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The Stability of Ferrocenylmethyl Derivatives: Further Attempts to Synthesize Ferrocenylacetone

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Attempts have been made to synthesize ferrocenylacetone by various routes. The reaction of ferrocene and chloroacetone in the presence of boron trifluoride etherate was investigated as a potential route but this gave 2,2-diferrocenylpropane and not ferrocenylacetone as reported in the literature. Several other attempts to synthesize ferrocenylacetone also failed and possible reasons for the instability of this and of other ferrocenylmethyl derivatives are discussed.

Keywords: ferrocenylacetone; ferrocenylmethyl derivatives; thermal stability

INTRODUCTION

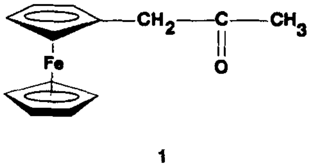
There has recently been an upsurge of interest in the potential use of organometallic molecules, particularly ferrocene derivatives, as new compounds for use in materials such as liquid crystals,[1-10] non-linear optical materials,[11-18] magnetic materials[19] and electronic materials.[20] Clearly, if these molecules are to be useful in devices, they must have reasonable thermal and photostability. It is also desirable that they are stable to oxidizing conditions (in air). There has not previously been a comprehensive study on the factors affecting the stability of ferrocene derivatives although it is possible to deduce from past literature some general trends.

1. Electron-withdrawing groups adjacent to a ferrocenyl group weaken the Fe–Cp (substituted) bond to an extent and lead to compounds of lower thermal stability than ferrocene.[21] Despite this the compounds can usually be isolated. For example, nitroferrocene,[22] cyanoferrocene[23] and 1,1′-dicyanoferrocene[24] are all high-melting solids.
2. Electron-donating groups adjacent to a ferrocenyl group lead to compounds which are prone to oxidation and therefore exhibit air instability. Examples are hydroxyferrocene,[25] aminoferrocene[26] and 1,1′-diaminoferrocene.[27] These compounds are usually not isolated but are used directly in a synthetic sequence.
3. Ferrocenes bearing a *partial positive* charge in an α-position are highly unstable photochemically. There are many documented examples of this[28-32] and we have recently observed a similar behaviour for benzyldiphenylferrocenylphosphonium salts in solution.[33]
4. Ferrocenes exhibit photoinstability in certain halogenated solvents.[34] For example, ferrocene in tetrachloromethane decomposes rapidly in sunlight.

Points (1)–(3) summarize the effect of substituent groups directly attached to ferrocenes on their stability but it is apparent that less is known concerning the effects of more distant groups on the stability of ferrocenes.

It was during our investigation of whether haloferrocenes could undergo $S_{RN}1$[35] reactions that we were drawn to the apparent unusual instability of certain ferrocenylmethyl derivatives.

One of the products expected from the reaction



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of iodoferrocene and acetone enolate by an $S_{RN}1$ reaction is ferrocenylacetone (**1**). Initially, we expected that the synthesis of **1** would be straightforward. This proved not to be the case and the previous literature recorded for **1** is not consistent. The first attempt to synthesize **1** was reported in 1969 by Nugent and co-workers[36] from the reaction of ferroceneacetic acid and methyllithium. The product was described as being highly unstable and was not isolated. In 1972, two further attempts to synthesize **1** were reported. The first of those methods involved the reaction of ferrocenecarboxaldehyde and dimethyloxosulphonium methylide.[37] The elemental analysis of the product from the reaction was low in carbon, hydrogen and iron and this was attributed again to the instability of the product. The second route to **1** published in 1972 was by the reaction of chloromercuriferrocene, palladium(II) chloride and isopropenyl acetate in ethanol, in which it was claimed that **1** was isolated in a yield of 27%. The product was a low-melting solid (m.p. 46–47 °C).[38] Two further reports on the synthesis of **1** appeared in 1973. Ali *et al.*[39] claimed to have obtained **1** as a stable solid (m.p. 130–131 °C) from the reaction of ferrocene and chloroacetone in the presence of boron trifluoride. In the final report on compound **1**, Toma and Salisova reported that it was unstable in air at room temperature, being easily oxidized to 1-ferrocenyl-1,2-propanedione.[40] In our desire to synthesize **1** for our free-radical work, we have attempted to synthesize **1**, firstly using some of the aforementioned literature methods and secondly by using new routes. Our results show that **1** is particularly difficult to isolate pure and also that some of the previous characterizations for **1** are incorrect. We discuss the possible reasons for the instability of **1** by comparing its properties with the properties of a series of ferrocenylmethyl derivatives, this comparison shows that a small alteration of the electron density adjacent to the ferrocenylmethyl group gives unstable molecules.

