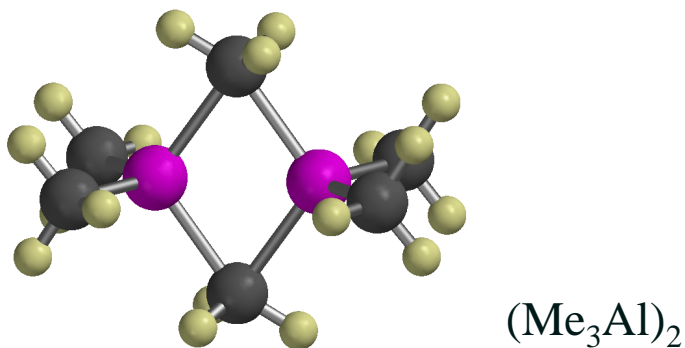
↻ auxiliaries in organic synthesis

↻ source of organic groups for transition metals

- ❖ Strong preference for s-donor groups but Cp is often p-bound (deceptively like with transition metals)

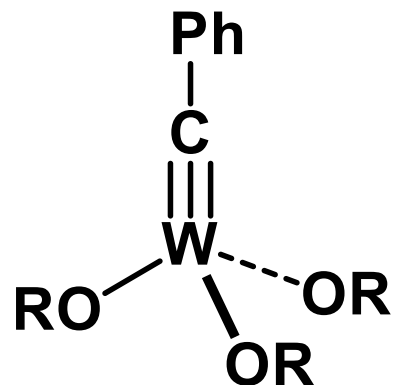
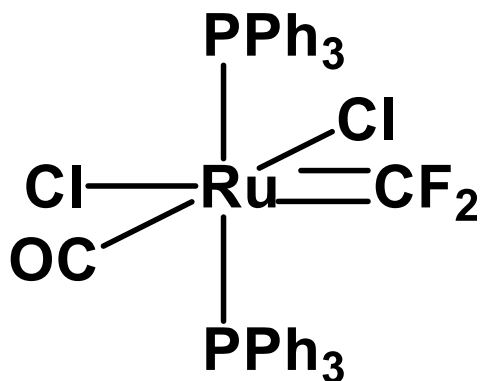
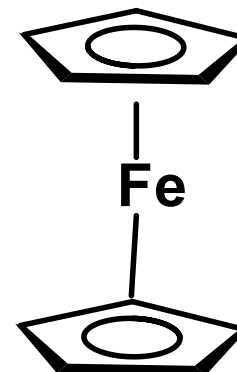
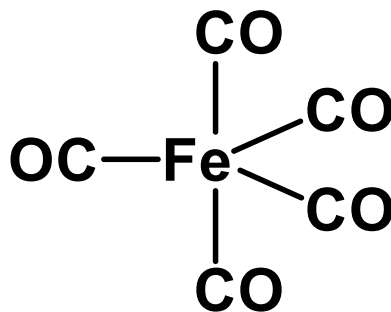
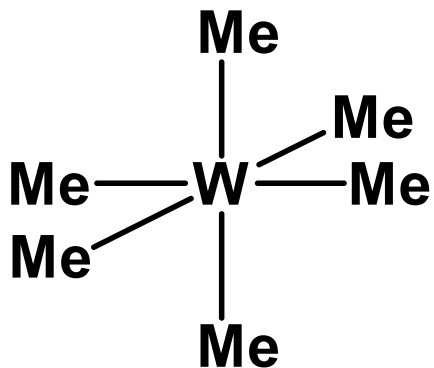


- ❖ Electropositive metals: often  $3c-2e$  or  $4c-2e$  hydrides/alkyls



*Chemistry:* structures, bonding and properties of molecules.

Transition metal compounds

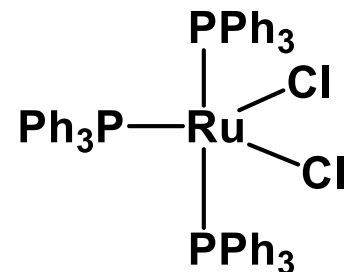
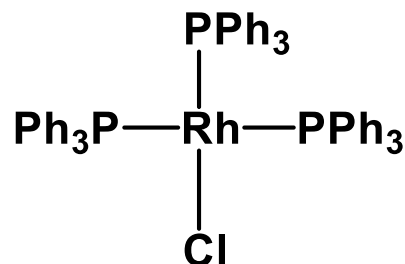
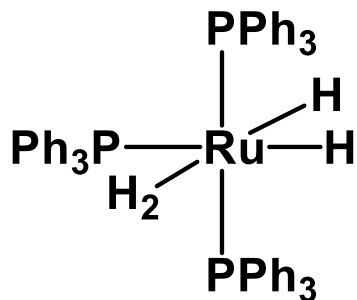
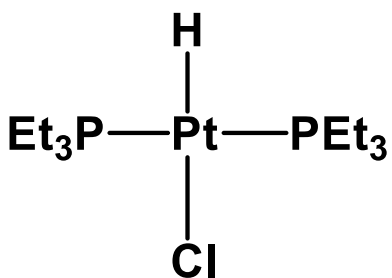


$\text{MeLi}$

$\text{PhMgBr}$

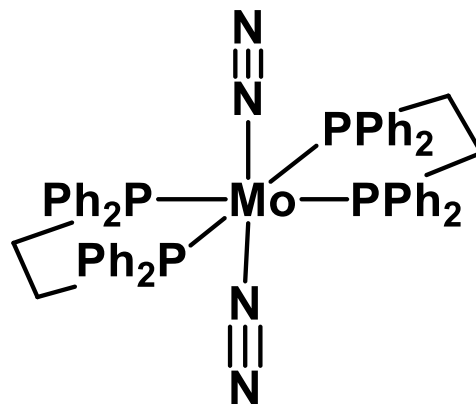
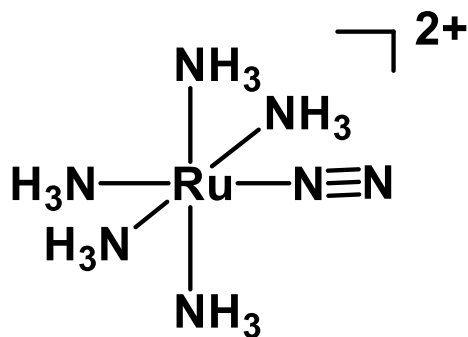
Some compounds do not contain metal-carbon bond, but they are usually included in the field of organometallic chemistry. They include:

- Metal hydride complexes, *e.g.*



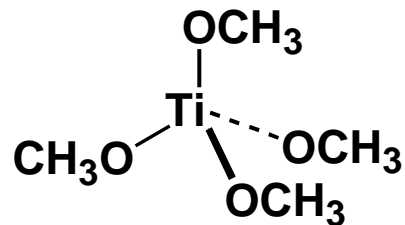
- Phosphine complexes, *e.g.*

- N<sub>2</sub>-complexes, *e.g.*

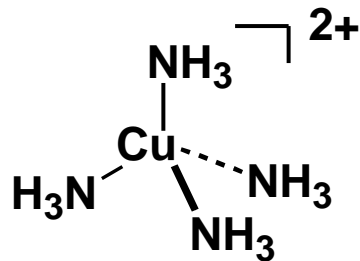


Exercise. Which of the following compounds is an organometallic compound?

