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Synthesis and Reactions of Ferrocene



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Objectives

The principal aims of these experiments are to provide experience in the synthesis, isolation, purification and characterisation of organometallic compounds. Purification techniques include distillation, sublimation, chromatography and crystallisation. The main characterisation technique used in these experiments is ^1H NMR spectroscopy using the benchtop Spinsolve spectrometer. Furthermore, students will also develop their synthetic skills using inert atmosphere techniques.

Introduction

The archetypal organometallic compound ferrocene, $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$, is of historical importance since its discovery and structural characterisation in the early 1950s sparked extensive research into the chemistry of metal sandwich compounds.¹ Two of the chemists who first proposed the correct structure of ferrocene (Figure 1), Geoffrey Wilkinson and Ernst Otto Fischer, were awarded the Nobel Prize in Chemistry in 1973 for their pioneering work on the chemistry of sandwich complexes.

Ferrocene is an example of a π -complex in which interactions between the d-orbitals of the Fe^{2+} metal centre with the π -orbitals of the two planar cyclopentadienyl ligands (C_5H_5^-) form the metal-ligand bonds. Thus, all the carbon atoms in the cyclopentadienyl rings are bonded equally to the central Fe^{2+} ion. Ferrocene exhibits aromatic properties and is thermally very stable. It is also resistant to acidic and basic reagents.

In this series of experiments, you will synthesise ferrocene and then perform several reactions with it. The various products prepared will be characterised by ^1H NMR spectroscopy.

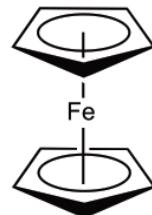


Figure 1. Ferrocene $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$



Preparation of ferrocene

There are two parts to this experiment: first, prepare freshly distilled cyclopentadiene (C_5H_6), and second, use it immediately to synthesise ferrocene. Both parts should be done in the fumehood.

Safety

Dicyclopentadiene, cyclopentadiene and 1,2-dimethoxyethane (DME) are toxic. Avoid breathing vapour and contact with skin. Dimethyl sulfoxide (DMSO) is dangerous because it increases the permeability of the skin to other substances. Avoid all contact with skin and clothing. HCl and KOH are very corrosive, handle with extreme caution. Iron(II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) and ferrocene can be harmful, handle with care. Deuteriochloroform ($CDCl_3$) is toxic, handle with caution and do not ingest or inhale.

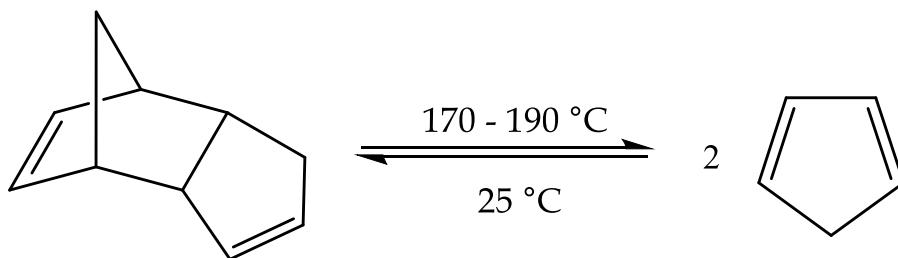
a) Cracking of dicyclopentadiene

Monomeric cyclopentadiene (C_5H_6) dimerises rapidly at room temperature to dicyclopentadiene by a Diels-Alder reaction. Thus, commercial dicyclopentadiene is thermally decomposed (cracking process) to obtain cyclopentadiene by fractional distillation (Scheme 1).² The apparatus is set up using a Vigreux column and a 100 mL round bottom flask charged with 30 mL of dicyclopentadiene.[†] Monomeric cyclopentadiene is collected in the 40–42 °C range and is kept cool using an ice bath until required. Take an aliquot (1 mL) for 1H NMR. You will need 4.25 mL for part b.

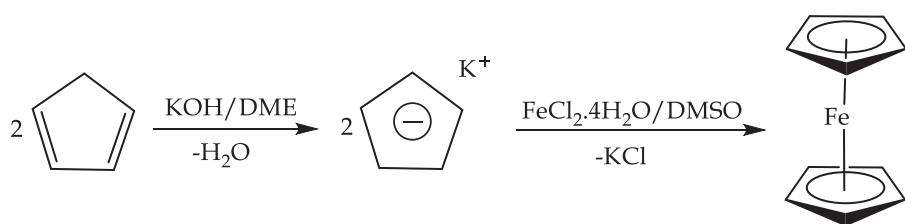
[†] In a laboratory session, it might be convenient to set up one fractional distillation apparatus to carry out the cracking process of dicyclopentadiene.

b) Ferrocene synthesis³

Charge a 250 mL 3-neck round bottom flask equipped with a dropping funnel, magnetic stirrer and nitrogen inlet, with DME (50 mL) and 4.25 mL of freshly distilled cyclopentadiene (Figure 2). Stir the solution and flush with nitrogen.^{4,5} Take an aliquot (1 mL) for 1H NMR. Add finely ground KOH (20 g) and stir the mixture vigorously for 15 min to form a coloured mixture, which includes the cyclopentadienyl anion. Take an aliquot (1 mL) for 1H NMR. Prepare a solution of finely powdered $FeCl_2 \cdot 4H_2O$ (5 g) in 20 mL of DMSO under nitrogen and transfer the solution into the dropping funnel. Add the iron(II) chloride solution slowly over a period of 30 min with efficient stirring. Take an aliquot (1 mL) for 1H NMR after 2/3 of the $FeCl_2$ /DMSO solution has been added, then another aliquot (1 mL) at the end of addition. Continue stirring the reaction mixture for a further 15 min then pour the dark slurry into a beaker containing crushed ice (80 g) and hydrochloric acid (75 mL, 6 M). Stir the mixture thoroughly to dissolve and neutralise any remaining KOH. Filter the precipitate and wash with water. Collect the crude orange ferrocene and dry in the air. Purify by sublimation to obtain orange crystalline material and record your yield (see Figure 3).²



Scheme 1. Cracking of dicyclopentadiene



Scheme 2. Formation of ferrocene.

