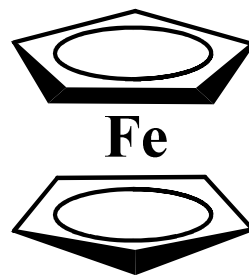
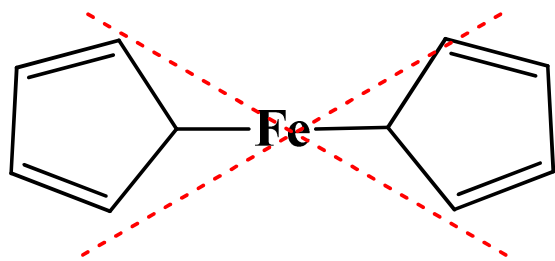


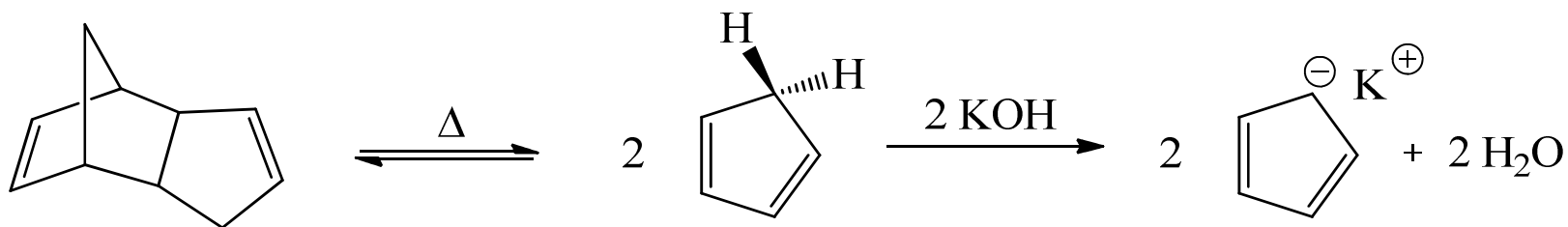
# Organometallic Chemistry

- Organometallic compounds combine an organic moiety with a metal in a molecule that has direct metal-carbon bonds.
- Ferrocene, first prepared in 1951, ushered in the modern era of organometallic chemistry.
- Originally called “dicyclopentadienyliron.”
- Subsequent X-ray analysis proved that ferrocene consisted of an iron(II) ion sandwiched between two parallel cyclopentadienyl (Cp) rings.
- The cyclopentadienyl ligand is just one example of many where the  $\pi$ -system of an organic compound binds directly to a metal atom via a  $d-\pi$  interaction.
- The term ***hapticity***, denoted  $\eta$ , describes the number of ligand atoms coordinated to the central metal atom, e.g.  $(\eta^5\text{-Cp})_2\text{Fe}$

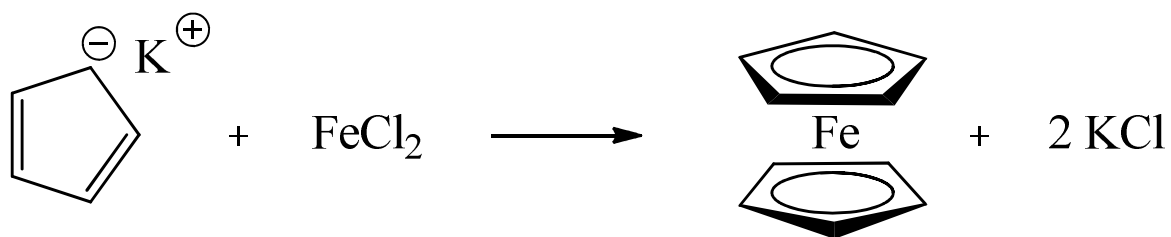


# Ferrocene Synthesis

- Cyclopentadiene (b.p. 42.5 °C) is produced by cracking dicyclopentadiene (b.p. 170 °C).
- Cyclopentadiene slowly dimerizes back to dicyclopentadiene at room temperature.
- The burgundy-red cyclopentadienyl ion,  $C_5H_5^-$ , can be produced by reaction of cyclopentadiene with KOH in solvent 1,2-dimethoxyethane (ethylene glycol dimethyl ether)

