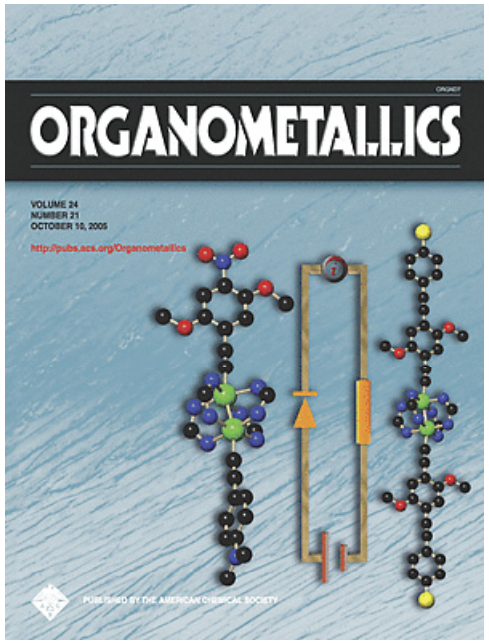
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NUMBER 21
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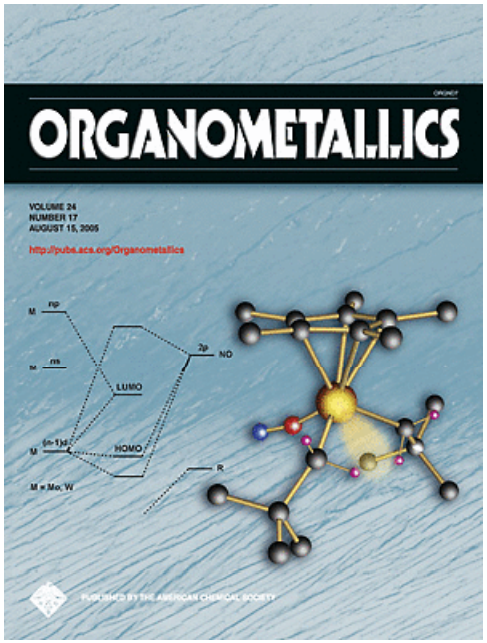
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LUMO
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NUMBER 24
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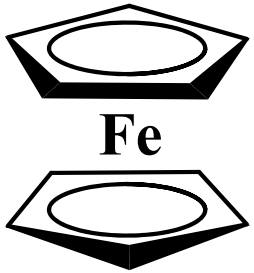
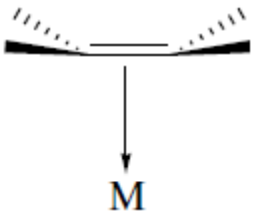
Organometallic Chemistry

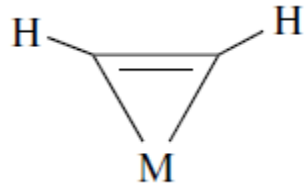
- Organometallic compounds combine an organic moiety with a metal in a molecule that has direct metal-carbon bonds.
- Ferrocene, first prepared in 1951, ushered in the modern era of organometallic chemistry.
- Originally called “dicyclopentadienyliron.”
- Subsequent x-ray analysis proved that ferrocene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



π bonded ligands

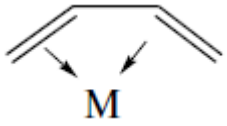


alkene complexes



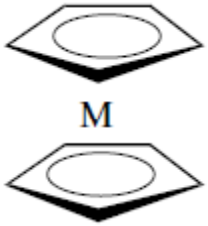
alkyne complexes

allyl complexes



diene complexes

cyclopentadienyl complexes



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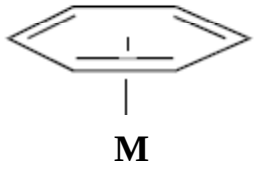
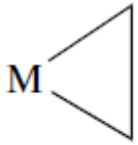
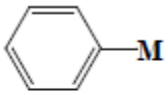
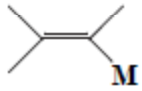
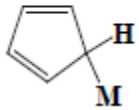
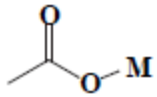
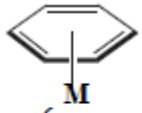
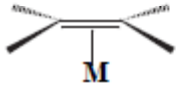
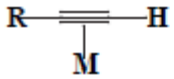
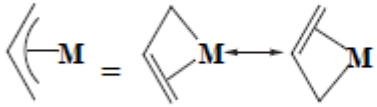
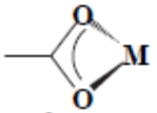


metallacycles



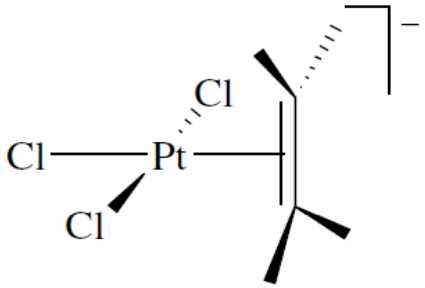
η^1-coordination	Formal	# of e- donated
 η^1-aryl	-1	2
 η^1-alkenyl	-1	2
 η^1-alkynyl	-1	2
 η^1-Cp (cyclopentadienyl)	-1	2
 η^1-allyl	-1	2
 η^1-acetate	-1	2