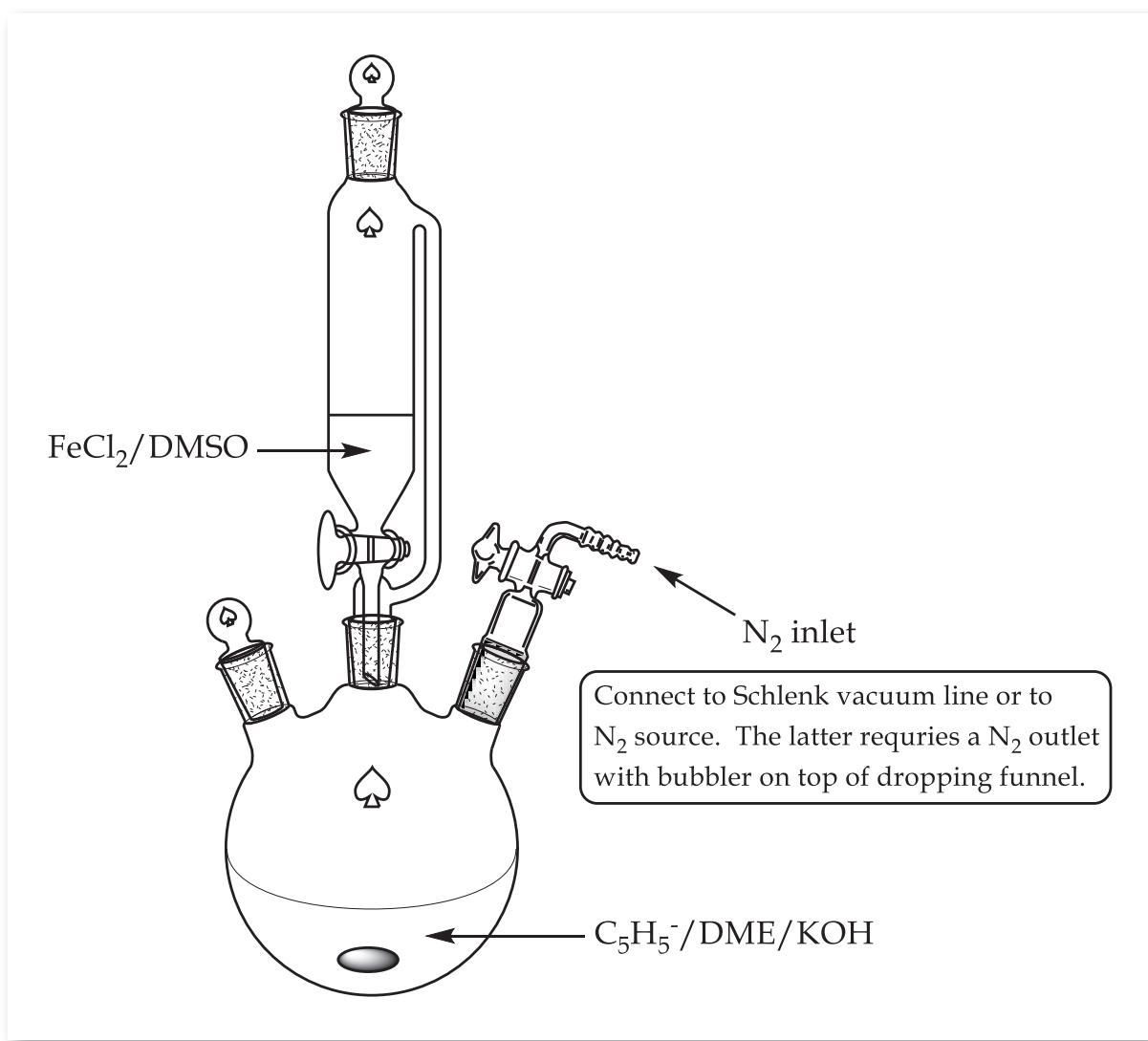


Figure 2. Experimental setup for ferrocene synthesis.



(a) Crude ferrocene



(b) Sublimed ferrocene

Figure 3(a)-(b). Purification of crude ferrocene via sublimation.

Tasks

- Determine the theoretical and percentage yields of ferrocene.
- Record the ^1H NMR spectra of all aliquots taken during the synthetic procedure using the Spinsolve NMR spectrometer.
- Record the ^1H NMR spectrum of purified ferrocene using the Spinsolve NMR spectrometer. Prepare the NMR sample using 50 mg of ferrocene in 1 mL of CDCl_3 .
- Record an IR spectrum of ferrocene.

Questions

- Why is it crucial to use freshly distilled cyclopentadiene for the synthesis of ferrocene?
- If all the reagent are stable to air before the reaction begins and the product ferrocene is also stable to air, why must the experiment be done under a nitrogen (inert) atmosphere?
- What makes ferrocene sublime easily?
- Assign the IR and NMR spectra of ferrocene.
- Explain how the spectra support the sandwich structure of ferrocene.
- Generally, aromatic protons resonate between 6.5-8.5 ppm in the ^1H NMR spectrum. Explain why the C_5H_5^- protons in ferrocene resonate upfield at 4.16 ppm.

¹H NMR Spectra

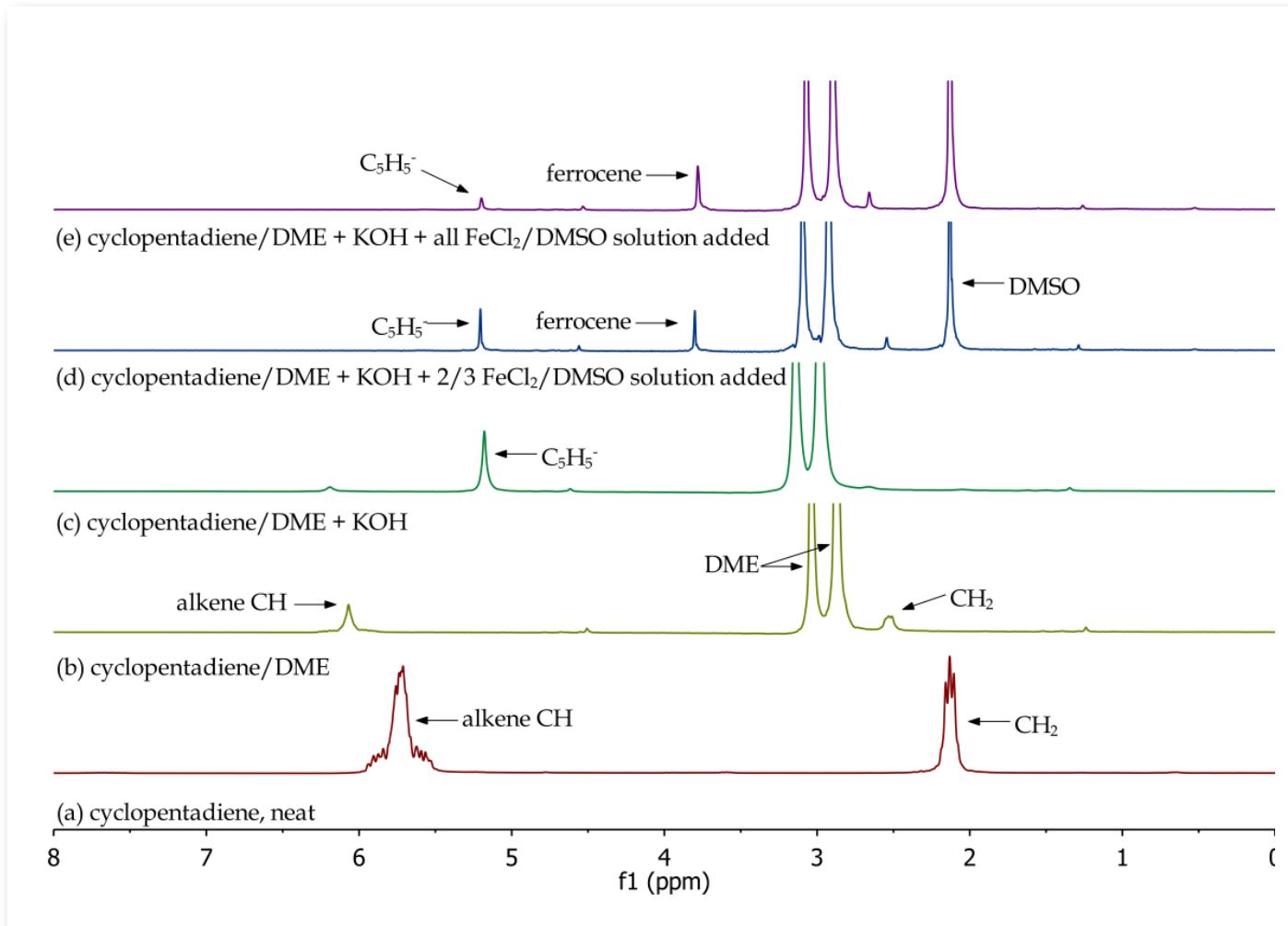


Figure 4. Overlay of ¹H NMR spectra of reactants and reaction mixtures during the synthesis of ferrocene.

The different synthetic stages involved in the preparation of ferrocene can be easily monitored using the Spinsolve NMR spectrometer. By analysing the different aliquots collected during the synthetic procedure, the disappearance of reactants and formation of products can

be observed. In Figure 4, we can confirm the monomeric nature of cyclopentadiene (a and b), the formation of the cyclopentadienyl anion (c) and its disappearance and formation of ferrocene (d and e).

