A brief description of the 18 electron rule

A valence shell of a transition metal contains the following: 1*s* orbital, 3 *p* orbitals and 5 *d* orbitals; 9 orbitals that can collectively accommodate 18 electrons (as either bonding or nonbonding electron pairs). This means that, the combination of these nine atomic orbitals with ligand orbitals creates nine molecular orbitals that are either metal-ligand bonding or non-bonding, and when metal complex has 18 valence electrons, it is said to have achieved the same electron configuration as the noble gas in the period.

In some respect, it is similar to the octet rule for main group elements, something you might be more familiar with, and thus it may be useful to bear that in mind. So in a sense, there's not much more to it than "electron bookkeeping"

18 electron rule is more useful in the context of organometallics.

Two methods are commonly employed for electron counting:

1. Neutral atom method: Metal is taken as in zero oxidation state for counting purpose
2. Oxidation state method: We first arrive at the oxidation state of the metal by considering the number of anionic ligands present and overall charge of the complex

Neutral Atom Method

The major premise of this method is that we remove all of the ligands from the metal, but rather than take them to a closed shell state, we do whatever is necessary to make them neutral. Let's consider ammonia once again. When we remove it from the metal, it is a neutral molecule with one lone pair of electrons. Therefore, as with the ionic model, ammonia is a neutral two electron donor. But we diverge from the ionic model when we consider a ligand such as methyl. When we remove it from the metal and make the methyl fragment neutral, we have a neutral methyl radical. Both the metal and the methyl radical must donate one electron each to form our metal-ligand bond. Therefore, the methyl group is a one electron donor, not a two electron donor as it is under the ionic formalism. Where did the other electron "go"? It remains on the metal and is counted there. In the covalent method, metals retain their full complement of d electrons because we never change the oxidation state from zero; i.e. Fe will always count for 8 electrons regardless of the oxidation state and Ti will always count for four.

Ligand Electron Contribution (for neutral atom method)

a. Neutral Terminal (eg. CO,PR3,NR3) : 2 electrons

b. Anionic Terminal (eg. $X-$,$R2P-$,$Ro-$) : 1 electron

c. Hapto Ligands (eg. $\eta 2-C2R4$,$\eta 1-$allyl): Same as hapticity

d. Bridging neutral (eg. $\mu 2-CO$) : 2 electrons

e. Bridging anionic (eg. $\mu 2-CH3$) (no lone pairs): 1 electron

f.Bridging anionic (eg. $\mu 2-Cl$,$\mu 2-OR$) (with 1 lone pair)): 3 electrons *(with 1 lone pair)*

or, $\mu 2-Cl$(with 2 lone pairs): 5 electrons

g. Bridging alkyne 4 electrons

h. NO linear 3 electrons

i. NO bent (lone pair on nitrogen): 1 electron

j. Carbene (M=C): 2 electron

k.Carbyne (M≡C): 3 electron

Determining # Metal-Metal bonds

Step 1: Determine the total valence electrons (TVE) in the entire molecule (that is, the number of valence electrons of the metal plus the number of electrons from each ligand and the charge)-- I'll call this T (T for total, I'm making this up)

Subtract this number from $n \times 18$

where n is the number of metals in the complex, i.e $(n \times 18) - T$

-- call this R (R for result, nothing fancy)

(a) R divided by 2 gives the total number of M–M bonds in the complex. (b) T divided by n gives the number of electrons per metal.

If the number of electrons is 18, it indicates that there is no M–M bond; if it is 17 electrons, it indicates that there is 1 M–M bond; if it is 16 electrons, it indicates that there are 2 M–M bonds and so on.

At this point, let's apply this method to a few examples

a) Tungsten Hexacarbonyl

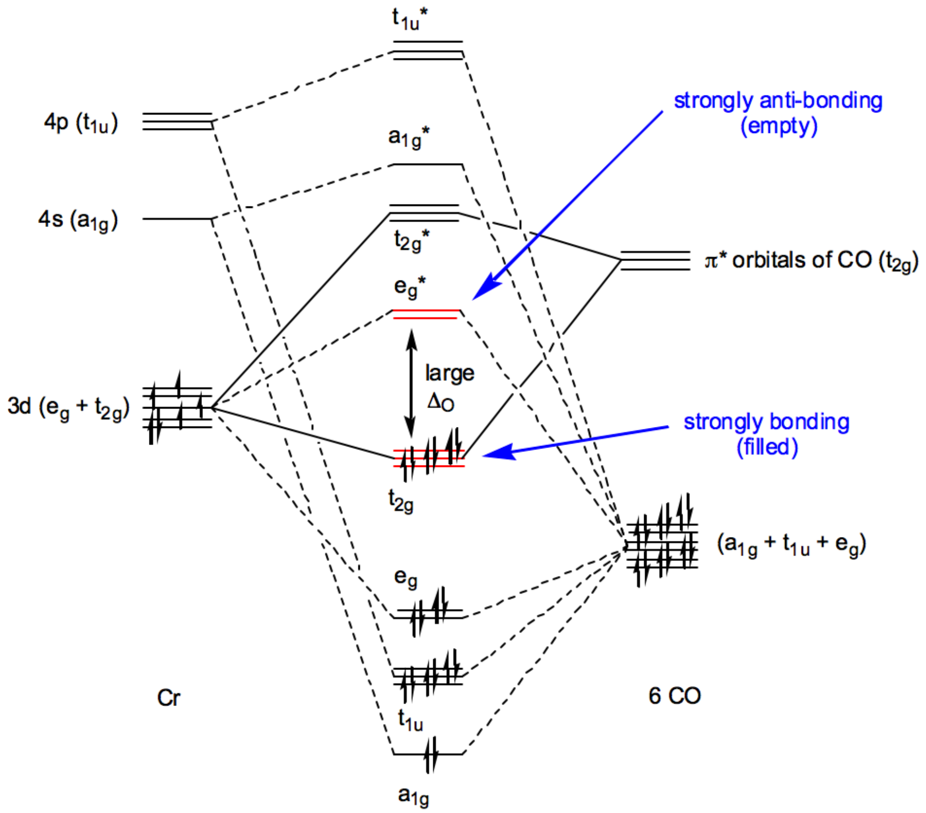
Let's use the neutral atom method, W has 6 electrons, the carbonyls donate 12 electrons and we get a total of 18. Of course there can be no metal metal bonds here.

(b) Tetracobalt dodecacarbonyl, here let's figure out the no. of metal-metal bonds. T is 16, R is 12, Total # M-M bonds is 6, # electrons per metal is 15, so 3 M-M bonds.

A few examples where the "18 electron Rule" works

I. **Octahedral Complexes with strong π- acceptor ligands**

eg. [Cr(CO)6]



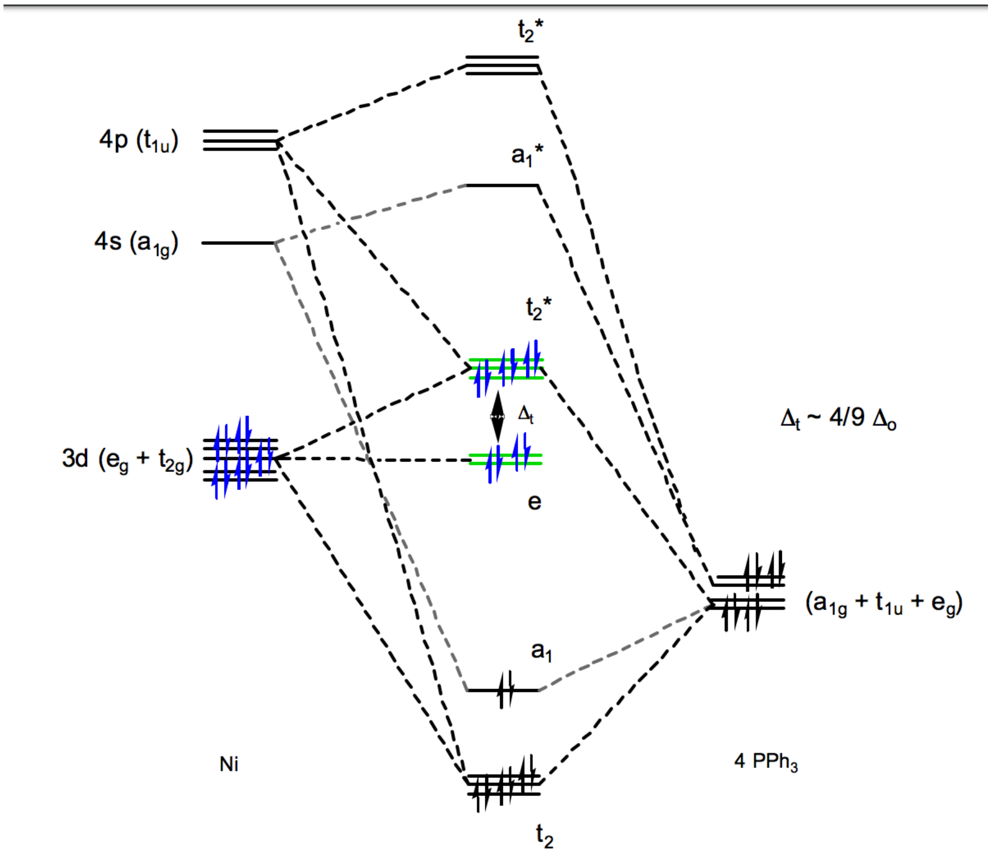
Here, *t2g* is strongly bonding and is filled and, *eg* is strongly antibonding, and empty. Complexes of this kind tend to obey the 18-electron rule irrespective of their coordination number. Exceptions exist for *d*8, *d*10

systems (see below)

II. Tetrahedral Complexes

e.g. [Ni(PPh3)4]

(Ni0, *d*10 18-electron complex



Tetrahedral complexes cannot exceed 18 electrons because there are no low lying MOs that can be filled to obtain tetrahedral complexes with more than 18 electrons. In addition, a transition metal complex with the maximum of 10 d-electrons, will receive 8 electrons from the ligands and end up with a total of 18 electrons.

Violations of 18 electron rule

I. Bulky ligands : (eg. Ti(neopentyl)4

has 8 electrons) Bulky ligands prevent a full complement of ligands to assemble around the metal to satisfy the 18 electron rule.