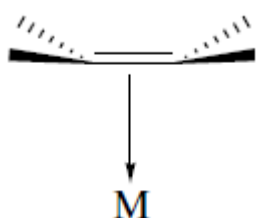


- A solution of  $\text{FeCl}_2$  in DMSO is slowly added to the solution containing  $\text{C}_5\text{H}_5^-$  ions, resulting in yellow-orange ferrocene:



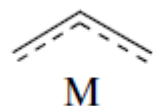
- An inert atmosphere ( $\text{N}_2$ ) is necessary to avoid air oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , which cannot effectively form ferrocene.
- The  $\text{FeCl}_2$  solution is prepared by dissolving  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  in DMSO.
- An open bottle of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (pale green) oxidizes over time to form brown  $\text{Fe(III)}$ . (***Do not leave container open and unattended***).
- The solution must be prepared and held under an inert atmosphere ( $\text{N}_2$ ) to avoid oxidation.
- $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  dissolves slowly - start preparing the solution early and use *mild heating* to speed up the process.

# $\pi$ bonded ligands



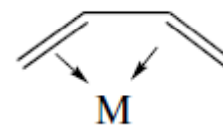
alkene complexes

alkyne complexes

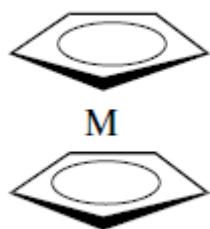


allyl complexes

diene complexes

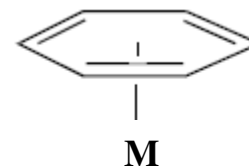
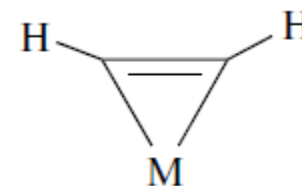
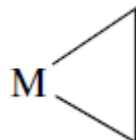


cyclopentadienyl complexes



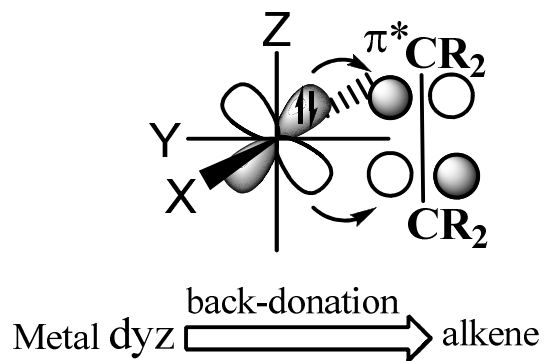
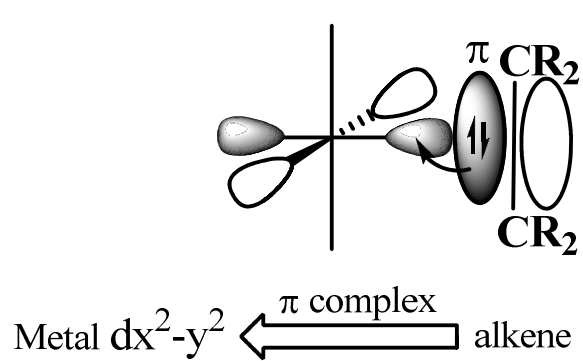
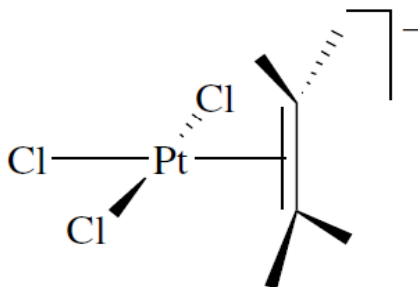
arene complexes