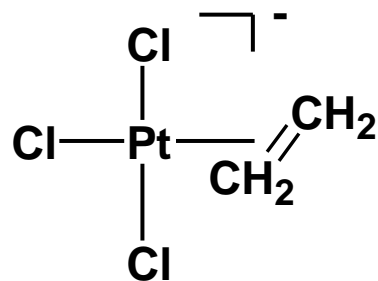
a)



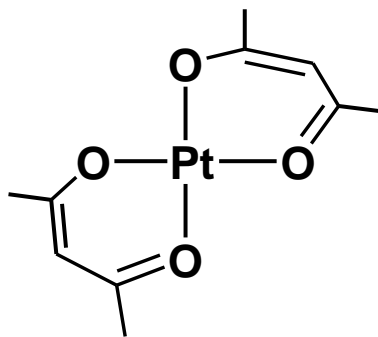
b)



c)



d)

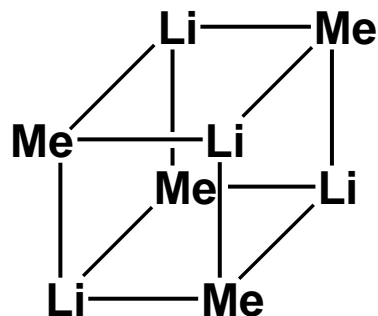


In general, metals in organometallic compounds include:

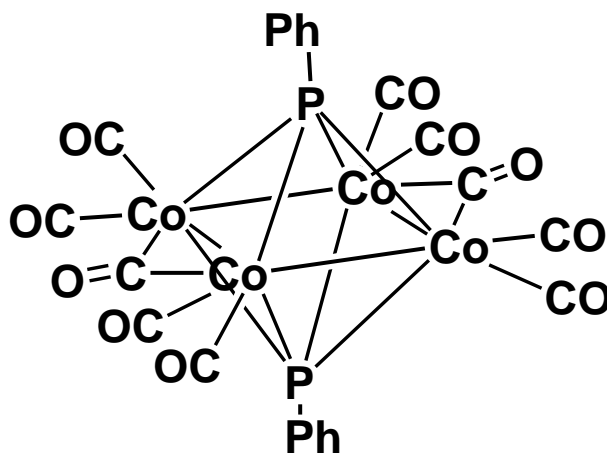
- *main group metals*
- *transition metals*
- *f-block metals*

In this course, transition metals are our main concern.

e)



f)





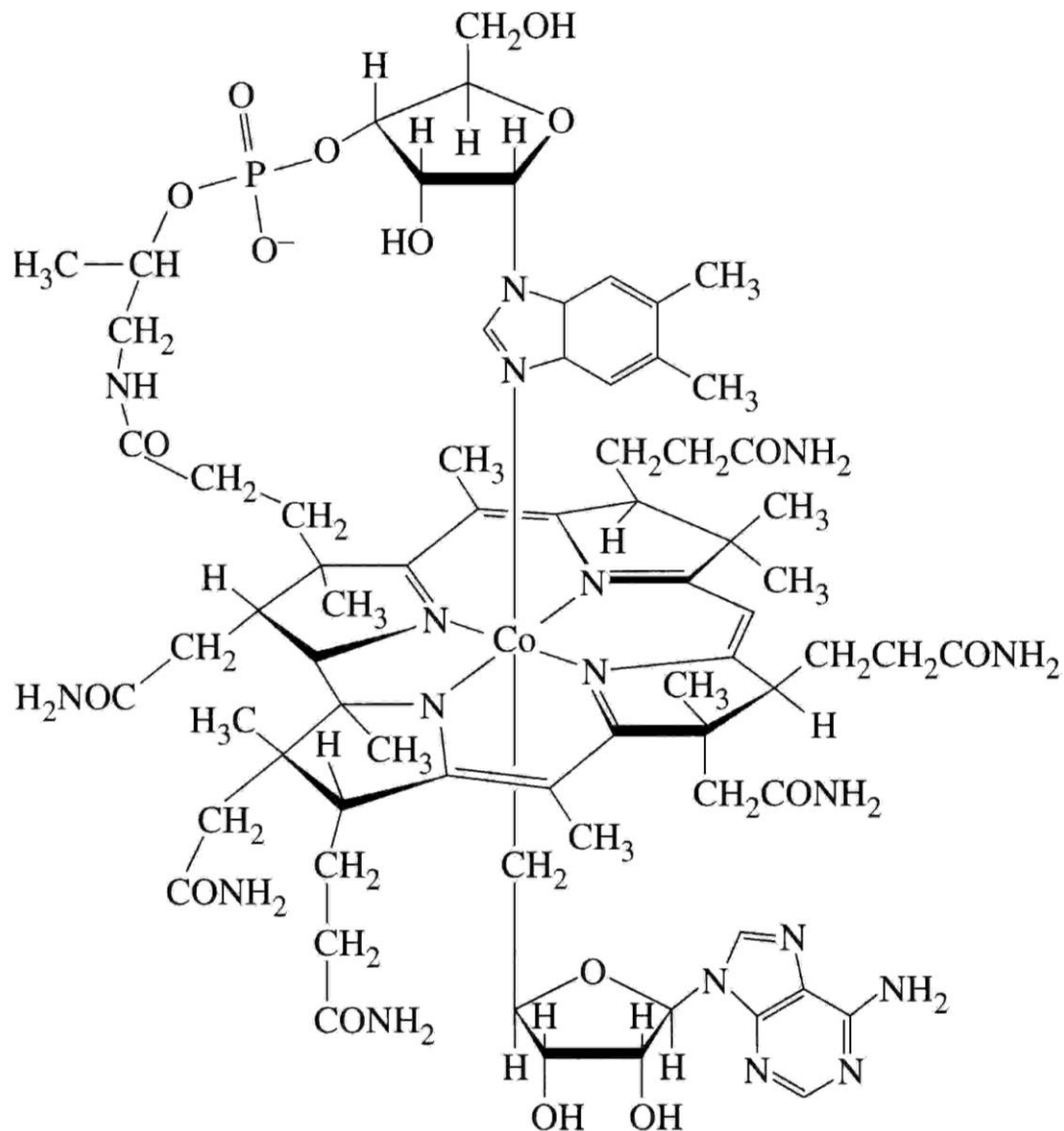
# A brief history of organometallic chemistry