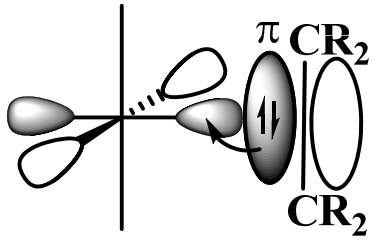
η^x-coordination	Formal	# of e- donated
 η^6-arene	0	6
 η^2-alkene	0	2
 η^2-alkyne	0	2
 η^5-Cp (cyclopentadienyl)	-1	6
 η^3-allyl	-1	4
 η^2-acetate	-1	4

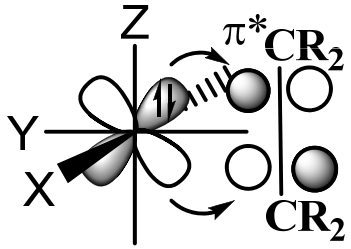
- **Common unsaturated π donating ligands encountered in organotransition-metal chemistry together with the respective numbers of electrons relevant to the application of the 18 VE rule.**

Transition metal alkene complexes

- 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.

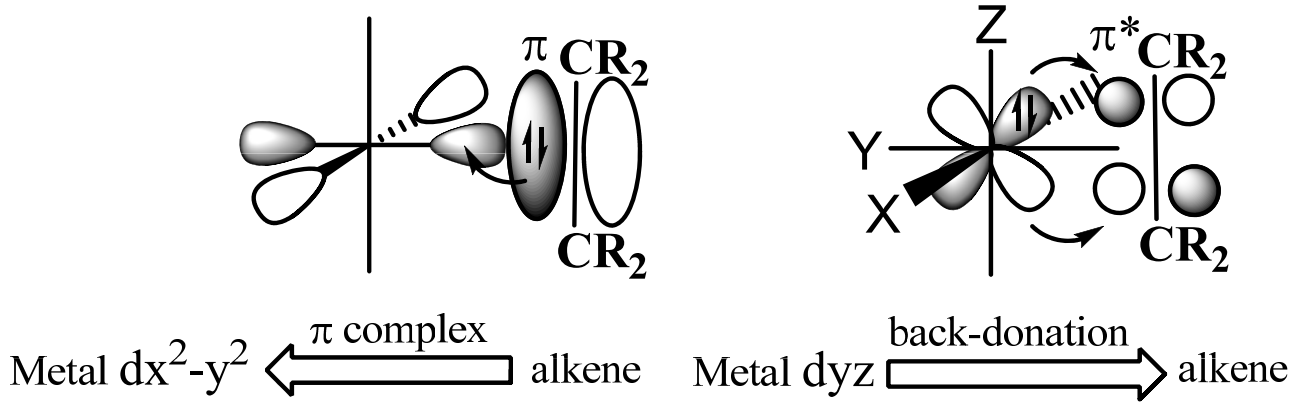






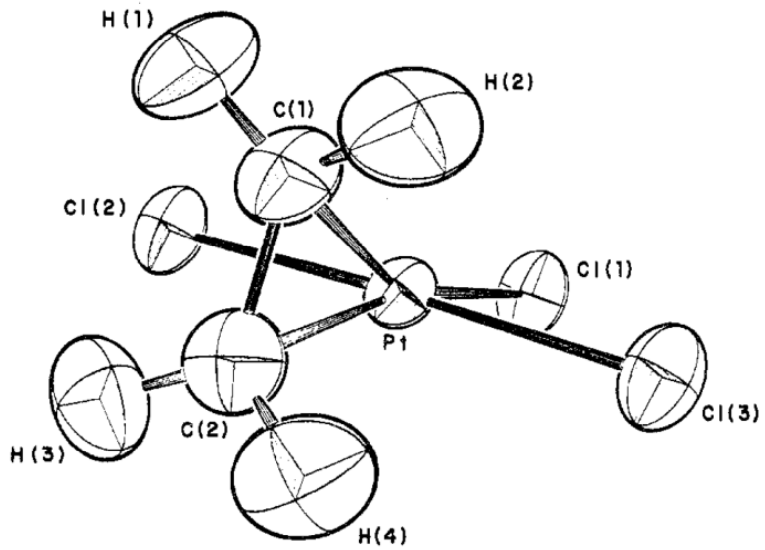
Metal dx^2-y^2 ⟸ (π complex) alkene

Metal dyz ⟹ (back-donation) alkene



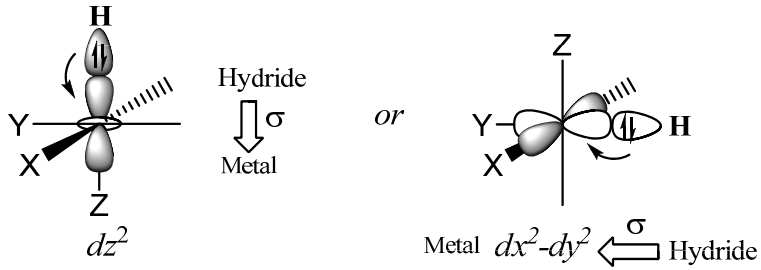
- The ***Dewar-Chatt-Duncanson model*** explains the type of chemical bonding between an unsaturated ligand and a metal forming a π complex.
- The π-acid ligand donates electron density into a metal *d*-orbital from a π-symmetry bonding orbital between the carbon atoms.
- The metal donates electrons back from a filled t_{2g} *d*-orbital into the empty π^* antibonding orbital of the ligand (hence the description π-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)

