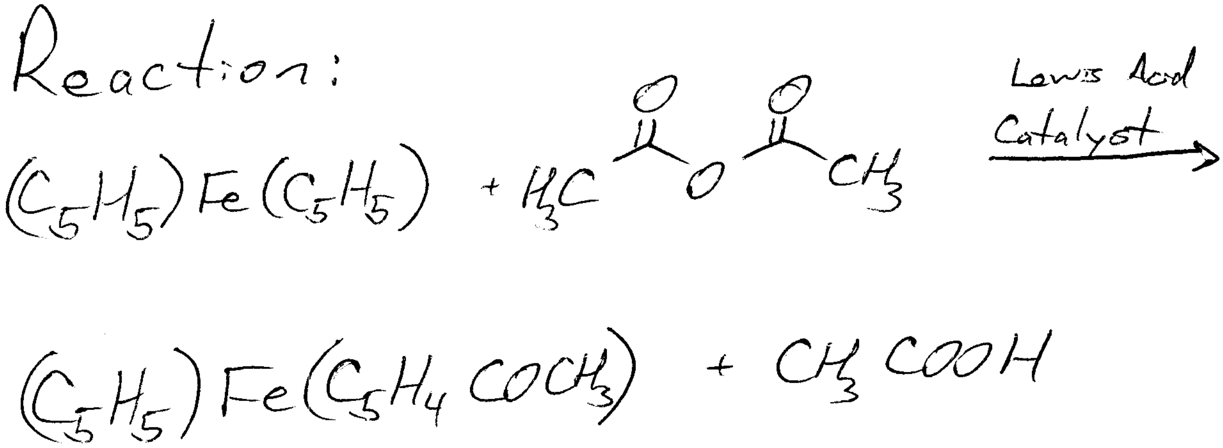
Notes on the Friedel-Crafts Acetylation of Ferrocene:

- Reaction:



- The basic process:
  - We generate $H_3C-\overset{\oplus}{C}O$ or its equivalent
  - The acyl cation attacks an electron-rich Cp ring to give a new cation, then a proton is lost to give neutral product.

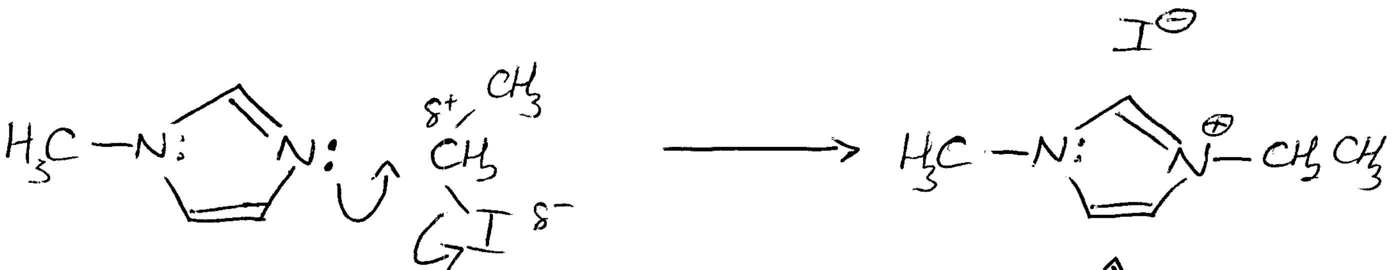
— The solvent:

- Formerly CH_2Cl_2 — toxic, high vapor pressure at room temperature.
- Now an ionic liquid — much lower toxicity, negligible vapor pressure.

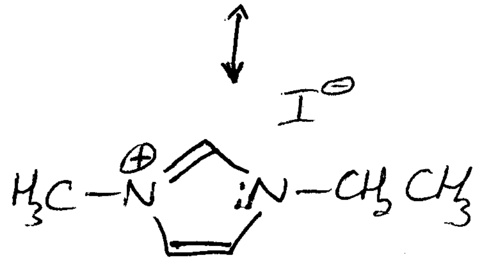
— Synthesis:

This lone pair is in the plane of the ring, not part of the aromatic π-system. It reacts with electrophiles.