Additionally, for early transition metals, (e.g in $d0$

systems), it is often not possible to fit the number of ligands necessary to reach 18 electrons around the metal. (eg. tungsten hexamethyl, see below)

II. Square Planar $d8$ complexes (16 electrons) and Linear $d10$ complexes (14 electrons)

For square planar complexes, $d8$

metals with 4 ligands, gives 16-electron complexes. This is commonly seen with metals and ligands high in the spectrochemical series

For instance, Rh+,Ir+,Pd2+,Pt2+

) are square planar. Similarly, Ni2+ can be square planar, with strong π

-acceptor ligands.

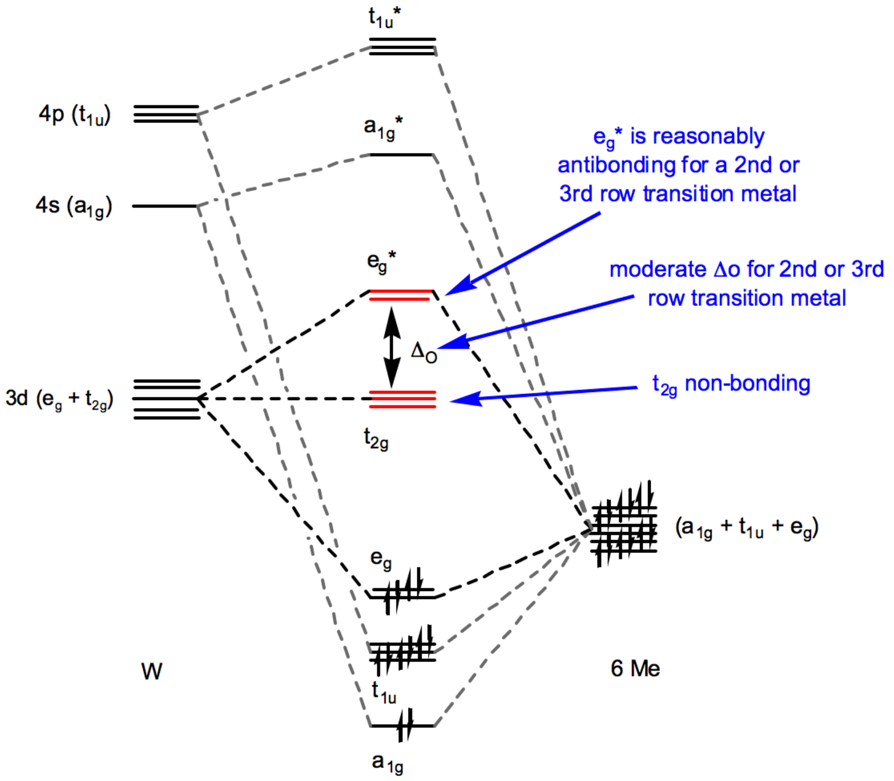
Similarly, $d10$

metals with 2 ligands, give 14-electron complexes. Commonly seen for for Ag+,Au+,Hg2+

III. Octahedral Complexes which disobey the 18 electron rule, but still have fewer than 18 electrons (12 to 18)

This is seen with second and third row transition metal complexes, high in the spectrochemical series of metal ions with σ

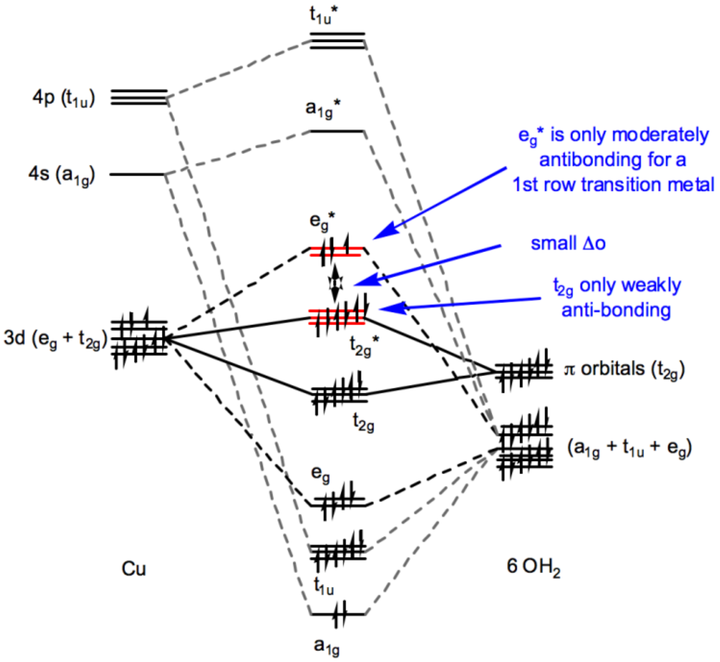
-donor or π-donor ligands (low to medium in the spectrochemical series). $t2g$ is non-bonding or weakly anti-bonding (because the ligands are either σ-donor or π-donor), and *t2g* usually contains 0 to 6 electrons. On the other hand, *eg* are strongly antibonding, and thus are empty.



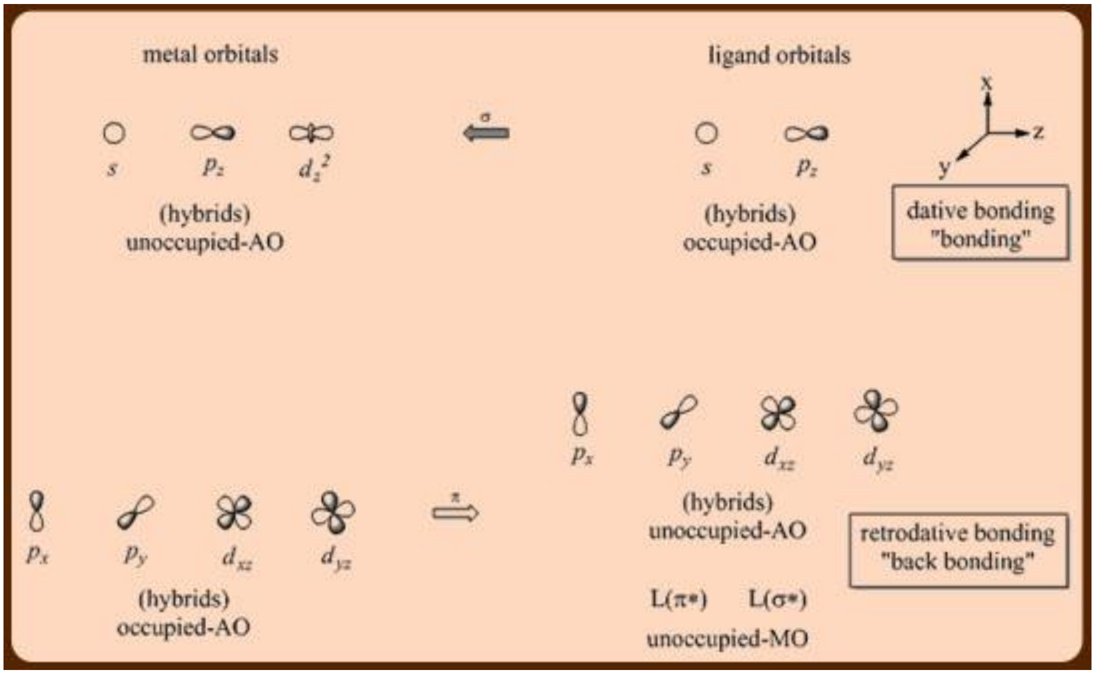
IV. Octahedral Complexes which exceed 18 electrons (12 to 22)

This is observed in first row transition metal complexes that are low in the spectrochemical series of metal ions, with σ

-donor or π-donor ligands Here, the *t*2*g* is non-bonding or weakly anti-bonding, but the *eg* are only weakly antibonding, and thus can contain electrons. Thus, 18 electrons maybe exceeded.

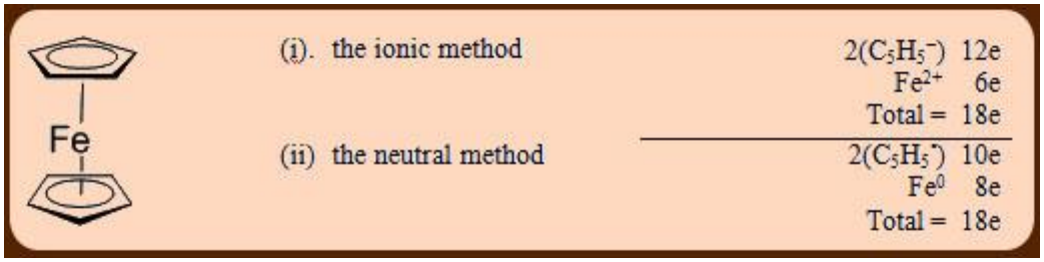


The transition metal organometallic compounds exhibit diverse structural variations that manifest in different chemical properties. Many of these transition metal organometallic compounds are primarily of interest from the prospectives of chemical catalysis. Unlike the main group organometallic compounds, which use mainly *ns* and *np* orbitals in chemical bonding, the transition metal compounds regularly use the $(n-1)d$, *ns* and *np* orbitals for chemical bonding (Figure 1). Partial filling of these orbitals thus render these metal centers both electron donor and electron acceptor abilities, thus allowing them to participate in σ-donor/π-acceptor synergic interactions with donor-acceptor ligands like carbonyls, carbenes, arenes, isonitriles and etc,.



The 18 Valence Electron (18 VE) Rule or The Inert Gas Rule or The Effective Atomic Number (EAN) Rule: The 18-valence electron (VE) rule states that thermodynamically stable transition metal compounds contain 18 valence electrons comprising of the metal *d* electrons plus the electrons supplied by the metal bound ligands. The counting of the 18 valence electrons in transition metal complexes may be obtained by following either of the two methods of electron counting, (*i*). the ionic method and (*ii*). the neutral method. Please note that a metal-metal bond contributes one electron to the total electron count of the metal atom. A bridging ligand donates one electron towards bridging metal atom.

