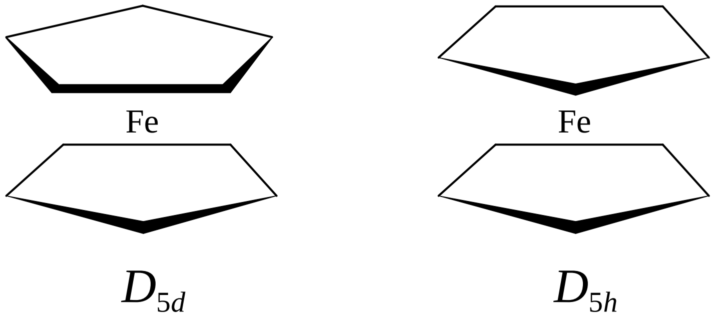
Organometallic Chemistry

- 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.[1]
  - Originally called "dicyclopentadienyliron."
  - Subsequent x-ray analysis proved that ferrocene consisted of an iron(II) ion sandwiched between two parallel pentadienyl rings.



  - Eclipsed and staggered configurations exist in the solid, and the barrier to rotation is low (<20 kJ/mol).

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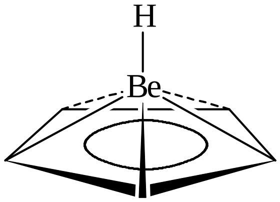
[1] P. L. Paulson and T. J. Kealy, *Nature*, **1951**, *168*, 1039.

Nomenclature

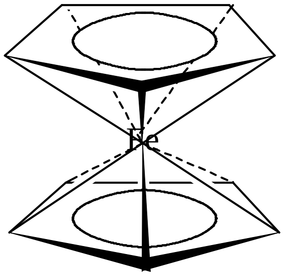
- Today, in organometallic chemistry the Greek-letter prefix η (eta) with an integer superscript is used to indicate the number of carbon atoms directly bonded to the metal, called the *hapticity*.
  - For example, (η^5-*Cp*)BeH has the following structure:



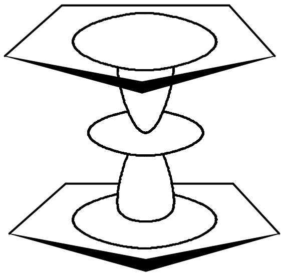
  - Ferrocene is systematically named

    bis(η^5-cyclopentadienyl)iron(II)

    implying the following bonding scheme:



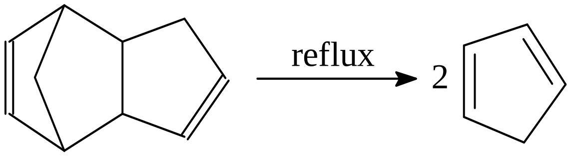
  - Carbon-metal bonding in sandwich compounds is less rigid than this model implies and is more nearly a less directed *d*-π interaction.



Cyclopentdienyl Ion (*Cp*$^-$), $C_5H_5^-$

- Cyclopentadiene, C_5H_6 (b.p. 42.5 °C), is produced by cracking dicyclopentadiene, $C_{10}H_{12}$ (b.p. 170 °C):

$$C_{10}H_{12} \xrightarrow{\text{reflux}} 2C_5H_6 \text{ (b.p. 42.5 °C)}$$



  - 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):

$$C_5H_6 + KOH \xrightarrow{\text{1,2-dimethoxyethane}} C_5H_5^- + K^+ + H_2O$$

Synthesis of Ferrocene

- A solution of $FeCl_2$ in DMSO is slowly added to the solution containing $C_5H_5^-$ ions, resulting in yellow-orange ferrocene:

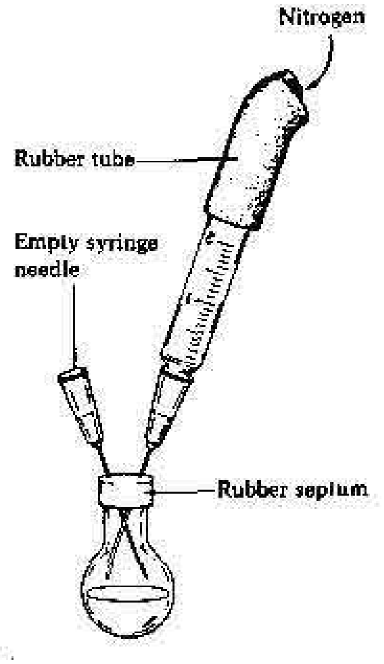
  $$2C_5H_5^- + Fe^{2+} \rightarrow (\eta^5\text{-}C_5H_5)_2Fe$$

  - 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 $FeCl_2 \cdot 4H_2O$ in DMSO.
  - An open bottle of $FeCl_2 \cdot 4H_2O$ (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.
  - $FeCl_2 \cdot 4H_2O$ dissolves slowly.
    - ☛ Start preparing the solution early and use *mild* heating (hot water bath) to speed up the process.

Micro-scale Synthesis of Ferrocene

✓ 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.

✓ Cyclopendadiene is injected into the r.b. 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 in the r.b. flask 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.

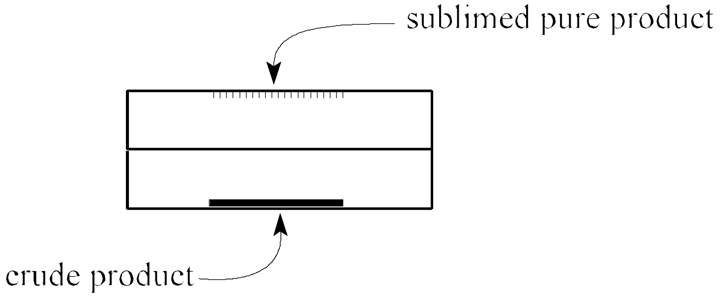
✓ Collect the crude product by filtration on a Hirsh funnel.

Purifying Ferrocene

- 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.

- Use the purified ferrocene to obtain an ATR-FTIR spectrum in the organic lab.