Key types of ligand in organometallic complexes

- σ-donor ligands:

(i) neutral: CO (carbonyl), PR_3 (phosphine), C(R)OR (Fischer carbene).

(ii) charged: CH_3^- (alkyl), H^- (hydride), Cl^- (halide), R_2C^{2-} (Alkylidene), RC^{3-} (Alkylidyne).

- π-donor ligands:

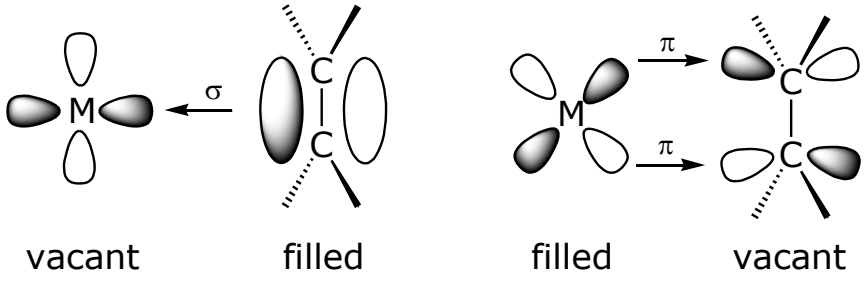
(i) alkene, alkyne, allyl, diene.

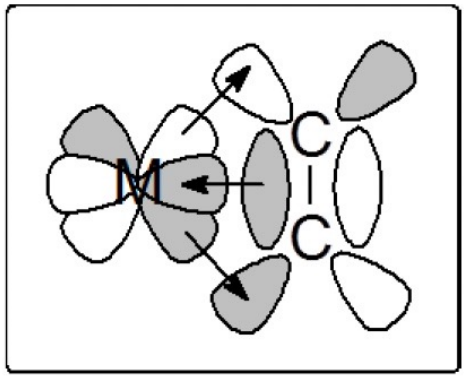
(ii)delocalised hydrocarbon rings:

cyclopentadienyl ($C_5H_5^-$), arene (C_6R_6), cycloheptatrienyl ($C_7H_7^+$ or $C_7H_7^{3-}$), cyclo-octatetraenyl ($C_8H_8^{2-}$).

- Most ligands also act as π-acceptors -synergic bonding.

Metal-Alkene Complexes:





. synergic

Bonding:

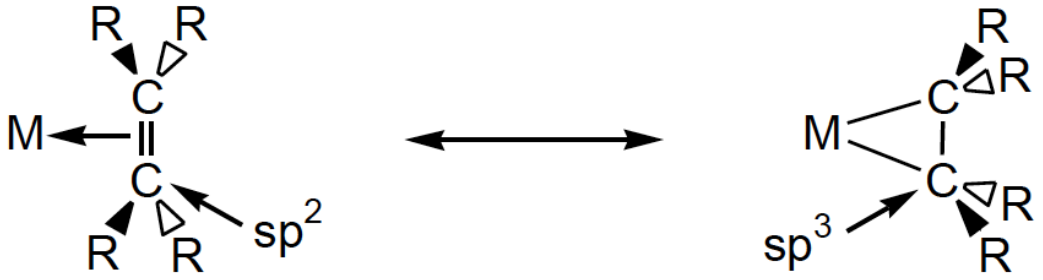
- The bonding is again the Dewar-Chatt-Duncanson model, i.e. *synergic.*

Two components:

- Donor – alkene HOMO π-bonding orbital.
- Acceptor – alkene LUMO π* antibonding orbital.

The two components of the bonding are better balanced than in metal carbonyl complexes.

Two extreme representations of the metal-alkene bond:



σ-donation from alkene to metal dominates
– little back donation
– slight lengthening of C=C bond
– any orientation of the alkene relative to the metal is allowed

π-donation from metal to alkene dominates
– considerable lengthening of C=C bond
– substituent bend away from metal as back bonding increases
– metallocyclopropane

Alkenes

Alkenes are typically relatively weakly coordinating ligands.

They are also extremely important substrates for catalytic reactions.

The strongest alkene-metal bonds occur with third row metals (as with almost all ligands) and when one can get more π-backbonding to occur.

The amount of π-backbonding depends strongly on:

-how electron-rich the metal center is

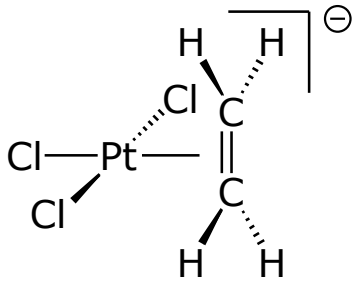
- whether or not there are electron-withdrawing groups on the alkene to make it a better acceptor ligand

-steric effects.

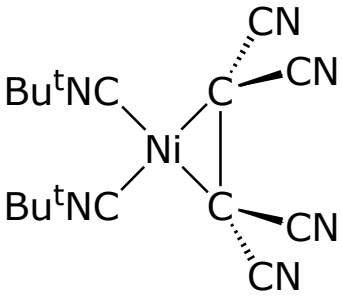
Consequences of backbonding:

- Lengthening of the C=C bond.
- Reduction of angles at C from ~120° (sp^2) to ~109° (sp^3).

C=C = 1.337(2) Å



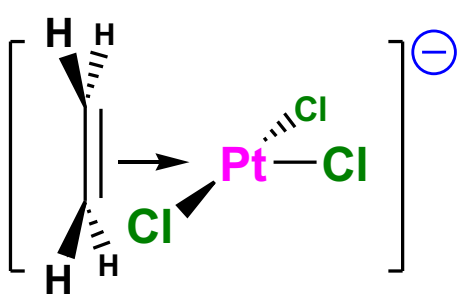
C=C = 1.354(2) Å



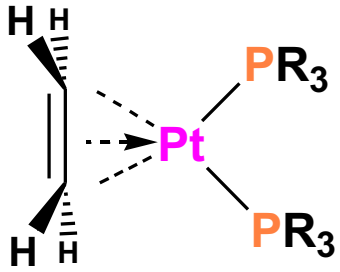
C=C = 1.480(2) Å

Electron withdrawing groups increase π-backdonation and decrease the σ-donation.