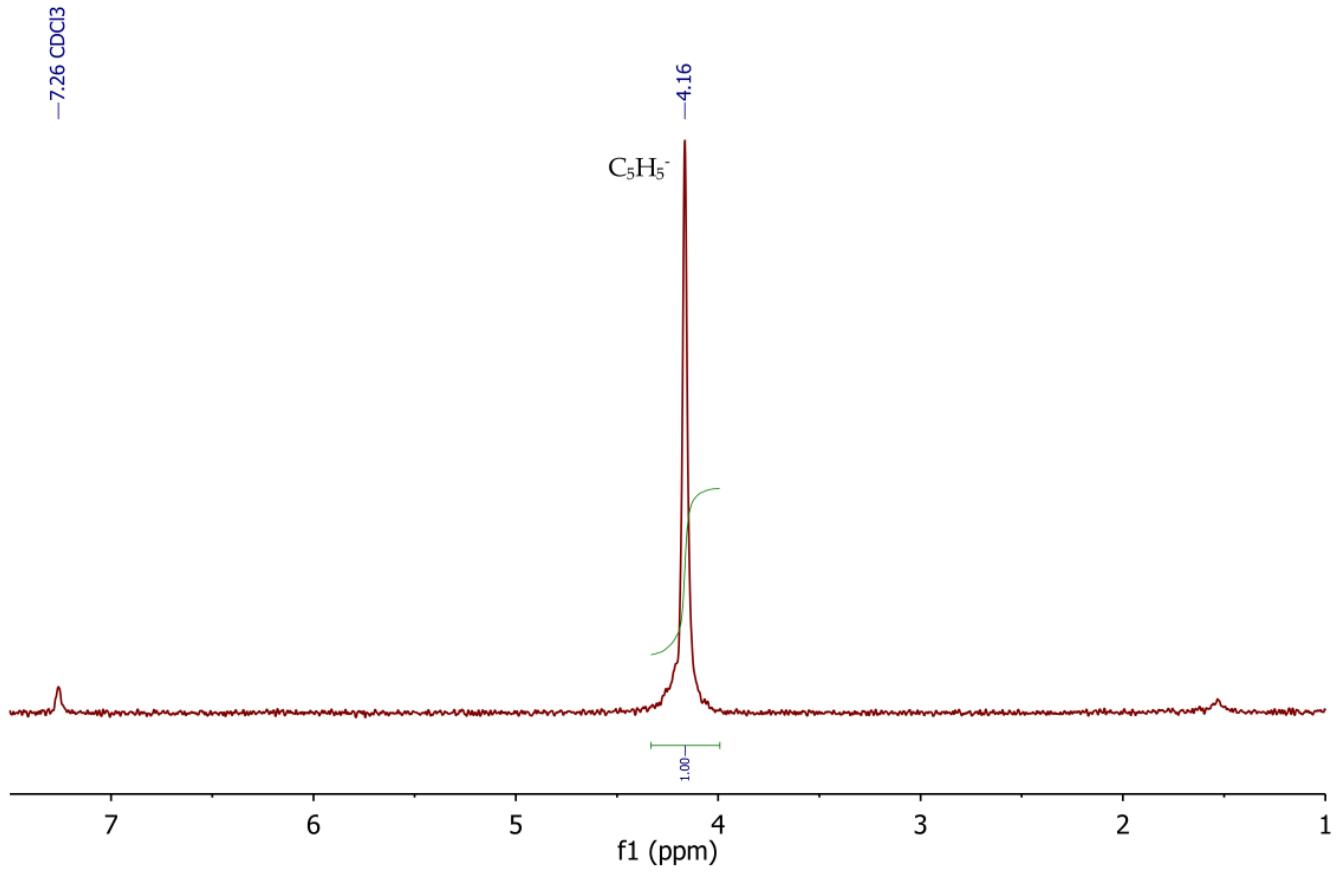


Figure 5. ¹H NMR spectrum of ferrocene, $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$, CDCl_3 .

The ¹H NMR spectrum of ferrocene (Figure 5) shows ten equivalent aromatic protons as a singlet at 4.16 ppm.

Acetylation of ferrocene

Due to the aromatic character of the cyclopentadienyl ligands, ferrocene can undergo electrophilic aromatic substitution reactions typical of aromatic compounds such as benzene. In this experiment you will acetylate ferrocene via the Friedel-Crafts acylation reaction.

Safety

Phosphoric acid (H_3PO_4) and acetic anhydride [$(CH_3CO)_2O$] are irritants. Avoid breathing and contact with skin. Acetylferrocene can be harmful, handle with caution. Alumina (Al_2O_3) is a lung irritant, avoid breathing the dust. Light petroleum ether and diethyl ether are highly flammable, handle with caution. Toluene is moderately toxic and flammable, avoid contact with skin and handle with care.

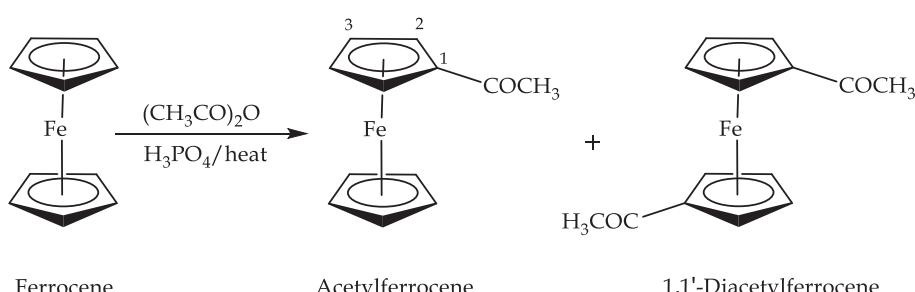
a) Acetylferrocene synthesis³

Charge a 25 mL round bottom flask with ferrocene (1 g) and acetic anhydride (3.3 mL). Carefully add phosphoric acid (0.7 mL, 85%) and heat the reaction mixture on a hot water bath for 20 min with stirring. Pour the hot mixture onto crushed ice (27 g). After all the ice has melted, neutralise the

solution with solid sodium bicarbonate and cool for a further 5 min. Collect the brown precipitate by filtration, wash with water and dry in the air. The solid obtained is a mixture of unreacted ferrocene and the monosubstituted product acetylferrocene (Figure 6). However, a third compound may also be present in very small amounts as the disubstituted product of acetylation (1,1'-diacetylferrocene).

b) Purification of acetylferrocene

Acetylferrocene is purified by column chromatography using a column prepared from alumina (or silica) suspended in light petroleum.² The crude solid is dissolved in the minimum amount of toluene and the solution is added carefully to the top of the column. Light petroleum ether is used to elute the first (yellow) band containing compound A. The second band (orange-red) is eluted using a 1:1 mixture of light petroleum ether and diethyl ether to obtain compound B. The fraction solvent is removed on the rotary evaporator to yield an orange solid in both cases. Collect the solids and record the yields of compounds A and B.



Scheme 3. Preparation of acetylferrocene.



Figure 6. Purified acetylferrocene.

Tasks & Questions

- Record the ^1H NMR spectra of compounds A and B using the Spinsolve NMR spectrometer. Prepare the NMR samples using 50 mg of each compound in 1 mL of CDCl_3 .
- Compare the ^1H NMR and IR spectra of compound A with the spectra of ferrocene from Part 1. What conclusion can you draw about the identity of compound A?
- Compare the ^1H NMR and IR spectra of compound B with the spectra of ferrocene from Part 1. Determine the structure of compound B and assign the spectra.
- Calculate the percentage yield of acetylferrocene taking into account the amount of unreacted ferrocene recovered.
- Record and assign the IR spectra of compounds A and B.
- Give a mechanism for the formation of acetylferrocene.

