A Second Year Blog on Benzene and the Friedel-Crafts' catalysts (for the week commencing the 27th of October 2019)

- Benzene has a melting point of 5.6°C therefore it is a (colourless) liquid at RTP. It is flammable volatile, toxic (inhalation will cause leukaemia and anaemia), and it is carcinogenic. Last year I told you that European chemists knew of the existence of Benzene in the first half of the 1800s (it was 'discovered' by the English scientist Michael Faraday in 1824), and in 1834 the German chemist Eilhard Mitscherlich worked out that its molecular formula was C_6H_6 – but (at that time) chemists were totally unaware of the **structural** formula of Benzene. One of the structures originally suggested for it was $CH_2=C=CH–CH=C=CH_2$, but Benzene does not have the properties that would be required for it to be a straight-chained Alkene. In 1865 it was then suggested by Kekulé that Benzene was a ring 'Alkene' and that it must therefore have three alternating single bonds and three double bonds. (However, I believe that there is a much earlier depiction of a Benzene ring in an Islamic scientific text from the Middle Ages[1], but sadly I cannot find it.)

- Double bonds are shorter than single bonds, and (from X-ray diffraction crystallography by Kathleen Lonsdale in the 1920s, mentored by the great Sir William Henry Bragg[2] and by Sir Christopher Ingold) we now know that all the bond lengths in Benzene *are exactly the same*, therefore we know that Benzene **CANNOT have alternating double and single bonds** because Benzene would then have to have sides of alternating lengths, and we know that all its sides are of the same length. (However, nothing was known about Resonance in those days.)

- We now know that Benzene exists as a Resonance structure, but it is often drawn as though it has alternating double and single bonds (as a cycloalkene with three double bonds might have), and in some circumstances Arenes[3] do *behave* like an Alkene (albeit at the higher temperatures and pressures that are needed to overcome the stability conferred by the delocalised π ring in Benzene).

- In addition, this apparent configuration of alternating double and single bonds is seen when Benzene and its derivatives behave like conjugated species. The entry for Benzene in Wikipedia below shows the proposals for the structure of Benzene by different chemists, and we now know that all of them were wrong (and we now know that Benzene has a delocalised π ring structure).

Historic benzene formulae (from left to right) by Claus (1867),[20] Dewar (1867),[21] Ladenburg (1869),[22] Armstrong (1887),[23] Thiele (1899)[24] and Kekulé (1865). Dewar benzene and prismane are different chemicals that have Dewar's and Ladenburg's structures. Thiele and Kekulé's structures are used today.

<— The representation on the right is **not** that of Kekulé. Kekulé's would have had to have sides of alternating lengths. I believe that the one on the right is that of Kathleen Lonsdale.

[1] In the Middle Ages when we in Europe were dressing up in suits of armour and killing each other (and slaughtering Muslims in the Crusades), **Muslim scholar**s were virtually the sole repository of almost every single piece of scientific knowledge in Europe. Sadly, from somewhere around the 13th century they then became distracted by belief rather than by **evidence**, and thus lost the position of scientific pre-eminence that they had earned. It was not until the 1700s that we in Europe began to understand that religious texts were not meant to be interpreted as scientific manuals, and thus was the 'scientific method' born in Europe.

[2] Very few Nobel Prizes have been won by both a father and his son. The only ones of which I am aware are the two Thomsons (JJ and GP) and the two Braggs (WH and WL).

[3] Arenes contain one or more Benzene rings.

NB The representation on the right on page 1 is not possible because, without Resonance, alternating double and single bonds **would give sides of unequal lengths** (cf. the diagram on page 3).
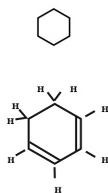
- I should however point out that even though Kekulé's proposition was a brilliant one, it was not until the giants of Physics and Chemistry in the early 20th century came along, that we at last understood the **true** nature of the structure of Benzene.