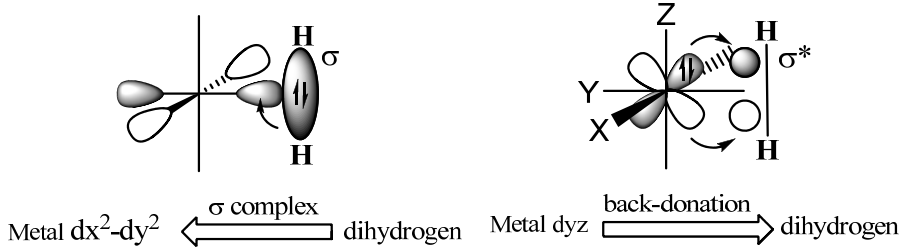


- The **$PtCl_3$** ***moiety forms a nearly planar group*** with the Pt atom.
- The Pt-Cl bond trans to the ethylene group (2.340 Å) is significantly longer than the cis Pt-Cl bonds (2.302 and 2.303 Å) – ***trans effect !!***
- The C atoms are approximately equidistant from the Pt atom (2.128 and 2.135 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_2H_4.
- ***Back-bonding is also indicated by a bending of the four hydrogen atoms away from the Pt atom.***

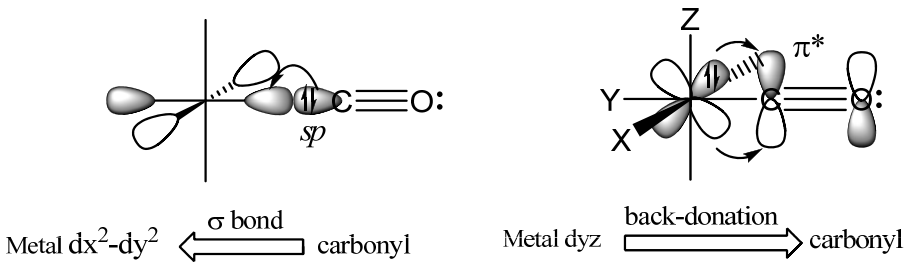
…some other classic examples of organometallic bonding interactions:



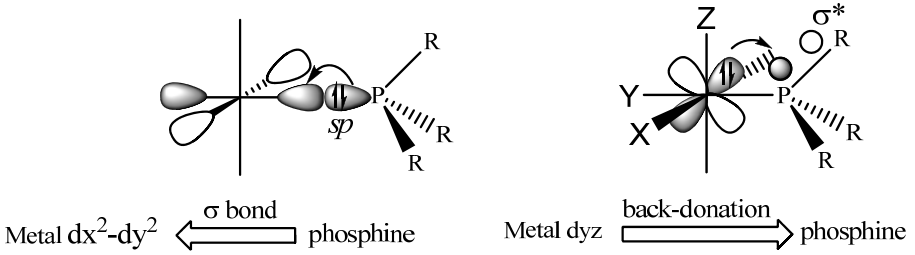
Metal Hydride



Metal Dihydrogen



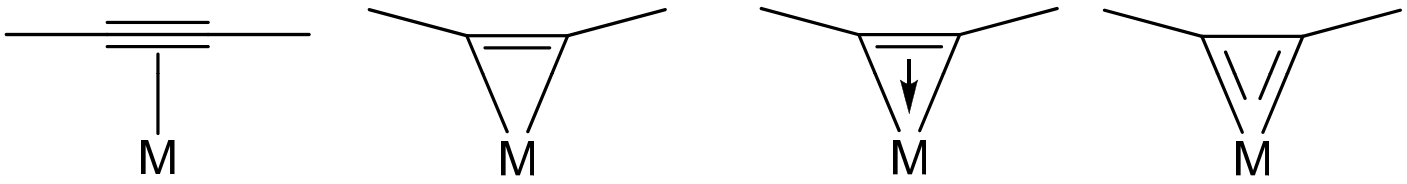
Metal Carbonyl



Metal Phosphine

Transition metal alkyne complexes

- Alkynes behave in ways broadly similar to alkenes, but being more electronegative, they tend to encourage back donation and bind more strongly.
- The substituents tend to fold back away from the metal by 30°–40° in the complex, and the M−C distances are slightly shorter than in the corresponding alkene complexes.