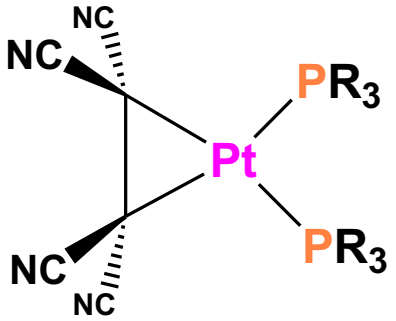
Note the olefin binds perpendicular to the $PtCl_3$ plane to overlap with the d_{yz} and avoid steric replusion with chlorides (Zeise's salt).



Pt(2+)
C=C = 1.37Å
Zeiss's Salt

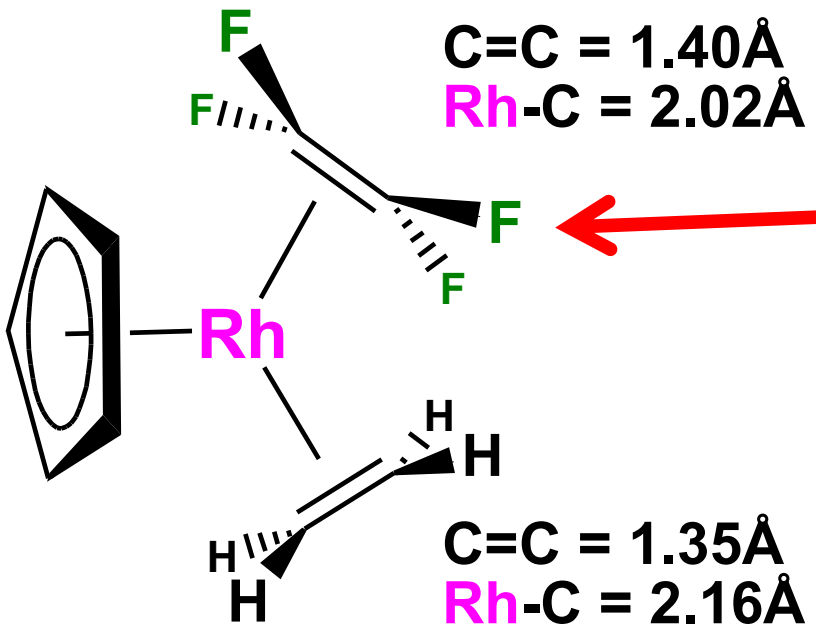


Pt(0)
C=C = 1.43Å



Pt(+2)
C--C = 1.49Å
metallocyclopropane

If the metal is electron-rich enough and/or if there are electron-withdrawing groups on the alkene, one can actually get a formal oxidation of the metal via the transfer of 2e- to the alkene to form a dianionic metallocyclopropane ligand that is now coordinated via two anionic alkyl s-bonds (thus the assignment of Pt(+2)).

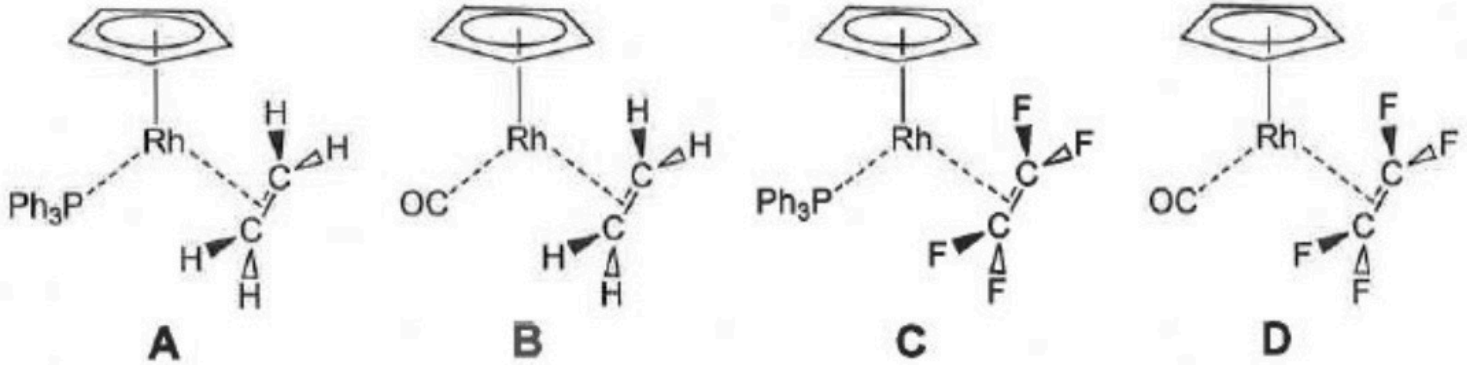


The electron-withdrawing fluorine groups on the $F_2C=CF_2$ alkene makes it a better π-acceptor ligand. This *weakens* the C=C bond, but ***strengthens*** the alkene-metal bond.

Electronic Effects

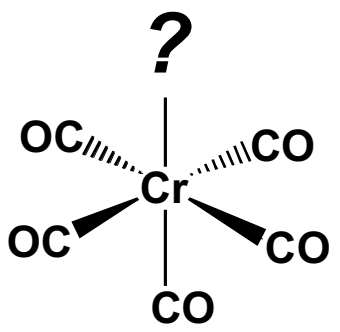
Ethylene Complex	$\nu C{=}C$ (cm^{-1})
Free Ethylene	1623
$[Ag(H_2C{=}CH_2)_2]^+$	1584
$Fe(CO)_4(H_2C{=}CH_2)$	1551
$[Re(CO)_4(H_2C{=}CH_2)_2]^+$	1539
$[CpFe(CO)_2(H_2C{=}CH_2)]^+$	1527
$Pd_2Cl_4(H_2C{=}CH_2)_2$	1525
$[PtCl_3(H_2C{=}CH_2)]^-$	1516
$CpMn(CO)_2(H_2C{=}CH_2)$	1508
$Pt_2Cl_4(H_2C{=}CH_2)_2$	1506
$CpRh(H_2C{=}CH_2)_2$	1493

In the following molecules, which alkene ligand will rotate most rapidly? Why?