NMR Spectra

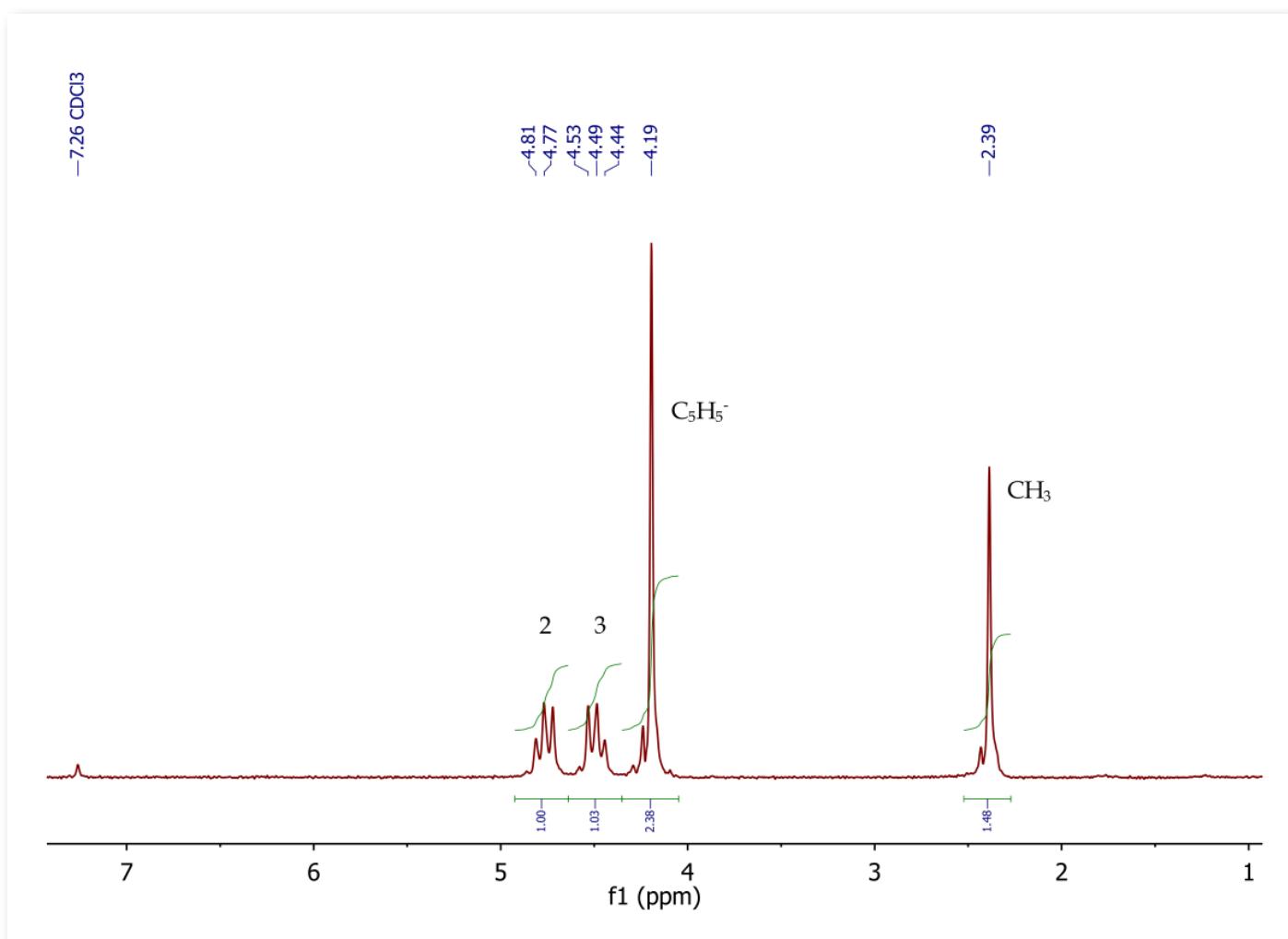


Figure 7. ^1H NMR spectrum of acetylferrocene, CDCl_3 . Refer to Scheme 3 for the annotated structure.

The ^1H NMR spectrum of acetylferrocene (Figure 7) shows five equivalent aromatic protons as a singlet at 4.19 ppm for the unsubstituted cyclopentadienyl ring. A singlet is observed at 2.39 ppm (3H) corresponding to the acetyl methyl group.

The substituted cyclopentadienyl ring protons appear as a second order AA'BB' system, with two multiplets centred at 4.49 and 4.77 ppm, integrating for two protons each.

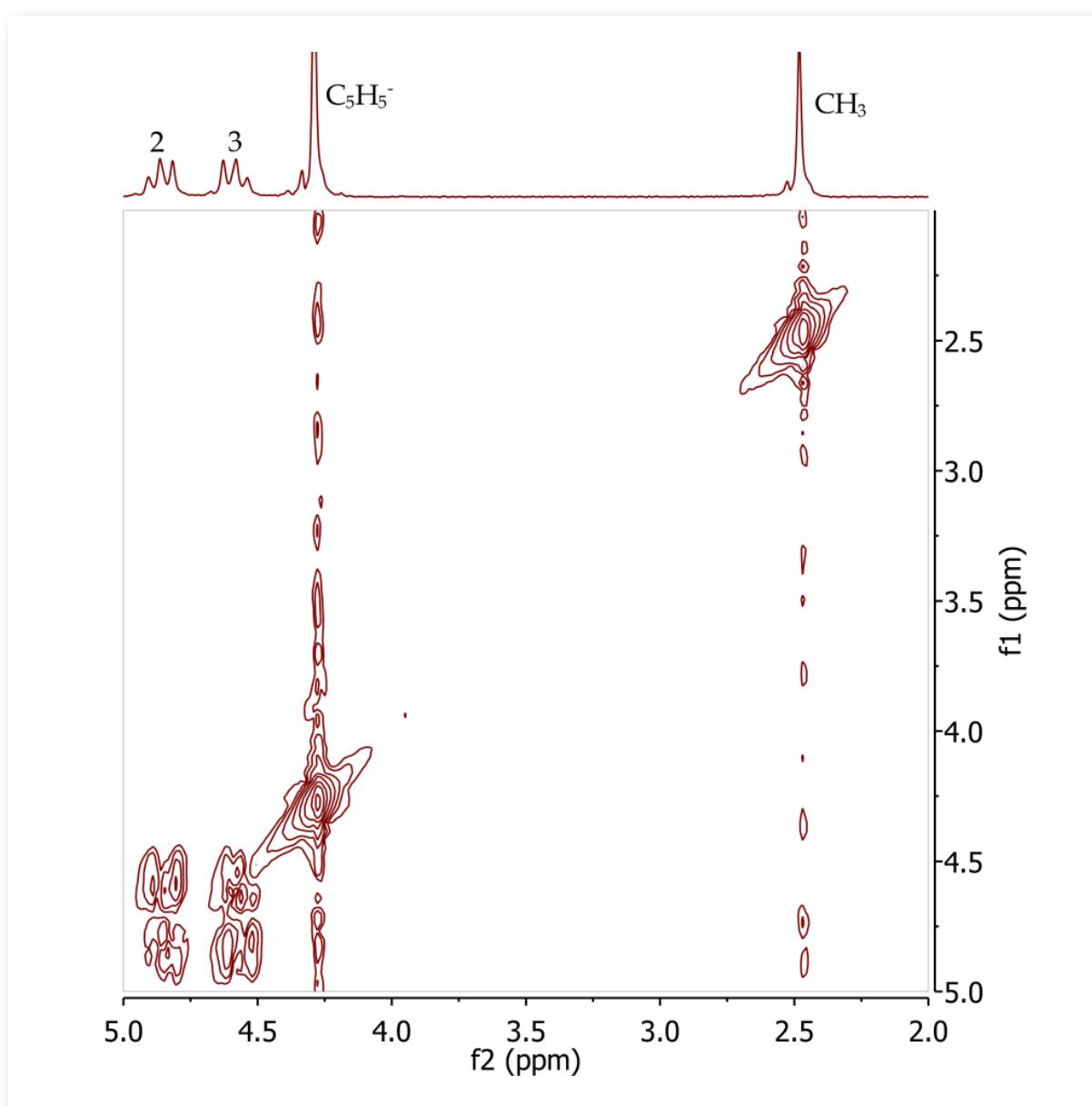


Figure 8. COSY spectrum of acetylferrocene, CDCl_3 . Refer to Scheme 3 for the annotated structure.