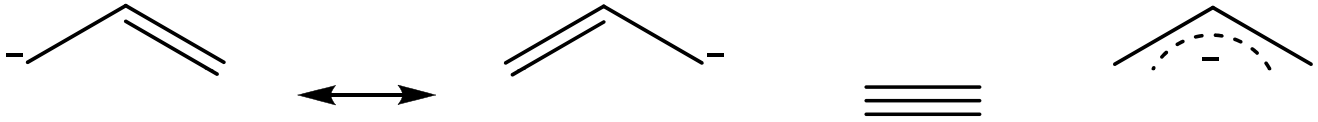


	η^1	η^2	η^2	η^2
Ionic model:	**2e (0)**	**4e (2-)**	**6e (2-)**	**8e (4-)**
Covalent model:	**2e (0)**	**2e (0)**	**4e (0)**	**4e (0)**

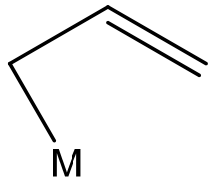
Why are alkynes more electronegative than alkenes?

Transition metal allyl complexes

- The allyl group, commonly a spectator ligand, binds in one of two ways.
- In the η^1 **form it is a simple X-type ligand** like Me
- In the η^3 **form it acts as a LX enyl ligand**.
- It is often useful to think in terms of the resonance forms **(2e + 1e donor)**

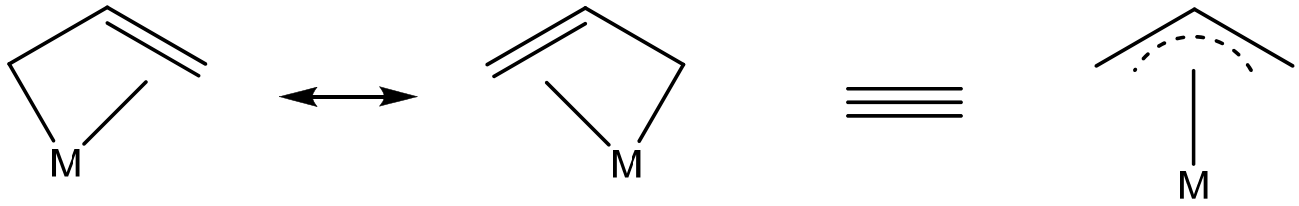


η^1



covalent model: 1e donor (0 charge)
ionic model: 2e donor (1- charge)

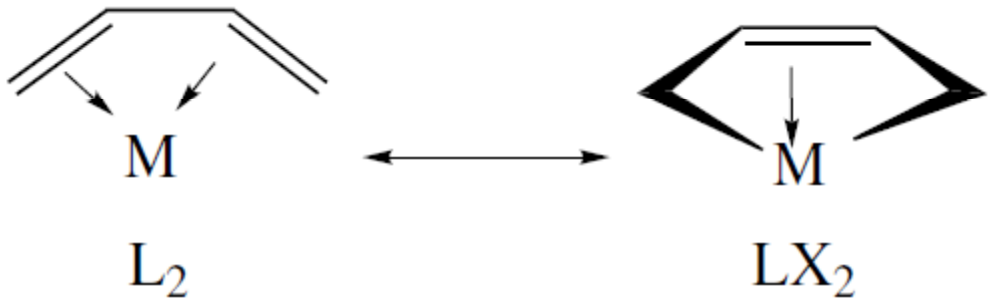
η^3



covalent model: 3e donor (0 charge)
ionic model: 4e donor (-1 charge)