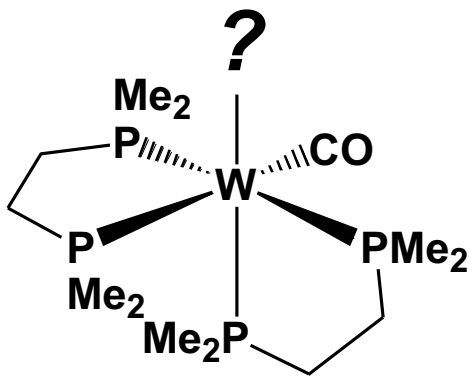


Problem: To which of the following (each with a single open coordination site) will **trifluoroethylene** bind to the most strongly? Why?

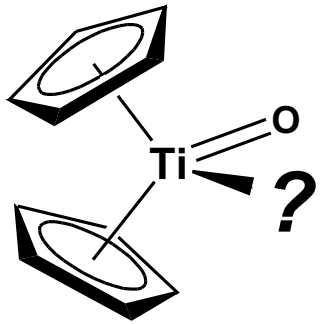
a)

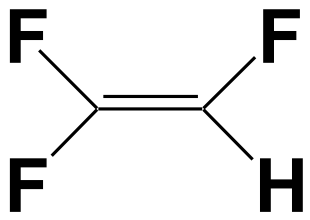


b)



c)

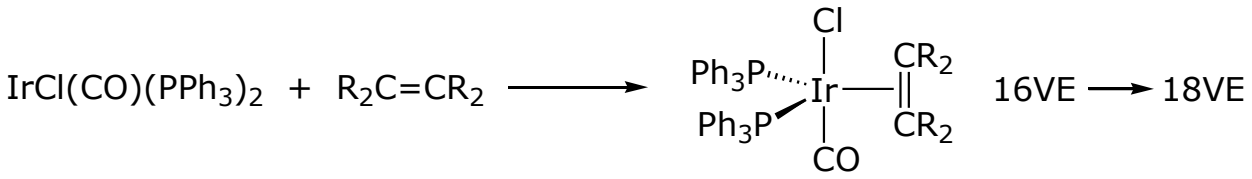




Synthesis:

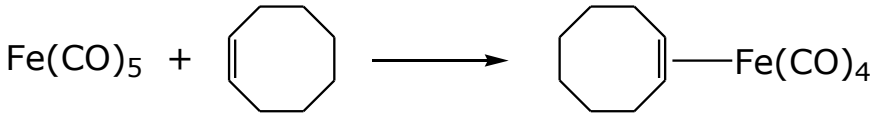
Addition:

e.g.

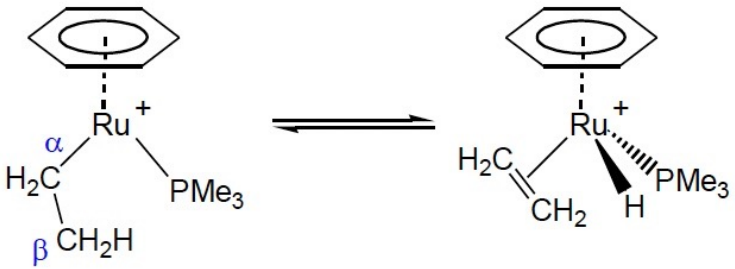


Substitution:

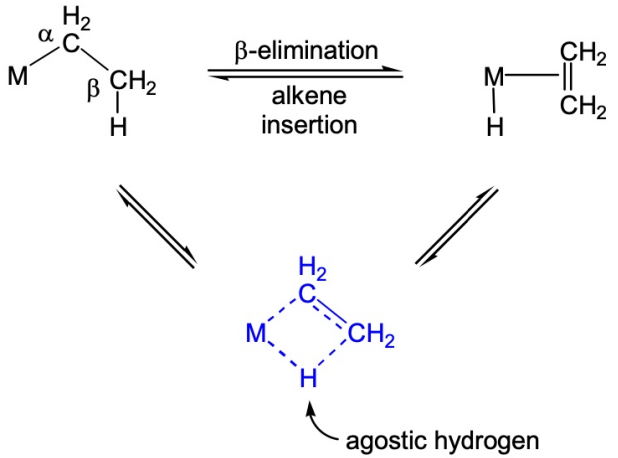
e.g.



β–Elimination

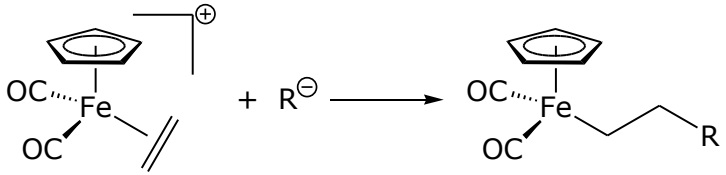


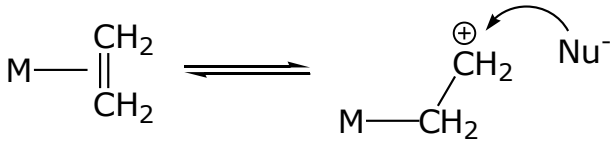
Ru(II), 16 VE Ru(II), 18 VE



Reactivity:

Reactivity with nucleophiles:
e.g.





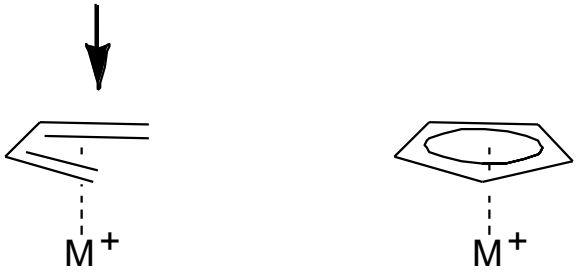
This can be intramolecular (via metal) or intermolecular (external attack).