1) Organometallic Chemistry has really been around for millions of years

Naturally occurring

Cobalimins contain Co—C bonds

Vitamin B12



2) Zeise's Salt synthesized in 1827 =  $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3] \cdot \text{H}_2\text{O}$

∞ Confirmed to have  $\text{H}_2\text{C}=\text{CH}_2$  as a ligand in 1868

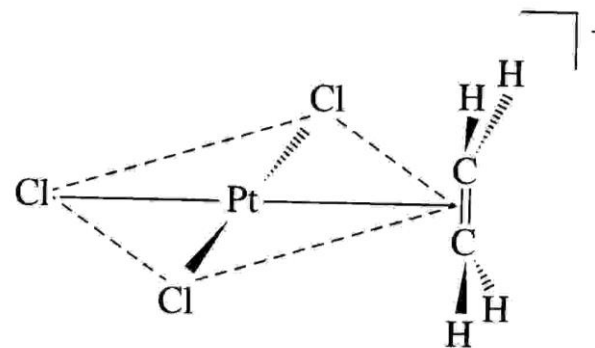
∞ Structure not fully known until 1975

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

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

∞ Accidentally produced while trying to make other compounds

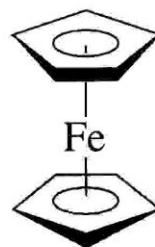
∞ Utility to Organic Synthesis recognized early on



5) Ferrocene synthesized in 1951

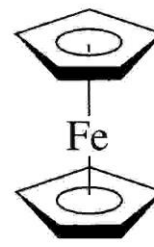
– **Modern Organometallic Chemistry begins with this discovery (Paulson and Miller)**

– **1952 Fischer and Wilkinson**



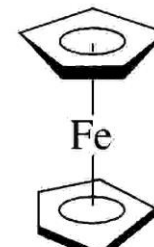
$D_{5d}$

Staggered rings



$D_{5h}$

Eclipsed rings



$D_5$

Skew rings

*Nobel -Prize Winners related to the area:*

Victor Grignard and Paul Sabatier (1912)

Grignard reagent

K. Ziegler, G. Natta (1963)

Ziegler-Natta catalyst

E. O. Fisher, G. Wilkinson (1973)

Sandwich compounds

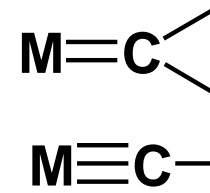
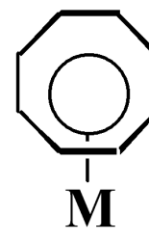
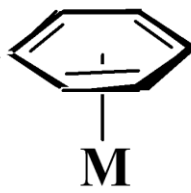
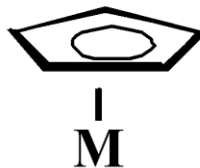
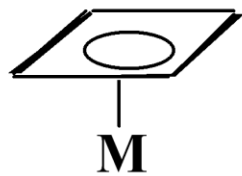
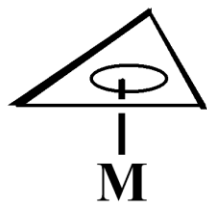
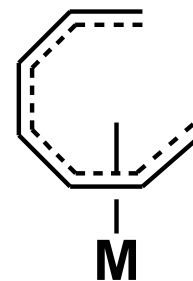
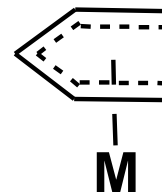
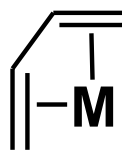
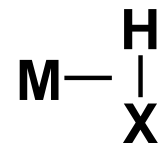
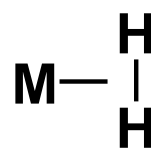
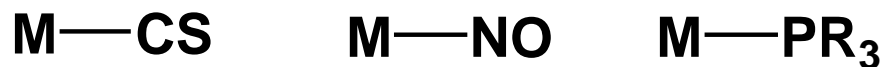
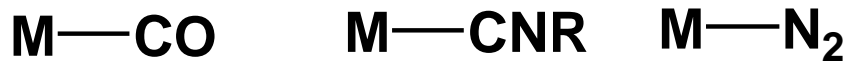
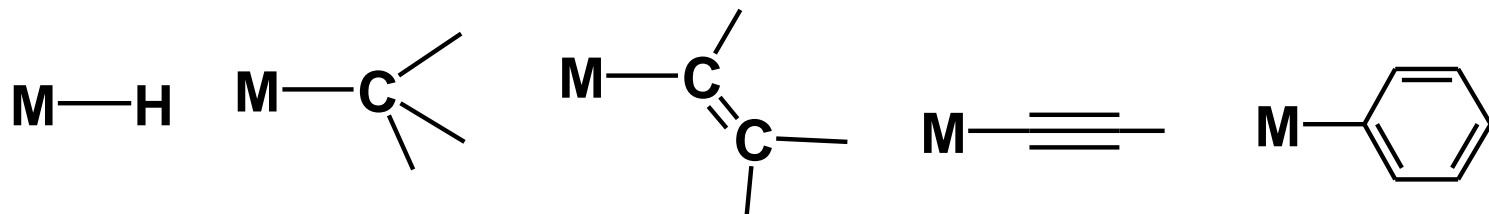
K. B. Sharpless, R. Noyori (2001)