- In the second half of the 19th century, after Kekulé had posited his revolutionary theory about the ring structure of Benzene, and after chemists had begun to recognise the existence of double and triple bonds, chemists started to recognise that Benzene and its sister "aromatic" compounds (i.e. the Arenes) were *different* from the group of compounds that we now call Alkenes because Benzene and its sister compounds did not react in the same way as Alkenes. The classic tests for unsaturated compounds are the decolourisation of (i) Bromine water and (ii) $KMnO_4$ – and Benzene will do **neither** at RTP.

- As it happens, we now know that Arenes have **a delocalised π ring that gives them an extra amount of stability** when compared to Alkenes[4], and in a sense, the one thing that underlies all the things that we have talked about so far viz. Resonance/Inductive effects/Mesomeric effects/etc is Delocalisation, and it is this extra stability that prevents Arenes from reacting in exactly the same way as Alkenes[5]! **It is the delocalised π ring that makes Benzene what it is.**

- Although the Kekulé idea for Benzene, i.e. a closed ring with alternating double and single bonds, is incorrect (in fact *Benzene has a delocalised π ring structure and not alternating double and single bonds*) – nevertheless the alternating double and single bond way of drawing a Benzene ring is very frequently used in Chemistry (albeit with sides of equal length) in order to ask the reader to think of Benzene, in specific situations, as a conjugated species (i.e. a species with alternating double and single bonds).
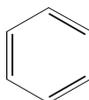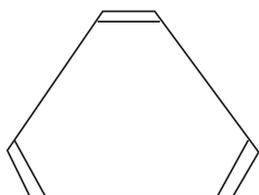

- **If (like an Alkene) Benzene had double bonds in it, then it would react with Bromine in an addition reaction – and this it does NOT do.**

- **It does NOT do so**, or at least it does not *readily* undergo Addition reactions (as Alkenes do) – and **it certainly does NOT decolourise Bromine water nor $KMnO_4$ in the dark at RTP**.

- **Benzene is thus not an Alkene! It may be Alkene's close-relative, but it is not an Alkene.**

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[4] Benzene is about 151 kJ mol^{-1} more stable than it would be if it had alternating double and single bonds.
[5] The great Linus Pauling also contributed to the understanding of the true nature of the configuration of Benzene when he did his work on Resonance in the 1930s.
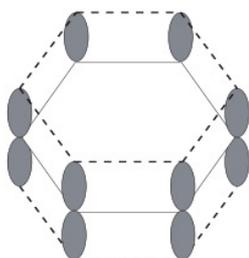
Please take careful note of the difference between Cyclohexane/ Cyclohexene/and Benzene – all of which species have six C atoms in their molecules, **but each one of these substances has different chemical properties**. [NB Here "cyclo" means "circular" or "in the form of a circle".] A **cyclohexane** is merely a hexane where the Carbon atoms at the opposite ends of the chain have joined together thus forming a circle or a ring – and please remember (when you are drawing the molecule) that each C atom can have only **four bonds**. The topmost molecule to the left of this text is cyclohexane, C_6H_{12}, *and please note that the standard **skeletal** diagram of carbon molecules does not show any of the H atoms, nor any of the C–H bonds.* Similarly a **cyclohexene** is a circular hexene, therefore it must have at least one double bond, and if it has more than one double bond, then the name must state that fact, and it must define the location of the double bonds. The name of an Alkene must be one which gives the smallest numbers for the location of the double bonds e.g. the molecule towards the top left of this text is 1,3-cyclohexadiene, (C_6H_8). *[In this diagram I have for clarity shown all the H atoms and the C–H bonds.]*

Shown below is the old-fashioned representation of Benzene in which only three pairs of unhybridised 'p' orbitals overlap, and there are alternating double and single bonds in the molecule. Kekulé's concept would have required long single bonds and shorter double bonds.