EXPERIMENTAL

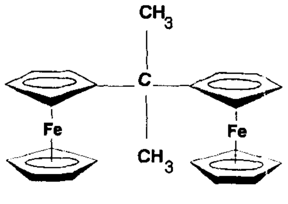
Equipment

All reactions were carried out under nitrogen. Silica gel was used for column chromatography. IR spectra were recorded using a Perkin–Elmer 397 spectrometer. Microanalyses were performed by the microanalytical department of the University of Strathclyde. Mass spectra were recorded using an MSS mass spectrometer connected to an Elliot 905 computer. ^1H NMR and ^{13}C NMR spectra were recorded using either a Perkin–Elmer R32 90 MHz spectrometer or a Bruker AC 300 spectrometer. Melting points were recorded using a Gallenkamp apparatus. Ferrocenylacetonitrile was prepared according to the method of Osgerby and Pauson.[41]

Attempted synthesis of ferrocenylacetone

From ferrocene and chloroacetone

Ferrocene (3.0 g, 16 mmol) was dissolved in anhydrous dichloromethane (40 ml) and chloroacetone (1.5 g, 16 mmol) was added. Boron trifluoride etherate (10.0 g, 70 mmol) was added to the solution dropwise. The solution was stirred overnight, following which aqueous sodium acetate (50 ml) was added. The aqueous layer was separated, washed twice with dichloromethane (2 × 20 ml), and the washings were combined with the original organic layer. The combined organic layer was washed with 20% aqueous sodium carbonate (2 × 30 ml), three times with water (3 × 30 ml), and then dried over anhydrous calcium chloride. The solvent was removed by evaporation and the orange residue was chromatographed on silica gel, eluting initially with light petroleum, (b.p. 40–60 °C). Ferrocene (0.6 g, 20%) was recovered from the first yellow fraction. A second yellow fraction was removed from the column using diethyl ether. After evaporation of the solvent, an orange residue remained and this was sublimed at 100 °C/0.01 mmHg to give a bright orange solid identified as 2,2-diferrocenylpropane **2** (0.4 g, 15%), m.p. 129 °C. Found: C, 67.3; H, 6.0; M^+, 412.058. $C_{23}H_{24}Fe_2$ requires C, 67.0; H, 5.9%; M, 412.145; IR (KBr), cm^{-1}: 3095 (m), 1460 (m), 1440 (m), 1240 (m), 1100 (s), 1000(s), 900 (s), 820 (vs). ^1H NMR ($CDCl_3$), ppm: 4.10 (s, 10H, $C_5H_5 \times 2$), 4.05 (s, 8H,



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$C_5H_4 \times 2$), 1.62 (s, 6H, $CH_3 \times 2$). MS, *m/z*: 412.058 (M^+, 52%), 397.030 (15), 347.015 (7), 240.941 (4), 186.013 (4).