The COSY spectrum of acetylferrocene (Figure 8) clearly shows that protons at position 2 and 3 are

within the same spin system, i.e. the substituted cyclopentadienyl ring.

Preparation of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$

In this experiment, you will perform a ligand exchange reaction between one of the cyclopentadienyl rings in ferrocene and benzene to form a cationic iron π complex, which is then precipitated as the hexafluorophosphate (PF_6^-) salt.⁶

Safety

Benzene is carcinogenic and flammable, avoid all contact with the skin and handle with extreme caution in the fumehood. Aluminium trichloride (AlCl_3) is corrosive and hygroscopic, avoid contact with skin and clothing and keep the container tightly sealed. Potassium hexafluorophosphate (KPF_6) is harmful, handle with care. Aluminium powder is an irritant and reacts violently with water. Keep dry and handle with care. Acetonitrile and dichloromethane are flammable and toxic. Tetrachloroethane is toxic and may cause cancer, do not ingest or inhale and handle with caution. Acetone-d₆ is flammable and an irritant, handle with care.

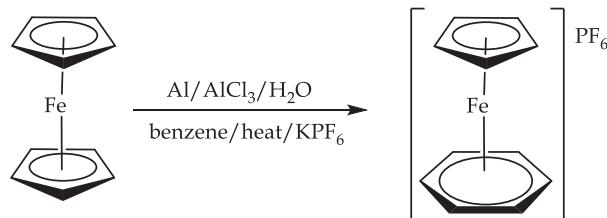
a) Synthesis of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$

Dissolve 2.0 g of ferrocene in 10 mL of benzene in a 50 mL round bottom flask. With continuous stirring add aluminium powder (0.3 g), AlCl_3 (4 g) and water (0.2 mL). Place a reflux condenser on top of the flask and heat the reaction mixture under reflux for 45 min with efficient stirring. Thorough mixing of the heterogeneous reaction mixture is vital to the success of this synthesis. Cool the dark brown mixture in an ice bath then add ice cold water (25 mL) cautiously as considerable heat is generated. Place the reaction mixture in a 100 mL separating funnel. The aqueous layer is collected in a beaker and made up to 50 mL with water. Finely ground KPF_6 (2.5 g) is added and the mixture is stirred for 10 min. The green precipitate is filtered, washed with some water, ethanol and diethyl ether and allowed to dry in the air.

b) Purification of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$

Dissolve the crude green solid in 10 mL of acetonitrile and filter under gravity into a small

round bottom flask. Add 3 mL of tetrachloroethane and evaporate the acetonitrile on a rotary evaporator until a green solid forms and only about 3 mL of liquid remains. Collect the solid by filtration, wash with some dichloromethane and record your yield.



Scheme 4. Ligand exchange of ferrocene with benzene.

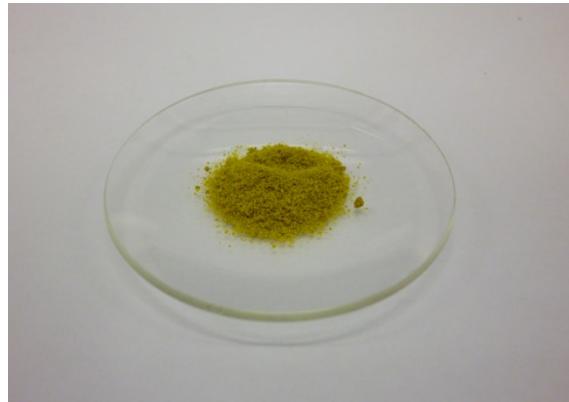


Figure 9. $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$.

Tasks

- Calculate the percentage yield of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$.
- Record the ^1H NMR spectrum of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ using the Spinsolve NMR spectrometer. Prepare the NMR samples using 50 mg of each compound in 1 mL of acetone-d₆.
- Record the IR spectrum of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$.

Questions

- Assign the ^1H NMR and IR spectra of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$.
- Comment on the chemical shift of the C₆H₆ protons in $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ relative to protons in free benzene.

¹H NMR Spectrum

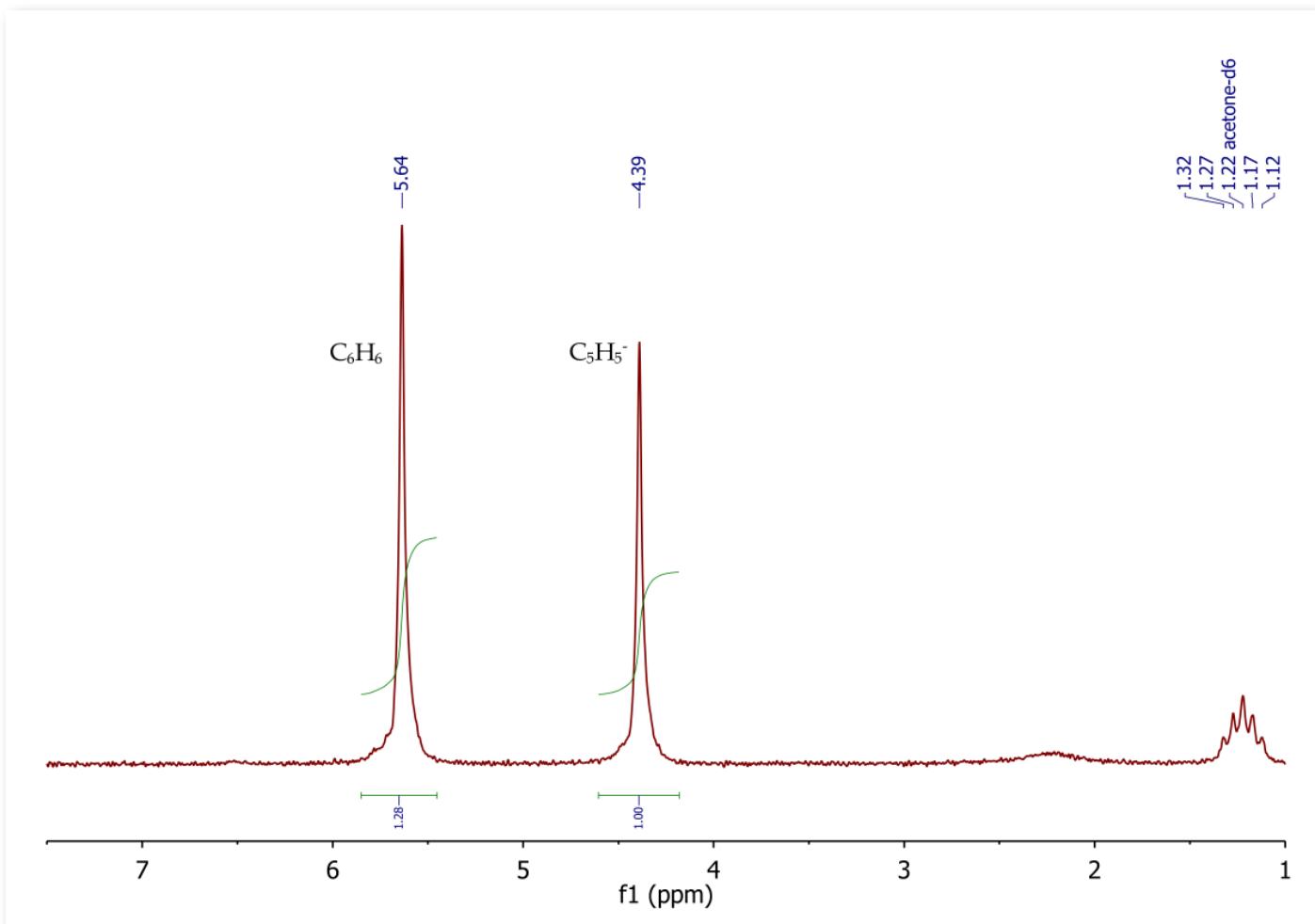


Figure 10. ¹H NMR spectrum of [Fe(η-C₅H₅)(η-C₆H₆)]PF₆ complex, acetone-d₆.