Hydrogenation and oxidation

Yves Chauvin, Robert H. Grubbs, Richard R. Schrock (2005) Metal-catalyzed alkene

metathesis

# Common organometallic ligands

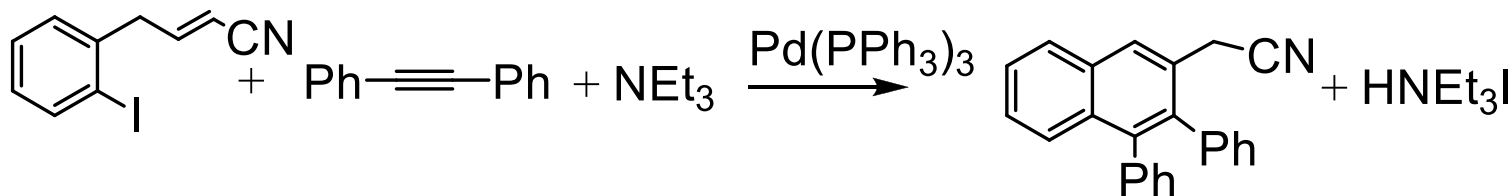
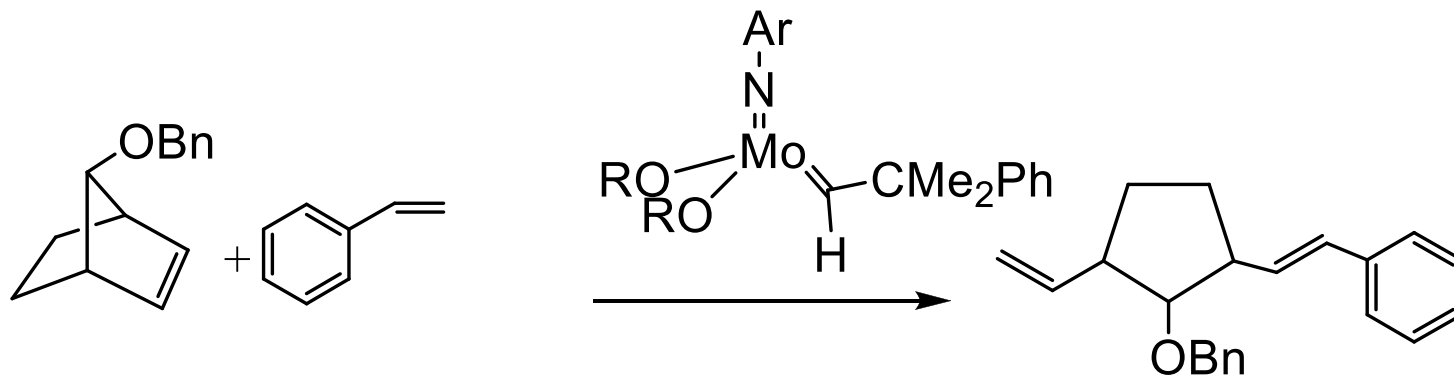


# Why organometallic chemistry ?

a). *From practical point of view:*

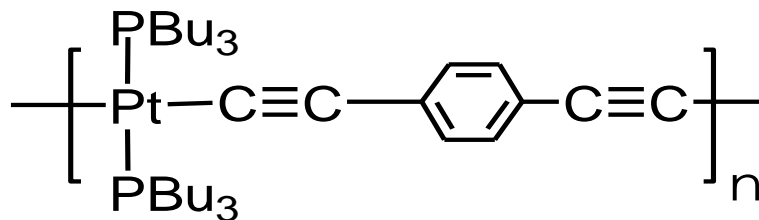
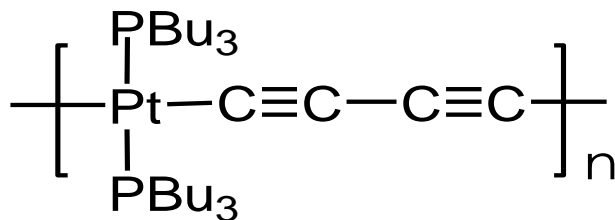
\* OMC are useful for chemical synthesis, especially catalytic processes, *e.g. In production of fine chemicals*

*In production of chemicals in large-scale reactions could not be achieved traditionally*



\* Organometallic chemistry is related to material sciences.

*e.g. Organometallic Polymers*



*Small organometallic compounds:*

*Precursors to films for coating (MOCVD)*

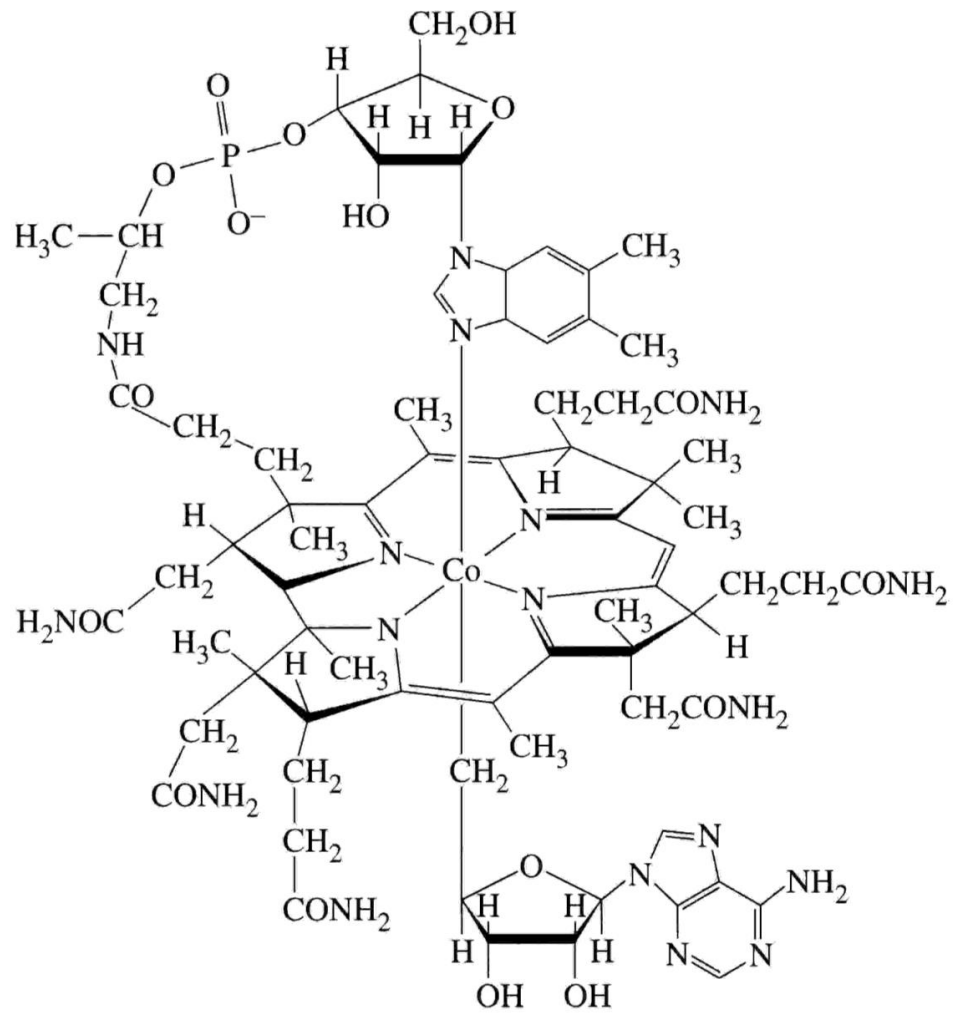
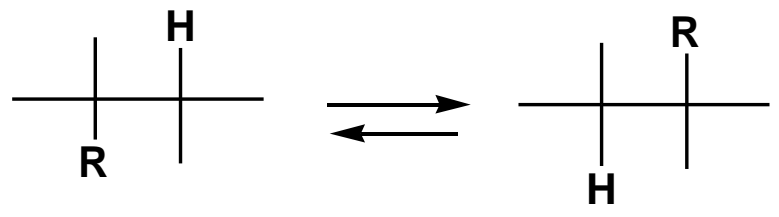
$(\text{h}^3\text{-C}_3\text{H}_5)_2\text{Pd} \text{ -----} > \text{ Pd film}$