This lone pair is perpendicular to the ring. Lines up with the double bond π-orbitals ⟹ 6 π electrons in the ring. N-Methylimidazole is aromatic.

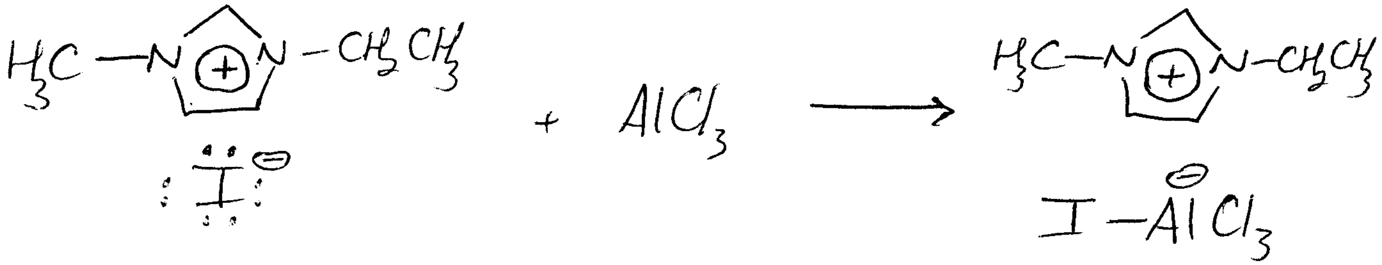


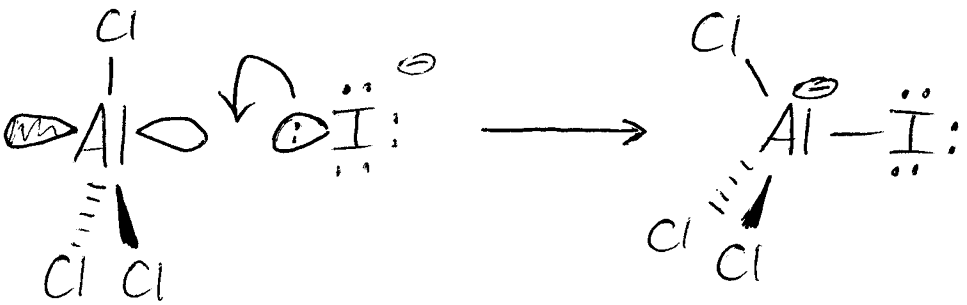
- Note: The product salt is still aromatic, with two major resonance forms.



— Synthesis of the Ionic Liquid, cont'd:

When $AlCl_3$ is added, a new anion is formed. The imidazolium cation stacks poorly with it, so the salt melts below room temperature.