Transition metal diene complexes

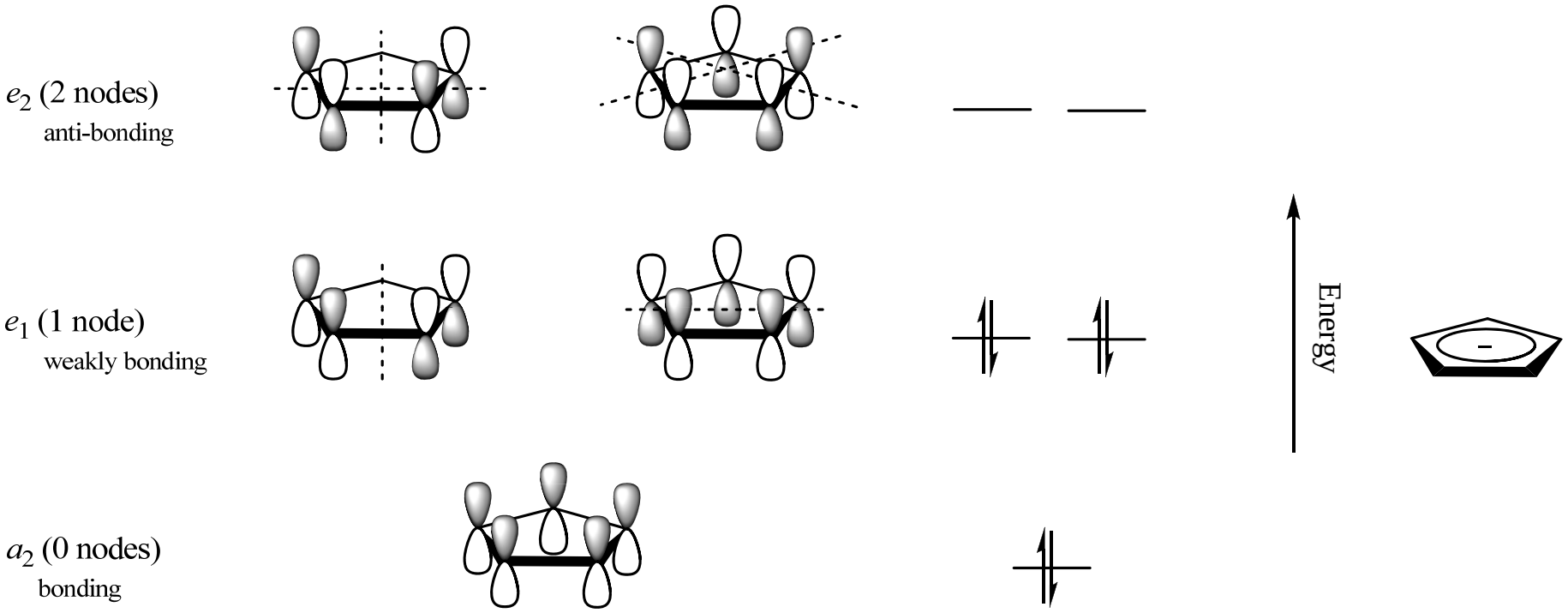
- The η^4 diene ligand usually acts as a 4e donor in its cisoid conformation (L_2 form).
- The corresponding enediyl (LX_2) form can also be described as a ***metalacyclopropane***.



- The L_2 form is rarely seen with the LX_2 form becoming more important as the back donation increases.

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 (~ 4 $kJmol^{-1}$) and ground state structures of ferrocene may show either of these conformations.
- There is also very little difference in electronic states between the D_{5h} and D_{5d} symmetries however the D_{5d} point group representations are used here in the description of the electronic structure of ferrocene as they simplify the symmetry matching of ligand molecular orbitals and metal atomic orbitals.
- The primary orbital interactions that form the metal-ligand bonds in ferrocene occur between the Fe orbitals and the π-orbitals of the Cp ligand.
- 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 Cp ring (D_{5h} symmetry) can be combined to produce five molecular orbitals.



The π-molecular orbitals of the cyclopentadienyl ring (D_{5h})

- 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 planar nodes at right angles to the plane of the ring.
- The relative energies of these orbitals increase as the number of nodes increases.
- The a_2 and e_1 orbitals are both fully occupied in the electronic configuration of the Cp^- anion whereas the e_2 orbitals are net anti-bonding and are unfilled.
- For a bis-cyclopentadienyl metal complex (η^5-Cp)$_2$M , such as ferrocene, the π-orbitals of the two Cp ligands are combined pairwise to form the symmetry-adapted linear combination of molecular orbitals (SALC's).

- To do this, 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.

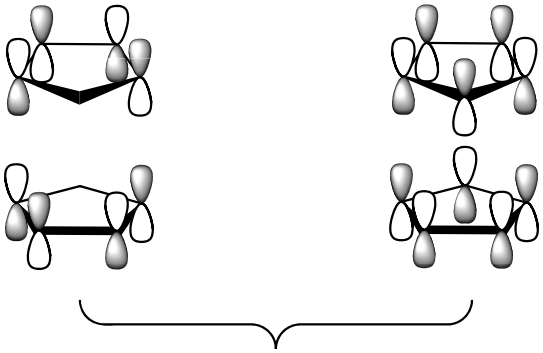
- Overall, this gives rise to three sets of ligand molecular orbitals of gerade (*g*) and ungerade (*u*) symmetry *with respect to the centre of inversion*;