$\text{CH}_3\text{C} \equiv \text{C} - \text{Au} - \text{C} \equiv \text{NMe} \text{ -----} > \text{ Au film}$

*Luminescent materials*

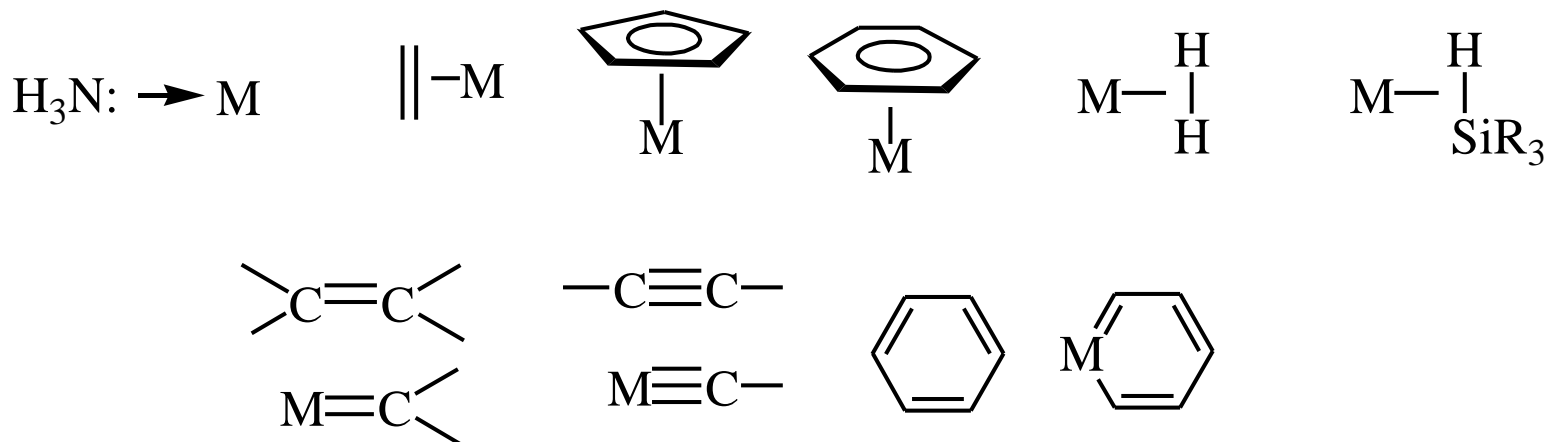
**\* Biological Science. Organometallic chemistry may help us to understand some enzyme-catalyzed reactions.**

*e.g. B12 catalyzed reactions.*



b). From academic point of view:

\* Organometallic compounds display many unexpected behaviors- discover new chemistry- *new structures* e.g.



*New reactions, reagents, catalysts, e.g.*

Ziegler-Natta catalyst, Wilkinson catalyst

Reppe reaction, Schwartz's reagent

Sharpless epoxidation, Tebbe's reagent



# Types of bonds possible from Ligands

Language: All bonds are coordination or coordinative

Remember that all of these bonds are weaker than normal organic bonds (they are dative bonds)

Simple ligands *e.g.*  $\text{CH}_3^-$ ,  $\text{Cl}^-$ ,  $\text{H}_2$  give s bonds

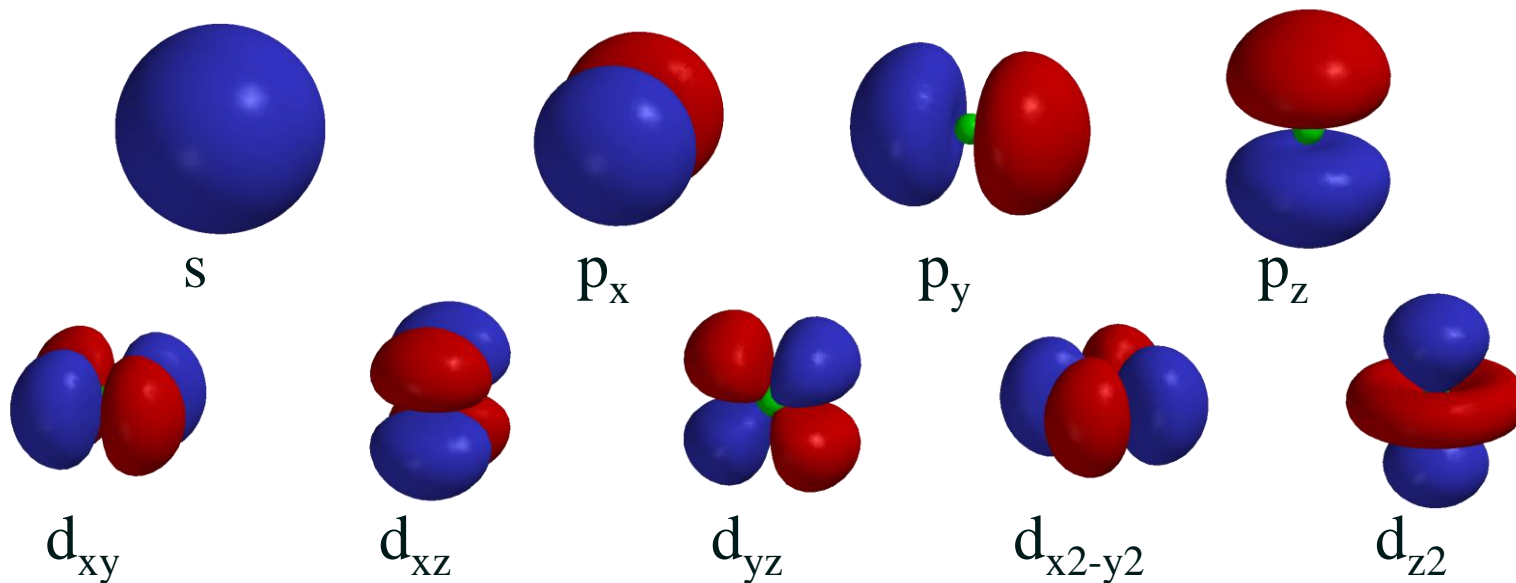
$\pi$  systems are different *e.g.* CO is a s donor and p acceptor

Bridging ligands can occur two metals

Metal-metal bonds occur and are called d bonds – they are weak and are a result of *d-d* orbital overlap

# 18 Electron Rule (Sidgwick, 1927)

- OM chemistry gives rise to many “stable” complexes - how can we tell by a simple method
- Every element has a certain number of valence orbitals:
  - 1 { 1s } for H
  - 4 {  $ns$ ,  $3'np$  } for main group elements
  - 9 {  $ns$ ,  $3'np$ ,  $5'(n-1)d$  } for transition metals