From chloromercuriferrocene, palladium(II) chloride and isopropenyl acetate

First experiment

A lithium chloropalladite solution was prepared by stirring anhydrous lithium chloride (0.1 g, 2.4 mmol) and anhydrous palladium chloride (0.21 g, 1.2 mmol) overnight at room temperature in dry ethanol (20 ml). To this solution was added a mixture of chloromercuriferrocene (0.5 g, 1.2 mmol) and isopropenyl acetate (0.45 g, 4.5 mmol). The mixture was stirred at room temperature for 12 h. The solution was then filtered to remove palladium salts and the solvent was removed under reduced pressure. Chromatography of the residue on silica gel using petroleum ether (40–60 °C) and then benzene as the eluant afforded one fraction. On removing the solvent *in vacuo*, an orange solid was obtained and identified as biferrocenyl (50 mg, 11%); m.p. 238–240 °C (lit., m.p. 239–240 °C dec.[42]) IR (KBr), cm^{-1}: 1685 (br), 1409 (m), 1261 (m), 1102 (vs), 1032 (m), 1000 (vs), 814 (vs), 482 (vs). ^1H NMR ($CDCl_3$), ppm: 3.97 (s, 10H, $C_5H_5 \times 2$), 4.15 (t, 4H, $C_5H_4 \times 2$), 4.33 (t, 4H, $C_5H_4 \times 2$). ^{13}C NMR ($CDCl_3$), ppm: 69.01, 67.59, 66.36, 65.30. MS, *m/z*: 370 (M^+).

Second experiment

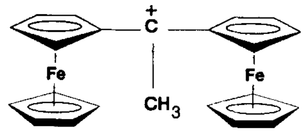
The procedure was as for the first experiment except that oxygen was bubbled through the solution after the 12 h stirring period. A GC/MS of the reaction residue was recorded prior to separation of the components using flash chromatography. The GC/MS indicated that there were three main components: (1) *m/z* = 243 (10%), 242 (63%), 200 (17%), 199 (100%), 121 (74%); (2) *m/z* = 257 (9%), 256 (39%), 214 (7%), 213 (37%), 186 (13%), 185 (100%); (3) *m/z* = 371 (39%), 370 (100%), 305 (46%), 185 (13%). The reaction residue was subjected to flash chromatography using benzene as the eluant and two fractions were collected. The first fraction contained biferrocenyl (16 mg, 4%). The product from the second fraction was identified as 1-ferrocenyl-1,2-propanedione (9 mg, 3%). ^1H NMR ($CDCl_3$), ppm: 2.46 (s, 3H, CH_3), 4.21 (s, 5H, C_5H_5) 4.67 (t, 2H, C_5H_4), 5.01 (t, 2H, C_5H_4). ^{13}C NMR ($CDCl_3$), ppm: 29.71, 65.84, 70.34, 71.17, 74.20, 207.22, 208.80. MS, *m/z*: 257 (9%), 256 (39%), 214 (7%), 213 (37%), 186 (13%), 185 (100%).

From ferrocenylacetonitrile and methyl-lithium

In a 50 ml flask equipped with stirrer, dropping funnel and nitrogen inlet were placed ferrocenylacetonitrile (0.10 g, 0.4 mmol) and anhydrous diethyl ether (30 ml). The reaction mixture was cooled to −5 °C and methyl-lithium (0.5 ml of a 1.4 M solution in diethyl ether) was added to the solution dropwise. A static pressure of nitrogen was maintained over the reaction mixture, which was stirred at high speed. After the reaction mixture had been allowed to stand for 2 h at −5 °C, it was heated under reflux for 5 h. Stirring was then discontinued and the mixture was allowed to stand at room temperature overnight. Phosphoric acid (1 ml, 5%) was added with stirring. The ether layer was separated, washed with water then saturated sodium hydrogen carbonate solution, and finally it was dried over anhydrous sodium sulphate. Evaporation of the solvent left a brown oil [IR(I_f), cm^{-1}: 1710 (CO)] which darkened on exposure to air.

RESULTS AND DISCUSSION

The simplest route to ferrocenylacetone **1** from easily available starting materials was considered to be that described by Ali *et al.*[39] This involved reacting ferrocene and chloroacetone in the presence of boron trifluoride. This reaction gave an orange solid; the melting point and NMR spectrum of this compound were identical to those cited in the literature. However, an IR spectrum of the product showed no absorption in the carbonyl region and thus it could not be **1**. This compares with the literature compound for which an IR was reported to give a carbonyl absorption



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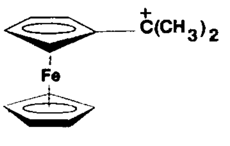

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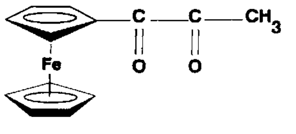

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band at 1725 cm^{-1} in DMSO. A mass spectrum of the orange solid indicated that the molecular ion was 412.058, corresponding to a molecular formula, $C_{23}H_{24}Fe_2$.

The spectrum did not contain a peak at *m/z* 242 (molecular weight of ferrocenylacetone) and this observation confirmed that this product was not **1**. The mass spectrum contained other peaks at *m/z* 410, 397, 241, 227, 226, 206, 186, and 120. Spectral evidence together with analytical data confirmed that the product was 2,2-diferrocenylpropane, **2**.

The ions with *m/z* values 397 and 227 probably correspond to the ions shown as structures **3a** and **3b**. Compound **2** was synthesized once previously by Nesmeyanov *et al.*[43] by the reaction of ferrocene and acetone in the presence of boron trifluoride and concentrated hydrochloric acid although, on that occasion, it was not fully characterized. The mass spectrum of that compound showed a similar fragmentation pattern to the one exhibited by our compound. We can conclude therefore that the reaction of ferrocene and chloroacetone in the presence of boron trifluoride is not a viable route to **1**. On the other hand, the reaction represents one of the simplest procedures for synthesizing a diferrocenyl compound direct from ferrocene and could prove of use in the emerging field of materials chemistry.

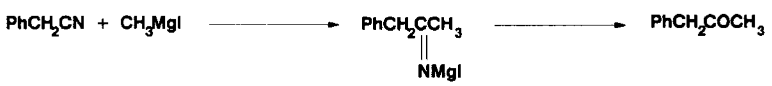
Next, we attempted to repeat the procedure described by Kasahara *et al.*[38] This involved reacting chloromercuriferrocene and lithium chloropalladite with isopropenyl acetate. This reaction was performed in duplicate with a modification of the literature procedure in the second reaction. From the first reaction, only biferrocenyl was isolated. Decomposition of a significant proportion of the reaction mixture residue on the column was observed. In the second reaction, oxygen was bubbled through the solution after the 12 h period of stirring and we expected that if **1** was forming, it would undergo efficient oxidation to 1-ferrocenyl-1,2-propanedione (**4**), a reaction previously reported by Toma and Salisova.[40] A GC/MS analysis of the reaction mixture prior to chromatographic separation indicated the presence of three ferrocene-containing products. One of these was biferrocenyl showing a molecular ion at $m/z = 370$. Another fraction showed MS signals at $m/z = 243$, 242, 200 and 19, whilst the third fraction had signals at $m/z = 257$, 256, 214, 213, 186, 185. These fragmentation patterns suggest that the products are **1** and **4**. Two fractions were isolated from chromatography of the second reaction. The first again contained biferrocenyl whilst the second did indeed contain 1-ferrocenyl-1,2-propanedione (**4**).

The Japanese group claimed to have isolated **1** as a low-melting solid from their reaction. However, their spectroscopic evidence for compound **1** is far from convincing. For example, the chemical shift values in the ^{1}H NMR of their material are not consistent with those expected for **1**. The NMR shifts are given as 2.21 (CH_3), 3.92 (CH_2), and 4.12 (ferrocenyl; Fc). The benzene analogue of **1**, phenylacetone has ^{1}H NMR shifts at 2.11 (CH_3), 3.65 (CH_2), and 7.0–7.4 (Ph). The ferrocenyl group is more electron-donating than the phenyl group and usually causes an upfield shift of the NMR signals with respect to a phenyl group. Clearly, this is not the case for their compound, where the ferrocenyl group shows the reverse trend.

The next attempt to prepare **1** was based on the reaction in Scheme 1.[44] Reaction of ferrocenylacetonitrile with methylmagnesium iodide gave a large quantity of starting material back and analysis of the reaction residue showed that it did not contain a ketone.

The final attempt involved the reaction of ferrocenylacetonitrile with methyl-lithium. In this instance, the reaction gave after work-up a dark brown oil which darkened further on exposure to air. The IR spectrum of this material showed a strong absorption at 1710 cm^{-1} but isolation of pure **1** was not achieved.

The evidence from these experiments supports the work of other groups that show **1** is not a particularly stable compound at room temperature in air and this conclusion correlates with the behaviour of many other ferrocenylmethyl deri-



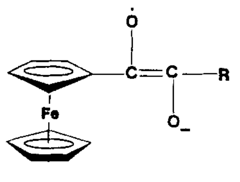
$$PhCH_2CN + CH_3MgI \longrightarrow PhCH_2\underset{\|\atop NMgI}{C}CH_3 \longrightarrow PhCH_2COCH_3$$

Scheme 1 Route to the synthesis of phenylacetone from phenylacetonitrile.

Table 1 Properties of substituted ferrocenylmethyl derivatives ($FcCH_2X$)

Substituent group, X	M.p. (B.p.) (°C)	Stability[a]
$COCH_3$		Unstable[40]
COPh	80–82	Unstable[45]
CN	81–83	Unstable[46]
CHO		Unstable[37]
Cl		Unstable[47]
SO_2Ph	163–165	Stable[48]
COFc	159–161	Stable[49]
Ph	76	Stable[50]
OCH_3	(106–107.5)	Stable[51]
OH	76	Stable[24]
COOH	152–155	Stable[46]
$N(CH_3)_2$	200	Stable[41]
NH_2	30–35	Stable[52]
N_3	32–34	Light-sensitive[53]

[a] The compounds marked as stable are easily isolated and can be kept at room temperature in air without undergoing considerable decomposition or oxidation.



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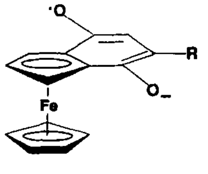
R= -Me, -Et, -Pr^i, -Bu^t, Ph



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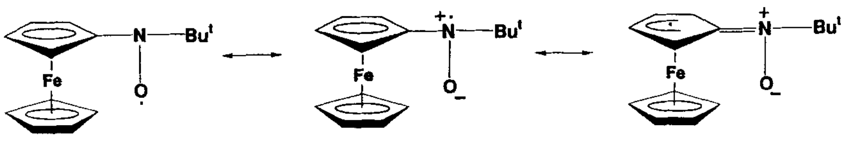
R= -H, -Me, -Et, -Pr^i

vatives (Table 1). Many of the compounds listed in Table 1 are unstable in the solid state at room temperature and all have a methylene group between the ferrocene ring and an electron-withdrawing group. According to the models outlined in the Introduction concerning the general factors leading to unstable ferrocenes, the instability of **1** and compounds of similar structure cannot be reconciled with any of the categories (1)–(3). The electron-withdrawing effect of the acetyl group in **1** should not be efficiently translated through the methylene group to cause disruption of the Fe–Cp bond (Cp = cyclopentadienyl). Compound **1** is air-sensitive (the CH_2 group is oxidized quite easily to a carbonyl group) but according to the models in the Introduction, **1** would not be expected to be unstable in air or (in other words) be susceptible to oxidation to ferrocenium ions which subsequently break down. Compounds such as **1** contain acidic hydrogen atoms and the generation of α-ferrocenylmethyl carbanions from them is quite a facile process.[48] Carbanions of this type would be stabilized by charge delocalization into the carbonyl group to give an enolate ion. Interactions between the negatively charged oxygen and the ferrocenyl moiety in such an enolate should not be sufficient to disrupt the bonding between the metal and the Cp ligands. Several groups conducting previous studies on compounds in which such interactions are possible reported that the ferrocene compounds are reasonably stable in solution. For example, McDonnel and Pochopien formed stable semidiones **5** and **6** which were found to be reasonably stable.[54,55] Forrester *et al.*[56] reported on the synthesis of t-butylferrocenyl nitroxide (**7**), one of the few stable radicals containing a ferrocenyl group. The radical can be represented as shown in Scheme 2; the compound was reported to be stable as a solid for months and in solution for weeks (the solvent was not specified). Cais *et al.*[57] have reported on the formation of nitroxides **8** from α-ferrocenylmethyl carbocations. Again, these species are reasonably stable.