Example 1: Ferrocene $Fe(C_5H_5)_2$



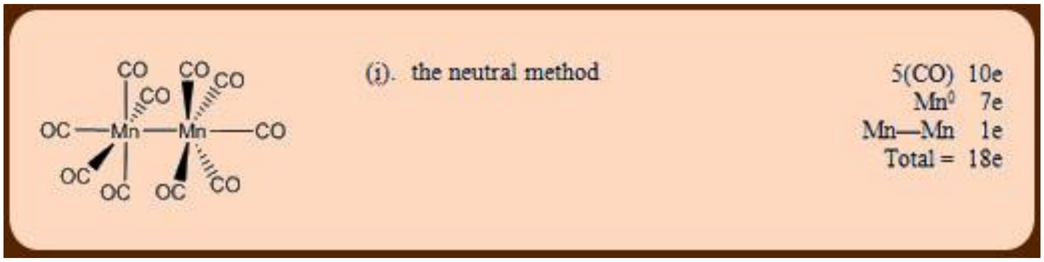
(i). the ionic method

$2(C_5H_5^-)$ 12e
Fe^{2+} 6e
Total = 18e

(ii) the neutral method

$2(C_5H_5^{\cdot})$ 10e
Fe^0 8e
Total = 18e

Example 2. $Mn_2(CO)_{10}$



(i). the neutral method

5(CO)	10e
Mn^0	7e
Mn—Mn	1e
Total =	18e

Transition metal organometallic compounds mainly belong to any of the three categories.

a. **Class I** complexes for which the number of valence electrons do not obey the 18 VE rule.
b. **Class II** complexes for which the number of valence electrons do not exceed 18.
c. **Class III** complexes for which the valence electrons exactly obey the 18 VE rule.

The guiding principle which governs the classification of transition metal organometallic compounds is based on the premise that the antibonding orbitals should not be occupied; the nonbonding orbitals may be occupied while the bonding orbitals should be occupied.

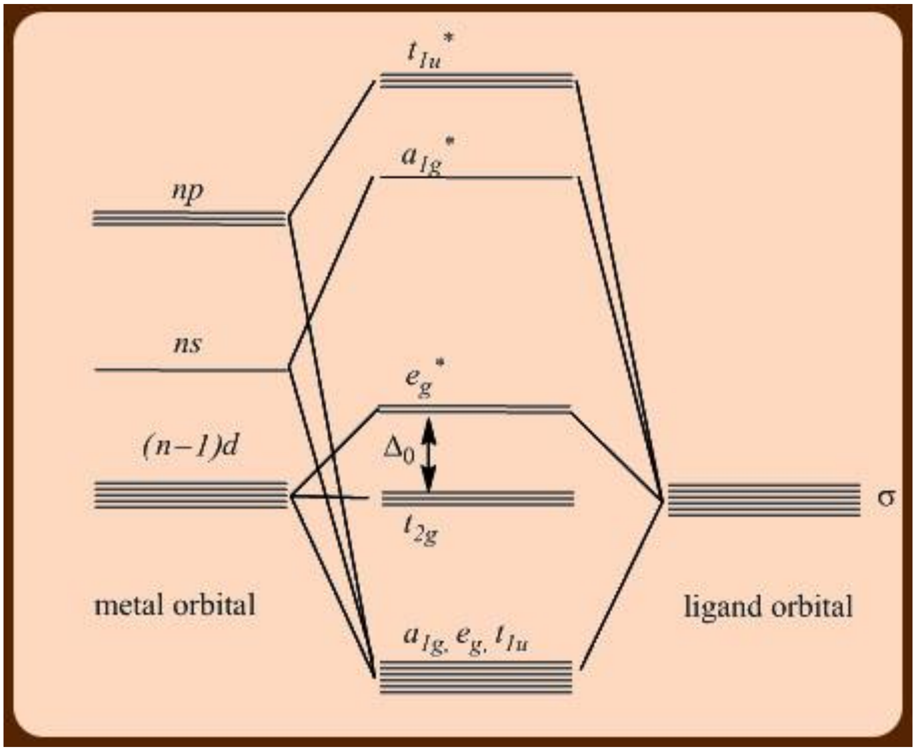


Figure 2. A simplified molecular orbital diagram for an octahedral transition metal complex showing σ−interactions only.

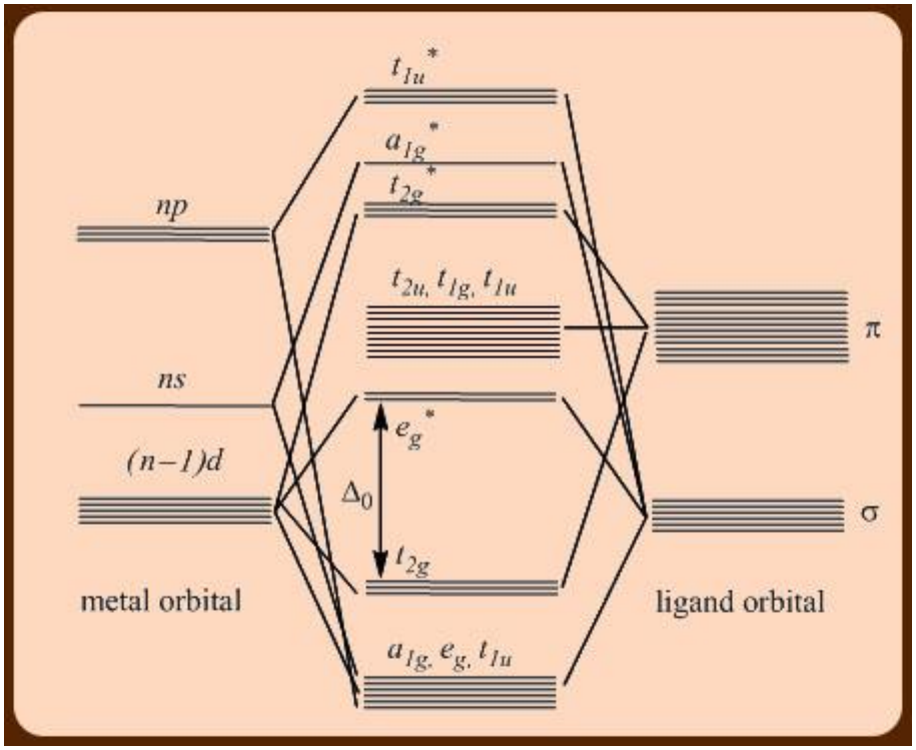


Figure 3. A simplified molecular orbital diagram for an octahedral transition metal complex showing σ−and π−interactions only.

Class I:

In **class I** complexes, the Δ_o splitting is small and often applies to *3d* metals and σ ligands at lower end of the spectrochemical series. In this case the t_{2g} orbital is nonbonding in nature and may be occupied by 0−6 electrons (Figure 2). The e_g* orbital is weakly antibonding and may be occupied by 0−4 electrons. As a consequence, 12−22 valence electron count may be obtained for this class of compounds. Owing to small Δ_{tetr} splitting energy, the tetrahedral transition metal complexes also belongs to this class.

Class II:

In **class II** complexes, the Δ_o splitting is relatively large and is applicable to *4d* and *5d* transition metals having high oxidation state and for σ ligands in the intermediate and upper range of the spectrochemical series. In this case, the t_{2g} orbital is essentially nonbonding in nature and can be filled by 0−6 electrons (Figure 3). The e_g* orbital is strongly antibonding and is not occupied at all. Consequently, the valence shell electron count of these type of complexes would thus be 18 electrons or less.

Class III:

In **class III** complexes, the Δ_o splitting is the largest and is applicable to good σ donor and π acceptor ligands like CO, PF_3, olefins and arenes located at the upper end of the spectrochemical series. The t_{2g}orbital becomes bonding owing to interactions with ligand orbitals and should be occupied by 6 electrons. The e_g* orbital is strongly antibonding and therefore remains unoccupied.

Problems

State the oxidation state of the metal and the total valence electron count of the following species.

1. $V(C_2O_4)_3^{3-}$

Ans: +3 and 14 2. $Mn(acac)_3$ Ans: +3 and 16 3. $W(CN)_8^{3-}$ Ans: +5 and 17 4. $CpMn(CO)_3$ Ans: 0 and 18 5. $Fe_2(CO)_9$ Ans: 0 and 18 Self Assessment test

State the oxidation state of the metal and the total valence electron count of the following species.

1. TiF_6^{2-}

Ans: +4 and 12 2. $Ni(en)_3^{2+}$ Ans: +2 and 20 3. $Cu(NH_3)_6^{2+}$ Ans: +2 and 21 4. $W(CN)_8^{4-}$ Ans: +4 and 18 5. $CH_3Co(CO)_4$ Ans: 0 and 18

Summary

The transition metal complexes may be classified into the following three types. (i). The ones that do not obey the 18 valence electron rule are of class I type (ii). the ones that do not exceed the 18 valence electron rule are of class II and (iii). the ones that strictly follow the 18 valence electron rule. Depending upon the interaction of the metal orbitals with the ligand orbitals and also upon the nature of the ligand position in spectrochemical series, the transition metal organometallic compounds can form into any of the three categories.

The 18-electron rule is used primarily for predicting and rationalizing formulae for stable metal complexes, especially organometallic compounds. The rule is based on the fact that the valence shells of transition metals consist of nine valence orbitals (one s orbital, three p orbitals and five d orbitals), which collectively can accommodate 18 electrons as either bonding or nonbonding electron pairs. This means that, the combination of these nine atomic orbitals with ligand orbitals creates nine molecular orbitals that are either metal-ligand bonding or non-bonding. When a metal complex has 18 valence electrons, it has achieved the same electron configuration as the noble gas in the period. The rule and its exceptions are similar to the application of the octet rule to main group elements.

This rule applies primarily to organometallic compounds, and the 18 electrons come from the 9 available orbitals in d orbital elements (1 s orbital, 3 p orbitals, and 5 d orbitals). The rule is not helpful for complexes of metals that are not transition metals, and interesting or useful transition metal complexes will violate the rule because of the consequences deviating from the rule bears on reactivity. If the molecular transition metal complex has an 18 electron count, it is called **saturated**. This means that additional ligands cannot bind to the transition metal because there are no empty low-energy orbitals for incoming ligands to coordinate. If the molecule has less than 18 electrons, then it is called **unsaturated** and can bind additional ligands.

Electron counting

Two methods are commonly employed for electron counting:

1. Neutral atom method: Metal is taken as in zero oxidation state for counting purpose
2. Oxidation state method: We first arrive at the oxidation state of the metal by considering the number of anionic ligands present and overall charge of the complex

To **count electrons** in a transition metal compound:

1. Determine the oxidation state of the transition metal and the resulting d-electron count.
    - Identify if there are any overall charges on the molecular complex.
    - Identify the charge of each ligand.
2. Determine the number of electrons from each ligand that are donated to the metal center.
3. Add up the electron counts for the metal and for each ligand.