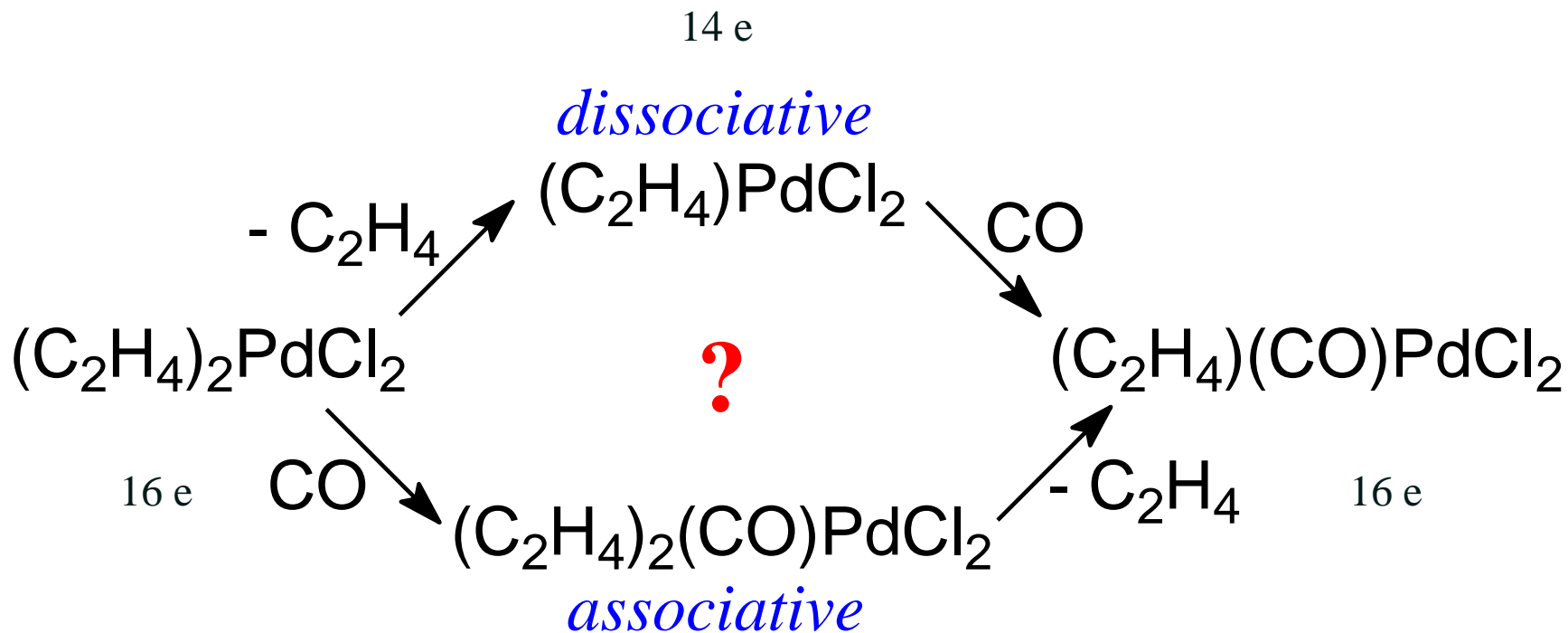


- Therefore, every element wants to be surrounded by 2/8/18 electrons
  - For main-group metals (8-*e*), this leads to the standard Lewis structure rules
  - For transition metals, we get the 18-electron rule
- Structures which have this preferred count are called *electron-precise*
- Every orbital wants to be “used”, *i.e.* contribute to binding an electron pair

The strength of the preference for electron-precise structures depends on the position of the element in the periodic table

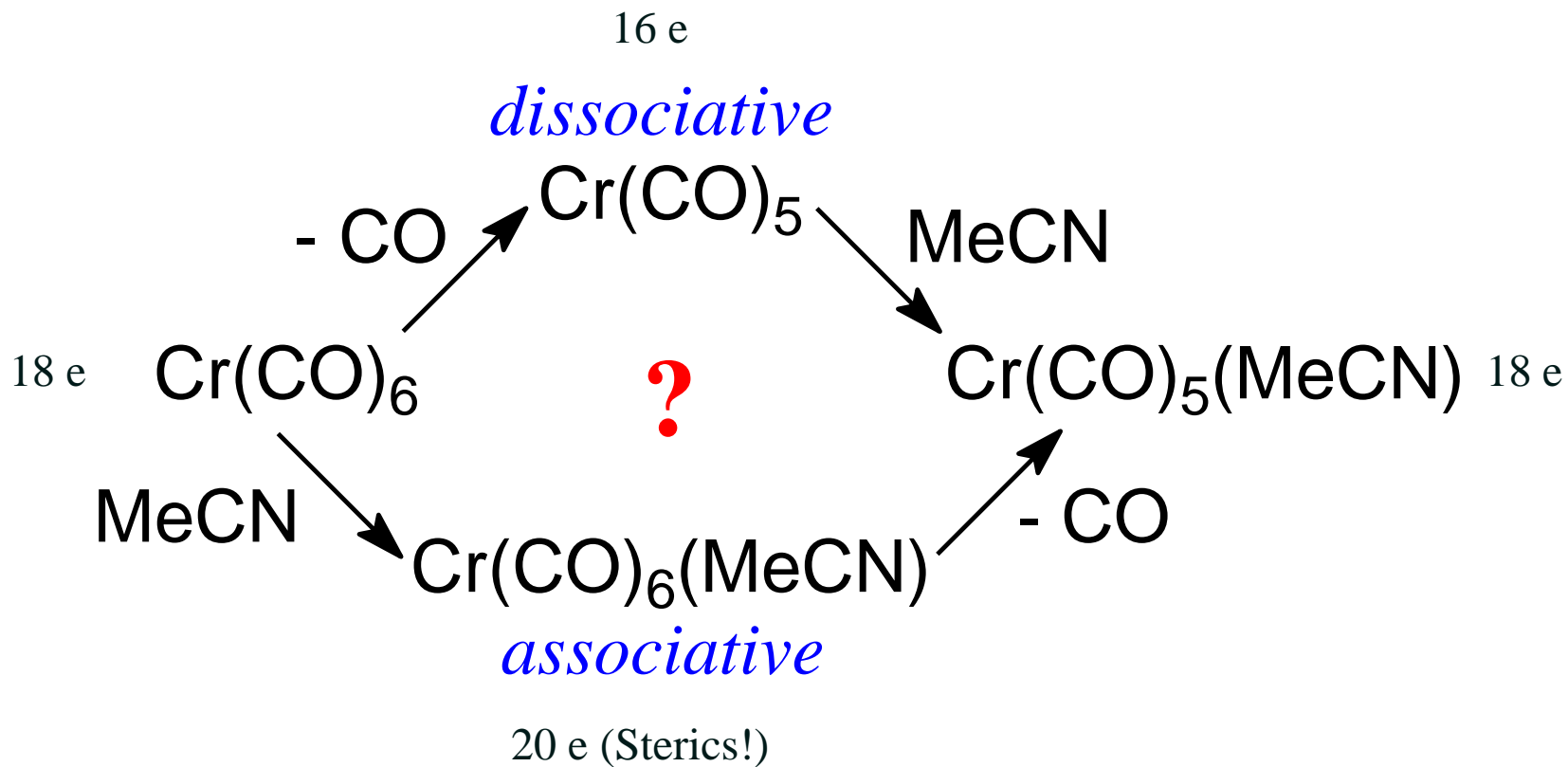
- For early transition metals, 18-*e* is often unattainable for steric reasons - the required number of ligands would not fit
- For later transition metals, 16-*e* is often quite stable (square-planar  $d^8$  complexes)
- Addition of 2 $e^-$  from 5th ligand converts complex to 5 CN 18 $e^-$  , marginally more stable