The ¹H NMR spectrum of [Fe(η-C₅H₅)(η-C₆H₆)] (Figure 10) shows five equivalent aromatic protons as a singlet at 4.39 ppm for the cyclopentadienyl ring. Another singlet is also observed at 5.64 ppm (6H) corresponding to the benzene ring.

Reaction of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ with nucleophiles

In these experiments, you will study the reaction of the iron benzene π -complex prepared in part 3 with LiAlH_4 and LiAlD_4 , sources of H^- and D^- ions respectively.⁶ Arenes, such as benzene, are typically more susceptible to attack by electrophiles than nucleophiles. However, association with a metal often alters the reactivity of organic ligands. Thus, we will examine the reactivity of the benzene ligand in the iron π -complex towards the nucleophiles H^- and D^- .

Safety

Lithium aluminium hydride (LiAlH_4) and lithium aluminium deuteride (LiAlD_4) are toxic and corrosive, avoid all contact with skin and clothing. These compounds also react violently with water, thus the need to weigh them rapidly and keep the containers tightly sealed. Tetrahydrofuran (THF) is carcinogenic and flammable, handle with extreme caution. Ethanol is toxic and flammable, handle with care.

a) Reaction of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ with LiAlH_4

Charge a 50 mL round bottom flask with $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ (1 g) in dry THF (20 mL). Cautiously add LiAlH_4 (0.25 g) in small portions while stirring the reaction mixture. Continue stirring until the last traces of the yellow starting material have disappeared. Cool the reaction mixture in an ice bath, and destroy any excess LiAlH_4 by adding ethanol dropwise until vigorous bubbling ceases. Transfer the mixture into a separating funnel and carefully add water (30 mL) and light petroleum ether (30 mL). Run the aqueous layer from the bottom of the funnel, but collect the organic layer from the top of the funnel. Evaporate the organic fraction to dryness using a rotary evaporator to obtain a red solid (Figure 11). Purify the crude product by sublimation and record your yield.²

b) Reaction of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ with LiAlD_4

Follow the same procedure as above, but use LiAlD_4 instead of LiAlH_4 .

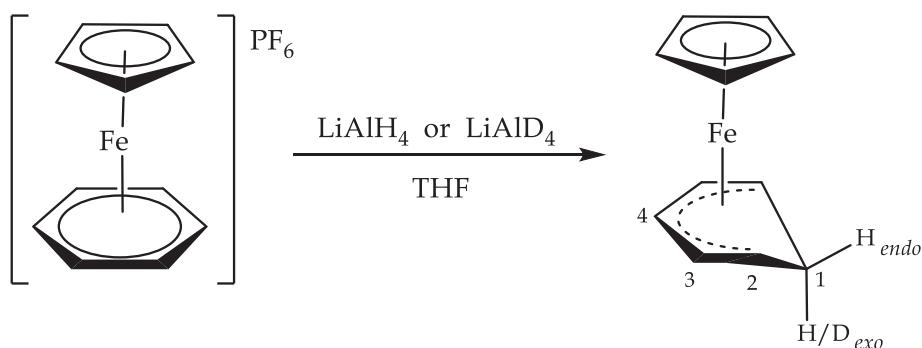
Tasks

- Calculate the theoretical yields for the products of hydride and deuteride attack on $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ complex.
- Record the ^1H NMR spectra of the products of hydride and deuteride attack on $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ complex using the Spinsolve NMR spectrometer. Prepare the NMR samples using 50 mg of each compound in 1 mL of CDCl_3 .
- Record the COSY and 2D J-resolved (2DJRes) spectra of the product of hydride attack on $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ complex using the Spinsolve NMR spectrometer.
- Record the IR spectra of the products of hydride and deuteride attack on $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ complex.

Questions

- Sketch three plausible structures for the product of hydride attack on $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ complex, and consider how many signals would be expected in the ^1H NMR spectrum for each structure. Remember, nucleophilic attack on either ring can occur on the same side as the metal (*endo*), or from the opposite side (*exo*). Also, the *endo* and *exo* positions in such a ring are fixed in space.
- Analyse the ^1H NMR spectrum of the product of hydride attack on $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ complex. Can you eliminate any of the proposed structures based on the number of signals and their intensities? Remember, there is a solvent peak and some peaks may overlap.
- Analyse the COSY spectrum to determine the correlations between the different proton environments in the product of hydride attack on $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ complex. You should also be able to confirm that some signals are partly obscured.
- Analyse the 2D J-resolved spectrum of the product of hydride attack on $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ complex to further confirm the proton coupling patterns and the overlap of signals.

- Analyse the ^1H NMR spectrum of the product of deuteride attack on $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ complex. Can you identify the signal of the incoming nucleophile? Which other signal is it strongly coupled to in the COSY spectrum?
- Analyse and compare the IR spectra of the products of hydride and deuteride attack on $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ complex. Can you identify the main vibration arising from the incoming H/D nucleophile? Does this allow you to eliminate any of the proposed structures? Is the $\nu(\text{D})$ vibration where you would expect relative to the $\nu(\text{H})$ vibration?
- Assign the NMR and IR spectra of the products of hydride and deuteride attack on $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ complex. Discuss how the spectroscopic data supports the proposed structure, including how the site of nucleophilic attack was determined and whether the attack was on the *endo* or *exo* face of the ring.



Scheme 5. Nucleophilic attack on the benzene ring of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]$.



(a) $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_6\text{H}_7)]$



(b) $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_6\text{H}_6\text{D})]$

Figure 11(a)-(b). Purified nucleophilic reaction products.