  - a low lying filled bonding pair of a_{1g} and a_{2u} symmetry

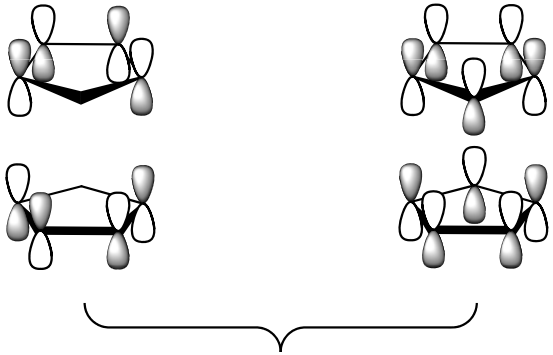
  - a filled weakly bonding pair of e_{1g} and e_{1u} symmetry

  - an unfilled anti-bonding pair of e_{2g} and e_{2u} symmetry.

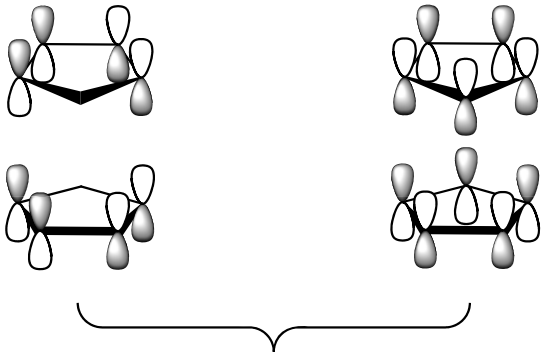
SALC's for a (η^5-Cp)$_2$M complex; $\Gamma_\pi = A_{1g} + A_{2u} + E_{1g} + E_{1u} + E_{2g} + E_{2u}$