# Predicting reactivity



Most likely *associative*

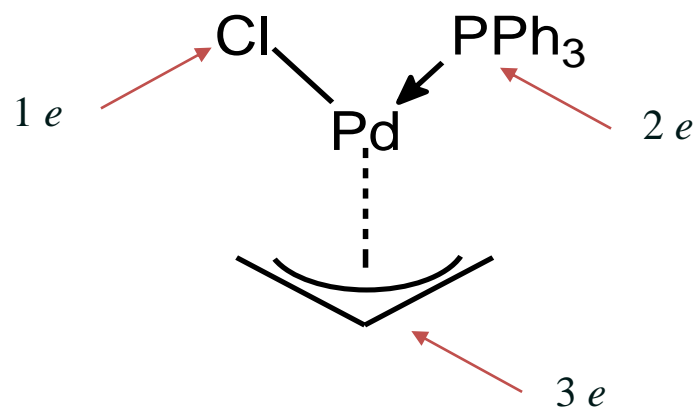
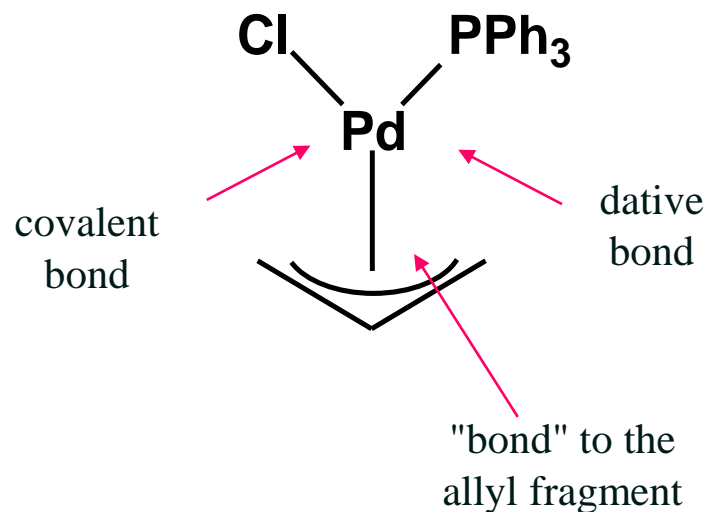
# Predicting reactivity



Most likely *dissociative*

*N.B.* How do you *know* a fragment forms a *covalent* or a *dative* bond?

- Chemists are "sloppy" in writing structures. A "line" can mean a covalent bond, a dative bond, recognise/understand the bonding first
- Use analogies ("PPh<sub>3</sub> is similar to NH<sub>3</sub>").
- Rewrite the structure properly before you start counting.



Pd =	10
Cl <sup>3/4</sup> =	1
P <sup>Ⓡ</sup> =	2
allyl =	3
	+ 3/4 <sup>3/4</sup>
e-count	16

"Covalent" count: (ionic method also useful)

1. Number of valence electrons of central atom.
  - from periodic table
2. Correct for charge, if any
  - but only if the charge belongs to that atom!
3. Count 1 *e* for every *covalent* bond to another atom.
4. Count 2 *e* for every *dative* bond *from* another atom.
  - no electrons for dative bonds *to* another atom!
5. Delocalized carbon fragments: usually 1 *e* per C (hapticity)
6. Three- and four-center bonds need special treatment
7. Add everything

*N.B.* Covalent Model:

$$18 = (\# \text{ metal electrons} + \# \text{ ligand electrons}) - \text{complex charge}$$

The number of metal electrons equals it's row number (*i.e.*, Ti = 4e, Cr = 6 e, Ni = 10 e)

## Hapto (h) Number (hapticity)

For some molecules the molecular formula provides insufficient information with which to classify the metal carbon interactions

The hapto number (h) gives the number of carbon (conjugated) atoms bound to the metal

It normally, but not necessarily, gives the number of electrons contributed by the ligand

We will describe to methods of counting electrons but we will employ only one for the duration of this module



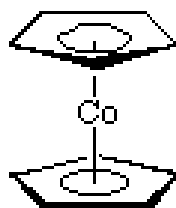
The two methods compared:  
some examples

*N.B.* like oxidation state assignments,  
electron counting is a formalism and does not  
necessarily reflect the distribution of  
electrons in the molecule – useful though

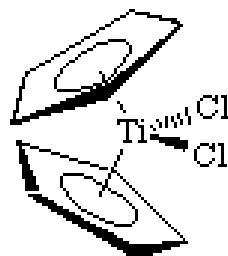
Some ligands donate the same number of  
electrons

Number of *d*-electrons and  
donation of the other ligands  
can differ

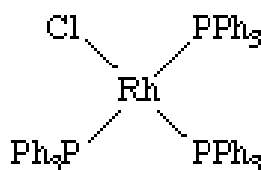
Now we will look at practical  
examples on the black board



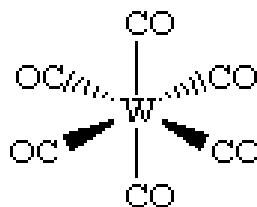
ionic		covalent	
Co <sup>II</sup>	7 e <sup>-</sup>	Co	9 e <sup>-</sup>
2 Cp <sup>-</sup>	12 e <sup>-</sup>	2 Cp <sup>•</sup>	10 e <sup>-</sup>
<b>Total</b>	19 e <sup>-</sup>	<b>Total</b>	19 e <sup>-</sup>