- ***Nucleophilic attack***
- **Favored when the metal fragment L_nM is a poor π base but a good π acid.**
- e.g. if L_nM bears a net positive charge or has electron-withdrawing ligands, one of the ligands L may be depleted of electron density to such an extent that a nucleophile, Nu^- (e.g., LiMe, OH^-, etc.), can attack L.

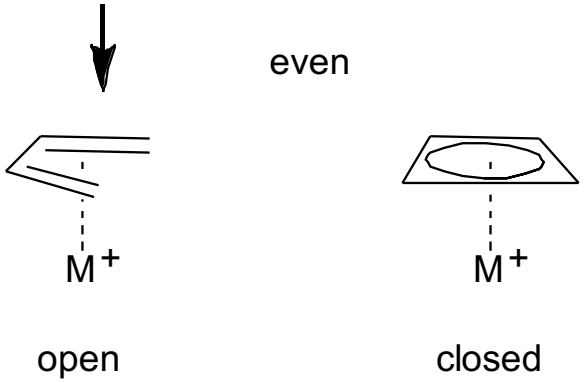
The Davies-Green-Mingos Rules: allow predictions of the direction of nucleophilic attack at 18-electron cationic metal complexes.

Rule 1. Nucleophilic attack occurs preferentially at EVEN coordinated polyenes (polyenes before polyenyls)

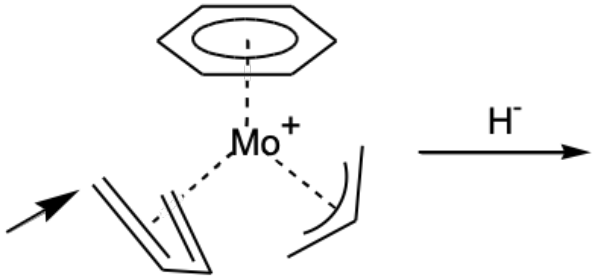
Apply rule 1 before rule 2



Rule 2. Nucleophilic attack occurs preferentially at OPEN coordinated polyenes before closed.

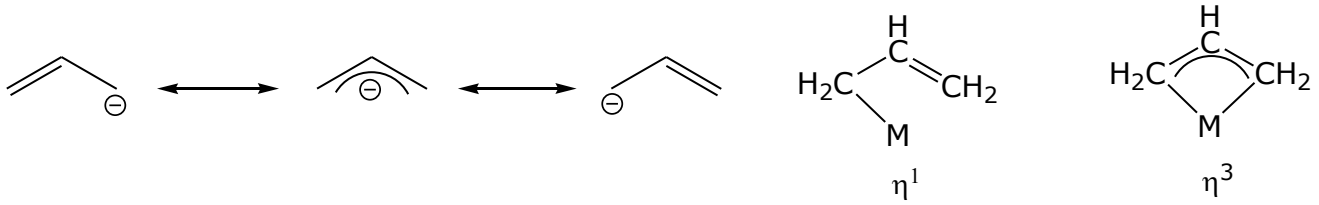


Rule 3. For EVEN OPEN polyenes, nucleophilic attack always occurs at the terminal carbon atom, For ODD OPEN polyenyls, attack at the terminal carbon occurs only if L_nM^+ is strongly electron withdrawing.



Metal-Allyl Complexes

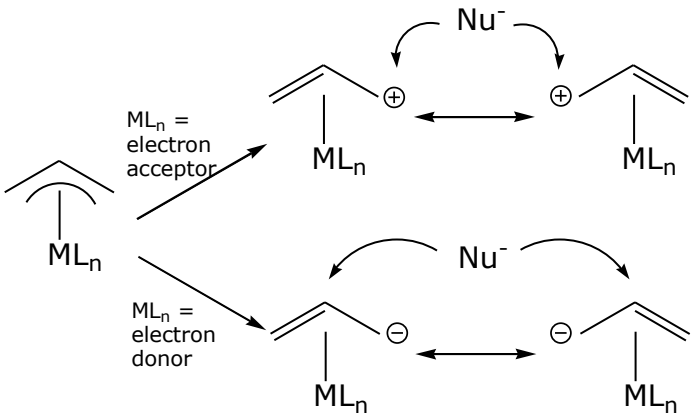
Bonding modes:



Nucleophilic attack:

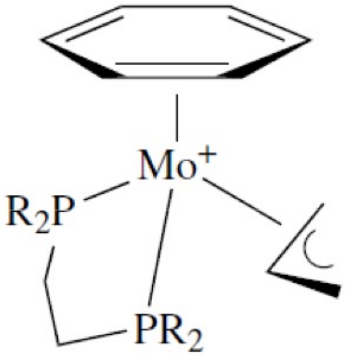
e.g.

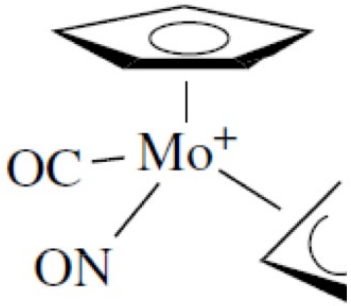
Rule 3. For EVEN OPEN polyenes, nucleophilic attack always occurs at the terminal carbon atom, For ODD OPEN polyenyls, attack at the terminal carbon occurs only if L_nM^+ is strongly electron withdrawing.

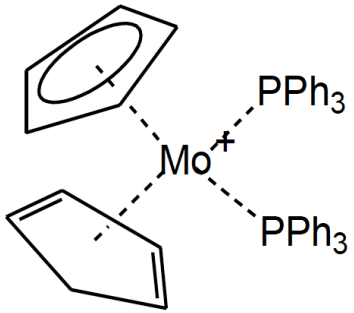


- 1,3-attack with cationic allyls (late metals)
- 2-attack for anionic allyls (early metals).