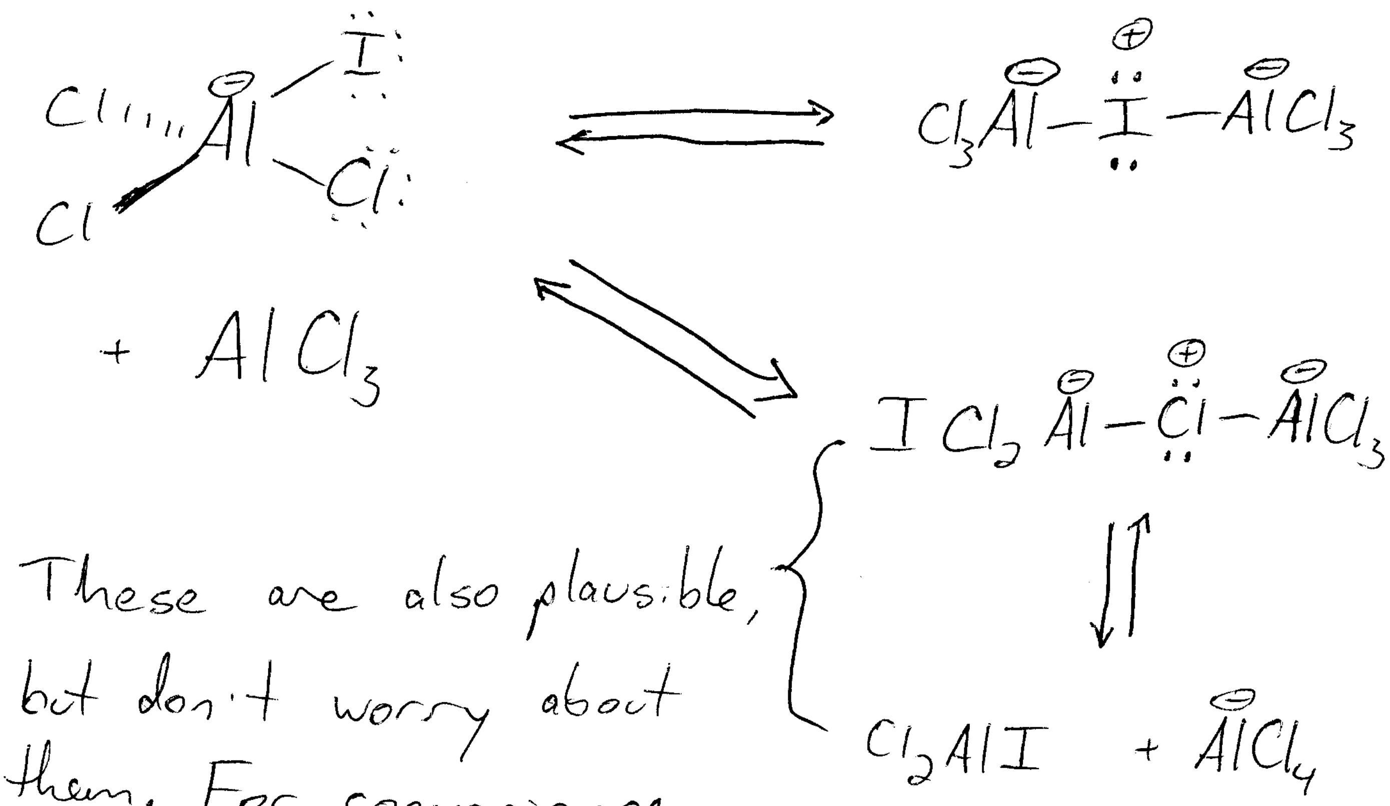




- Aluminum in $AlCl_3$ has an empty orbital; iodide has lone pairs to share with it.
- Iodine in $Cl_3\overset{\ominus}{Al}I$ still has lone pairs, but they are less readily shared: The iodine is no longer negatively charged.

— The Lewis Acid:

- As you add more than one equivalent of $AlCl_3$ to the iodide salt, you get more complex anions:

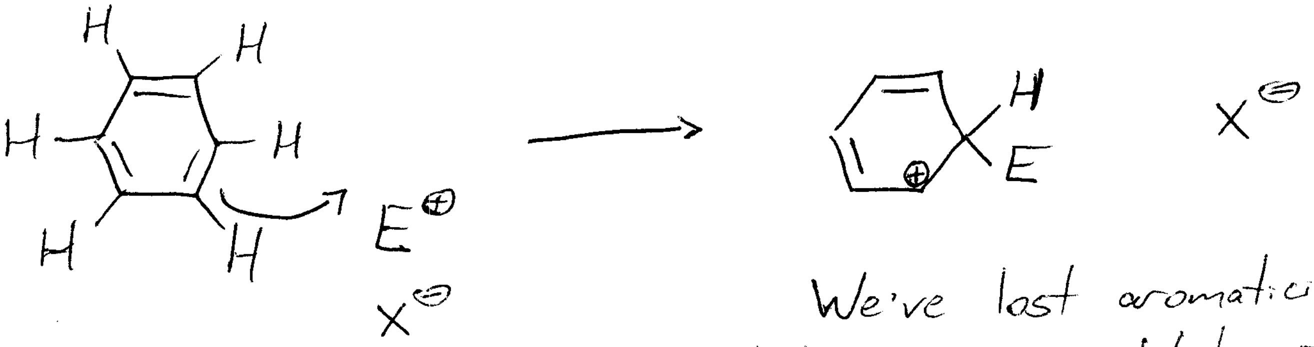


These are also plausible, but don't worry about them. For convenience, we'll take the relevant equilibrium to be the top one.