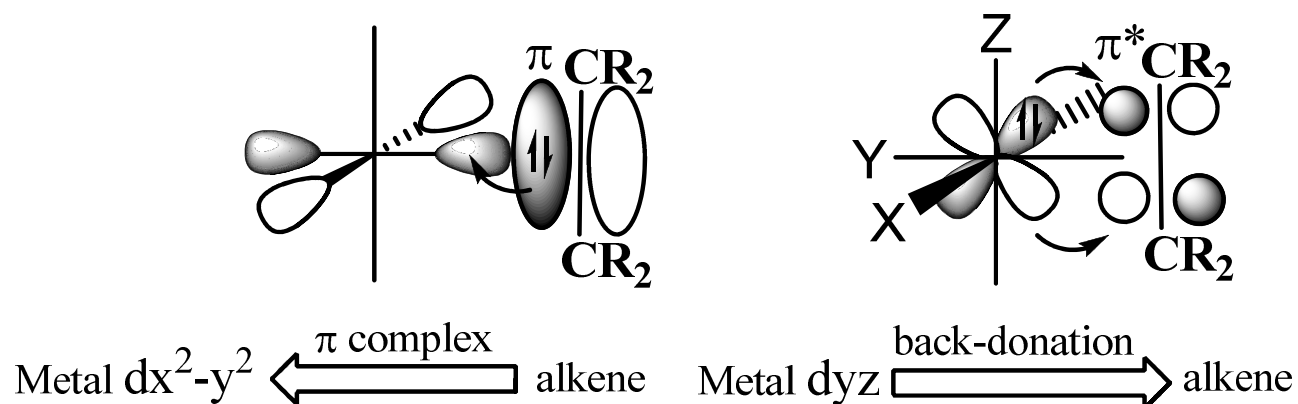
metallacycles



## Dewar-Chatt-Duncanson model

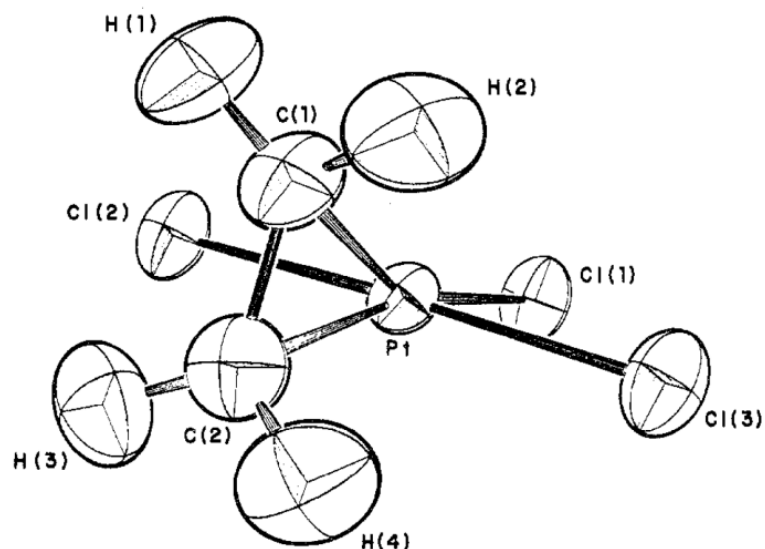
- Zeise's salt was the first organometallic compound to be isolated in pure form (1825 by William Zeise). The structure was not confirmed until 1838.
- This discovery spawned a tremendous growth in organometallic chemistry and still serves as the simplest example of transition metal-olefin complexation.
- Zeise's salt has become one of the most cited examples of the **Dewar-Chatt-Duncanson model** for metal-olefin complexation.





- The **Dewar-Chatt-Duncanson model** explains the type of chemical bonding between an unsaturated ligand and a metal forming a  $\pi$  complex.
- The  $\pi$ -acid ligand donates electron density into a metal  $d$ -orbital from a  $\pi$ -symmetry bonding orbital between the carbon atoms.
- The metal donates electrons back from a filled  $t_{2g}$   $d$ -orbital into the empty  $\pi^*$  antibonding orbital of the ligand (hence the description  $\pi$ -acid ligand).
- Both of these effects tend to reduce the C-C bond order, leading to an elongated C-C distance and a lowering of its vibrational frequency.
- The interaction can cause carbon atoms to "rehybridize", for e.g in metal alkene complexes from  $sp^2$  towards  $sp^3$ , which is indicated by the bending of the hydrogen atoms on the ethylene back away from the metal.
- Often the reactivity of the ligand is reversed from its free state – "**umpolung**".