Ti <sup>IV</sup>	0 e <sup>-</sup>	Ti	4 e <sup>-</sup>
2 Cl <sup>-</sup>	4 e <sup>-</sup>	2 Cl <sup>•</sup>	2 e <sup>-</sup>
2 Cp <sup>-</sup>	12 e <sup>-</sup>	2 Cp <sup>•</sup>	10 e <sup>-</sup>
<b>Total</b>	16 e <sup>-</sup>	<b>Total</b>	16 e <sup>-</sup>



Rh <sup>I</sup>	8 e <sup>-</sup>	Rh	9 e <sup>-</sup>
Cl <sup>-</sup>	2 e <sup>-</sup>	Cl <sup>•</sup>	1 e <sup>-</sup>
3 PPh <sub>3</sub>	6 e <sup>-</sup>	3 PPh <sub>3</sub>	6 e <sup>-</sup>
<b>Total</b>	16 e <sup>-</sup>	<b>Total</b>	16 e <sup>-</sup>



W <sup>0</sup>	6 e <sup>-</sup>	W	6 e <sup>-</sup>
6 CO	12 e <sup>-</sup>	6 CO	12 e <sup>-</sup>
<b>Total</b>	18 e <sup>-</sup>	<b>Total</b>	18 e <sup>-</sup>

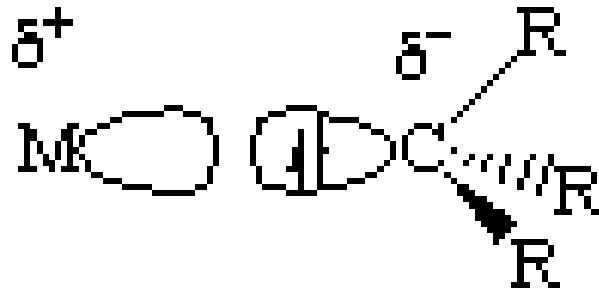
Alkyl ligands:

Transition metal alkyl complexes important for catalysts *e.g.* olefin polymerization and hydroformylation thermodynamic

Problem is their weak kinetic stability

(Thermally fine: M-C bond dissociation energies are typically 40-60 kcal/mol with 20-70 kcal/mol)

Simple alkyls are sigma donors, that can be considered to donate one or two electrons to the metal center depending on which electron counting formalism you use



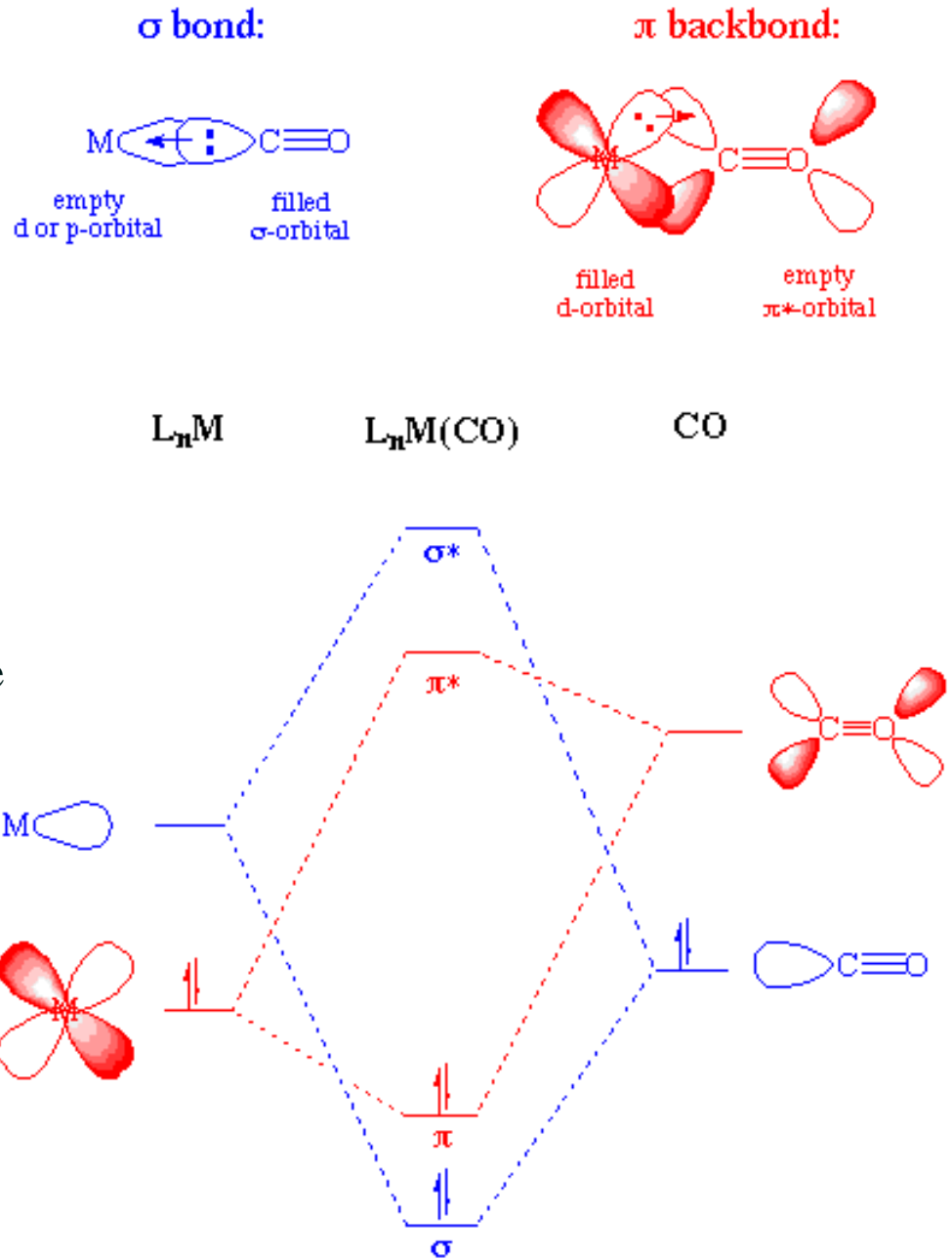
# Carbonyl Complexes

## Bonding of CO

Electron donation of the lone pair on carbon s This electron donation makes the metal more electron rich - compensate for this increased electron density, a filled metal *d*-orbital may interact with the empty *p*\* orbital on the carbonyl ligand

*p*-backbonding or *p*-backdonation or synergistic bonding

Similar for alkenes, acetylenes, phosphines, and dihydrogen.



## Main characterization methods:

- X-ray diffraction  $\text{P}$  (static) structure  $\text{P}$  bonding
- NMR  $\text{P}$  structure en dynamic behaviour
- EA  $\text{P}$  assessment of purity
- (calculations)

## Useful on occasion:

- IR
- MS
- EPR

## Not used much:

- GC
- LC

THANK YOU!!!