In the 19th century, scientists worked out that the molecular formula of Benzene was C_6H_6, and at first they did not realise that Benzene was a ring molecule; and, then in 1865, a scientist called Kekulé had the blinding insight that Benzene was a ring molecule with **alternating double and single bonds** (as in the diagram alongside this text). However, since a double bond must have a π bond (but Kekulé did not know anything about π bonds) and a π bond itself requires the **overlap** of two unhybridised 'p' orbitals, then it must follow that three pairs of neighbouring Carbon atoms had to be close enough for their unhybridised 'p' orbitals to overlap – but the other three pairs of neighbouring C atoms were NOT close enough for **their** orbitals to overlap. This meant that diagrams of Kekulé's molecule would have had to have three long sides and three short sides! Kekulé's concept was a brilliant idea; but, when scientists were later on able to measure the lengths of the sides of molecules, they discovered that ALL the sides of a Benzene molecule are **equal** in length – therefore Kekulé had not quite got it right, and (as we now know) Benzene has a resonance structure with a delocalised π ring.

The structure below represents the modern view of Benzene in which ALL the adjoining unhybridised 'p' orbitals overlap and there is therefore a continuous delocalised π ring above and below the ring of σ bonds.

Kekulé had not known anything about delocalised electrons and he had therefore not appreciated the true structure of Benzene. However, if all the sides of a Benzene molecule are equal in length and the unhybridised 'p' orbitals of every pair of adjoining C atoms overlap, then there would be SIX double bonds in Benzene (and Benzene could then not be C_6H_6). It was only THEN that scientists at last realised that the true structure of Benzene **was a ring molecule where all the sides are of equal length**, *and **all** the unhybridised 'p' orbitals (of adjoining C atoms) overlap* – BUT, instead of forming six double bonds, the electrons in the unhybridised 'p' orbitals become delocalised and are *shared* by ALL the Carbon atoms. **Therefore it is as though there is one big continuous π bond encircling the whole of the Benzene ring (above and below it)!** If you have a look at a 3-D model of a Benzene molecule (in your Chemistry lab at school/college) you will see exactly how it is constructed.

- Benzene does **not** have alternating double and single bonds – **but it behaves as though it does have them**!

- Let me show you the delocalisation stabilisation calculations given by the German website Chemgapedia. The amount of energy involved in the delocalisation of Benzene is shown as 150.7 kJ mol^{-1}.

