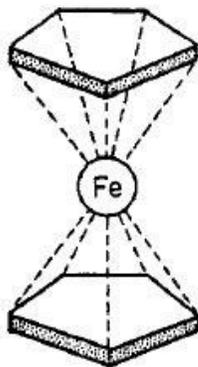
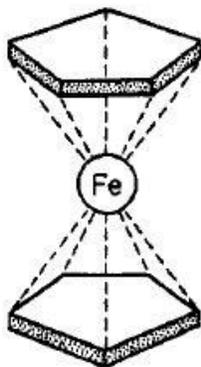


Experiment 4

Acetylation of ferrocene and reduction of acetylferrocene

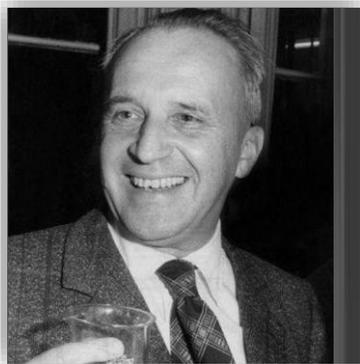
Ferrocene (Cp_2Fe)



Ferrocene was first prepared in 1951 by Pauson & Kealy; *Nature* 1951, 168, 1039-1040.

Staggered (D_{5d}) or eclipsed (D_{5h}): *JACS* 1952, 74, 2125-2126.

Nobel Prize in 1973: Ernst-Otto Fisher in Munich and Geoffery Wilkinson in London

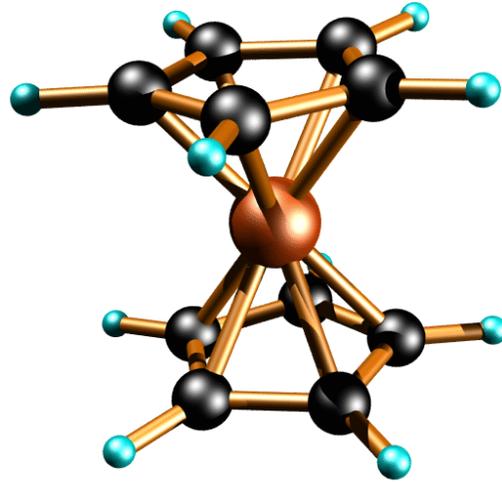


Ernst-Otto Fisher



Geoffery Wilkinson

Ferrocene (Cp_2Fe)