NMR Spectra

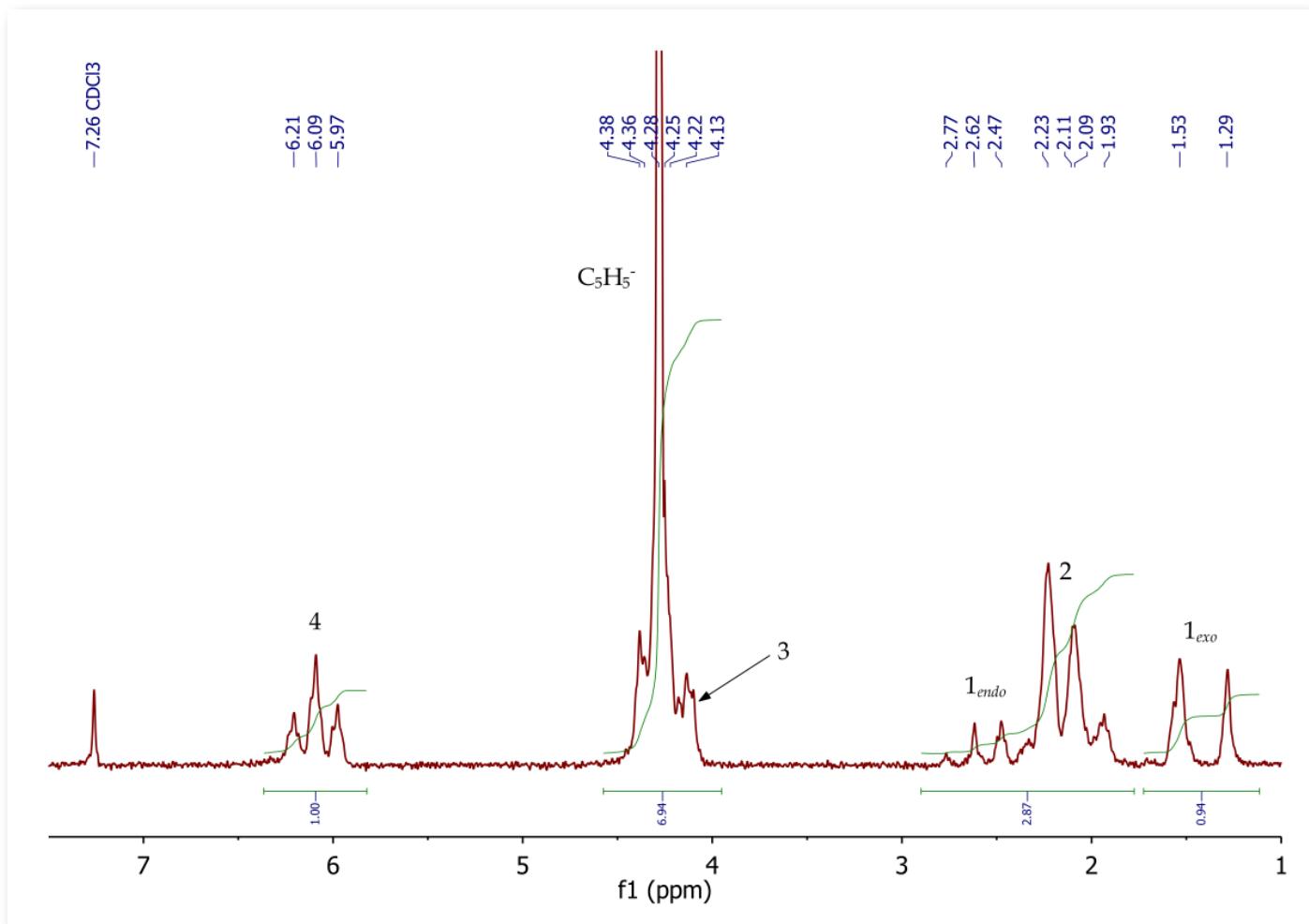


Figure 12. ^1H NMR spectrum of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_6\text{H}_7)]$ complex, CDCl_3 . Refer to Scheme 5 for the annotated structure.

The ^1H NMR spectrum (Figure 12) of the product of hydride attack on $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ complex shows four signals in a 1:3:7:1 ratio, with two sets of overlapping signals between 1.93–2.77 and 4.13–4.38 ppm. Therefore, the nucleophilic attack has occurred on the benzene ring, which is an even closed cyclic polyene, rather than at

an odd system, i.e. cyclopentadienyl anion. The expected number of signals with no overlap would be six in the ratio 1:2:1:2:5:1. The exo proton at position 1 resonates as a doublet (10.6 Hz) at 1.55 ppm, whereas the endo proton appears as a multiplet centred at 2.47 ppm. These two protons are also strongly coupled in the COSY spectrum (Figure 14).

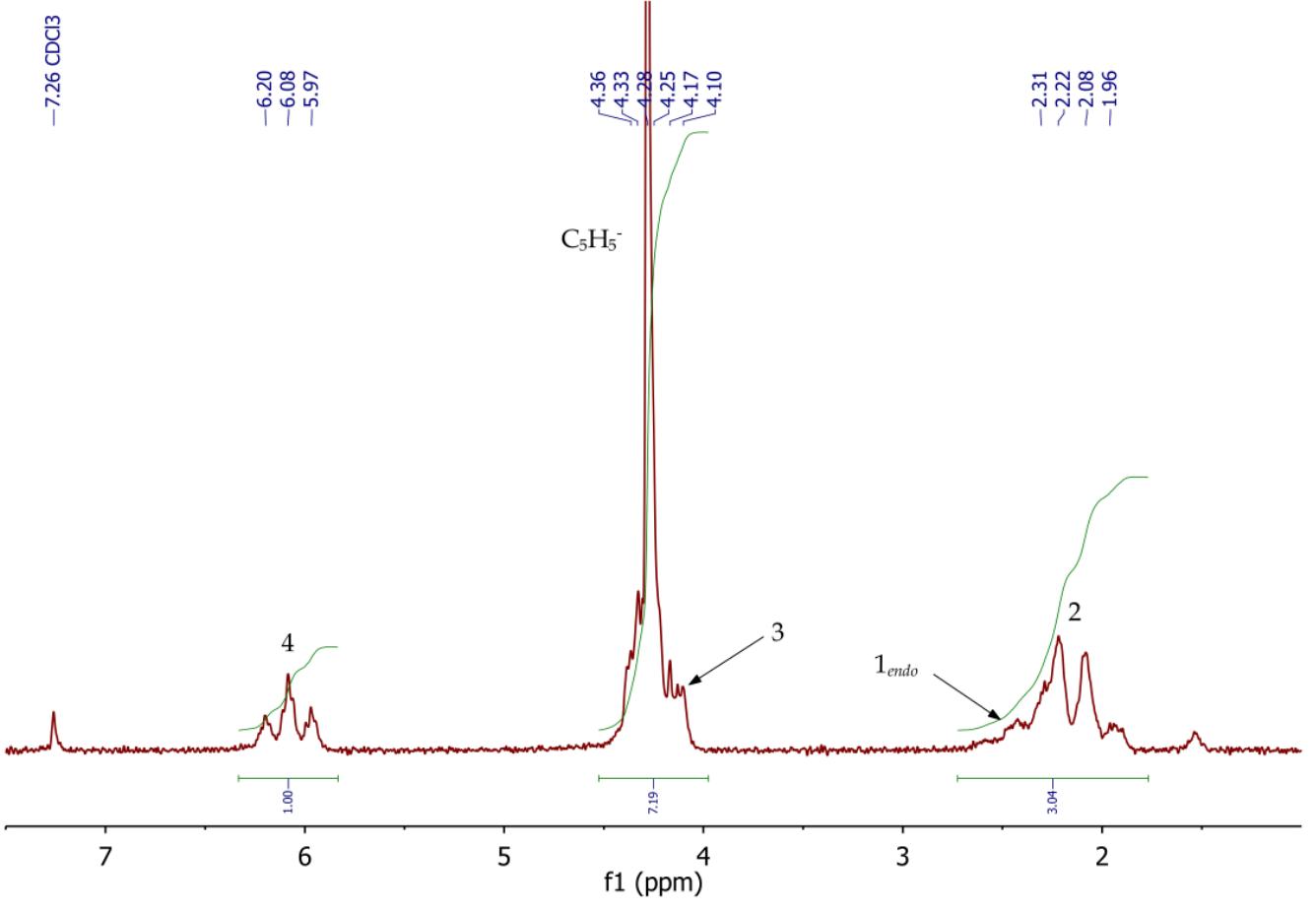


Figure 13. ^1H NMR spectrum of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_6\text{H}_6\text{D})]$ complex, CDCl_3 . Refer to Scheme 5 for the annotated structure.

The ^1H NMR spectrum (Figure 13) of the product of deuteride attack on $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_6\text{H}_6)]\text{PF}_6$ complex shows three signals in the ratio 3:7:1, with two sets of overlapping signals between 1.96–2.31 and 4.10–4.36 ppm. Therefore, the site of nucleophilic attack is exclusively exo as the signal for the exo proton at 1.55 ppm (Figure 12) has

disappeared. The expected number of signals with no overlap would be five in the ratio 2:1:2:5:1. The *endo* proton resonates as a broad multiplet centred at approximately 2.30 ppm. The *endo* proton signal is obscured by the proton signal at position 2 and is further complicated by deuterium coupling.