Problem: Predict nuclephilic attack using The Davies-Green-Mingos Rules

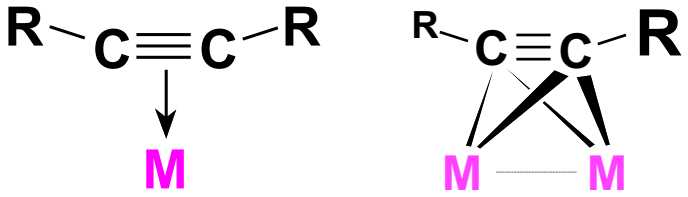






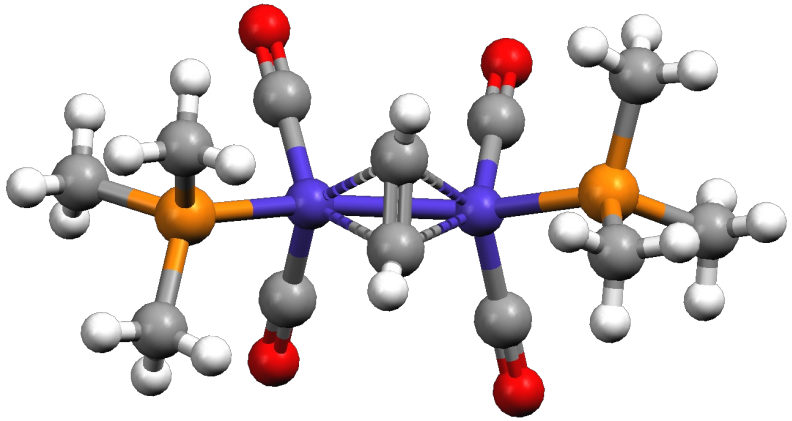
Alkynes

Alkynes are stronger donor than alkenes, with two orthogonal π-bonds. Thus they can act as neutral 2 or 4 e- donors, depending on the needs of the metal center. They are also much better bridging ligands because of this second set of π-electrons.

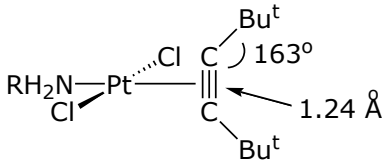


Note how the bridging alkyne is drawn. This indicates a perpendicular bridging mode and that both carbons are interacting equally with both metals (the alkyne is donating 2e- to each metal). It dos NOT indicate that each carbon has 6 bonds to it !!

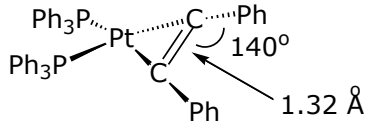
When alkynes bridge, they almost always do so perpendicular to the M-M axis, the parallel bridging mode is known, but is quite rare:



The extent of backbonding is heavily dependent on how electron rich the metal is.

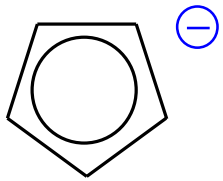


Pt(II), d^8, weak backbonding

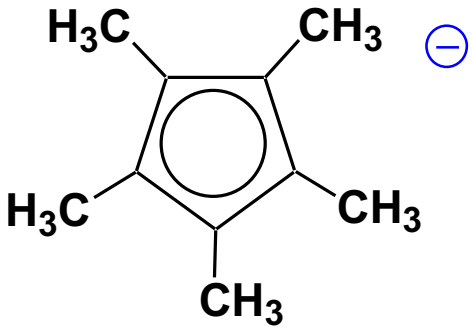


Pt(0), d^{10}, strong backbonding

Cyclopentadienyl ligands – Cp's

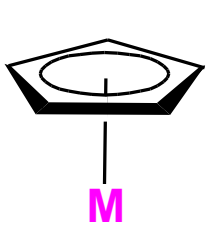


6e- strong donor

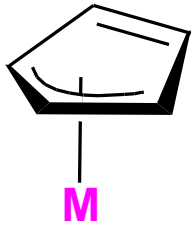


6e- stronger donor bulky ligand

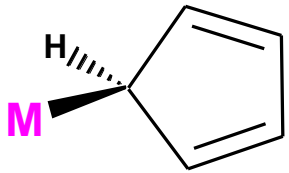
Cp **Cp***



η^5



η^3

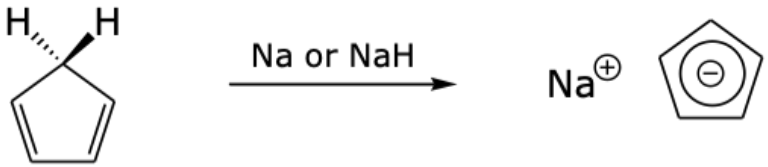


η^1

Metallocenes do not rigorously obey the 18 electron rule.

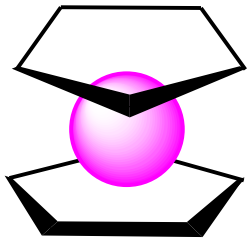
- Very stable and versatile, easy to derivatise.

EPFL **Synthesis :**

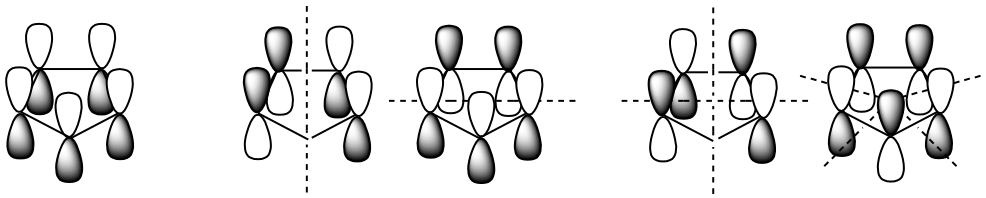


cyclopentadiene cyclopentadienyl anion

$$FeCl_2 + 2\ NaCp \longrightarrow FeCp_2 + 2\ NaCl$$



- MCp_2 complexes are referred to as metallocenes.
- Cp* is a much stronger electron donor than Cp (and a poorer electron acceptor) so complexes with this ligand have their redox potential shifted
- to more negative values (i.e. easier to oxidise, more reducing).
- 5 p-orbitals combine to give 5 molecular orbitals
- Cp is a good σ- and π-donor .
- Cp is a weak δ-acceptor better π-acceptor.