The ease of oxidation of **1** with molecular oxygen compared with phenylacetone suggests that the metal may play some cooperative role in the oxidation process. Iron(II/III) is important in the Gif methods of alkane oxidation,[58] in which oxygen is believed to bind to the metal in the initial step. There are of course other possible scenarios. Scheme 3 shows one of these in which oxygen reacts with the enol form of **1** to give peroxyl radicals **9**. Similar intermediates could also form directly from the keto form of **1** by hydrogen abstraction by oxygen on **1** to give substituted ferrocenylmethyl radicals and hydroperoxyl radicals (HO—O$^{\bullet}$); subsequent addition



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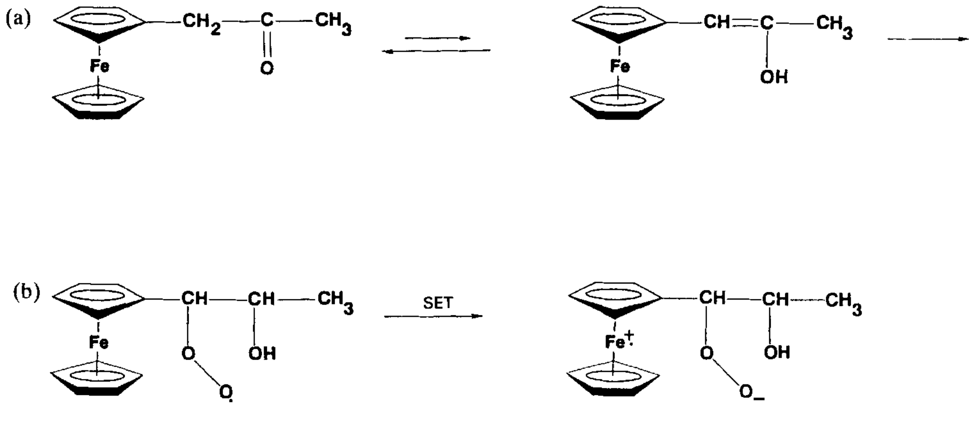
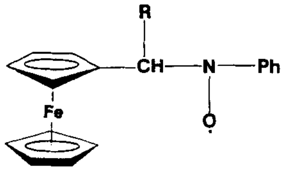
Scheme 2 t-Butylferrocenyl nitroxide, an inert radical containing a ferrocenyl group.



Scheme 3 Reaction of oxygen with ferrocenylacetone.



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of the substituted ferrocenylmethyl radicals to oxygen would give similar intermediates to **9** (the only difference being that the —OH group is replaced by an =O group). Radicals such as **9** normally form hydroperoxides which in turn often decompose to alcohols. Again, it is possible to speculate that there is some interaction between the metal and the oxygen atom in **9** which ultimately could produce an electron-transfer reaction.

CONCLUSIONS

This work has highlighted that the stability of ferrocenylmethyl derivatives is a tenuous affair and that if such molecules are to be useful in new devices, careful attention must be given to the choice of the substituent groups surrounding the organometallic core.

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