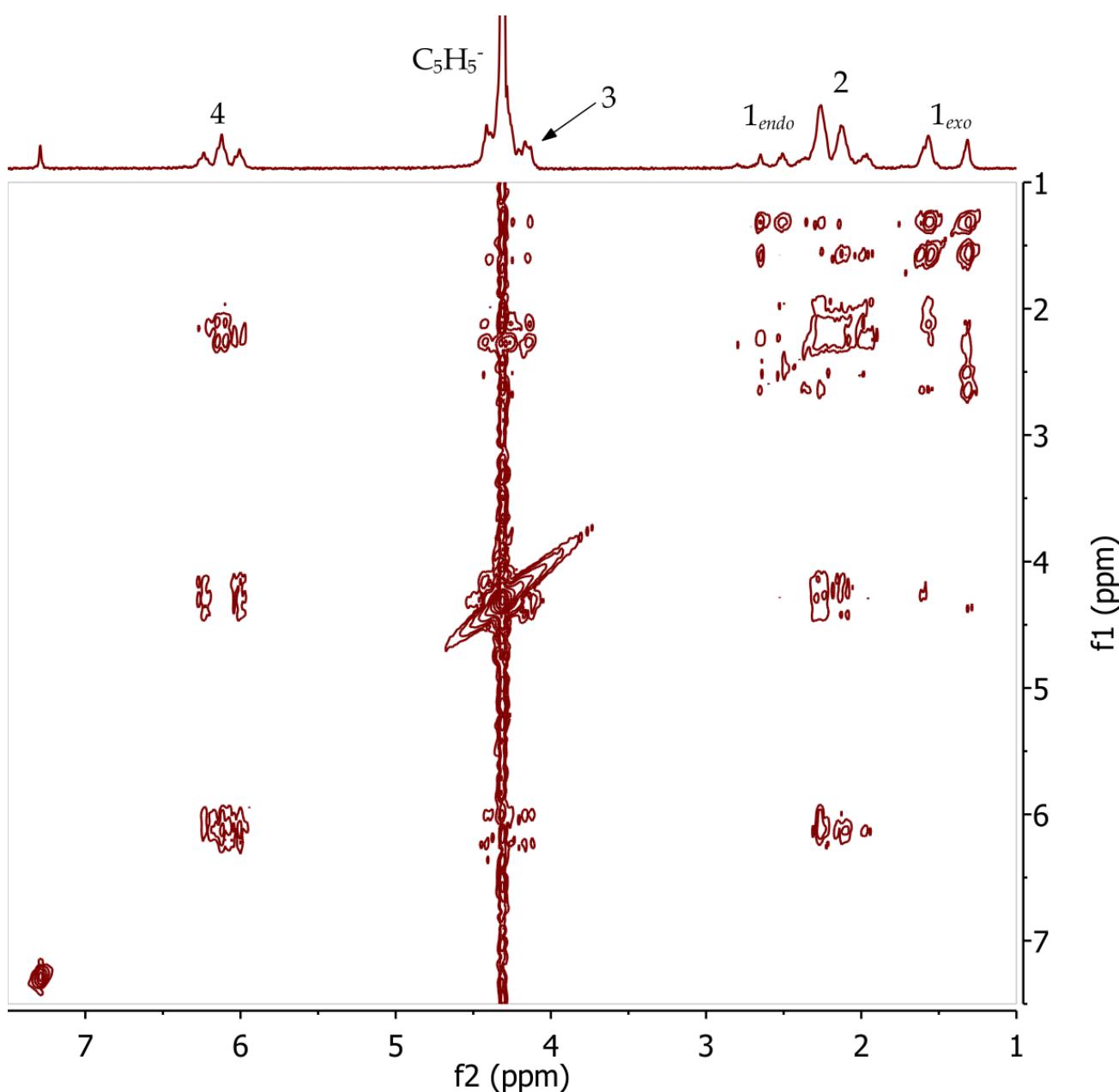


Figure 14. COSY spectrum of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_6\text{H}_7)]$ complex, CDCl_3 . Refer to Scheme 5 for the annotated structure.

Interpretation of the COSY spectrum of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_6\text{H}_7)]$ shows the resolution of the three-proton multiplet between 1.93-2.77 ppm. For example, the endo proton is strongly coupled to the exo proton at position 1, and in turn they

are both coupling to the protons at position 2. The COSY correlations also confirm the overlap of signals of the C_5H_5^- ring and the protons at position 3 between 4.13 and 4.38 ppm.

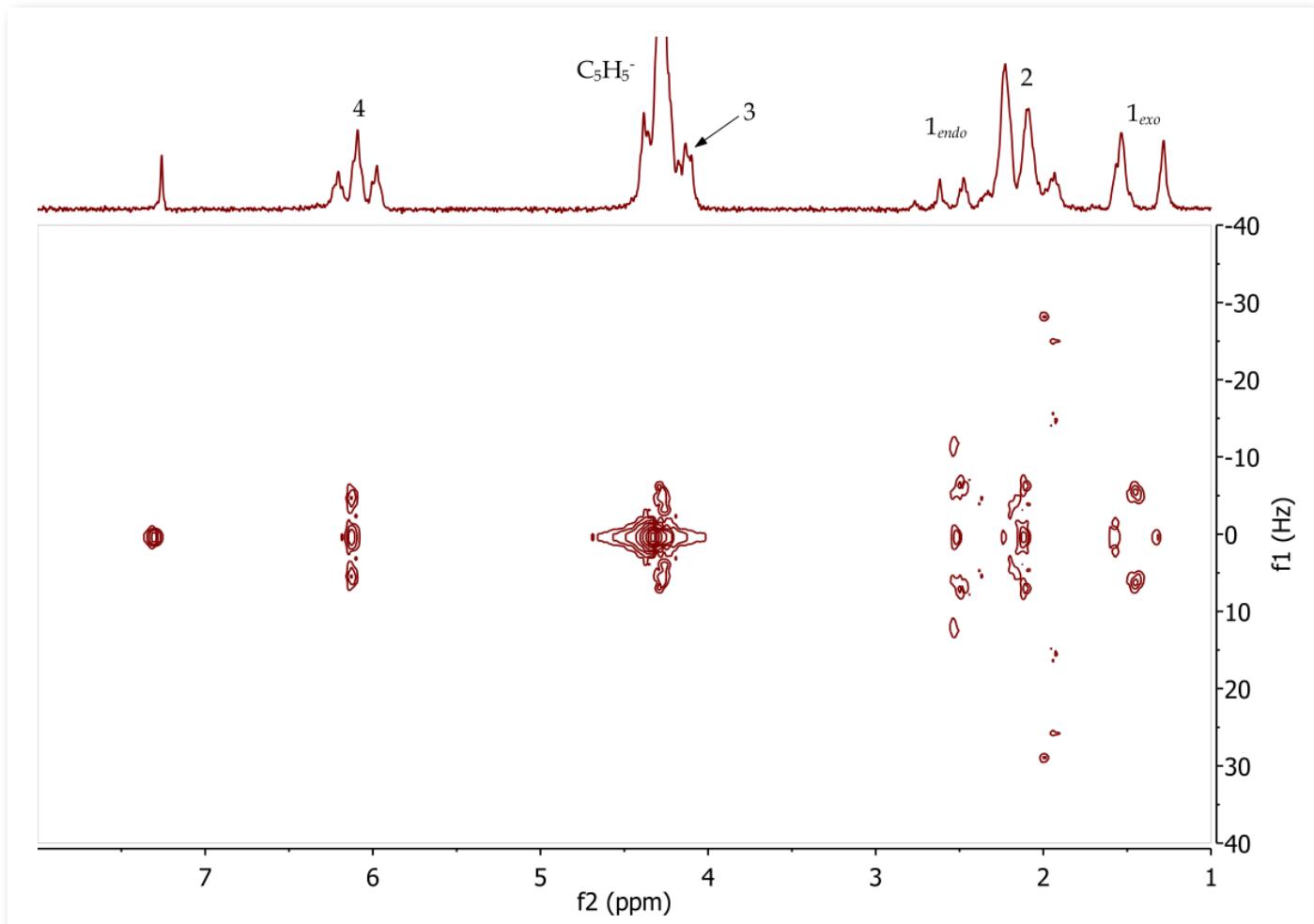


Figure 15. 2D J-resolved (2DJRes) spectrum of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_6\text{H}_7)]$ complex, CDCl_3 . Refer to Scheme 5 for the annotated structure.

The 2D J-resolved spectrum of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_6\text{H}_7)]$ (Figure 15) shows how the complex proton coupling patterns have been resolved in the second (f1) dimension. The overlap of signals of the endo proton and the protons at

position 2 between 1.93-2.77 ppm is also very clear, as well as the overlap of the signals of the C_5H_5^- ring and the protons at position 3 between 4.13-4.38 ppm.



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