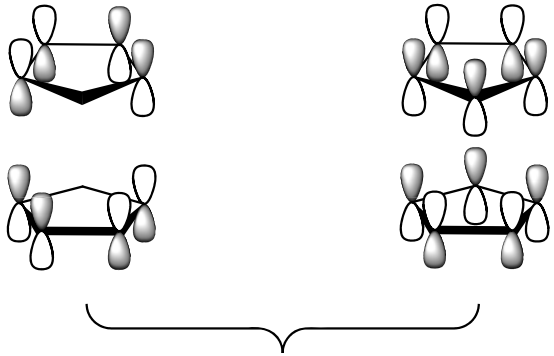
e_{2g}



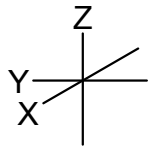
e_{2u}

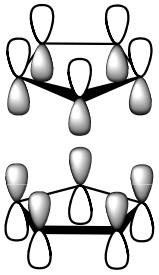


e_{1g}

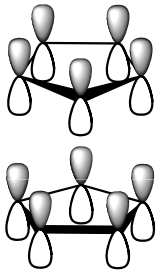


e_{1u}





a_{1g}



a_{2u}

- The metal orbitals transform as

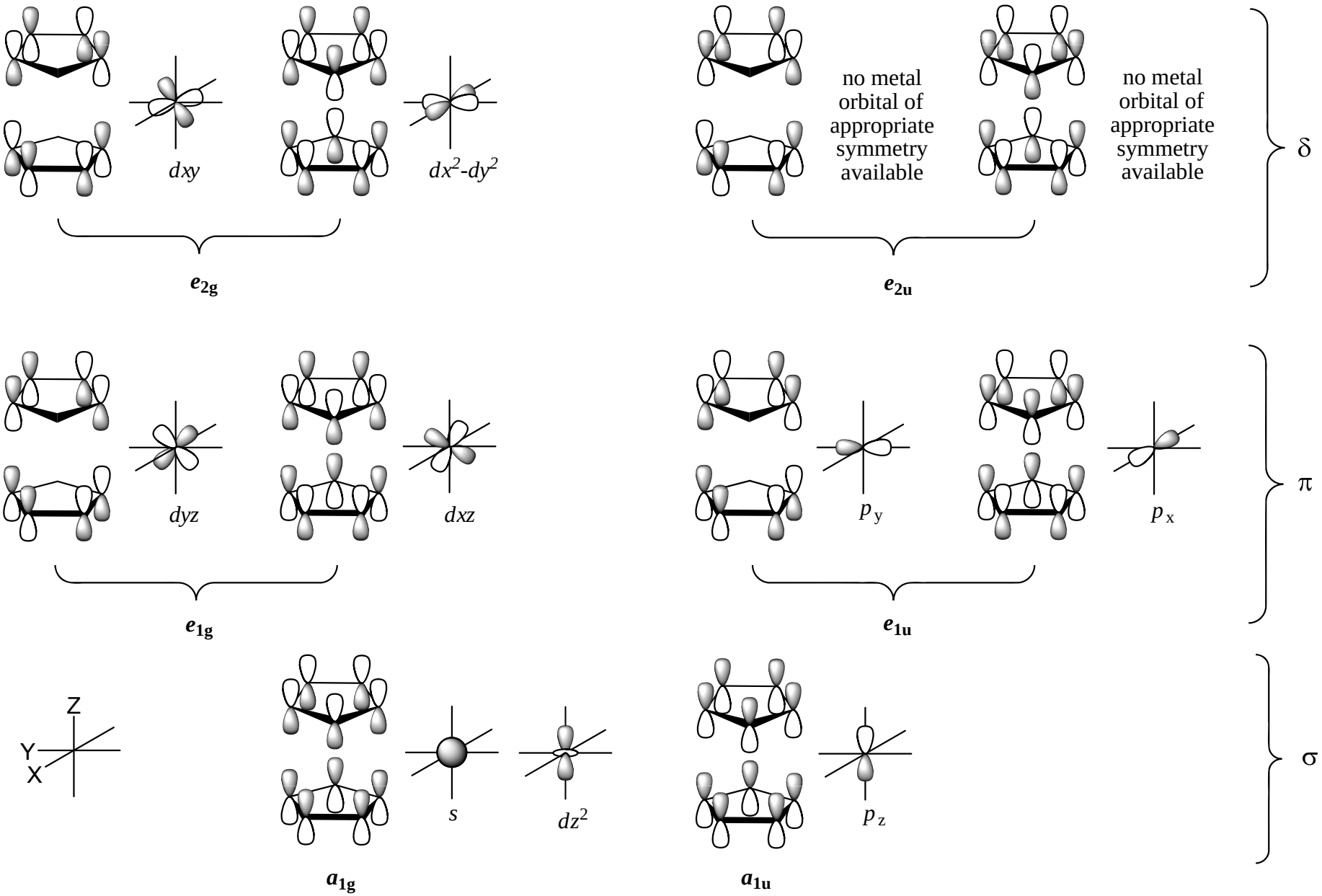
$$A_{1g}\,(d_z^2, s) + A_{2u}\,(p_z) + E_{1u}\,(p_x, p_y) + E_{1g}\,(d_{yz}, d_{xz}) + E_{2g}\,(d_x^2 - d_y^2, d_{xy})$$

- reducible representation of SALC's :

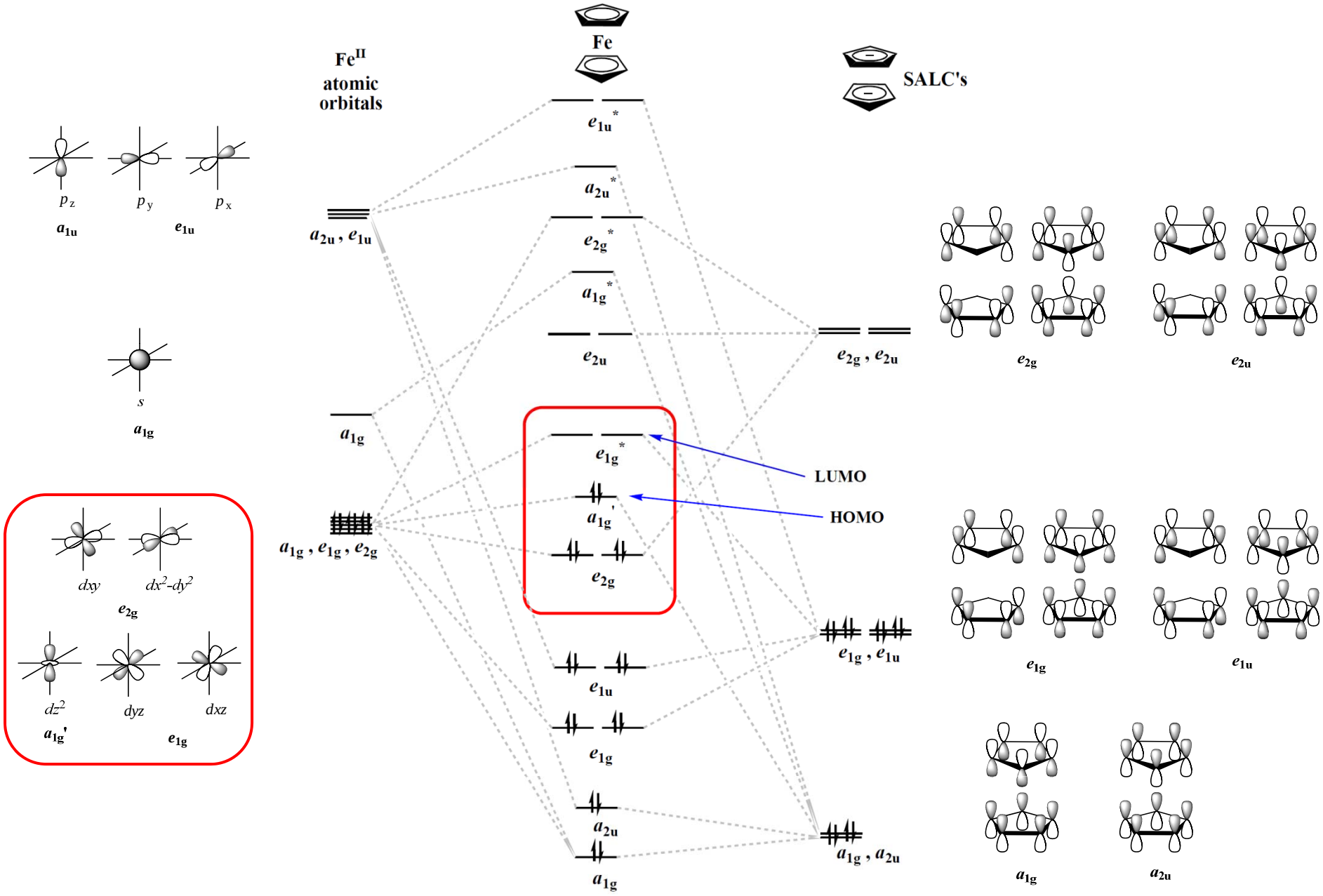
$$\Gamma_\pi = A_{1g} + A_{2u} + E_{1g} + E_{1u} + E_{2g} + E_{2u}$$