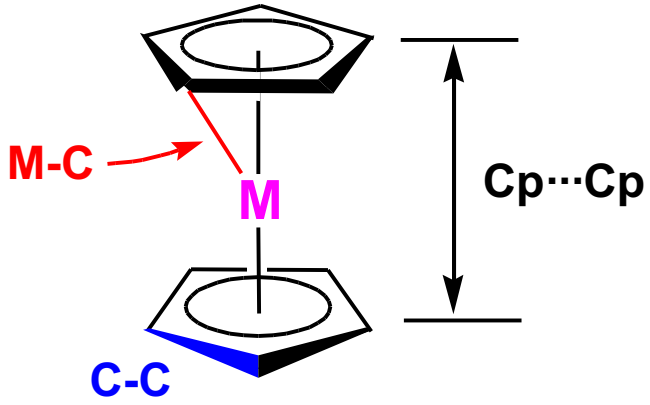


•the 18 electron rule is not obeyed for parallel metallocenes and most *bis*-Cp 3d-metal complexes exist, including nickelocene, which is a paramagnetic 20 VE complex!

Compound	Colour	m.p. (° C)	# of electrons (unpaired)	μ_{eff} (spin only, B.M.)	μ_{eff} found, B.M.
VCp_2	purple	167	15 (3)	3.87	3.84
$CrCp_2$	red	173	16 (2)	2.83	3.20
$MnCp_2$	amber/pink	173	17 (5)	5.92	5.81
$FeCp_2$	orange	173	18 (0)	0	0
$CoCp_2$	black-purple	174	19 (1)	1.73	1.76
$NiCp_2$	Green	173	20 (2)	2.83	2.86

Key rule: metallocenes do not rigorously obey the 18 electron rule.

Structural Features



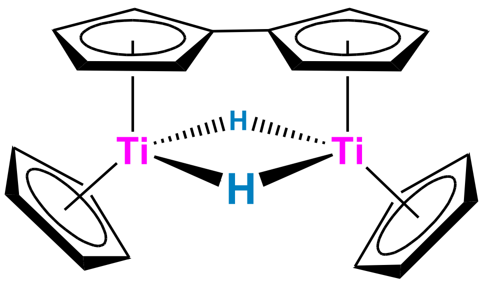
M	M-C	Cp…Cp	C-C
Fe	2.04	3.29	1.42
$[Fe]^+$	2.07	3.40	1.40
Ru	2.19	3.64	1.43
Os	2.19	3.61	1.45
Co	2.10	3.44	1.41
$[Co]^+$	2.03	3.24	1.42
Ni	2.18	3.63	1.41

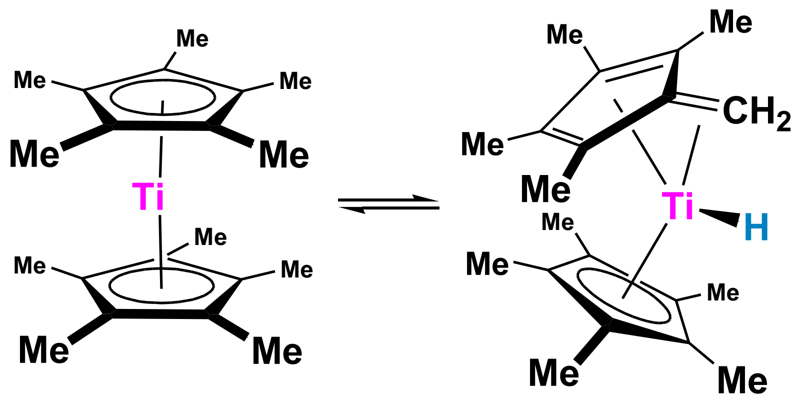
The changes in the neutral Fe, Co, Ni metallocenes are a direct result of going from 18e- (Fe) to 19e- (Co) to 20e- (Ni) counts. The extra electrons for the Co and Ni complexes are going into M-Cp antibonding orbitals, which are delocalized and progressively weaken the M-Cp bonding, leading to the increase in bond distances. This even though the metal's covalent radius is *decreasing* as going from Fe to Ni.

Problem: Explain why the Fe-C distance *lengthens* for $[Cp_2Fe]^+$, while the Co-C distance *shortens* for $[Cp_2Co]^+$.

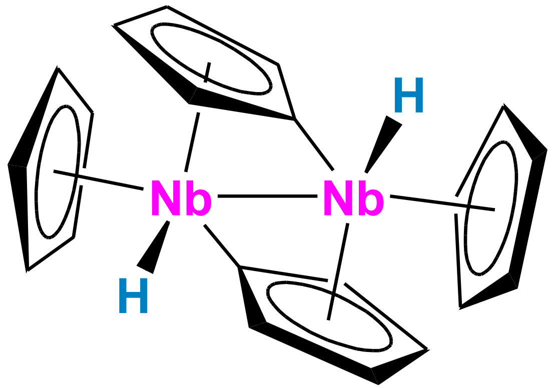
Bis-Cp Early TM Complexes

The simple neutral bis-Cp complexes of the early transition metals are quite different because they are in very low **+2** oxidation states (very electron-rich) and quite unsaturated. Thus, they are very reactive towards C-H oxidative additions and other reactions.





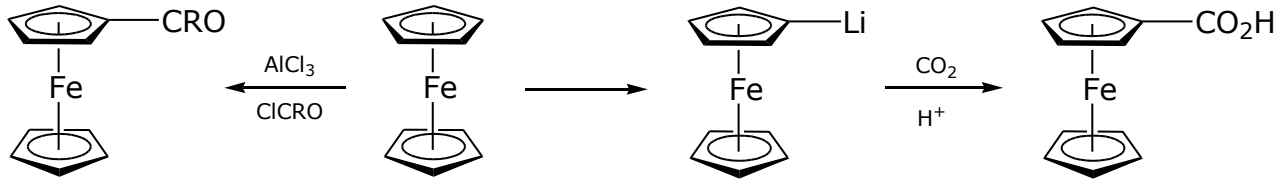
Problem: Electron-count this Ti_2 complex. Why is diamagnetic?