   Diagram: The amount of energy that would be required to convert different double-bonded structures into cyclohexane.
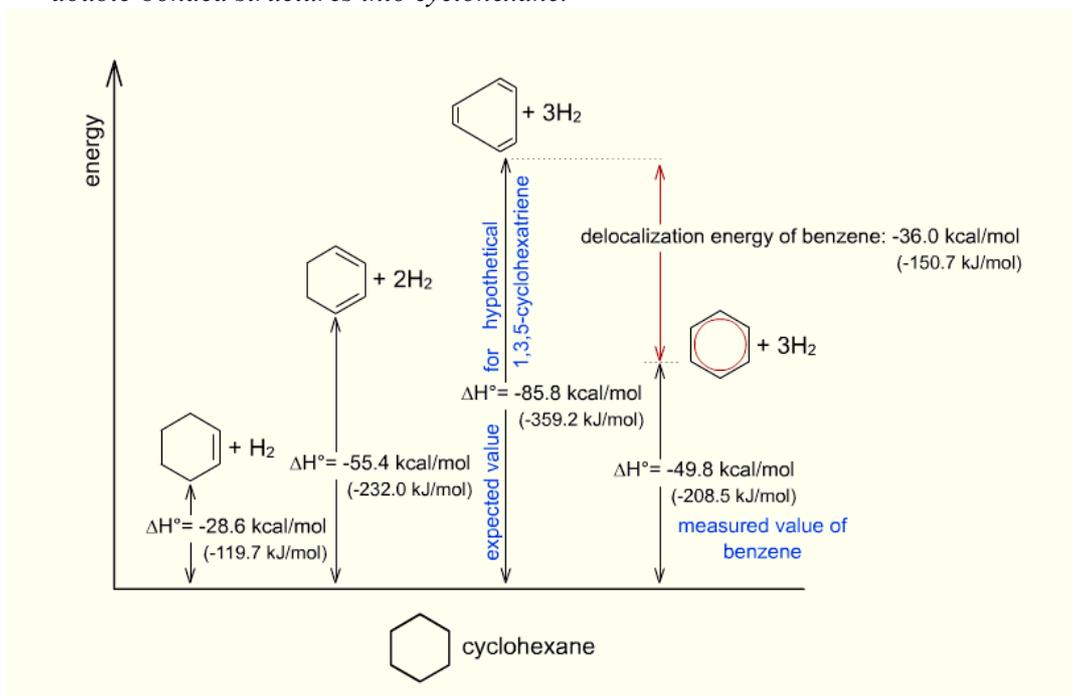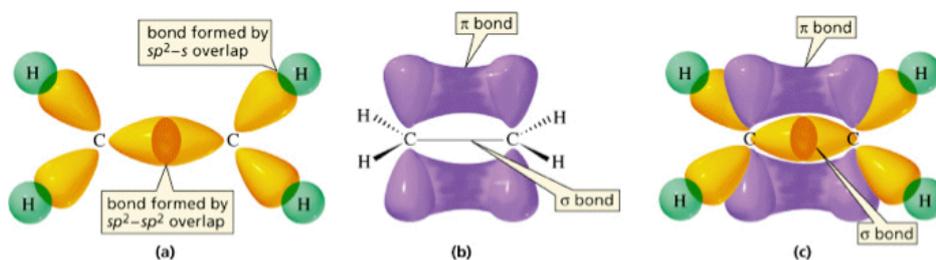

Source :
   http://www.chemgapedia.de/vsengine/vlu/vsc/en/ch/12/oc/vlu_organik/aromaten/aromaten/benzol_stabilitaet.vlu/Page/vsc/en/ch/12/oc/aromaten/aromaten/stabilitaet/stabilitaet.vscml.html

- We know today that Benzene has a ring structure where each one of the six C atoms has an unhybridised 'p' orbital that overlaps the unhybridised 'p' orbital of each of its two neighbours. This means that there is a continuous circle of overlapping unhybridised 'p' orbitals around the whole Benzene ring, and the six bonding electrons then cease to be located in one fixed spot between the overlapping orbitals of any two bonded Carbon atoms (as is the case with the two-carbon atom Ethene). Instead, the six electrons in Benzene become delocalised and are shared by **ALL** six of the Carbon atoms in the Benzene ring.

- Please compare the **fixed locus** of the two shared electrons in the π bond in Ethene and the six **delocalised** electrons in the π ring in Benzene. (The diagrams that follow have been taken from Professor Stephen Lower's excellent textbook.)

Linear LOCALISED π bond in Ethene

Source: http://www.chem1.com/acad/webtext/virtualtextbook.html)

Ring DELOCALISED π bond in Benzene
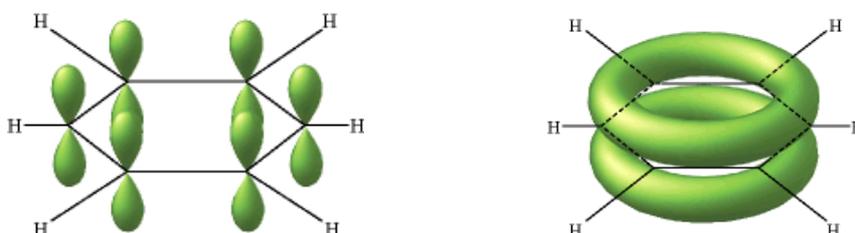
Fixed locus π electrons and delocalised π electrons