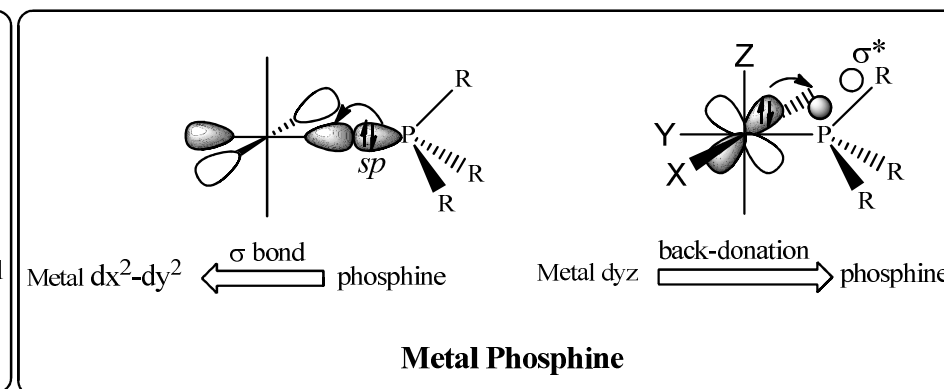
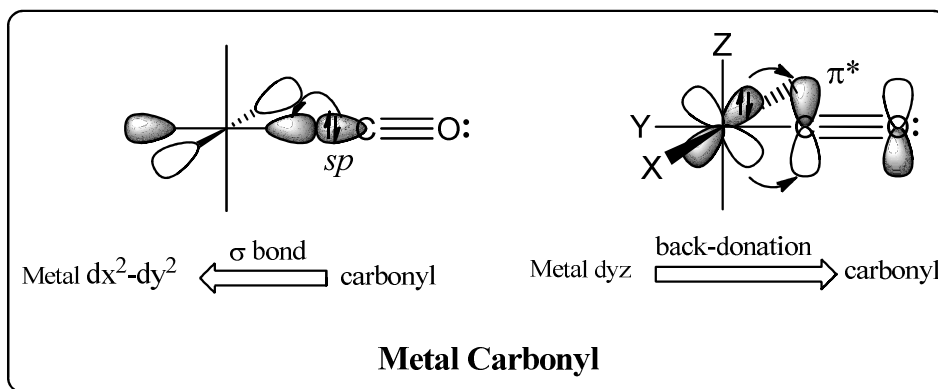
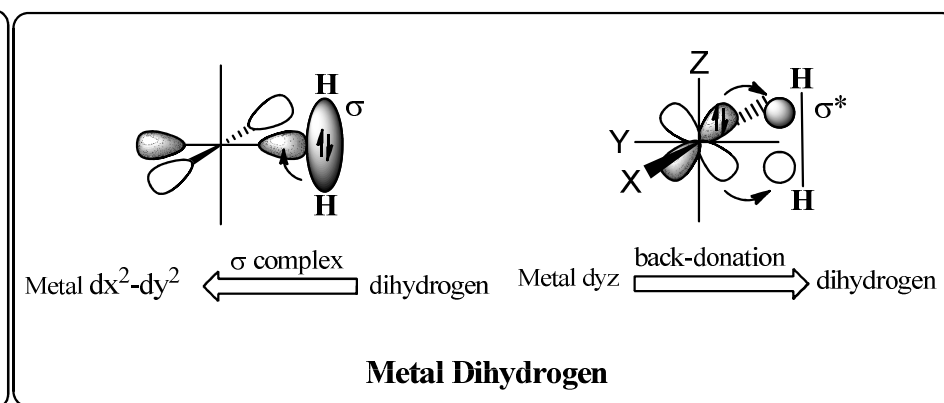
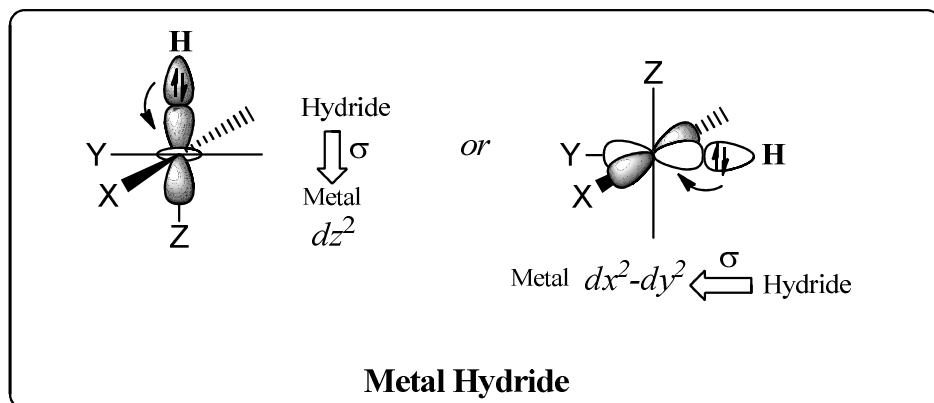
# Molecular geometry of Zeise's salt (neutron diffraction)