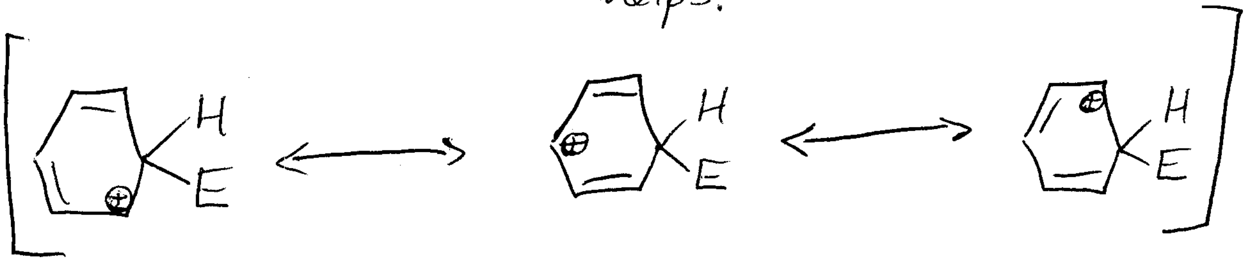
—Electrophilic Aromatic Substitution

- Net reaction:

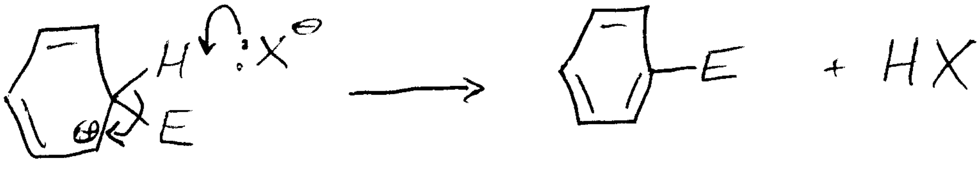
- Mechanism:



We've lost aromaticity, but resonance-stabilization helps:

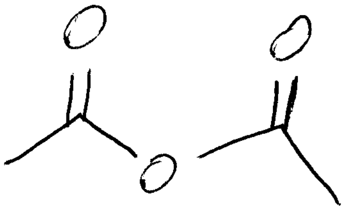
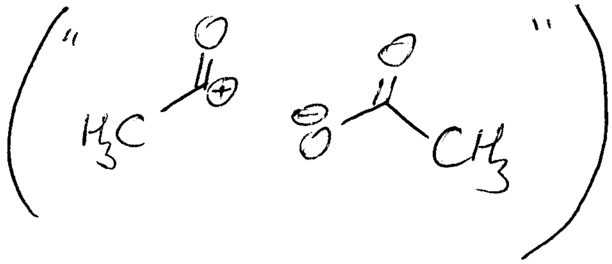


Rearomatization:

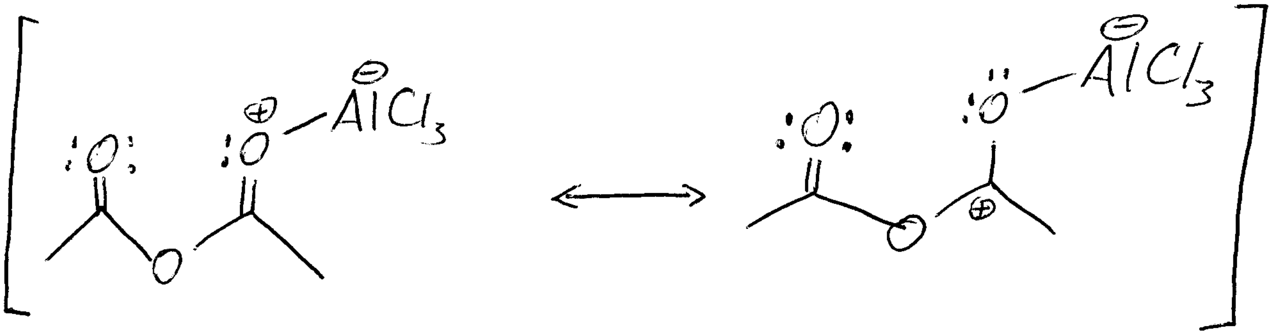


– So just what is $E^{\oplus}$?