- According to one accepted usage of the term, a **conjugated** species is one where there are alternating single and double bonds in the species.[6] For example, Butadiene has two double bonds and two single bonds in it and, if we ignore the Resonance structures of Butadiene for the moment, then Butadiene is a conjugated Alkene with alternating double and single bonds as in any one of Dickerson & Geis' diagrams (B) to (E) of Butadiene overleaf, but if we were to take Butadiene's Resonance structures into account, then we would obtain a delocalised π structure over the whole of the Butadiene molecule as is shown in their first depiction, (A).
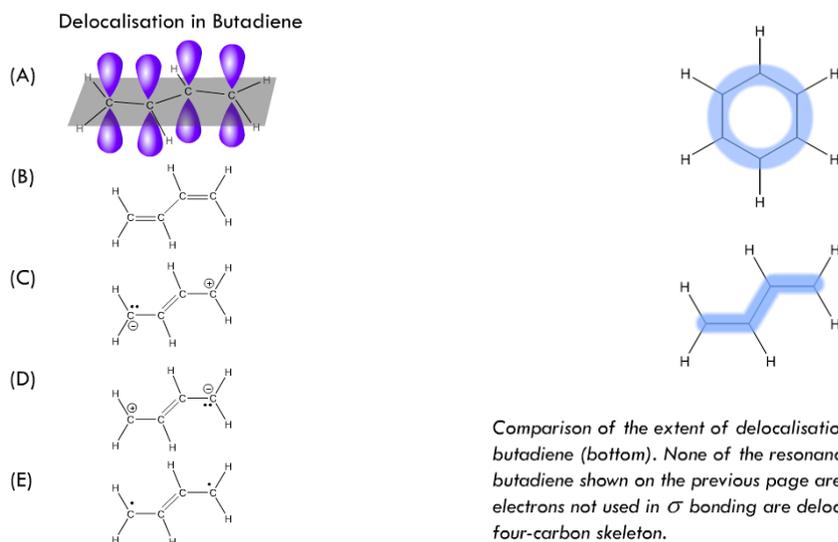
NB Butadiene is also found as a "dimer" (Source: Wikipedia)
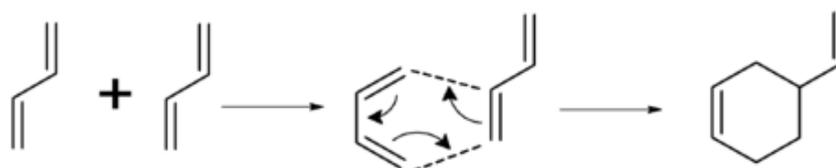
- Any **Alkene** that has more than two adjoining C atoms must (i) be a conjugated species and must (ii) have Resonance structures, and must therefore (iii) even though we rarely talk about it, have a delocalised π structure e.g. in Propene the middle C atom must treat the other two C atoms equally (i.e. with Resonance).

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[6] There are other definitions of "Conjugation".

- In contrast, a simple Alkene with just two C atoms (e.g. **Ethene**) will have just one double bond in it and cannot have any Resonance structures and thus **should not be thought of as having a delocalised π structure**.[7]

- In (A) below, the electrons in all the overlapping unhybridised 'p' orbitals become delocalised, whereas in (B) to (E) the Resonance structures have been drawn separately. In D&G's book, the diagram on the right and the one on the left were shown on different pages (therefore the wording of the legend is not quite correct).

Comparison of the extent of delocalisation in benzene (top) and butadiene (bottom). None of the resonance structures for butadiene shown on the previous page are correct; the four electrons not used in σ bonding are delocalised over the entire four-carbon skeleton.

Source : Dickerson & Geis' depiction of Butadiene in "Chemistry, Matter and the Universe".

The similarity between Alkenes and Aromatic Species (Benzene and its related species that have delocalised π rings are called "aromatic" species)

- As you can envisage, the Benzene molecule is surrounded/'protected' above and below by an area of high electron density and thus any species that reacts with Benzene will be (and in the vast bulk of cases) **HAS** to be an **electrophilic** species.

- **Neutrophiles** are species that possess a negative charge or a partial negative charge (or are rich in electron density) and the delocalised electron cloud on Benzene would repel such species!

- The delocalised π ring in Benzene creates a cloud of electron density above and below the Benzene molecule and there is therefore not an awful lot of the molecule that is left exposed to attack by anything other than an electrophilic species (which will come in and replace one or more H atoms in Benzene, and this gives rise to the generic description "**Electrophilic Aromatic Substitution reaction**"), and you will often see this referred to as an "EAS" reaction.

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[7] In more advanced Chemistry there are circumstances in which it is useful to think of delocalisation involving all the atoms in a molecule, but that is well beyond the scope of 'A' Level Chemistry.

- However, Benzene does undergo some **addition** reactions! For example, *boiling* Benzene will react (in the presence of u.v. light) with Halogen free radicals formed by homolytic bond fission by the u.v. light.

- In my second year book I talk about
A) the **Addition** reactions of Benzene, and then in greater detail about
B) the much more common *Electrophilic Aromatic* **SUBSTITUTION** **(EAS) reactions of Benzene.**

- However, before we can talk about either the Addition or the Substitution reactions of Benzene, we need to describe a group of chemicals called Friedel-Crafts' catalysts which could also be called Lewis acids (but such a description would lose the emphasis on the catalytic nature of these species).

Friedel-Crafts catalysts/Lewis Acids

- Some textbooks state that a Halogen carrier (and that name is self-explanatory viz. a species that carries a Halogen) or a Friedel-Crafts' catalyst works by dative bonding. However, there is a lot more to Halogen carriers/Friedel-Crafts catalysts' that is insufficiently explained in the textbooks, therefore I am going to describe their action in a fair amount of detail.

- At 'A' Level, Friedel-Crafts' catalysts/halogen carriers are very (or indeed are most) often used in the halogenation/or the alkylation/or the acylation of an aromatic molecule[8]. Acylation is something that is dealt with mainly at University, but **halogenation** (using a Hal-Hal / "X–X" diatomic molecule) and **alkylation** (using an Alkyl-Hal / "R–X" species) are both part of the 'A' Level syllabus, but here let us just consider the halogenation of a Benzene molecule using a halogen-carrier. However, let me warn you that Benzyl Halides are **TOXIC** species. As far as you are concerned therefore, this is just theoretical stuff. You will **not** be allowed to go anywhere near this sort of stuff in your school/college labs.

- Friedel-Crafts' catalysts/carriers **must have** a diminished octet (6 bonding electrons instead of 8) because it is this that creates the situation where a totally empty or vacant orbital can be used for dative bonding. Examples of substances that have diminished octets are **AlCl$_3$ / AlBr$_3$ / FeCl$_3$ / FeBr$_3$** (and also BF$_3$ / BeCl$_2$ / TiCl$_4$ / SbCl$_5$ / SnCl$_4$ / and so on).
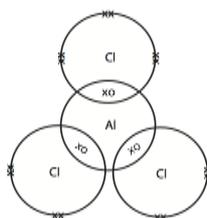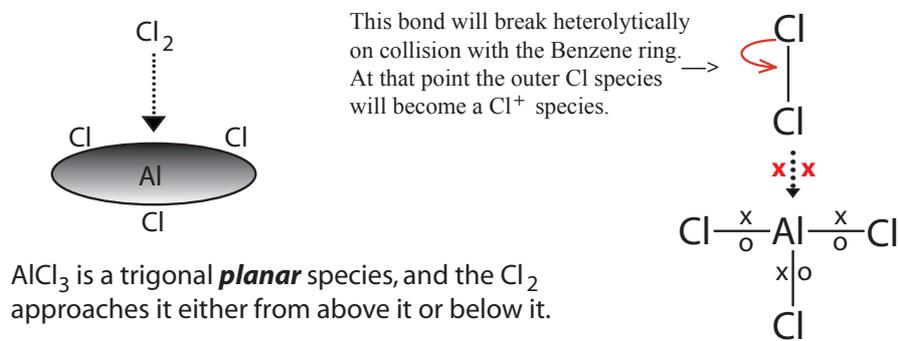

- If we examine AlCl$_3$ we can see that there are only three electron pairs on the central Al atom, and the Al atom in the AlCl$_3$ species therefore lacks the stability imparted by the Noble Gas Configuration of sharing in **FOUR** electron pairs (which is why AlCl$_3$ often forms the dimer Al$_2$Cl$_6$)[9].

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[8] Aromatic in the sense of a derivative of Benzene or any Arene molecule.

[9] "Dimers" have cropped up in 'A' Level exams. A dimer is a conjoined pair of similar *molecules* that exist together for greater stability. "Diatomic" means two conjoined atoms, and a "dimer" consists of two conjoined molecules.

- Al is in Group III, and in order to form three bonds, Al in $AlCl_3$ promotes one electron from 3s to 3p to form three sp^2 hybridised atomic orbitals which it uses to form 3 sigma bonds, one with each of the Cl atoms. This leaves its $2p_z$ unhybridised orbital able to accept a lone pair of electrons from a fourth Cl atom from, for example, a Cl–Cl molecule (to become, temporarily, $AlCl_4^-$ and Cl^+).

- Because F/Cl/and Br (but not Iodine) are sufficiently more electronegative than Al, then the four Cl (or whichever halogen) atoms in the $AlCl_4^-$ part of $AlCl_4^-Cl^+$ each become $Cl^{\partial-}$ species and the Al atom therefore becomes an $Al^{\partial+}$ species. In fact, because **four** $Cl^{\partial-}$ species are each drawing electron density off the Al species, the Al species becomes (almost) an $Al^{\partial+\partial+\partial+}$ species!

- Any diatomic Halogen molecule[10] such as Cl–Cl that approaches the Al in the $AlCl_3$ species *in the same plane as its existing $Cl^{\partial-}$ species*, will be hindered in its planar approach by one of the existing three physically big $Cl^{\partial-}$ species, and the diatomic Halogen molecule can therefore approach the $AlCl_3$ species *only either from above or from below* $AlCl_3$.[11]

I have drawn $AlCl_3Cl_2$ in only *one* of its Resonance forms

AlCl$_3$ is a trigonal ***planar*** species, and the Cl$_2$ approaches it either from above it or below it.

This bond will break heterolytically on collision with the Benzene ring. At that point the outer Cl species will become a Cl^+ species.

- If you look at Br$_2$ overleaf you will see another possible resonance structure for Br$_2$ or for Cl$_2$.

- The Cl atom nearer the AlCl$_3$ species will then become partially polarised by the $Al^{\partial+}$ species, and it will thus become a $Cl^{\partial-}$ species, and its companion Cl atom will thus automatically become a $Cl^{\partial+}$ species – **and it is THIS $Cl^{\partial+}$ species that will be attracted to the area of high electron density that encircles the Benzene molecule**.

- Other than in very rare circumstances, it is only an electrophile that can bond easily with a Benzene molecule – and that is precisely what $Cl^{\partial+}$ is. It is an **ELECTROPHILE** and it will be attracted to the nucleophile Benzene. **All the other four Cl species are $Cl^{\partial-}$ species, and they cannot bond with Benzene.**

- On impact with the Benzene molecule, the diatomic Cl– Cl molecule that has become a partially polarised molecule will break by **heterolytic bond fission** with the $Cl^{\partial-}$ species becoming a full Cl^- species, and the $Cl^{\partial+}$ **species breaks away as a full Cl^+ electrophile** – and it is THIS species that then takes part in the electrophilic substitution reaction with Benzene.