Typically for most compounds, the electron count should add up to 18 electrons. However, there are many exceptions to the 18 electron rule, just like there are exceptions to the octet rule.

Reactivity

The 18 electron rule allows one to predict the reactivity of a certain compound. The associative mechanism means that there is an addition of a ligand while a dissociative mechanism means that there is a loss of a ligand. When the electron count is less than 18, a molecule will most likely undergo an associative reaction. For example: $(C_2H_4)PdCl_2$

- 16 electron count
- Would it more likely lose a C_2H_4 or gain a CO? Losing a C_2H_4 results in a 14 electron complex while gaining a CO gives an 18 electron complex. From the 18 electron rule, we will expect that the compound will more likely undergo an associative addition of CO.

Example 24.3.1

:

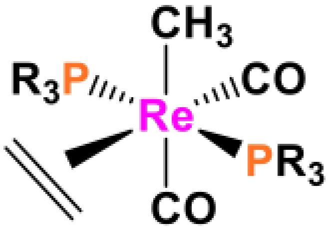


Figure 24.3.1

: Saturated Re metal complex with 18 electron count. Image used with permission (CC SA-BY 4.0; Derrekli)

1. There is no overall charge on the molecule and there is one anionic ligand (CH_3^-)
    - The Re metal must have a positive charge that balances out the anionic ligand charge to equal the 0 overall molecular charge. Since there is a -1 charge contribution from the methyl ligand, the Re metal has a +1 charge.
    - Because the Re metal is in the +1 oxidation state, it is a d^6 electron count. It would have been its regular d^7 electron count if it had a neutral (0) oxidation state.
2. The CH_3^- ligand contributes 2 electrons. Each CO ligand contributes 2 electrons. Each PR_3 ligand contributes 2 electrons. The H2C=CH2 ligand contributes 2 electrons.
3. Adding up the electrons:
    - Re(1): 6 electrons
    - CH_3^-: 2 electrons
    - 2 x CO: 2 x 2 electrons = 4 electrons
    - 2 x PR_3: 2 x 2 electrons = 4 electrons
    - $H_2C=CH_2$: 2 electrons
    - Total: 18 electrons

In this example, the molecular compound has an 18 electron count, which means that all of its orbitals are filled and the compound is stable.

Example 24.3.2

: $[M(CO)_7]^+$

The 18 electron rule can also be used to help identify an unknown transition metal in a compound. Take for example $[M(CO)_7]^+$. To find what the unknown transition metal M is, simply work backwards:

1. 18 electrons
2. Each (CO) ligand contributes 2 electrons
    - 7 x 2 electrons = 14 electrons
3. 18 - 14 = 4 electrons
4. d^4
5. M(I) oxidation state
6. The unknown metal M must be V, Vanadium

Example 24.3.3

: $[Co(CO)_5]^z$

Similarly to Example 2, the 18 electron rule can also be applied to determine the overall expected charge of an molecule. Take for example $[Co(CO)_5]^z$. To find the unknown charge z:

1. 18 electrons
2. Each CO ligand contributes 2 electrons
    1. 5 x 2 electrons = 10 electrons
3. Co is typically d^9
4. 9 + 10 = 19 electrons
5. To satisfy the 18 electron rule, the $[Co(CO)_5]^z$ compound must have a charge of z = +1.

Ligand Contributions

Below is a list of common organometallic ligands and their respective electron contributions.

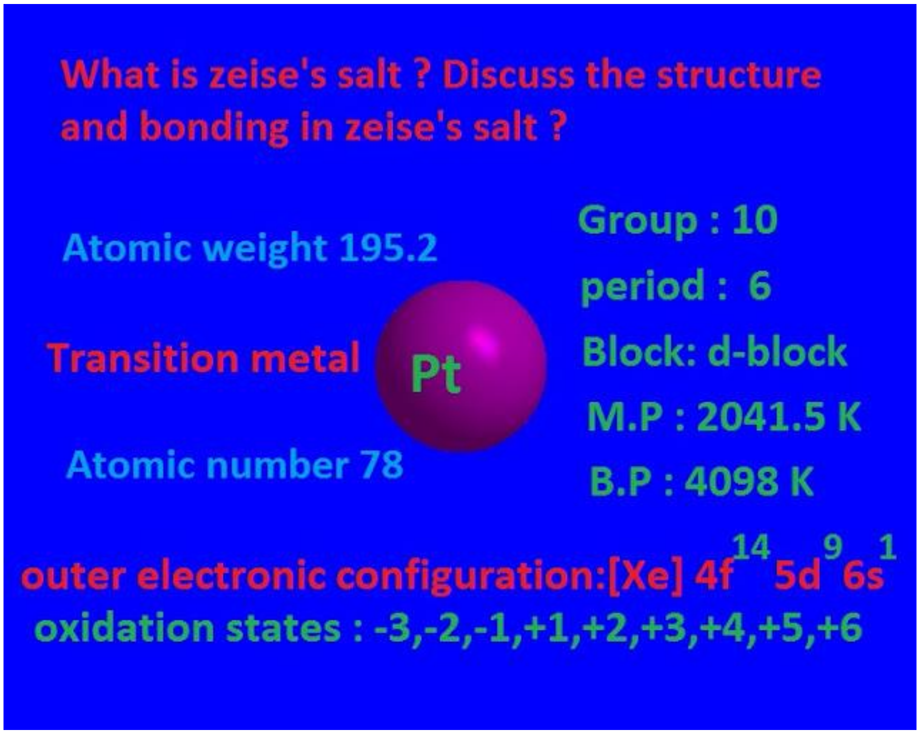
Neutral 2e donors	**Anionic 2e donors**	**Anionic 4e donors**	**Anionic 6e donors**
PR_3 (phosphines)	X^- (halide)	$C_3H_5^-$ (allyl)	Cp^- (cyclopentadienyl)
CO (carbonyl)	CH_3^- (methyl)	O^{2-} (oxide)	O^{2-} (oxide)
alkenes	CR_3^- (alkyl)	S^{2-} (sulfide)	
alkynes	Ph^- (phenyl)	NR^{2-} (imide)	
nitriles	H^- (hydride)	CR_2^{2-} (alkylidene)	
	R_nE^- (silyl, germyl, alkoxo, amido etc.)	OR^- (alkoxide, bridging ligand)	
		SR^- (thiolate, bridging ligand)	
		NR_2^- (inorganic amide, bridging ligand)	
		PR_2^- (phosphide, bridging ligand)	

Exceptions

Generally, the early transition metals (group 3 to 5) could have an electron count of 16 or less. Middle transition metals (group 6 to group 8) commonly have 18 electron count while late transition metals (group 9 to group 11) generally have 16 or lower electron count. When a structure has less than an 18 electron count, it is considered electron-deficient or coordinately unsaturated. This means that the compound has empty valence orbitals, making it electrophilic and extremely reactive. If a structure has "too many electrons," that means that not all of the bonds are covalent bonds, and thus some has to be ionic bonds. These bonds are weaker compared to covalent bonds. However, these organometallic compounds that have an electron count greater than 18 are fairly rare.

Zeise’s Salt

Platinum (Pt) , a 4d transition metal, which forms a large number of organo- metallic compounds . **Zeise’s salt** is one of them. The salts containing the ion [$C_2H_4PtCl_3$] $^{-1}$ are known as **Zeise’s salt** after the name of discover such salts may be $K[C_2H_4PtCl_3]$, $Na[C_2H_4PtCl_3]$, $NH_4[C_2H_4PtCl_3]$ etc.



What is zeise's salt ? Discuss the structure and bonding in zeise's salt ?

Atomic weight 195.2

Transition metal

Atomic number 78

Group : 10

period : 6

Block: d-block

M.P : 2041.5 K

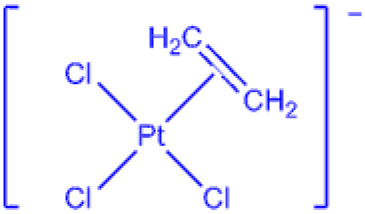
B.P : 4098 K

outer electronic configuration:[Xe] $4f^{14}\ 5d^{9}\ 6s^{1}$

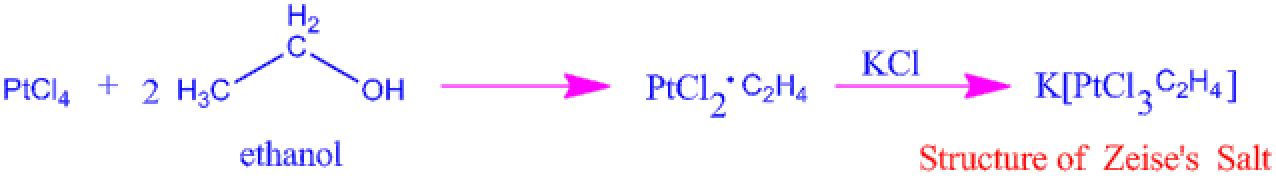
oxidation states : -3,-2,-1,+1,+2,+3,+4,+5,+6

Preparation of Zeise’s salt :

When platinum tetra chloride is react with ethanol an adduct is formed , which react with KCl gives **Zeise’s salt.** The following two method for preparation of **Zeise’s salt** are shown below,



Structure of Zeise's Salt



Structure of Zeise's Salt

$$K_2PtCl_4 \xrightarrow[\text{in HCl medium}]{C_2H_4 \text{ is passed}} K[PtCl_3C_2H_4]$$

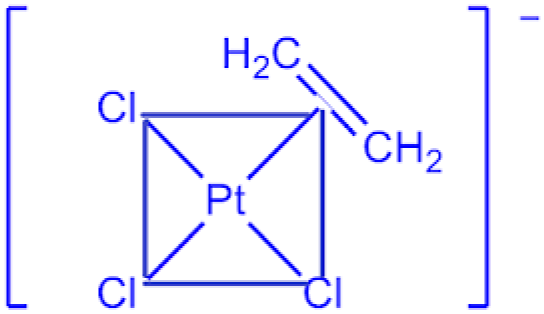
Structure of Zeise's Salt

The nature of bonding in such olefinic compound like **Zeise's salt** is still imperfectly understood, but it is clear that localized σ-bond between the metal atoms and carbon do not exist.