In this case, several possibilities:

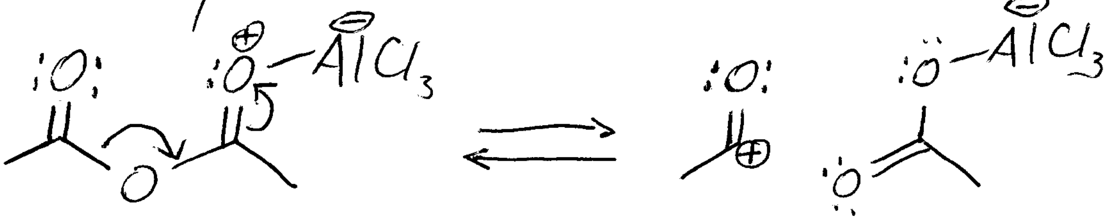
-  

  Not electrophilic enough. This is why we need $AlCl_3$.

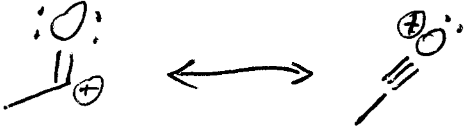
- 

  Has carbocation-like character: good electrophile.

- Acetyl cation:

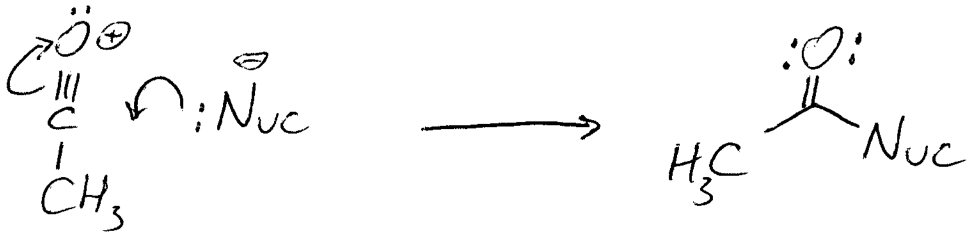


Acetyl would be a terrible (high-energy) cation, but is accessible due to resonance:

