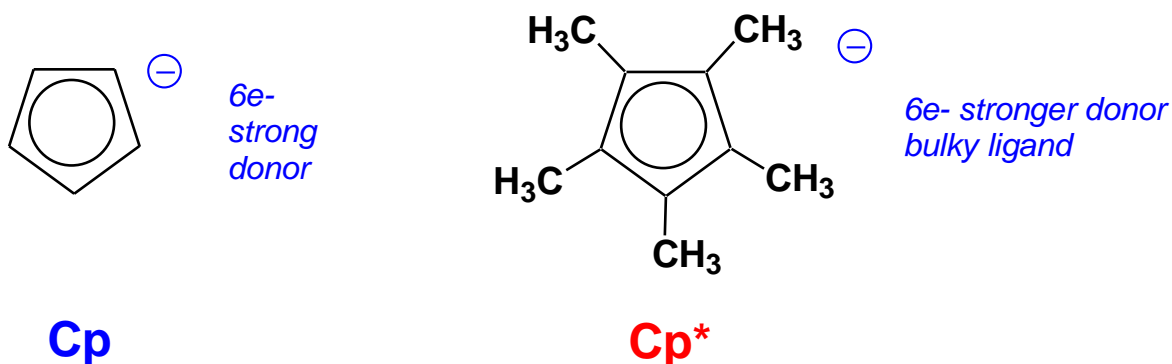
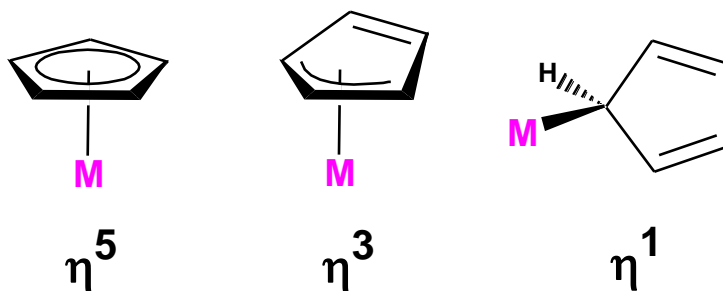


# Cyclopentadienyl - Cp

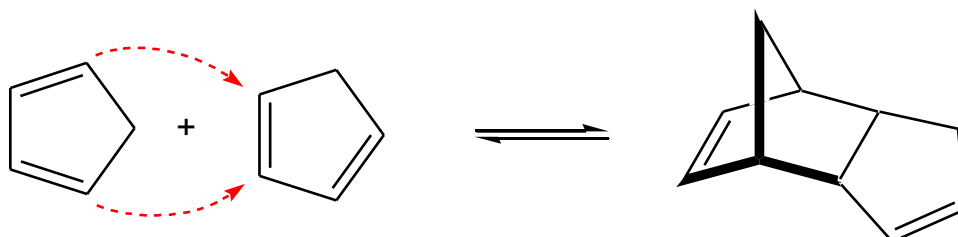
The cyclopentadienyl ligand is one of the most common and popular ligands in organometallic chemistry.



It is an anionic ligand that normally coordinates in an  $\eta^5$  mode as a 6e<sup>-</sup> donor, but it can adopt  $\eta^3$ - and  $\eta^1$ -coordination modes.



Free neutral cyclopentadiene, which is deprotonated with a strong base to generate the  $\text{Cp}^-$ , is unstable and reacts with itself via a **Diels-Alder** reaction to make the dicyclopentadiene. One typically regenerates cyclopentadiene by distilling (“cracking”) it from the high boiling dimer solution and storing it in a refrigerator, but it slowly re-dimerizes to make dicyclopentadiene.



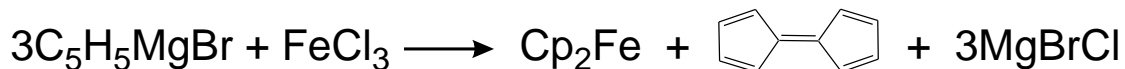
## Brief History of Ferrocene:

1901 Synthesis of  $\text{KC}_5\text{H}_5$  from K and  $\text{C}_5\text{H}_6$

1951 Miller, Tebboth & Tremaine

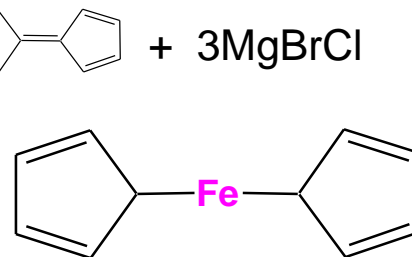
Synthesis of  $\text{Fe}(\text{C}_5\text{H}_5)_2$  from the reaction of  $\text{C}_5\text{H}_6$  with freshly reduced Fe at  $300^\circ\text{C}$

1951 Kealy & Pauson



They were trying to make fulvalene!

They proposed that they had made:

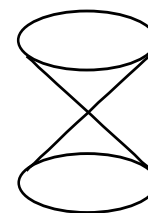


1952 E. O. Fischer proposes a “*Double-cone structure*”

X-ray structural data

Diamagnetism

Chemical behavior

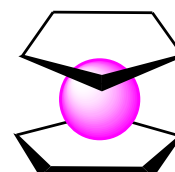


1952 Geoffrey Wilkinson & Robert Woodward: “*Sandwich Structure*”

IR spectroscopy

Diamagnetism

Dipole moment = 0



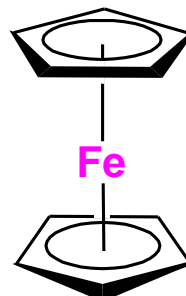
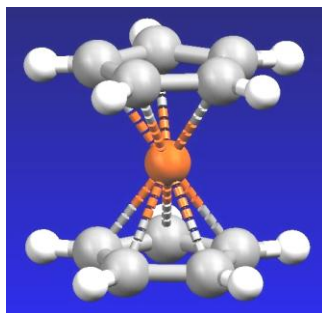
Woodward noted that the Cp rings were susceptible towards electrophilic substitutions, similar to the aromatic behavior of benzene.

Thus the common name: **ferrocene**

1973 Fischer & Wilkinson receive the Nobel Prize in Chemistry for their “discovery” of ferrocene, which played a key role in opening up the new area of organometallic chemistry.

For a short historical account see *Chemical & Engineering News*, Dec 3, 2001 (I have copies of the article) or the special Ferrocene issue of *Journal of Organometallic Chemistry*, Vol 637-639, Issue 1, 3 December 2001.

The structure of ferrocene does have a sandwich structure with a bonding interaction from each ring carbon to the metal, although virtually all researchers only draw a single bond from the metal to the middle of the Cp ring(s) as shown below in the structural diagram.



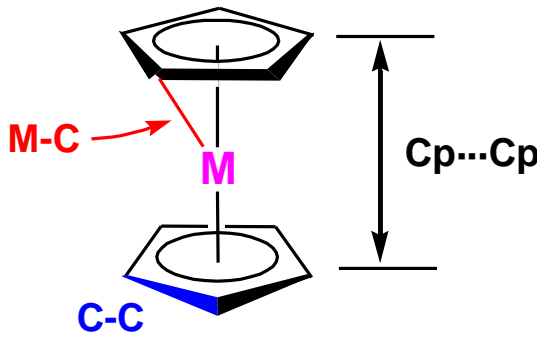
### Some Properties of Metallocenes

Complex	Color	mp/°C	Miscellaneous
"Ti(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> "	green	200 (decomp.)	bimetallic with two m-H bridges and a fulvalene bridging ligand (structure shown later)
V(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	purple	167	very air-sensitive, paramagnetic
"Nb(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> "	yellow	-	bimetallic with η <sup>1</sup> ,η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> bridges and terminal hydrides (structure shown later).
Cr(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	scarlet	173	very air-sensitive
"Mo(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> "	Black	-	several bimetallic isomers with fulvalene and h <sup>1</sup> ,h <sup>5</sup> bridges and terminal hydrides (structures shown later), diamagnetic, air-sensitive.
"W(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> "	yellow-green	-	same as Mo
Mn(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	brown	173	air-sensitive and easily hydrolyzed, interesting high-spin to low-spin interconversion
Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	orange	173	<b>air-stable</b> , can be oxidized to blue-green [Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ] <sup>+</sup> which, in turn, is a good "inert" oxidizing agent.
Co(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	purple-black	174	air-sensitive, paramagnetic 19e- complex, can be oxidized to the air-stable 18e- yellow [Co(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ] <sup>+</sup>
Ni(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	green	173	20e- complex, slow oxidation in air to the labile, orange cation [Ni(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ] <sup>+</sup>

Adapted from Elschenbroich & Salzer, "Organometallics", VCH, 1989

## Structural Features

The parallel sandwich structures have the following structural features:



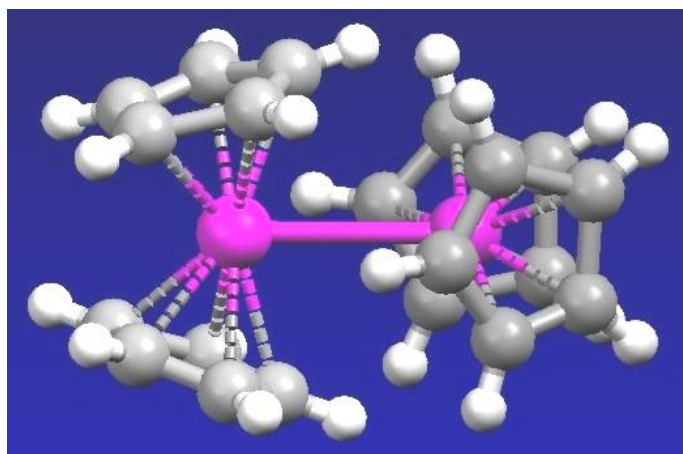
M	Distances (Å)		
	M-C	Cp...Cp	C-C
Fe	2.04	3.29	1.42
[Fe] <sup>+</sup>	2.07	3.40	1.40
Ru	2.19	3.64	1.43
Os	2.19	3.61	1.45
Co	2.10	3.44	1.41
[Co] <sup>+</sup>	2.03	3.24	1.42
Ni	2.18	3.63	1.41

Note the various trends in the bond distances. 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 in spite of the fact that the metal's covalent radius is *decreasing* as one goes from Fe  $\longrightarrow$  Ni (effective atomic number contraction effect).

**Problem:** Explain why the Fe-C distance *lengthens* for  $[\text{Cp}_2\text{Fe}]^+$ , while the Co-C distance *shortens* for  $[\text{Cp}_2\text{Co}]^+$ .

Oxidation of  $\text{Cp}_2\text{Os}$  does not produce a simple cationic monomer as seen for Co and Fe. Instead one gets dimerization to produce the following bimetallic complex that has an Os-Os bond (3.04 Å).

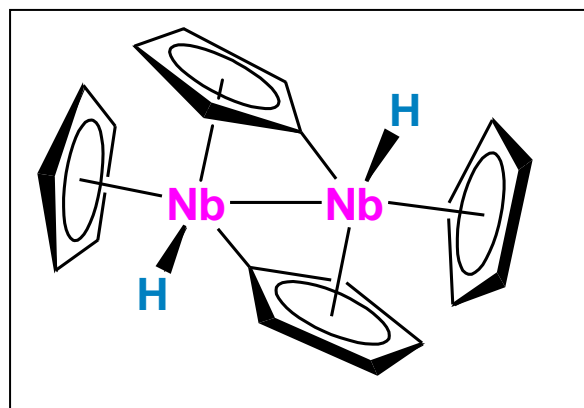
**Problem:** Is this complex para- or diamagnetic?



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 **oxidative addition** and other reactions.

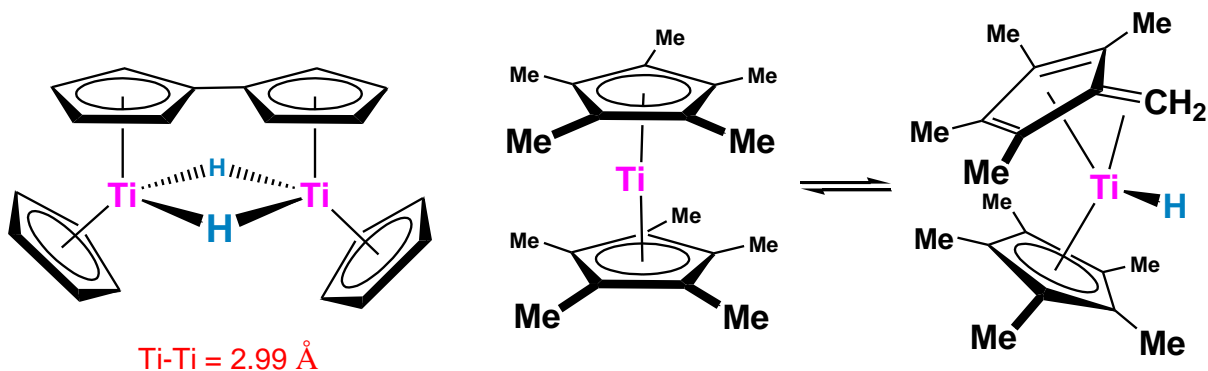
“ $\text{Nb}(\text{C}_5\text{H}_5)_2$ ”, for example, is nominally a 15 e- complex with a highly reactive  $d^3$  Nb electronic configuration.

Two molecules of niobocene react with one another via C-H bond activation (**oxidative addition**) to produce the structure shown to the right. Note that two of the Cp rings are dianionic forming both a traditional anionic  $\eta^5$  **6e-  $\pi$ -type donor** to one metal, while



bridging over and acting as an **anionic 2e-  $\sigma$ -donor** to the other metal center. **Practice your electron counting on this.**

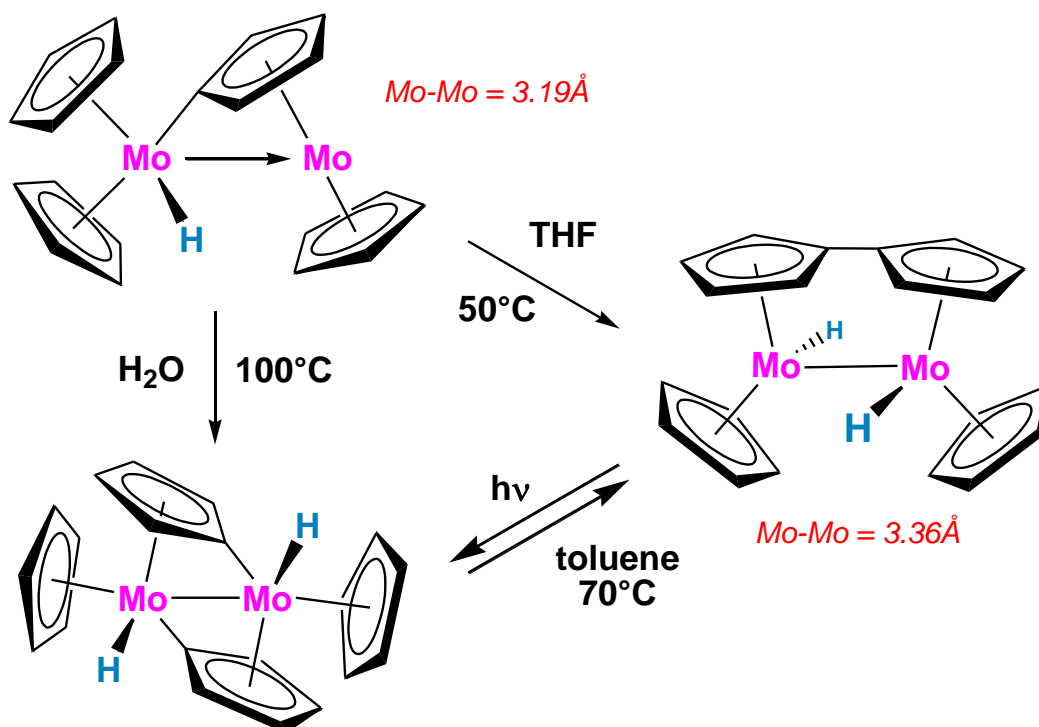
“ $\text{Ti}(\text{C}_5\text{H}_5)_2$ ”, is nominally a 14 e- complex with a highly reactive  $d^2$  electronic configuration. Two molecules of titanocene also react with one another via C-H bond activation (**oxidative addition**) to produce a bimetallic complex that may well look just like the niobium complex just discussed. But it has a further reaction (perhaps due to steric crowding brought on by the smaller Ti centers) leading to the coupling of the two  $\sigma$ -bound Cp's to produce C-C bound bis-Cp and the complex shown below. The more sterically crowded pentamethyl-Cp ( $\text{Cp}^*$ ) complex simply does a **hydride abstraction** and stops at the complex also shown below.



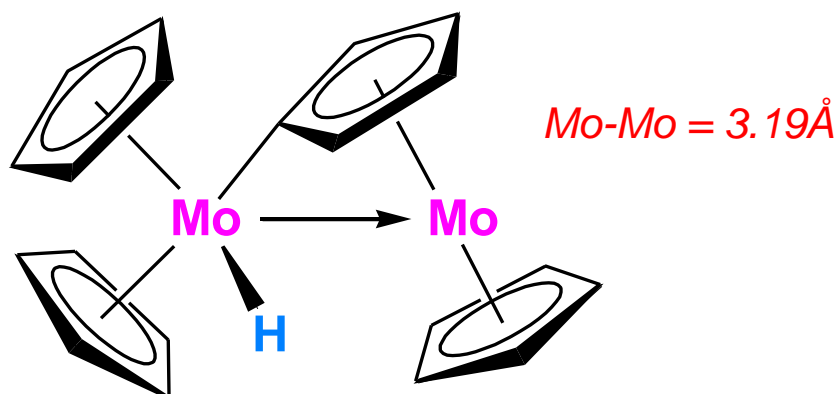
**Problem:** Electron-count the bimetallic Ti complex to the above left. Should it have a Ti-Ti bond or not? Show your electron counting.

**Problem:** What advantage does the  $\text{Cp}^*_2\text{Ti}$  complex (above middle) gain by doing a hydride abstraction to produce the hydride complex to the above right (previous page)?

The “ $\text{Mo}(\text{C}_5\text{H}_5)_2$ ” and “ $\text{W}(\text{C}_5\text{H}_5)_2$ ” complexes might appear to have a “reasonable” 16 e- count, but they are quite reactive, like their early transition metal cousins, and also self react with one another via C-H bond activations to produce several isomeric bimetallic complexes shown below.

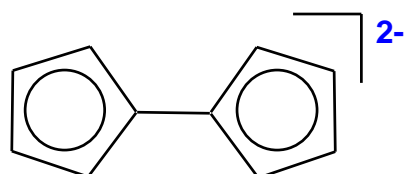


**Problem:** Electron-count the following complex. What does the arrow between the two Mo atoms indicates? It is NOT a covalent Mo-Mo bond. What name for this type of bonding would you use?

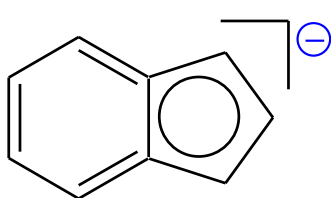


## Cp Variants

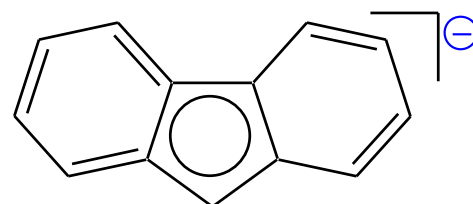
*these have special bonding properties important in substitution reactions (see that chapter)*



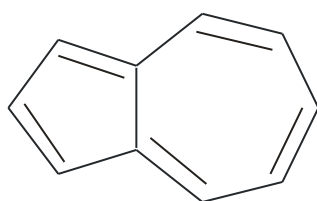
fulvalenediyl (2-)



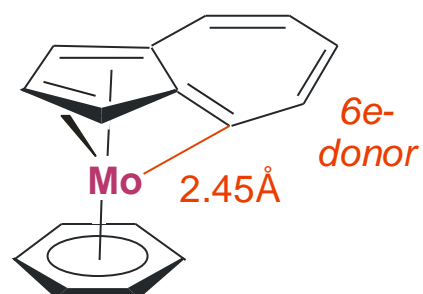
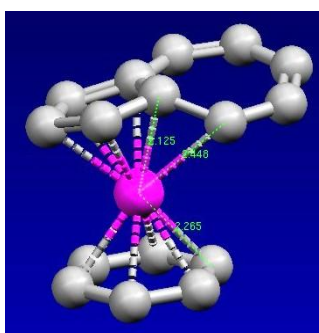
indenyl (-)



fluorenyl (-)



azulene



Behrens, *Angew. Chem.*, 1987

Azulene is neutral, so  $\eta^5$ -coordination of the  $C_5$  ring only provides  $5e^-$ , to get  $6e^-$  one needs to use one of the  $C_7$  ring carbon  $\pi$ -orbitals!