- The **PtCl<sub>3</sub> moiety forms a nearly planar group** with the Pt atom.
- The Pt-Cl bond trans to the ethylene group (2.340 Å) is significantly longer than the cis Pt-Cl bonds (2.302 and 2.303 Å) – **trans effect !!**
- The C atoms are approximately equidistant from the Pt atom (2.128 and 2.135 Å).
- The distance from the midpoint of the C-C bond to the Pt atom is 2.022 Å.
- The **C-C distance, 1.375 Å, is slightly longer than the value found in free ethylene (1.337 Å)**, indicating some dπ-pπ\* back-bonding from the platinum atom to C<sub>2</sub>H<sub>4</sub>.
- **Back-bonding is also indicated by a bending of the four hydrogen atoms away from the Pt atom.**

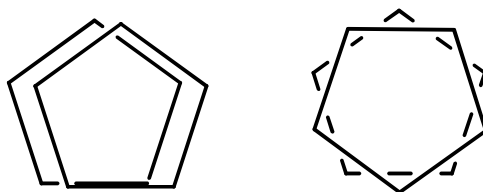


...some other classic examples of organometallic bonding interactions:



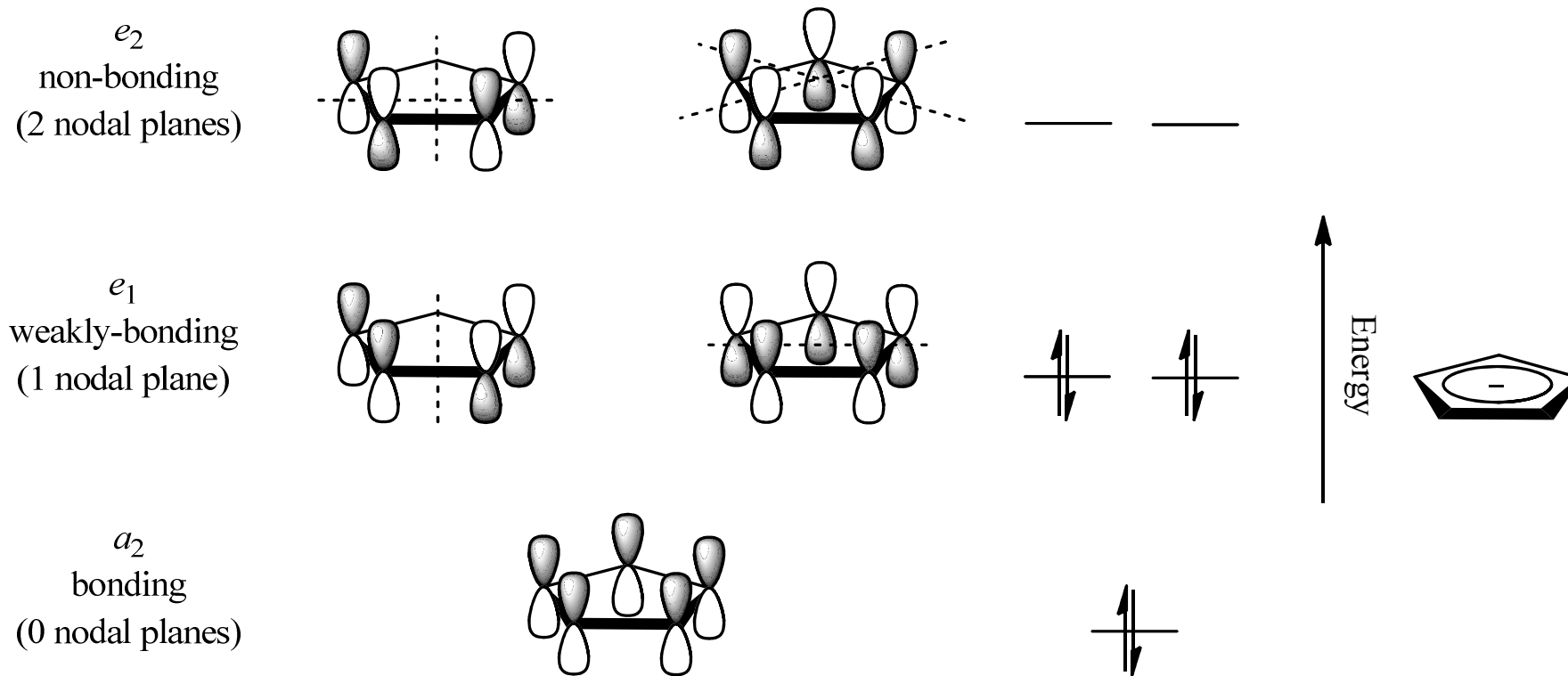
# The Electronic Structure of Ferrocene

- The two cyclopentadienyl (Cp) rings of ferrocene may be orientated in the two extremes of either an eclipsed ( $D_{5h}$ ) or staggered ( $D_{5d}$ ) conformation.