Reactivity:

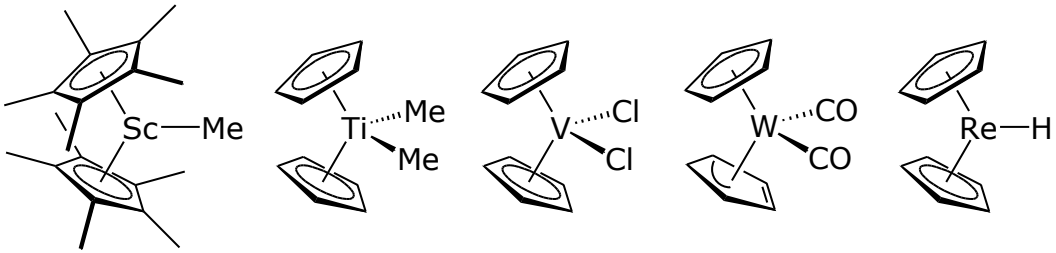
• **For parallel metallocenes, the reactivity occurs at the RING.**

The number of ferrocene derivatives is vast due to its highly stable nature and air- and moisture-stability. Ferrocene may be regarded as an electron rich arene;



Bent Metallocenes:

• Bending a metallocene raises its energy, but this is offset by the energetic stabilisation gained from forming additional M–L bonds.



d^0, 14VE d^0, 16VE d^1, 17VE d^4, 18VE d^4, 18VE

Reactivity:

• **For bent metallocenes, the reactivity occurs at the METAL.**

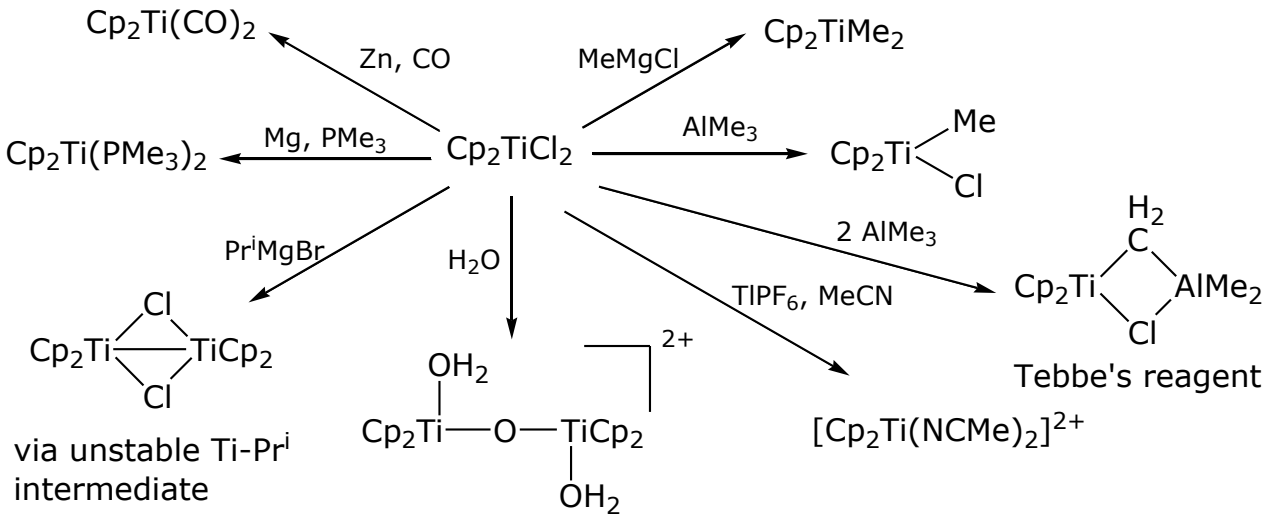
Metallocene dihalides:

These are an important class of compound, synthetically and for their *in vitro* activity against cancer cells and use in homogeneous catalysis.

$MCl_4 + 2\ NaCp \rightarrow Cp_2MCl_2 + 2\ NaCl$ (M = Ti, Zr, Hf)

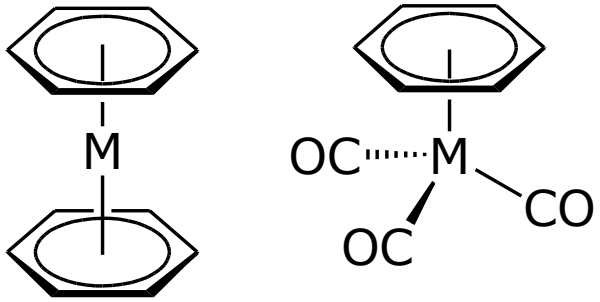
Reactions include:

- alkylations
- reductions
- exchange reactions with donor ligands



Metal-Arene Complexes:

Structures:



typically coordinate in an $\eta 6$ fashion and as such are **neutral 6 e- donors**, although they can adopt lower coordination modes (η^4 and η^2).

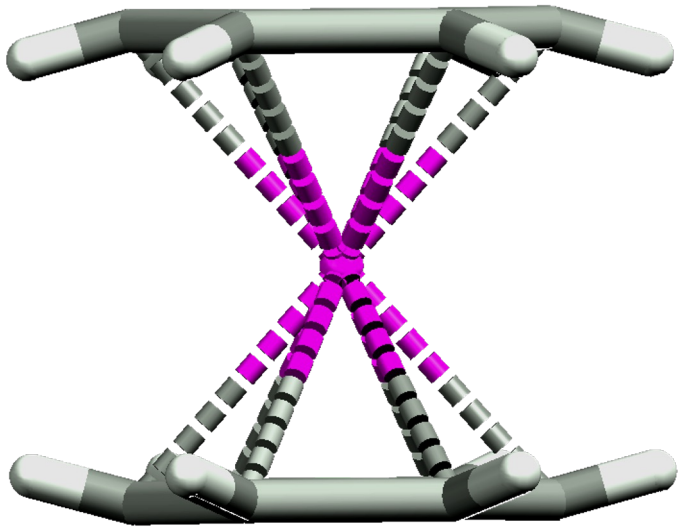
- The bonding in arene-metal complexes is qualitatively very similar to metallocenes, but since the arene is NEUTRAL all the bonding electrons come from the arene. Complexes with 16-21VE are known.
- Because there is no charge, and therefore less electrostatic contribution to the bonding, metal-arene complexes are LESS stable than metallocenes.
- Thus, the first example was *bis*-(benzene)chromium (not iron), which is isoelectronic to ferrocene and obeys the 18-electron rule.

π-Backbonding

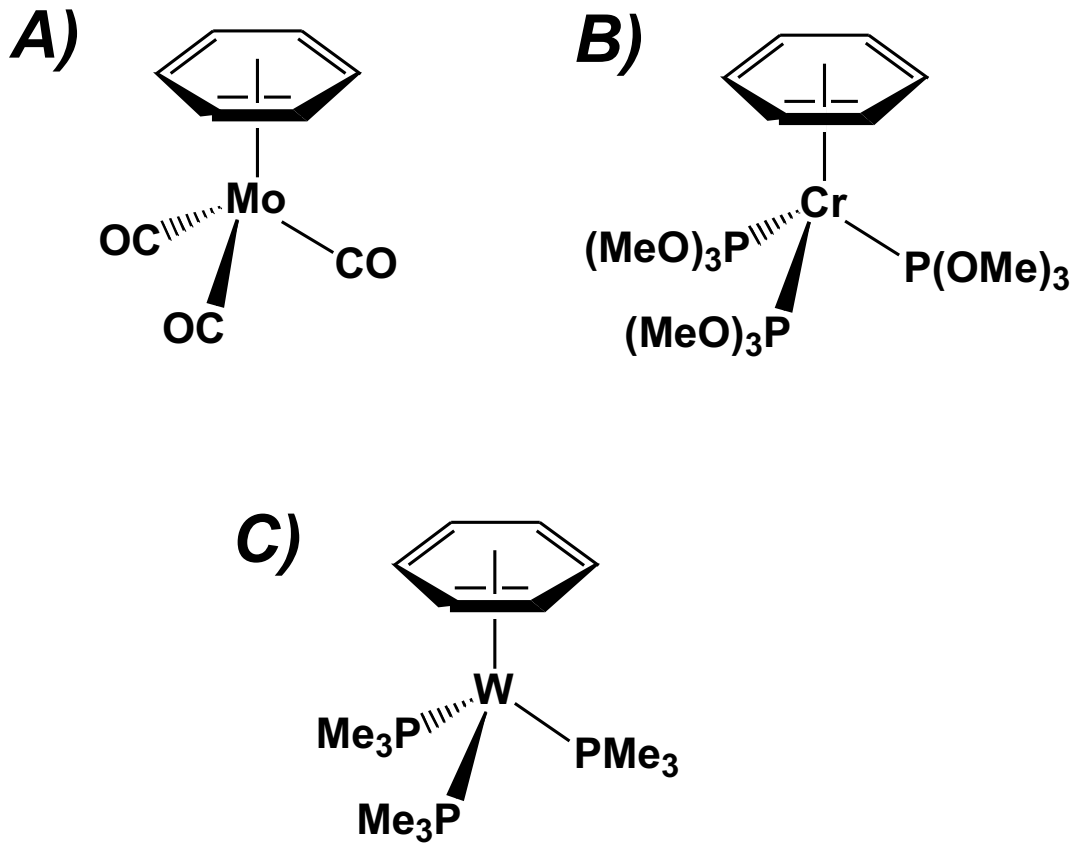
π-backdonation plays a relatively important role in arene bonding and chemistry. Arenes tend to favor metals in low oxidation states and often generate surprisingly stable complexes. $Cr(C_6H_6)_2$, for example, is kinetically inert to most substitution reactions, no doubt due to its 18 e- configuration, but also due to the mix of π-bonding and backbonding.

Remember that CO is far, far stronger π-backbonding ligand.

Problem: The crystal structure of $[Cr(C_6H_6)_2]^+$ clearly shows that the hydrogen atoms on the benzene distinctly lean in towards the metal center. Explain why.

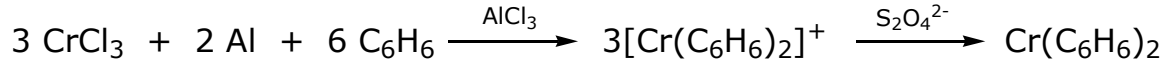


Problem: In which of the following complexes should the η^6-benzene ligand coordinate the strongest? Why??



Synthesis of bis-(arene)complexes:

Fischer-Hafner method:



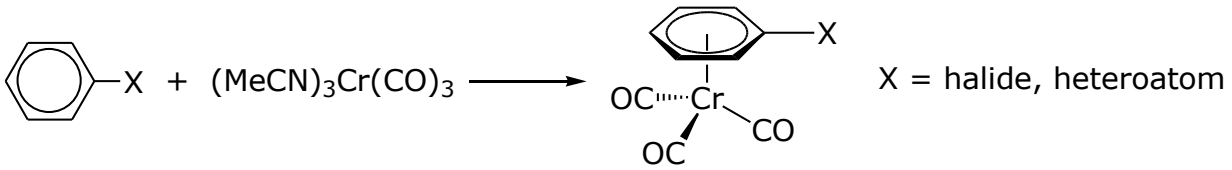
Works for: V, Cr, Mo, W, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni
But: the arene must be inert to $AlCl_3$

Metal vapour synthesis:

Co-condensation of metal and ligand vapours allows access to bis-(arene)metal complexes inaccessible by other means. Metals include: Ti, Zr, Hf, Nb, Mo, Sc, Y, Gd, Dy.

Synthesis of arene half-sandwich complexes:

By ligand displacement:



X = halide, heteroatom