- **THAT is what Halogen carrying is all about.**

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[10] or Alkyl-Hal/R–X.

[11] Some chemists talk of this and similar spatial reactions as a "backside" reaction. I do not do so because I find such terminology rather vulgar. If you insist on using such terminology, then please use the terms "frontal" attack, and "attack from the rear". I have chosen to draw the attack as occurring from **above** the plane of AlCl$_3$.

- The University of California (Davis) shows the use of Bromine in an FC catalyst thus (where the two structures in the brackets are Resonance Structures)
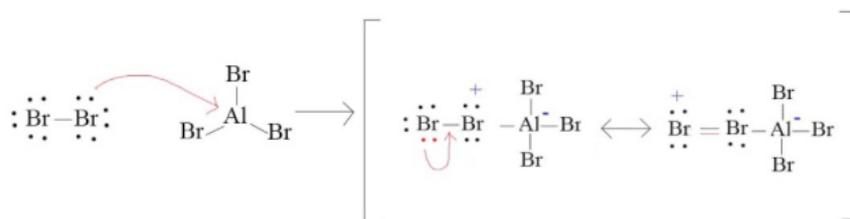
and Wikipedia shows the action of an FC catalyst thus (where R is what you want to add to C_6H_6).
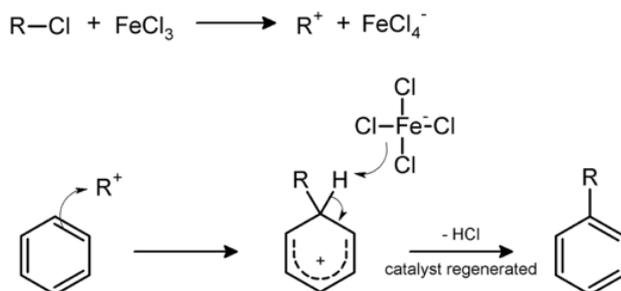
but so far I have explained only the first line in Wikipedia's representation.

- I have told you that Benzene is given considerable stability by its delocalised π ring – and it is therefore normally **not** reactive at room temperature and pressure (RTP).

- However, with a suitable Friedel-Crafts' catalyst acting as a Lewis acid (i.e. a species that accepts a lone pair of electrons) *the attacking electrophile will be made more reactive* and Benzene will *then* react with the attacking electrophile at RTP. Equally there are things that can be done to Benzene (e.g. we can increase the density of the electron cloud that surrounds the Benzene molecule by replacing an H atom on Benzene with a species that will "donate" electron density to Benzene (e.g. an Alkyl group/–NH_2/–OH/etc species)[12] *to make it more reactive,* and that will then make the Benzyl compound much more reactive.[13]

- We will talk about increasing the electron density of Benzene later, but could you please note that it is not really sensible to call a Friedel-Crafts (FC) catalyst simply a "halogen carrier" because an FC catalyst can also be used to make an *alkyl species* react with Benzene, and alkyl species are not halogens! *An FC catalyst thus may or may not be a halogen carrier.* My advice to you therefore is not to use the term "halogen carrier" at all. Catalysts such as $AlCl_3$ and $FeBr_3$ are more correctly called **Friedel-Crafts' catalysts**, or alternatively they can be described as **Lewis Acids** (but if you do so you then lose the importance of their function as catalysts).

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[12] An "activator" makes Benzene more reactive while a "deactivator" makes it less reactive (but the attacking species will still be an electrophile).

[13] Imperial College London says "Laurent, proposed that due to it being discovered in illuminating gas, it should instead be called pheno, from the Greek *phainein*, meaning to shine. This name never really gained acceptance, but persists to this day as phenyl - the name for the "$C_6H_5{}^{-}$" group – and nowadays when "Benzene" is used as an adjective we do call it a "phenyl ...." or "benzyl ....." species.