The is generally attributed to the interaction between π-electrons in the unsaturated molecule and the hybrid orbitals of metal atom.

Several olefin complexes have been studied by X-ray diffraction method.

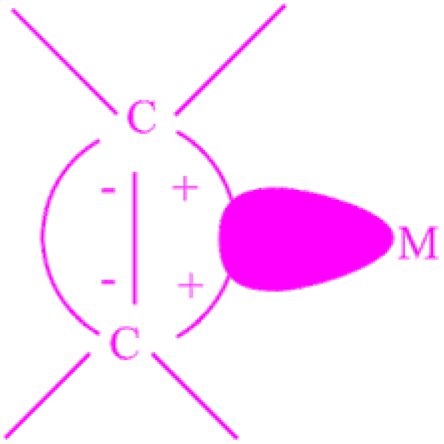
In complexes such as $[C_2H_4PtCl_2]_2$ and $[(C_2H_4)_2RhCl]_2$ the coordinated double bond is normal to the coordination plane and similar in the case for **$[C_2H_4PtCl_3]^{-1}$ ion.**



Structure of Zeise's Salt

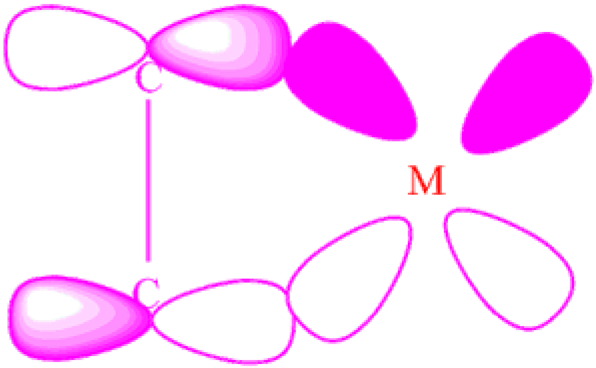
The bonding in **Zeise's salt** can be explained by the molecular orbital (M.O) approach. The theory assumes that the metal to olefin bond consists of two parts.

(I)overlap of the π-electron density of the olefin with a **σ-type acceptor** orbital on the metal atom.



Donation from filled π-orbitals to vacant metal orbital.

(II)A back bonding resulting from flow of electron density from filled metal dπ orbital into antibonding vacant orbitals of C-atom .



Back bonding from filled metal
orbital to accept π* orbitals

This view is similar to bonding in carbonyls , but some how different from that and this is known a μ-bonding.

Why the C –C olefinic bond length in Zeise's salt is greater than the C –C bond in free hydrocarbon ?

In Zeise's salt back bonding also takes place from suitable filled metal dπ orbital into the vacant antibonding π*orbital on the carbon atom. In the free C_2H_4 molecule, the C –C bond order should decrease .

As a consequence, the C –C bond length in **Zeise's salt** increases from free C_2H_4 molecule (1.34 Å) to coordinated **C_2H_4 molecule (1.4 -1.47 Å) .**

Why the ethylene molecule is perpendicular to the $PtCl_3$ molecular plane in Zeise's salt ?

In **Zeise's salt** the metal ion , Pt(II) contains three π-type filled d-orbital which are **d_{xy}, d_{yz}, and d_{xz}.**

When the coordinated ethylene molecule lies perpendicular to the molecular plane , the back bonding may take place either through **d_{yz} or d_{xz}** filled orbitals , but it may take place only through d_{xy} filled orbital.

When **C_2H_4** molecule exists in the plane of the molecule . As a consequence, C_2H_4 molecule lies lies perpendicular to the **$PtCl_3$** molecular plane for better scope of back bonding .

Why Cl^- ion trans to the ethylene has the large Pt –Cl bond distance than the other two Pt –Cl bond distance in Zeise's salt?

The above fact can be explained with the help of trans orienting power of ligands.

The metal olefin bond has multiple bond character due to back bonding and due to this multiple bond character **(π-bonding effect)** decreases the metal –carbon bond length.

As a result, the metal chlorine bond trans to the ethylene molecule weakens, that is, Pt –Cl bond length increases.

But **Pt –Cl** bond character cis to C_2H_4 molecule is not affected due to this π-bonding.

Therefore , Pt –Cl distance trans to C_2H_4 is larger than the other two Pt –Cl bond distance .

Is the rotation of C_2H_4 molecule in Zeise's salt hampering the stability of the complex ?

From bonding in **Zeise's salt** it can be said that ethylene molecule can either lie on the same plane to which the $PtCl_3$ unit belongs on lie perpendicular to the plane of the molecule.

In each case back bonding is possible . In first case back bonding takes place through filled d_{xy} metal orbital and in the second case it may take place either through **d_{yz} or d_{xz} metal orbitals.**

Since in the second case possibility of such back bonding is greater and hence the stability is more .

Experimental measurement has shown that stability difference is of the order of 5 – 6 kcal per mole , that is, the energy barrier of **C_2H_4 molecule** is only 5 – 6 kcal per mole .
So it is clear from the above explanation that free rotation of C_2H_4 molecule is possible in **Zeise's salt .**

Since the discovery and structural characterization of the compound ferrocene [Fe(η-C_5H_5)$_2$] in the 1950s, there was a large amount of research done on metal sandwich compound chemistry. Geoffrey Wilkinson and Ernst Otto Fischer, who defined the appropriate structure of ferrocene (Figure 1), received the Nobel Nobel Prize in Chemistry in 1973 for their work on sandwich complexes chemistry.

Ferrocene is a p-complex in which reactions between the d-orbitals of the Fe^{2+} metal centre with the p-orbitals of the two planar cyclopentadienyl ligands ($C_5H_5^-$) form the metal-ligand bonds. Hence there is equal bonding of all the carbon atoms in the cyclopentadienyl rings to the central Fe^{2+} ion.

Ferrocene shows aromatic properties and is very stable. This article covers the synthesis of ferrocene and several reactions done with it as well as characterizing the products with NMR spectroscopy.

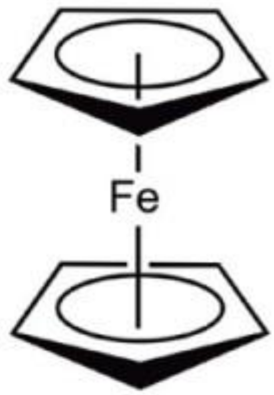


Figure 1. *Ferrocene [Fe(η-$C_5H_5)_2$]*

Preparation of Ferrocene

This experiment is done in two parts:

- Firstly freshly distilled cyclopentadiene (C_5H_6)is prepared
- Secondly, ferrocene is synthesized.

Both parts are done in the fumehood.

Safety

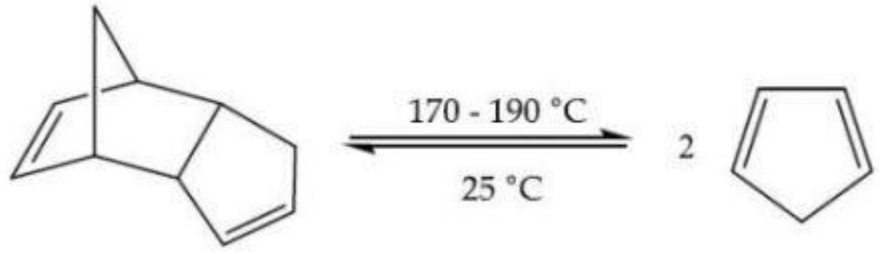
Most of the compounds, dicyclopentadiene, cyclopentadiene and 1,2-dimethoxyethane (DME) are toxic. While working with these compounds, one must take precautions to prevent contact with skin and breathe vapour.

Ferrocene Synthesis

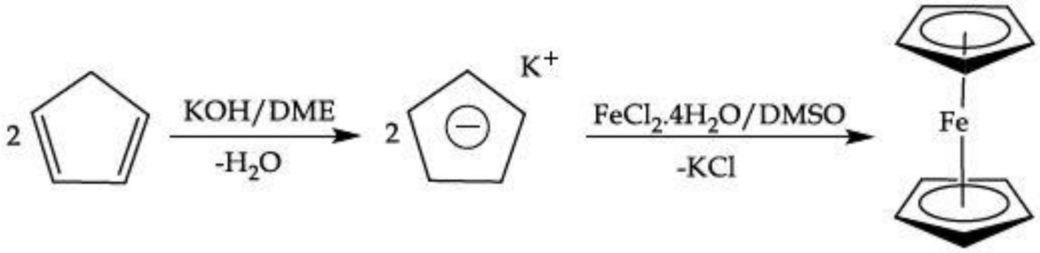
The method of synthesis is described below:

- A 250mL 3-neck round bottom flask having a dropping funnel, magnetic stirrer and nitrogen inlet is mixed with DME (50mL) and 4.25mL of freshly distilled cyclopentadiene (Figure 2).Stir the solution and flush with nitrogen.