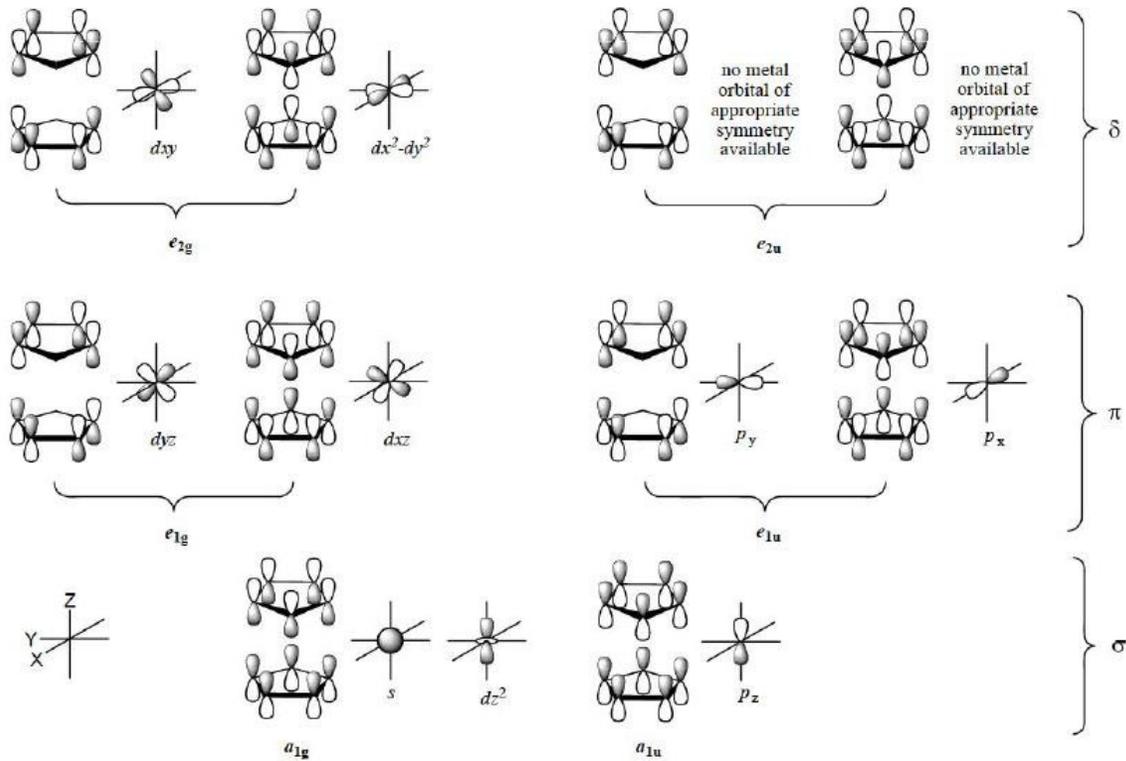


C-C distance is 1.40 Å, Fe-C distance is 2.04 Å by XRD

In the gas phase Cp rings are eclipsed, but the staggered conformation is stable in the condensed phase due to crystal packing

The Cp rings rotate with a low barrier about the Cp(centroid)-Fe-Cp(centroid) axis, as observed by measurements on substituted derivatives of ferrocene using ^1H and ^{13}C nuclear magnetic resonance spectroscopy

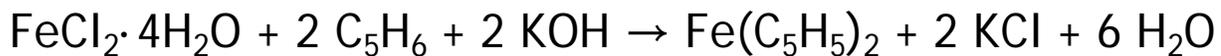
Ferrocene (Cp_2Fe)



The iron center in ferrocene is usually assigned to the +2 oxidation state, and each cyclopentadienyl (Cp) ring is then allocated a single negative charge, bringing the number of π -electrons on each ring to six, and thus making them aromatic. These twelve electrons (six from each ring) are then shared with the metal via covalent bonding. When combined with the six d-electrons on Fe^{2+} , the complex attains an 18-electron configuration.

Ferrocene (Cp₂Fe)

Preparation



Reaction

Ferrocene undergoes many reactions **characteristic of aromatic compounds**, enabling the preparation of substituted derivatives. A common undergraduate experiment is the Friedel-Crafts reaction of ferrocene with acetic anhydride (or acetyl chloride) in the presence of phosphoric acid as a catalyst

Redox Chemistry

Unlike the majority of organic compounds, ferrocene undergoes a one-electron oxidation at a low potential, around 0.5 V versus a saturated calomel electrode (SCE). This reversible oxidation has itself been used as standard in electrochemistry **Fc⁺/Fc = 0.64 V** versus the standard hydrogen electrode.

Acetylation of ferrocene

Acetylation of ferrocene

1. Add ferrocene (1.5 g) to acetic anhydride (5 ml) in 25 ml of a round bottom flask
 2. Add orthophosphoric acid (1 ml) dropwise
 3. Stir the mixture for 20 minutes in a boiling water bath
- * You should set a thermometer
4. Pour the hot mixture onto crushed ice (half of 250 ml beaker)
(Remained organic product in round bottom flask have to be washed out with 2nd distilled water)



Acetylation of ferrocene

5. Add 20~30 ml of saturated sodium bicarbonate solution

***Caution: The saturated solution should be added slowly**

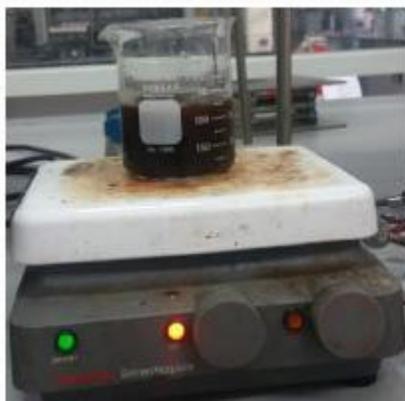
6. Cool the neutralized mixture in an ice bath for 5 minutes

7. Filter off the brownish yellow solid

8. Wash the product with petroleum ether

9. All volatiles are removed by rotary evaporator

10. Weigh your product and calculate yield (%)



Reduction of Acetylferrocene

Reduction of Acetylferrocene

1. Add acetylferrocene (0.5 g) to a 50 ml of Erlenmeyer flask and dissolve in ethanol (10 ml)
2. Dissolve NaBH_4 (0.4 g) in water (2 ml) and add NaBH_4 solution dropwise to the acetylferrocene solution
3. Stir the reaction mixture for 5 minutes at room temperature
4. Add distilled water (20 ml) and transfer to a separate funnel
5. The organic product was extracted with diethylether (20 ml X 2)
6. Dry the ether solution over magnesium sulfate and the precipitate is filtered by filter paper
7. Remove all volatiles including ether using rotary evaporator
8. Weigh your product and calculate yield (%)



To do

Prepare two NMR samples (Acetylferrocene, reduction of acetylferrocene)

Analyze of NMR, UV and IR spectra

Draw and explain the mechanism of acetylation and reduction

Explain why the acetylation of ferrocene is proceeded faster in ethanol than in benzene solution

Print your report after submit to turnitin