- The energy of rotation about the Fe-Cp axis is very small ( $\sim 4 \text{ kJmol}^{-1}$ ) and ground state structures of ferrocene may show either of these conformations.
- The primary orbital interactions that form the metal-ligand bonds in ferrocene occur between the Fe  $d$ -orbitals and the  $\pi$ -orbitals of the Cp ligand.
- The  $D_{5d}$  point group representations simplify the symmetry matching of ligand molecular orbitals and metal atomic orbitals.
- If  $D_{5d}$  symmetry is assumed, so that there is a centre of symmetry in the ferrocene molecule through the Fe atom there will be centro-symmetric ( $g$ ) and anti-symmetric ( $u$ ) combinations.

- The five  $p$ -orbitals on the planar  $\text{Cp}^-$  ring ( $D_{5h}$  symmetry) can be combined to produce five molecular orbitals.



- One combination has the full symmetry of the ring ( $a_2$ )
- There are two doubly degenerate combinations ( $e_1$  and  $e_2$ ) having one and two nodal planes orthogonal to the plane of the ring.
- The relative energies of these orbitals increase as the number of nodal planes (0, 1, 2) increases.
- The  $a_2$  and  $e_1$  orbitals are both fully occupied in the electronic configuration of the  $\text{Cp}^-$  anion whereas the  $e_2$  orbitals are net anti-bonding and are unfilled.
- For a bis-cyclopentadienyl metal complex  $(\eta^5\text{-Cp})_2\text{M}$ , such as ferrocene, **the  $\pi$ -orbitals of the two Cp ligands are combined pairwise to form the symmetry-adapted linear combination of molecular orbitals (SALC's).**

- To form the SALC orbitals, the sum and difference of corresponding molecular orbitals on the Cp ligand must be taken, e.g.  $(\psi_1+\psi_1)$ ,  $(\psi_1-\psi_1)$ ;  $(\psi_2+\psi_2)$ ,  $(\psi_2-\psi_2)$  etc.
- For example, ' $\psi_1+\psi_1$ ' gives rise to a molecular orbital of  $a_{1g}$  symmetry.
- Overall, this gives rise to three sets of ligand molecular orbitals of gerade ( $g$ ) and ungerade ( $u$ ) symmetry *with respect to the centre of inversion*;
  - a low lying filled bonding pair of  $a_{1g}$  and  $a_{2u}$  symmetry
  - a filled weakly bonding pair of  $e_{1g}$  and  $e_{1u}$  symmetry
  - an unfilled anti-bonding pair of  $e_{2g}$  and  $e_{2u}$  symmetry.

SALC orbitals for a  $(\eta^5\text{-Cp})_2\text{M}$  complex;  $\Gamma_\pi = A_{1g} + A_{2u} + E_{1g} + E_{1u} + E_{2g} + E_{2u}$