- Take a 1mL aliquot for ^{1}H NMR. Add 20g finely ground KOH and stir the mixture vigorously for 15min to form a colored mixture, which includes the cyclopentadienyl anion.
- Take another 1mL aliquot for ^{1}H NMR and prepare a finely powdered $FeCl_2.4H_2O$ (5g) solution in 20mL of DMSO under nitrogen and transfer the solution into the dropping funnel.
- Add the iron(II) chloride solution slowly over a period of 30 min with efficient stirring
- Take a 1mL aliquot for ^{1}H NMR after 2/3 of the $FeCl_2$/ DMSO solution has been added, then another aliquot (1mL) at the end of addition.
- The reaction mixture is again stirred for 15min then the dark slurry is poured into a beaker containing crushed ice (80g) and hydrochloric acid (75mL, 6M).
- The mixture is thoroughly stirred to dissolve and neutralize any remaining KOH.
- Filter the precipitate and wash with water. Collect the crude orange ferrocene and dry in the air.
- Purify by sublimation to obtain orange crystalline material and record your yield as shown in Figure 3



***Equation 1**. Cracking of dicyclopentadiene*



Equation 2. *Formation of Ferrocene*

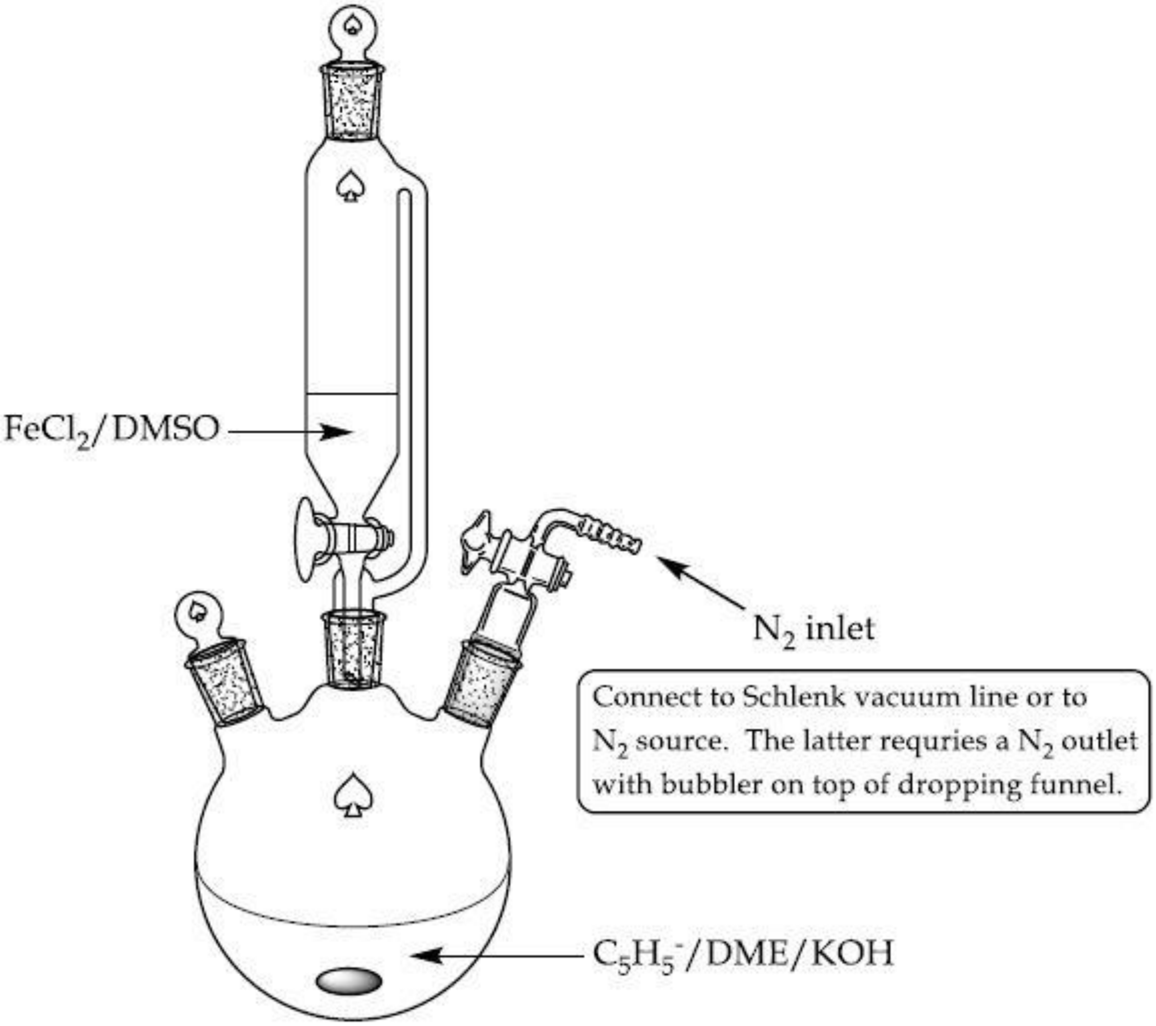


Figure 2. *Experimental setup for ferrocene synthesis*

Figure 3. *(a)-(b). Purification of crude ferrocene via sublimation. a) Crude ferrocene (b) Sublimed ferrocene*

The Spinsolve NMR spectrometer is used to monitor the different synthetic stages for preparing ferrocene. By studying the different aliquots collected during the synthetic procedure, the disappearance of reactants and formation of products can be observed. In Figure 4, the monomeric nature of cyclopentadiene (a and b), the formation of the cyclopentadienyl anion (c) and its disappearance and formation of ferrocene (d and e) are confirmed.

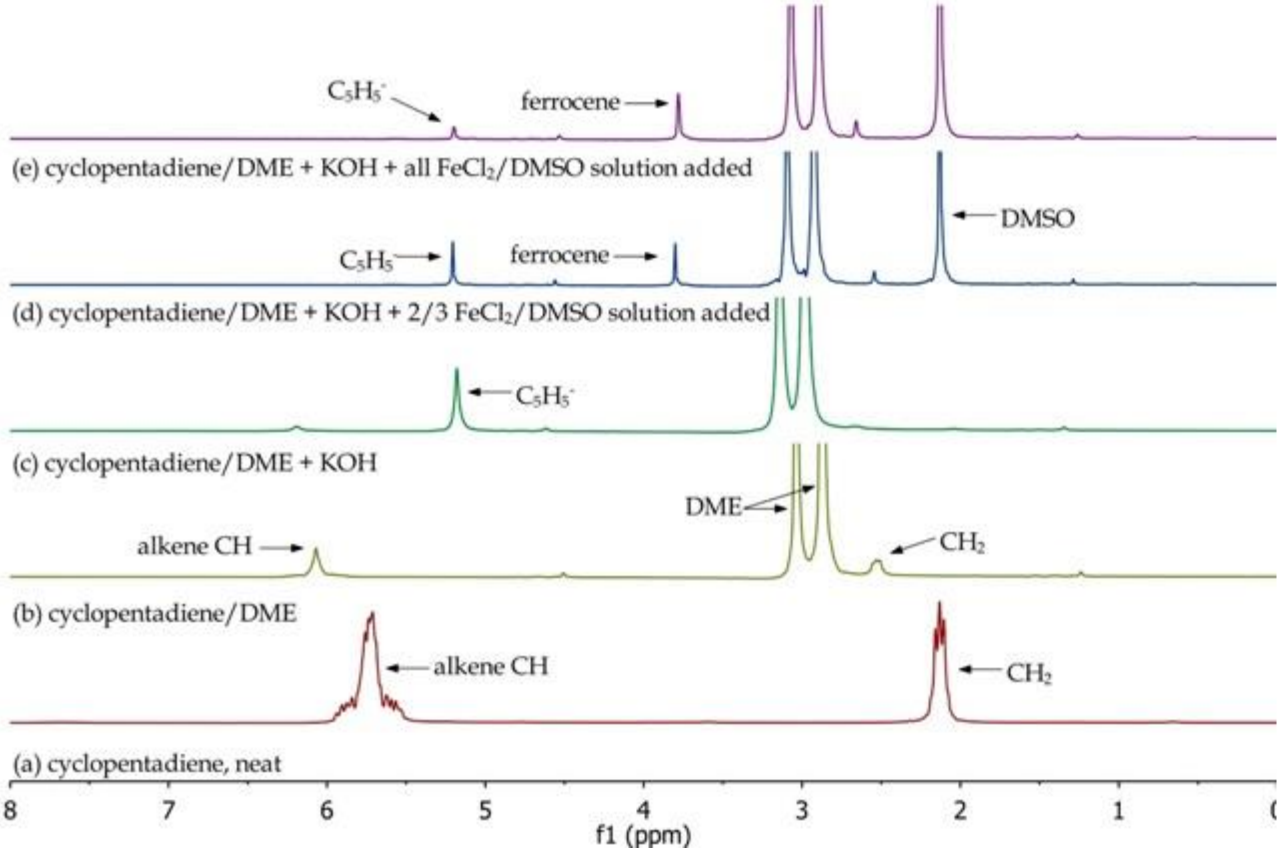


Figure 4. *Overlay of ^{1}H NMR spectra of reactants and reaction mixtures during the synthesis of ferrocene.*

The ^{1}H NMR spectrum of ferrocene (Figure 5) shows ten equivalent aromatic protons as a singlet at 4.16 ppm.

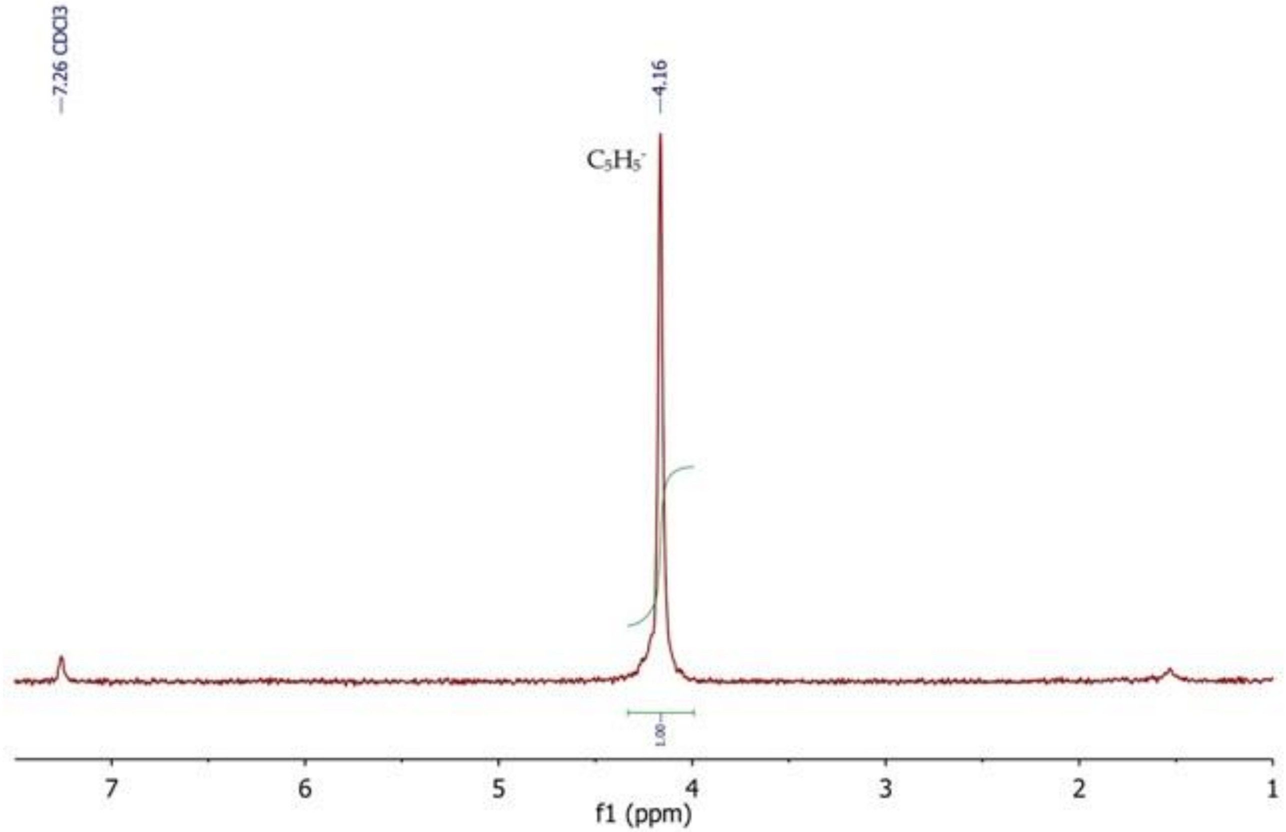


Figure 5. *^{1}H NMR spectrum of ferrocene, $[Fe(\eta\text{-}C_5H_5)_2]$, $CDCl_3$*

Acetylation of ferrocene

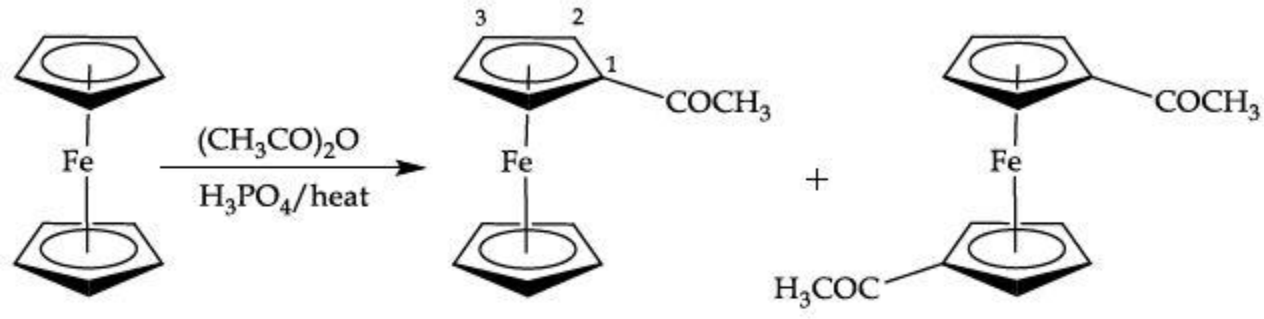
This experiment shows the Friedel-Crafts acylation reaction to obtain acetylateferrocene.

Acetylferrocene Synthesis

The synthesis of acetyl ferrocene is as follows:

- Charge a 25mL round bottom flask with ferrocene (1g) and acetic anhydride (3.3mL).
- Add phosphoric acid (0.7mL, 85%) and heat the reaction mixture on a hot water bath for 20min with stirring.
- Pour the hot mixture onto crushed ice (27g).

- After all the ice has melted, neutralize the solution with solid sodium bicarbonate and cool for a further 5min. Collect the brown precipitate by filtration, wash with water and dry in the air.
- The solid obtained is a mixture of unreacted ferrocene and the monosubstituted product acetylferrocene (Figure 6). However, a third compound may also be present in very small amounts as the disubstituted product of acetylation (1,1'-diacetylferrocene).



***Equation 3**. Preparation of acetylferrocene*

Figure 6 shows the ^{1}H NMR spectrum of acetylferrocene with five equivalent aromatic protons as a singlet at 4.19ppm for the unsubstituted cyclopentadienyl ring.

A singlet is observed at 2.39ppm (3H) corresponding to the acetyl methyl group. The substituted cyclopentadienyl ring protons are seen as a second order AA’BB’ system, with two multiplets centred at 4.49 and 4.77ppm, integrating for two protons each.

Figure 7 shows the COSY spectrum of acetylferrocene that protons at position 2 and 3 are in the same spin system, as in the substituted cyclopentadienyl ring.

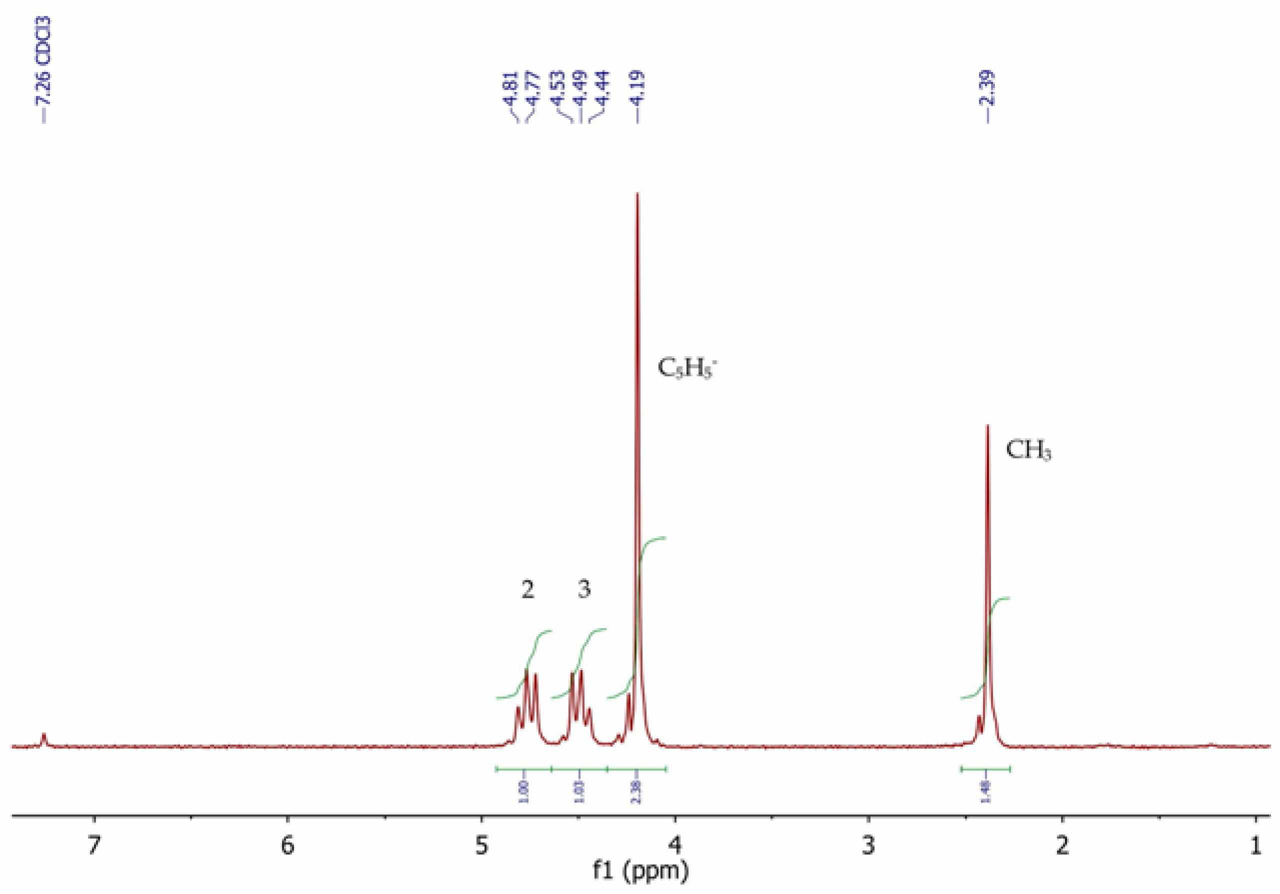


Figure 6. *^{1}H NMR spectrum of acetylferrocene, $CDCl_3$*

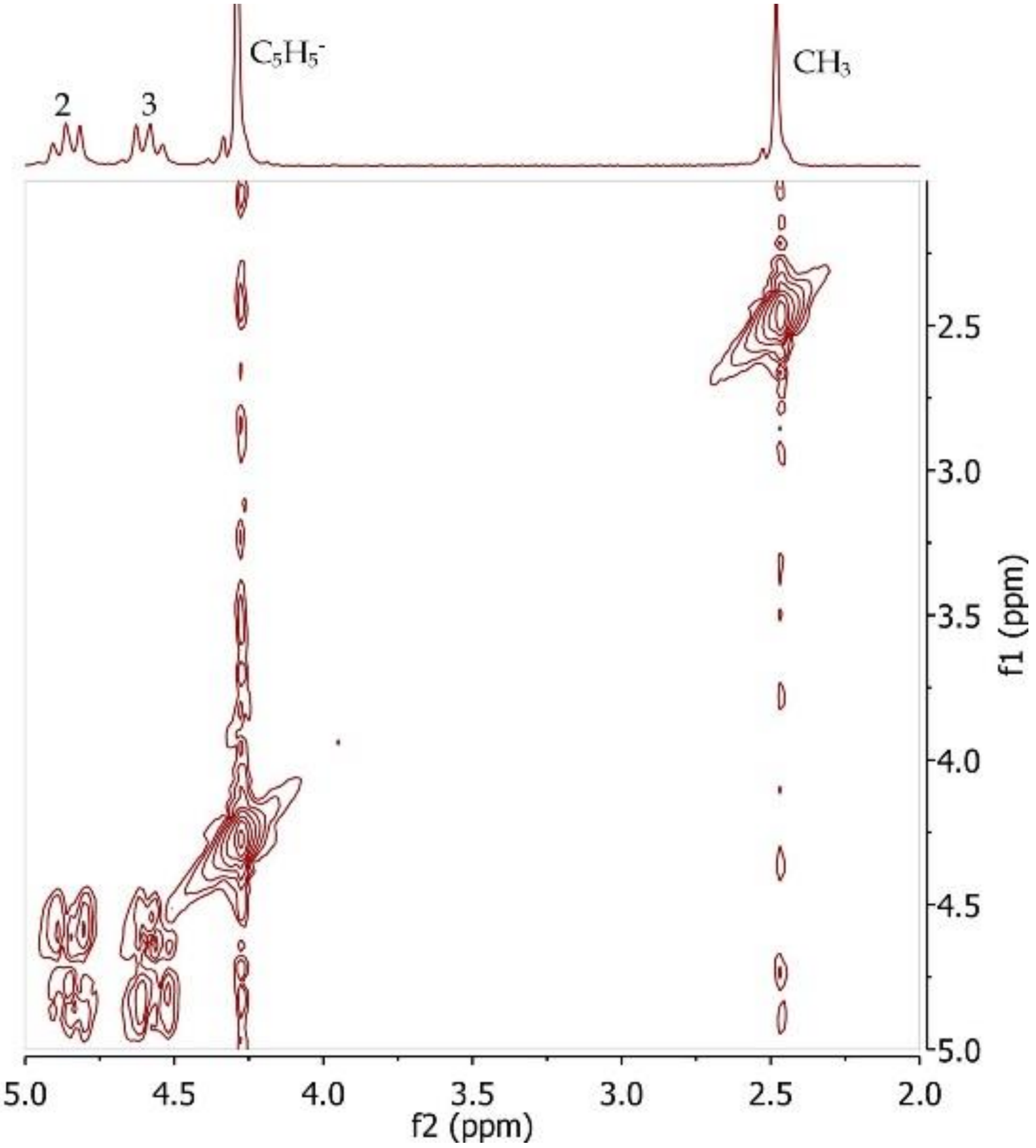


Figure 7. *COSY spectrum of acetylferrocene, $CDCl_3$. Refer to Equation 3 for the annotated structure.*

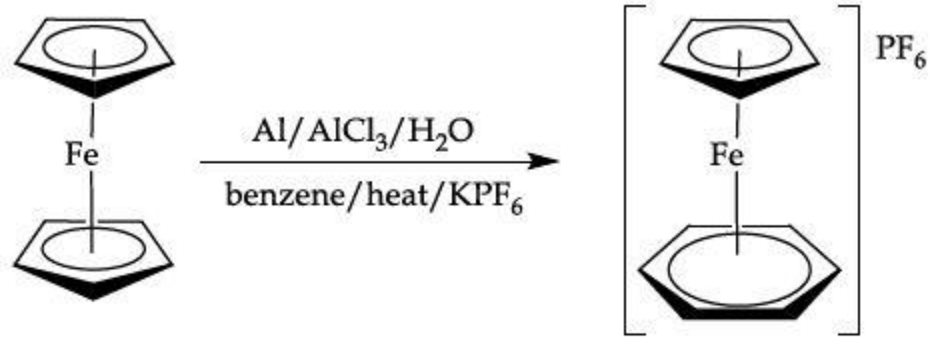
Preparation of [Fe(η-C_5H_5)(η-C_6H_6)]PF_6

This involves a ligand exchange reaction between one of the cyclopentadienyl rings in ferrocene and benzene to form a cationic iron p complex, which is then precipitated as the hexafluorophosphate (PF_6-)salt.

Synthesis of [Fe(η-C_5H_5)(η-C_6H_6)]PF_6

The synthesis method involves:

- 2.0g of ferrocene is dissolved in 10mL of benzene in a 50mL round bottom flask.
- With continuous stirring add aluminium powder (0.3g), $AlCl_3$ (4g) and water (0.2mL).
- Place a reflux condenser atop the flask and heat the reaction mixture under reflux for 45min with efficient stirring.
- Thorough mixing of the heterogeneous reaction mixture is vital to the success of this synthesis.
- Cool the dark brown mixture in an ice bath then add ice cold water (25 mL) cautiously as considerable heat is generated.
- Place the reaction mixture in a 100mL separating funnel. The aqueous layer is collected in a beaker and made up to 50mL with water.
- Finely ground KPF6 (2.5 g) is added and the mixture is stirred for 10min.
- The green precipitate is filtered, washed with some water, ethanol and diethyl ether and allowed to dry in the air.



***Equation 4**. Ligand exchange of ferrocene with benzene*

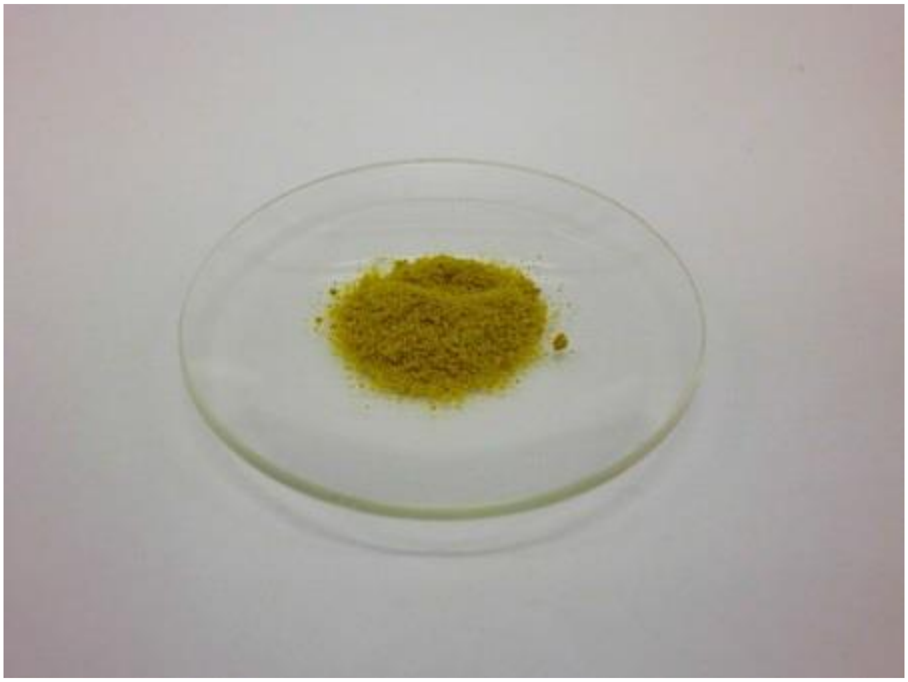


Figure 8. *[Fe(η-C_5H_5)(η-C_6H_6)]PF_6*

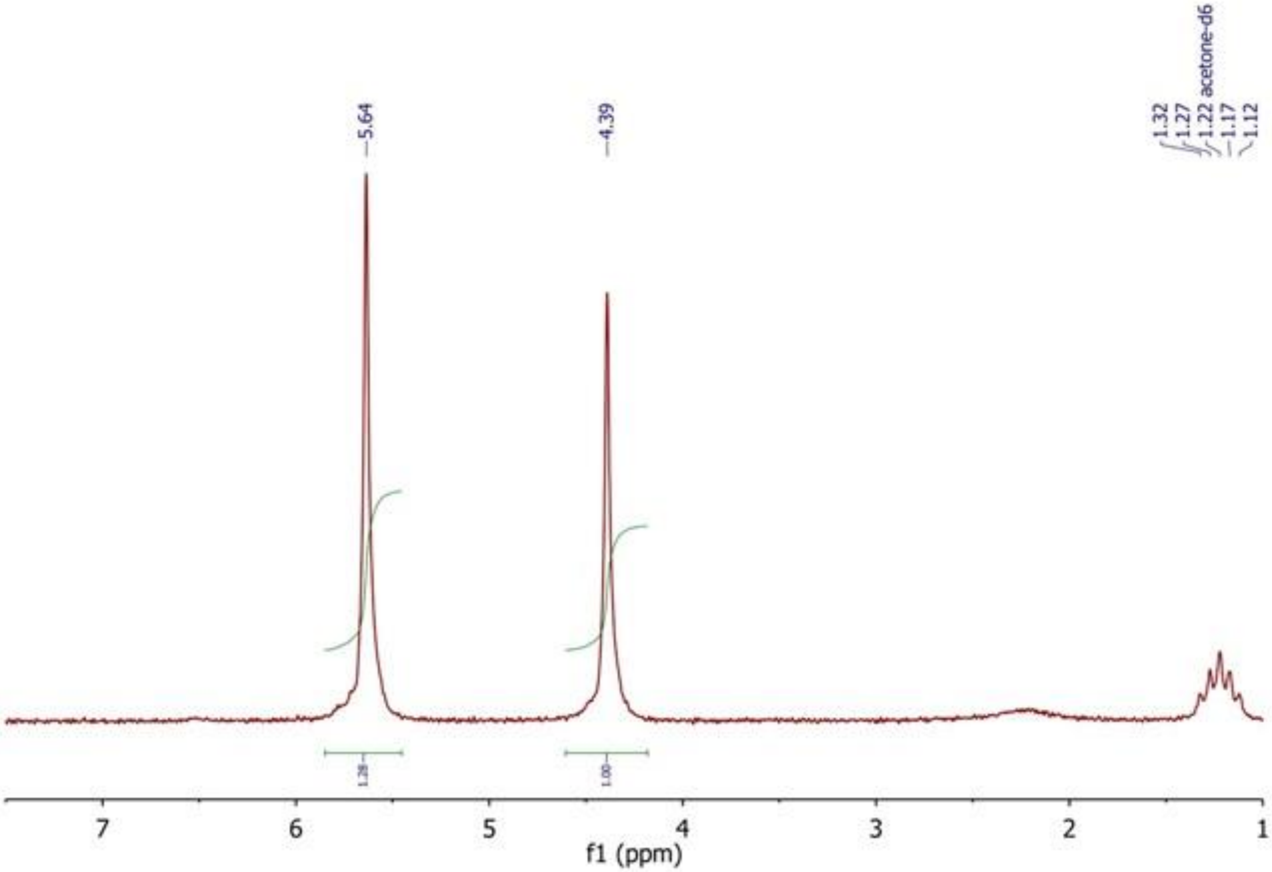


Figure 9. *^{1}H NMR spectrum of [Fe(η-C_5H_5)(η-C_6H_6)]PF_6 complex, acetone-d_6.*

Reaction of [Fe(η-C_5H_5)(η-C_6H_6)]PF_6 with Nucleophiles

The reaction of the iron benzene p-complex prepared in part 3 with $LiAlH_4$ and $LiAlD_4$, sources of H and D- ions respectively. Arenes, for instance benzene, are more susceptible to attack by electrophiles than nucleophiles. However, associating with a metal often alters the reactivity of organic ligands. Thus, the reactivity of the benzene ligand in the iron p-complex towards the nucleophiles H- and D- is examined.