Synthesis and Reactions of Ferrocene

The archetypal organometallic compound ferrocene, \([\text{Fe}(\eta^5\text{C}_5\text{H}_5)_2]\), is of historical importance since its discovery and structural characterisation in the early 1950s sparked extensive research into the chemistry of metal sandwich compounds. This document is a short summary of a detailed student lab guide which is available to Spinsolve for education users.

In this note, we show how the Spinsolve benchtop NMR spectrometer is used to monitor the different synthetic stages involved in the preparation of ferrocene. Moreover, the diverse chemistry of ferrocene is studied using 1D and 2D NMR experiments.

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Ferrocene is synthesised from the reaction of cyclopentadiene with sodium hydroxide (KOH) in 1,2-dimethoxyethane (DME) to produce the cyclopentadienyl anion (C$_5$H$_5^-$). This is then reacted with iron(II) chloride tetrahydrate (FeCl$_2$.4H$_2$O) in dimethyl sulfoxide (DMSO) to yield ferrocene (1). The disappearance of reactants and formation of products during the synthesis of ferrocene can be observed by sampling at different stages of the synthetic procedure. (Figure 1).

![Chemical structure of ferrocene synthesis](image)

Figure 1. $^1$H NMR spectra acquired at different stages of ferrocene synthesis, 42 MHz: cyclopentadiene in DME (a), formation of cyclopentadienyl anion (b) and formation of ferrocene (c).
Due to the aromatic character of the cyclopentadienyl ligands, ferrocene (1) can undergo the Friedel-Crafts acylation reaction to form acetylferrocene (2). Ferrocene can also undergo a ligand exchange reaction between one of the cyclopentadienyl rings and benzene to form complex 3. Nucleophilic attack on the benzene ring in 3 using LiAlH$_4$ affords the neutral compound 4. The analogous reaction with LiAlD$_4$ shows that the attack occurs on the exo face of the benzene ring to yield compound 5.

**Figure 2.** 1H NMR spectra of ferrocene derivatives, 42 MHz.
Figure 3. COSY spectrum of [Fe(η-C₅H₅)(η₅-C₆H₇)] (4), 42 MHz, CDCl₃. Interpretation of the COSY spectrum shows the resolution of the three-proton multiplet between 1.93-2.77 ppm. The COSY correlations also confirm the overlap of signals of the C₅H₅- ring and the protons at position 3 between 4.13 and 4.38 ppm.

Figure 4. 2D J-resolved (2DJRes) spectrum of [Fe(η-C₅H₅)(η₅-C₆H₇)] (4), 42 MHz, CDCl₃. The spectrum shows how the complex proton coupling patterns have been resolved in the second (f1) dimension.