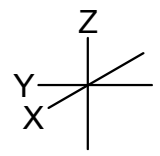
$e_{2g}$

$e_{2u}$



$e_{1g}$

$e_{1u}$



$a_{1g}$

$a_{2u}$

- The metal orbitals transform as

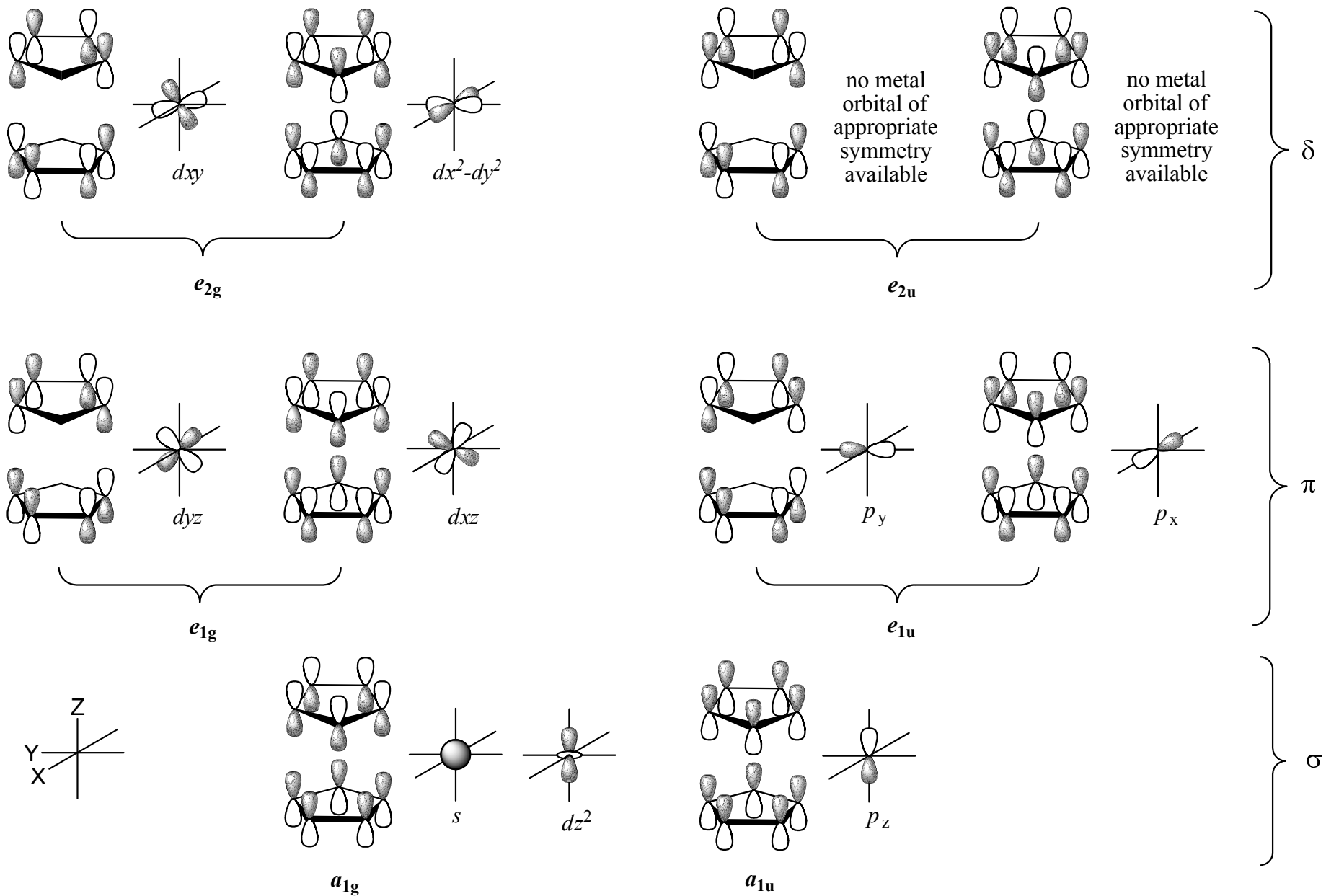
$$A_{1g} (d_z^2, s) + A_{2u} (p_z) + E_{1u} (p_x, p_y) + E_{1g} (d_{yz}, d_{xz}) + E_{2g} (d_x^2 - d_y^2, d_{xy})$$

- Reducible representation of SALC's :

$$\Gamma_{\pi} = A_{1g} + A_{2u} + E_{1g} + E_{1u} + E_{2g} + E_{2u}$$

- By considering the SALC orbitals and how overlap with metal atomic orbitals can be affected the molecular orbital bonding picture of ferrocene can be constructed.
- For example, the  $a_{1g}$  SALC orbital can in theory overlap with the Fe 4s and  $3d_{z^2}$  orbitals as they are also of  $a_{1g}$  symmetry. This interaction gives rise to the bonding and anti-bonding molecular orbitals of the complex  $a_{1g}$  and  $a_{1g}^*$  respectively.
- Each combination of ligand molecular orbitals and metal molecular orbitals leads to a bonding molecular orbital  $[(\psi_{\text{ligand molecular orbital}}) + (\psi_{\text{metal atomic orbital}})]$  and a corresponding anti-bonding molecular orbital  $[(\psi_{\text{ligand molecular orbital}}) - (\psi_{\text{metal atomic orbital}})]$  providing that the energies of the two component sets are sufficiently close for overlap.

# Symmetry matching of SALC orbitals with the metal atomic orbitals





# A qualitative molecular orbital diagram for ferrocene ( $D_{5d}$ )