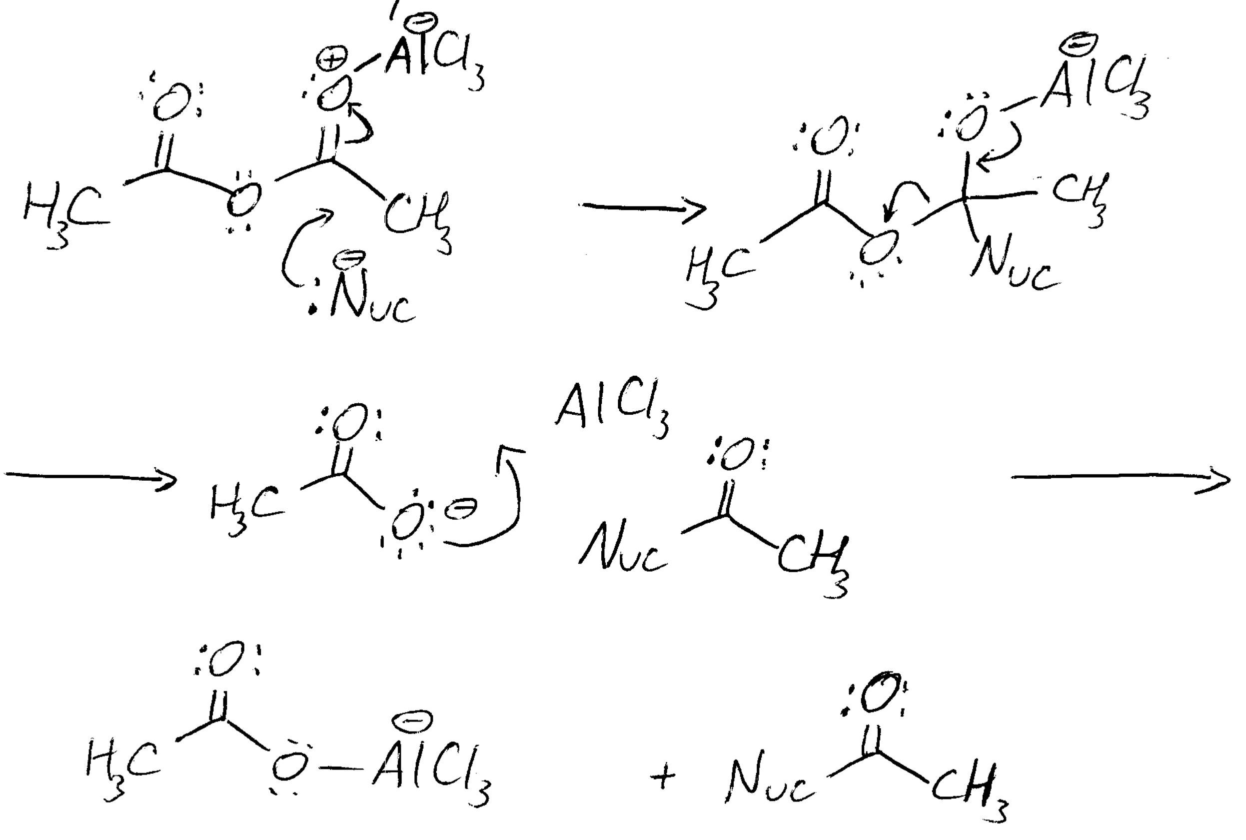


— Reaction of acetylating agents with nucleophiles:

- The acetyl cation is simple:

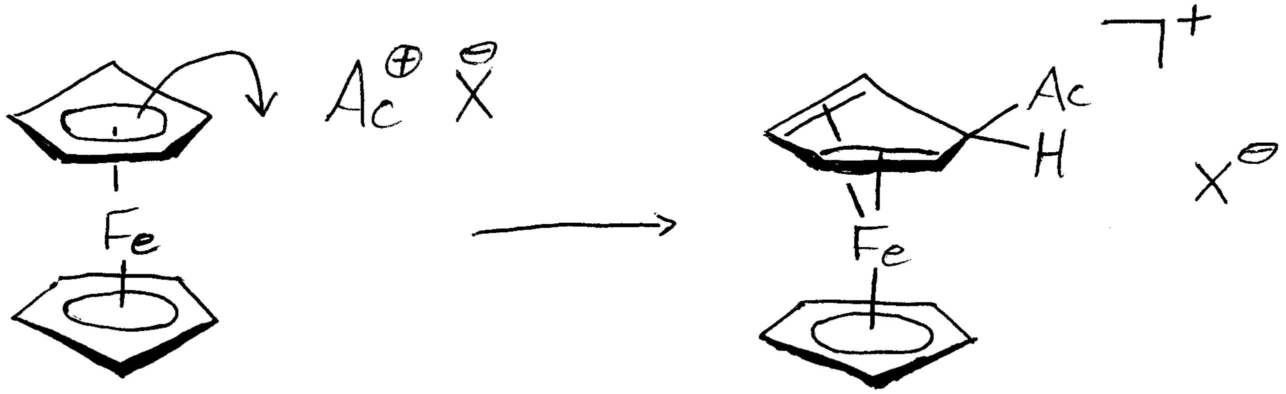


- Acetic anhydride — aluminum chloride:



In short, the $Ac_2O/AlCl_3$ complex reacts as if it were $[Ac^{\oplus}][AcO\overset{\ominus}{Al}Cl_3]$ $(Ac = CH_3CO)$.