- By considering these ligand molecular 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 $3dz^2$ 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 the SALC's with the metal atomic orbitals

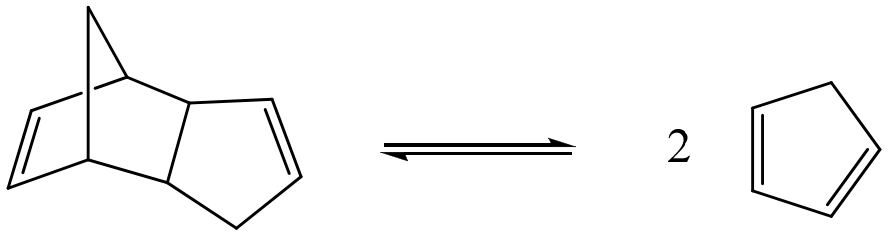


A qualitative molecular orbital diagram for ferrocene (D_{5d})



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 FeCl2 in DMSO is slowly added to the solution containing $C_5H_5^-$ ions, resulting in yellow-orange ferrocene:

$$2C_5H_5^- + Fe^{2+} \rightarrow (\eta^5\text{-}C_5H_5)_2Fe$$

- An inert atmosphere (N_2) is necessary to avoid air oxidation of Fe^{2+} to Fe^{3+}, which cannot effectively form ferrocene.
- The $FeCl_2$ solution is prepared by dissolving $FeCl_2.4H_2O$ in DMSO.
- An open bottle of $FeCl_2$.4H2O (pale green) oxidizes over time to form brown Fe(III).
  - Do not use any crystals that are brown.
- The solution must be prepared and held under an inert atmosphere (N_2) to avoid oxidation.
- $FeCl_2.4H_2O$ dissolves slowly - start preparing the solution early and use *mild heating* to speed up the process.

- Our synthetic procedure uses very small volumes in a 5-mL round bottom flask.
- An inert atmosphere is maintained by N_2 flow through a pair of hypodermic needles.
- First, a KOH/dimethoxymethane solution is prepared in the flask.
- A $FeCl_2$/DMSO solution is prepared in a test tube, also under N_2, for later addition.
- Cyclopentadiene is injected into the flask with the KOH solution, causing $C_5H_5^-$ ion (purple) to form.
- Injecting the $FeCl_2$/DMSO solution into the $C_5H_5^-$ solution causes ferrocene to form.
- To isolate the crude ferrocene, pour the dark slurry into a mixture of 4.5 mL of 6 M HCl solution and 5 g of ice in a 30-mL beaker.
- Collect the crude product by filtration on a Hirsh funnel.

- The crude ferrocene prepared in this synthesis is a dull yellow-orange powder.
- Pure ferrocene can be obtained by sublimation at atmospheric pressure.
- The easiest way to carry out the sublimation is with two small same-sized Petri dish halves, placed on top of each other, and ***mildly heated on a warm hot plate.***
- Overheating will scorch the crude product without sublimation, resulting in poor yield.
- Sublimed ferrocene has shiny, orange, crystalline flakes.
- The purified ferrocene will be used to record an IR spectrum and in a later experiment as a standard for cyclic voltammetry.