



A new insight into the problem of stabilisation of α -carbocationic centres in the ferrocene series

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Received 2 May 2002; revised 15 May 2002; accepted 16 May 2002

Abstract—Two different modes of stabilisation of the α -carbocationic centre in the diferrocenylcarbenium ion **4**, available from the [5]ferrocenophane **1** by sequential treatment with ferrocenyllithium and tetrafluoroboric acid, are clearly demonstrated by a combination of ¹H NMR and ⁵⁷Fe Mössbauer spectroscopies. © 2002 Elsevier Science Ltd. All rights reserved.

The phenomenon of the extraordinary ability of the ferrocenyl moiety, in addition to other cluster-based organometallic units, to alleviate electron deficiency at a neighbouring carbocationic centre has long been a matter of some controversy.¹ The point at issue is the exact mechanism by which such ions are stabilised. Several models have been suggested as appropriate for explaining the special stability of α -ferrocenylcarbenium ions: (a) interaction of the central metal ion with the π -electron system of the fulvene part with concomitant shift of the metal towards the exocyclic carbon atom;^{2b} (b) little or no interaction between the metal and the exocyclic carbon atom with the positive charge spread over the substituted cyclopentadienyl ring and stabilisation being due to ' σ - π conjugation' in accordance with the Traylor–Petit concept;³ (c) distortion and bending of bonds in the substituted ring so as to bring the exocyclic carbon atom near the metal ion to optimise the orbital overlap between the vacant p orbital on C_{exo} and a filled ϵ_2 orbital on iron.⁴ This type of 'bent' structure was predicted by an iterative extended Hückel calculation.⁵

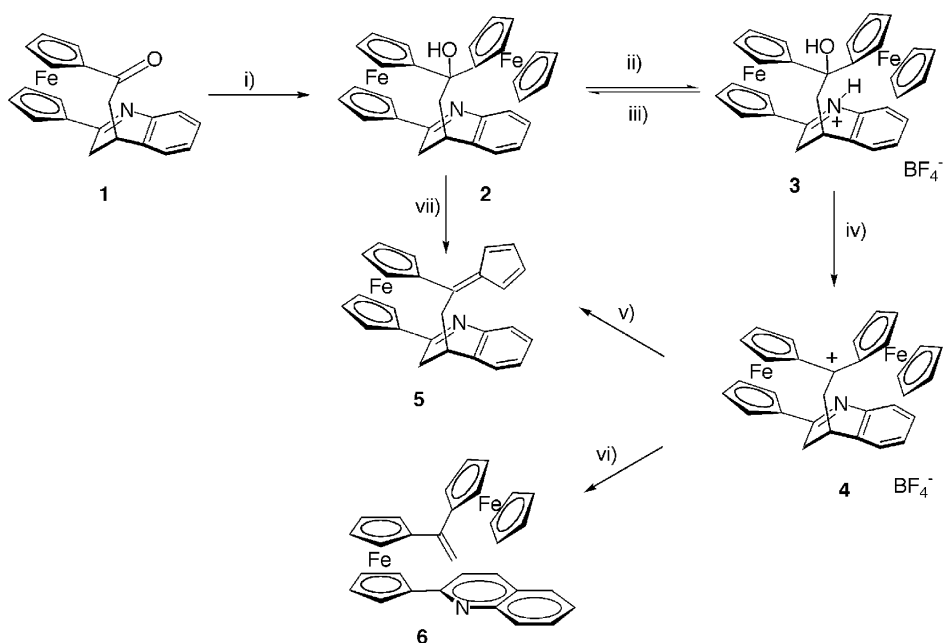
So far, only two crystal structures of ferrocenylcarbenium ions have been reported⁶ and in both cases the exocyclic carbon atom was bent out of the Cp ring plane towards the central iron atom. However, the Fe–C_{exo} distances are longer than the Fe–C σ bond,

this is not indicative of strong direct interaction between the metal atoms and the methine carbon atom.

Here, we report the preparation of a tertiary diferrocenylcarbenium ion in which the two ferrocene moieties have different environments and this will serve as an important benchmark for the study of the stabilisation of the α -carbocationic centre. The starting material of choice was the ferrocenophane **1**,⁷ which can be viewed either as a [5]ferrocenophane bearing a 2,4-bridged dihydroquinoline ring or [4](2,4)-dihydroquinolinophane containing a 1,1'-disubstituted ferrocene bridge. Reaction of compound **1** with ferrocenyllithium at room temperature provided the tertiary alcohol **2** in 80% yield. When the alcohol **2** was treated with 1 equiv. of HBF₄ in acetonitrile the *N*-protonated salt **3** was isolated as an unstable deep purple solid, which in turn can be deprotonated by potassium carbonate in methanol to give the starting alcohol **2**. Treatment of the salt **3** with 1 equiv. of HBF₄ in dichloromethane afforded the diferrocenylcarbenium salt **4** in 90% yield as a stable green solid. Direct conversion of alcohol **2** into **4** was affected by addition of 2 equiv. of HBF₄ in dichloromethane at room temperature. Further addition of 1 equiv. of HBF₄ to a solution of **4** in dichloromethane yielded the ferrocenylfulvene derivative **5** in 90% yield. This compound can also be prepared in almost quantitative yield directly from **2** by the action of dry hydrogen chloride. When this conversion was carried out in the presence of ammonium hexafluorophosphate the reaction rate was increased as well as the yield. We have also found that compound **4** in acetonitrile solution at room temperature is slowly transformed into **5** although in moderate yield.

Keywords: carbenium ions; ferrocenes; NMR; Mössbauer spectroscopy.

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Scheme 1. Reagents and conditions: (i) Fec-Li/THF , rt, 30 min, 80%; (ii) 0.1 M $\text{HBF}_4/\text{CH}_3\text{CN}$ (1 equiv.); (iii) $\text{K}_2\text{CO}_3/\text{MeOH}$, CH_3CN ; (iv) 0.1 M $\text{HBF}_4/\text{CH}_2\text{Cl}_2$ (1 equiv.), 90%; (v) a. 0.1 M $\text{HBF}_4/\text{CH}_2\text{Cl}_2$ (1 equiv.), 90%, b. SiO_2 , 10% $\text{Et}_3\text{N}/n$ -hexane; (vi) $\text{K}_2\text{CO}_3/\text{MeOH}$, CH_2Cl_2 , 30%; (vii) a. $\text{HCl (g)}/\text{CH}_2\text{Cl}_2/\text{NH}_4^+\text{PF}_6^-$, b. $\text{SiO}_2/10\%$ $\text{Et}_3\text{N}/n$ -hexane, 90%.

In spite of the high reactivity shown by the related (diferrocenyl)methyl carbocations towards methanol,⁸ the reaction of **4** with methanol in the presence of potassium carbonate provided the diferrocenylethylene derivative **6** in 30% yield instead of the expected methoxy derivative. This conversion can be understood by proton abstraction on the methylene group at position 4 of the bridge with concomitant aromatisation of the dihydroquinoline ring (Scheme 1).

The structure of the alcohol **2**, diferrocenylcarbenium ion **4**, and ferrocenylfulvene derivative **5** have been elucidated from their spectroscopic data.⁹ The high stability of carbenium ion **4** permits accurate mass detection by high resolution positive FAB-MS. The mass spectrum displayed an intense isotopic cluster peaking at m/z 524 assignable to the molecular ion. The relative abundance of the isotopic cluster was in good agreement with the simulated spectrum of M^+ . The room temperature 400 MHz ^1H NMR spectra of **2** and **4** were completely assigned (with the exception of the aromatic protons) by ^1H - ^1H COSY, NOESY and spin decoupled experiments. Immediately apparent from the ^1H NMR spectrum of **4** is the diastereotopism of all the protons of the three substituted Cp rings. (Table 1)

The assignment of the protons, corresponding to the different Cp rings present in the molecule as well as the four diastereotopic protons present in the two methylene groups of this structure, were achieved by inspection of the ^1H - ^1H COSY and two-dimensional NOESY spectra (Fig. 1). In addition to full characterisation of these protons it is worth noting some differences observed among the chemical shifts of the protons in the Cp_1 , Cp_2 , and Cp_3 rings. In the Cp_3 ring a large deshielding for the β and β' protons with reference to

that of α and α' protons is observed ($\Delta\delta_{3'',2''} = 0.78$ and $\Delta\delta_{4'',5''} = 1.1$ ppm), which is in agreement with this cation having an important resonance contribution from a η^6 -fulvene- η^5 -cyclopentadienyliron (II) unit, with additional π -bonding of the metal with the exocyclic double bond. In this context it is also important to underline that the δ values for $\text{H}3''$ and $\text{H}4''$ are the largest observed for this type of protons in α -ferrocenylcarbenium ions.^{2c,6a,10}

The direct metal participation in the stabilisation of the positive charge promotes a significant bending of the exocyclic carbenium atom out of the Cp ring plane towards the central iron atom (Fe2). Consequently, the electronic density on the 2'' and 5'' positions have been found to be significantly increased giving rise to a shielding of those protons with reference to $\text{H}3''$ and $\text{H}4''$, for this the opposite effect has been found^{2a} and they can be considered as fulvene-like protons. It is interesting to note that in the ^1H NMR spectrum of ferrocenylfulvene derivative **5**, the fulvene protons appear in the same region (6.4–6.7 ppm). Moreover, to the best of our knowledge, this is the first time in which a separation between the α and α' and β and β' protons is observed at room temperature.

Table 1. ^1H NMR (ppm) data for the three substituted Cp rings in compound **4**

	δH_5	δH_4	δH_3	δH_2	$\Delta\delta\text{H}_{5,4}$	$\Delta\delta\text{H}_{3,2}$
Cp_1	5.05	4.91	5.27	6.10	-0.14	-0.83
Cp_2	5.66	5.12	5.51	5.86	-0.54	-0.35
Cp_3	5.88	6.67	6.63	5.53	0.79	1.1

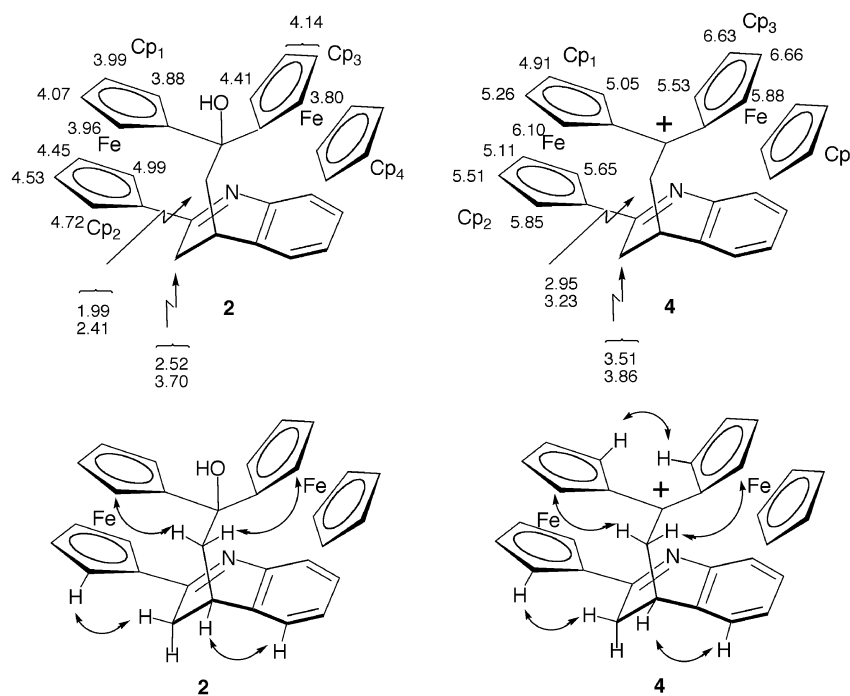


Figure 1. Chemical shifts and NOE observed for compounds **2** and **4**.

On the other hand, the chemical shifts corresponding to the protons of the Cp₁ moiety clearly indicate that, in this case, the iron atom within this ferrocene unit does not take part in the stabilisation of the positive charge. In such a case the expected δ values for the β and β' protons should be larger than those for the α and α' protons,^{2c} however, the observed situation is that the α and α' protons are unshielded with reference to the β and β' protons ($\Delta\delta_{5,4} = -0.14$ and $\Delta\delta_{3,2} = -0.84$), following the typical pattern of a ferrocene unit linked to an electron-withdrawing group.¹¹ Additionally, the δ values for the protons in this Cp₁ ring follow the sequence $\delta H_2 > \delta H_3 > \delta H_5 > \delta H_4$, the shielding of H5 is anomalous and can be perfectly explained by the influence of the iron(II) anisotropic field¹² on H5.

Finally, the pattern observed for the δ values of the protons in the Cp₂ ring are in accordance with those observed in ferrocene rings monosubstituted with an electron withdrawing group: $\delta H_2' > \delta H_5' > \delta H_3' > \delta H_4'$ ($\Delta\delta_{5',4'} = -0.54$ and $\Delta\delta_{3',2'} = -0.35$).

The Mössbauer data¹³ (Table 2), further support this view. The alcohol **2**, at 77 K, shows one quadrupole split doublet of narrow line width with an isomer shift (i.s.) and quadrupole splitting (q.s.) in the normal range for ferrocenes.¹⁴ There is no differentiation of the iron atoms as shown by Mössbauer. The cation **4**, at both 77 and 300 K, exhibits two, overlapping, quadrupole split doublets of equal relative intensity. The i.s. moves with temperature as expected and the q.s. values are independent of temperature. The i.s. is also typical of a ferrocene derivative.¹⁴ The smaller of the q.s. values of **4** is similar to that reported for diferrocenylmethylum tetrafluoroborate (2.10 mm s⁻¹ at 298 K),¹⁵ and is lower than that for the parent alcohol **2**. The other doublet of

4 has a q.s. exalted compared to **2** and similar to those found for a series of α -ferrocenylcarbenium ions.¹⁶ It has been postulated that exalted q.s. values (greater than that of ferrocene itself) in α -ferrocenylcarbenium systems are due to overlaps of the iron-based orbitals ϵ_2 with the empty p orbital on C_{exo} and values of about 2.6–2.7 mm s⁻¹ represent a maximal iron participation for such systems, whereas low q.s. values are due to electron withdrawal via ring-based orbitals ϵ_1 .¹⁶

The reported parameters are consistent with the two iron atoms having different partial charge. However, **4** can not be described as mixed-valence as, in this case, a much larger difference between q.s. values would be expected (e.g. in mixed-valence biferoceium derivatives, the difference between the q.s. value of Fe^{II} and Fe^{III} is more than 0.94 mm s⁻¹).¹⁷

In conclusion, the useful combination of ¹H NMR and ⁵⁷Fe Mössbauer spectroscopic data of the diferrocenylcarbenium ion **4** strongly suggests two different processes for stabilisation of the α -carbocationic centre. The monosubstituted ferrocene group can clearly be considered as a η^6 -fulvene- η^5 -cyclopentadienyliron (II) (desielding for β protons with respect to α protons) with iron participation (exalted q.s. value), whereas the

Table 2. ⁵⁷Fe Mössbauer parameters

Compound	T (K)	i.s.	q.s.	h.w.h.m
Alcohol 2	77	0.52	2.33	0.13
Cation 4	77	0.50	2.51	0.13
		0.51	2.11	0.14
	300	0.43	2.50	0.11
		0.44	2.14	0.13

disubstituted ferrocene group is acting only via cyclopentadienyl-based orbitals (deshielding for α protons with respect to β protons) without iron participation (low q.s. value). That the nature of diferrocenyl-carbenium ion **4** as pentafulvene complex is more than formal is demonstrated by its easy conversion to **5**, either spontaneously or under acid conditions. Compound **4** represents the first example reported in which two ferrocene groups linked to an α -carbocationic centre show different spectroscopic (both ^1H NMR and ^{57}Fe Mössbauer) characteristics. Compound **5** should be a versatile ligand for a large number of metals.¹⁸ Further research will be directed to synthesising heteronuclear metal complexes derived from **5**, with a possible metal–metal interactions.

Acknowledgements

We gratefully acknowledge the financial support of the DGI (Ministerio de Ciencia y Tecnología, Spain) (Project No. BQU2001-0014). The BBSRC, UK, are thanked for funding (D.J.E.).

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