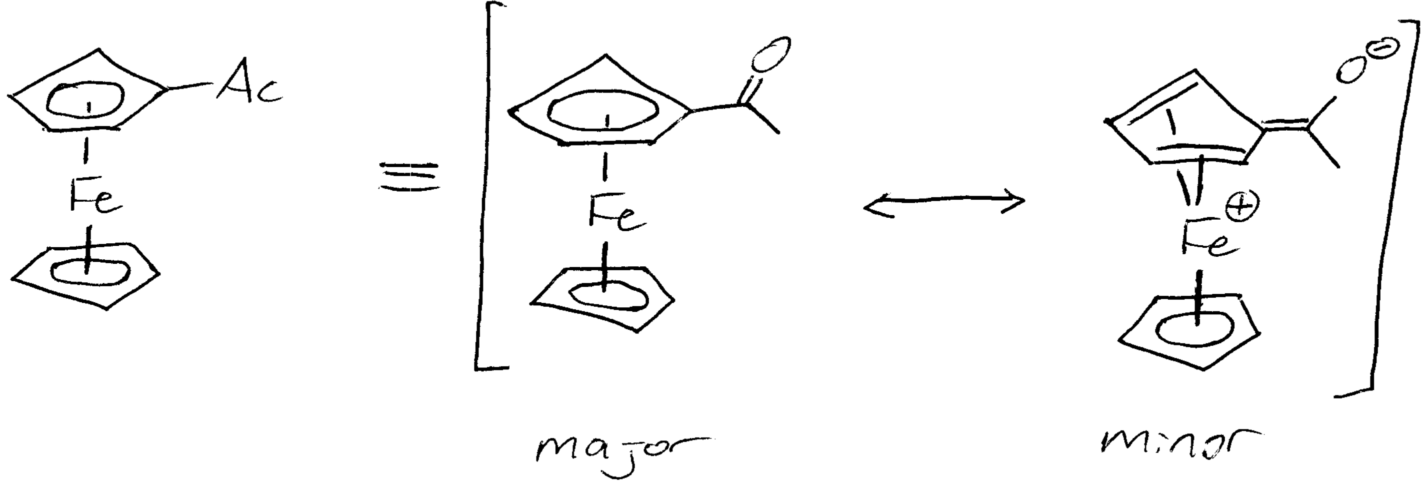
- Ferrocene reacts analogously to benzene:



- In the intermediate, the iron is coordinated to the two double bonds of the upper ring. If we think of it as Fe^{2+}, it is now coordinated to an anionic C_5H_5 ring, and a <u>neutral</u> cyclopentadiene. So the complex is cationic.

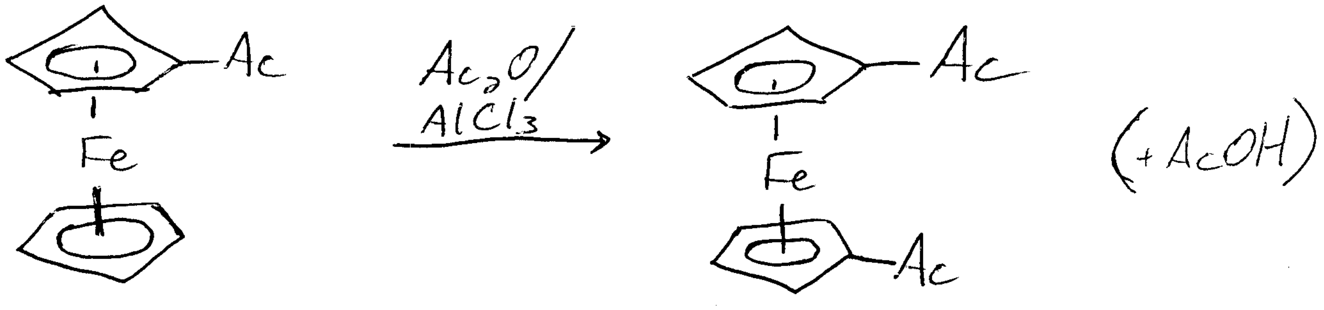
- "Rearomatization":

— Products:



- The upper ring is much less reactive toward electrophiles than in ferrocene.

- The lower ring is somewhat deactivated, but further reaction is still possible:



1,1'-diacetylferrocene

— Catalyst regeneration: