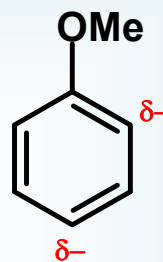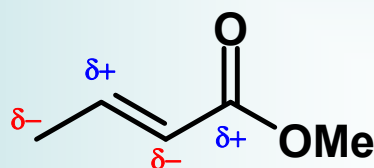# Organometallics in Organic Synthesis

1. So who cares (i.e., why?)

-Pattern of reactivity of organic compounds is imposed on
   molecule by existing functional groups

- By default, this limits what you can do with the compound

- Coordination of a metal fragment can change this completely

i.e., can render – an electrophilic species nucleophilic

- a nucleophilic species electrophilic

- can make a normally unstable molecule stable

- can make a stable molecule reactive

- can make impossible reactions possible

# The (Very) Basics of Organometallics

-The 18 Electron Rule

Most (middle) transition metal complexes prefer having

18 valence electrons (2s + 6p + 10d)

For transition metal complexes in the 0 oxidation state

4e	5e	6e	7e	8e	9e	10e
Ti	V	Cr	Mn	Fe	Co	Ni
Zr	Nb	Mo	Rc	Ru	Rh	Pd
Hf	Ta	W	Re	Os	Ir	Pt

-The 18 e rule is followed most closely in complexes of middle

transition metals (Cr to Co)

-As for early transition metal complexes, it's usually too difficult

to get enough ligands around the metal to get it to 18 e (i.e., Ti)

(16 e)   (Cp_2TiCl_2)
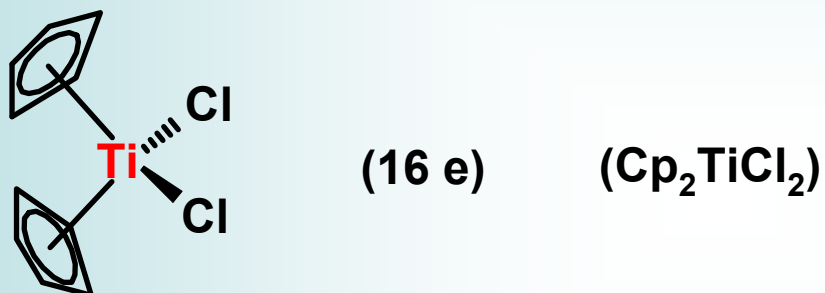
- As for late transition metal complexes (Ni, Pd, Pt), particularly

the square planar $M^{II}L_4$ complexes

- tend to be very stable as 16 e$^-$ complexes

- energy gap to 9th orbital is quite big; molecule is
quite willing <u>not</u> to fill that orbital

3

To count to 18 (or 16), need e⁻'s from ligands
   - I'll adopt a 'radical approach' – not only valid one

A) Inorganic Ligands

1e⁻   -X   -H   -R

2e⁻ $R_3P:$ $(RO)_3P:$ $R-C \equiv N:$ $R-N \equiv C:$

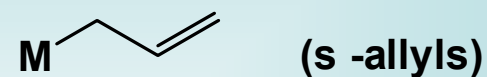 $R_3N:$ $R_2S:$ $R_2O:$

3e⁻   NO (usually)   nitrosyl complexes

4

Organic Ligands - Part 1
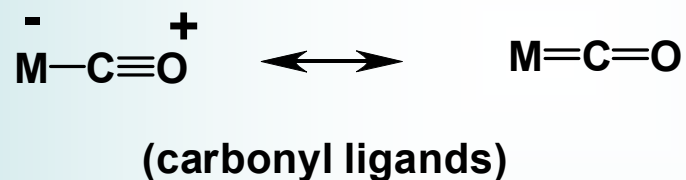
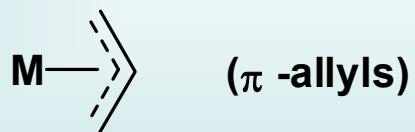η^1 (1 e⁻)   -R (alkyls)   -Ph (aryls)   M⌒⌒ (s -allyls)

η^2 (2 e-)   M⎯‖ (alkenes)   M⎯‖ (alkynes)

η^1 (2e⁻)   M⁻—C≡O⁺ ⟷ M=C=O   M=C(R)(R)

(carbonyl ligands)   (carbenes, alkylidenes)

η^3 (3e⁻)   M⎯⟩ (π -allyls)

η^1 (3e⁻)   M≡C—R   (carbynes)

5
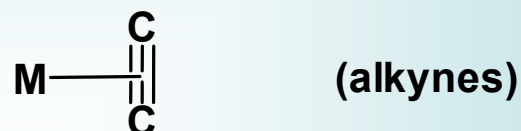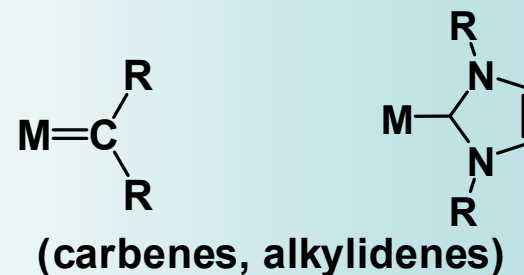
Organic Ligands, Cont'd.

η^4 (4e$^-$)
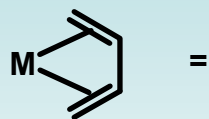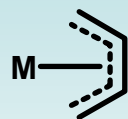
 = (dienes)

(trimethylenemethanes)
(TMM)

η^5 (5e$^-$)
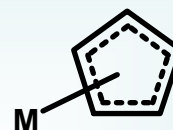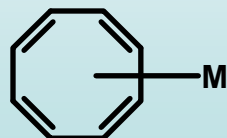
(dienyls)

(cyclopentadienyls)

η^6 (6e$^-$)

(arenes, trienes)

η^7 (7e$^-$)

(trienyls)

η^8 (8e$^-$)
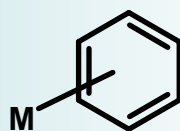
(cyclotetraenes) - rarely, usually η^4

So.....

The number of electrons on the free metal
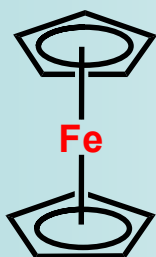
+ sum of the h number of the hydrocarbon ligands   + sum of the electrons donated by other ligands

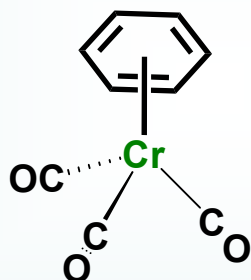**+ any negative charge on the complex   - positive charge on the complex**
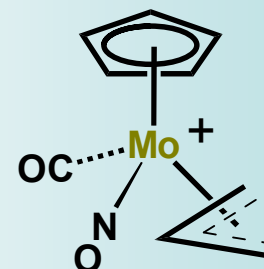
Should = 18 normally

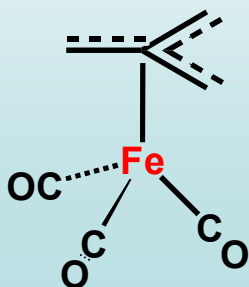**Many exceptions with early or late transition metals ; works best with middle transition metals**
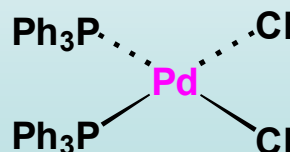
8 (Fe) + (2x5) = 18e⁻

6 (Cr) + 6 (Ph) + (3x2) = 18 e⁻

6 (Mo) + 5 (Cp) + 2 + 3 +3 -1 = 18 e⁻

8 + 4 (TMM) + (3x2) = 18 e⁻

10 (Pd) + (2x2) + (2x1) = 16 e⁻

Bonding of Hydrocarbon Ligands

- In its simplist form, bonding of the π- system to a transition metal fragment is based on the

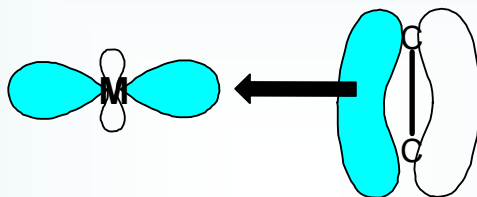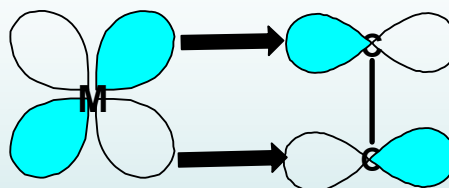## *Dewar-Chatt-Duncanson Model*

Consider

C
M———||
C
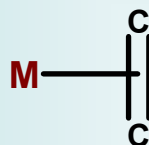
- There are two contributions to bonding

1) Ligand to Metal Donation

Note: this is <u>not</u> a π- bond, but rather a σ- bond

2) Metal to Ligand Back Donation

Note: this <u>is</u> a π- bond

Dewar, M. J. S. *Bull. Chim. Soc. Fr.* **1951**, C71.

Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

For higher level descriptions:

8

η^3, η^4, η^5 - see Yamamoto, A., p. 58-72
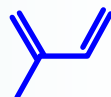
η^6 - see Collman, Hegedus, Norton, Finke p. 43-47

Consequences of Bonding of Hydrocarbon Ligands

1) - In the alkene, the C=C bond is made <u>weaker</u> by complexation

2) - The ligand may be made more *or* less electron rich by complexation
-depends on case

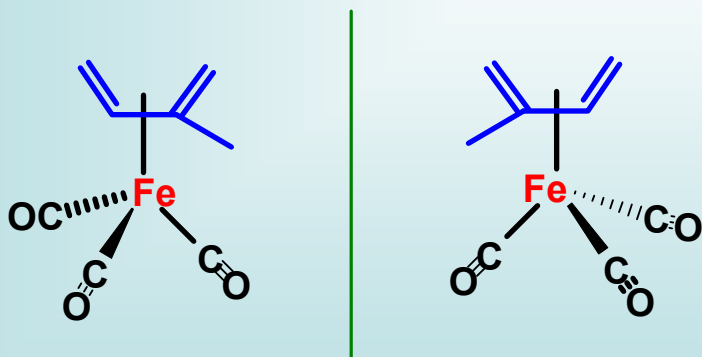**3) - The organic fragment often loses its only plane of symmetry**
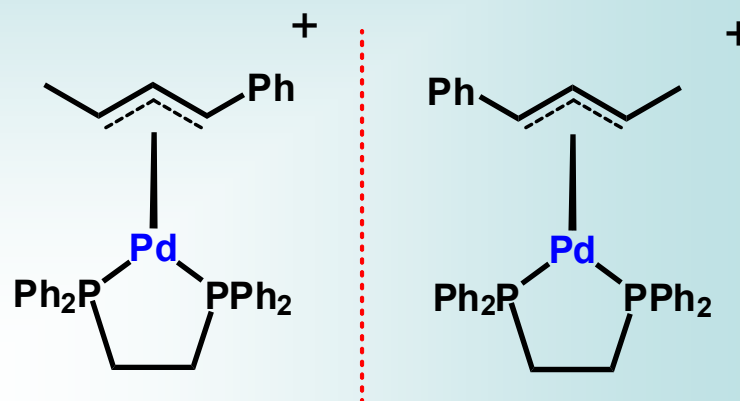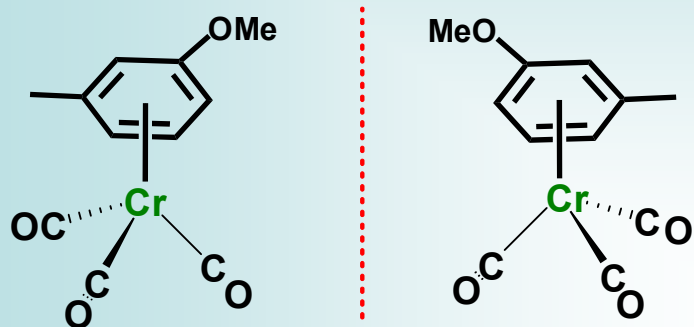**-for example**
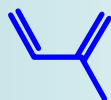
and **are the same compound**

But.......

These are not the same compound
- the plane of symmetry is destroyed

No non-superimposable mirror images
<u>Enantiomers</u>

mirror image

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Other examples

Same situation: Each pair is enantiomeric